

## Compressibility and Polygonization of Single-Walled Carbon Nanotubes under Hydrostatic Pressure

Jie Tang,<sup>1</sup> Lu-Chang Qin,<sup>2</sup> Taizo Sasaki,<sup>1</sup> Masako Yudasaka,<sup>2</sup> Akiyuki Matsushita,<sup>1</sup> and Sumio Iijima<sup>2,3,4</sup>

<sup>1</sup>National Research Institute for Metals, 1-2-1 Sengen, Tsukuba 305-0047, Japan

<sup>2</sup>JST-ICORP Nanotubelite Project, c/o NEC Corporation, 34 Miyukigaoka, Tsukuba 305-8501, Japan

<sup>3</sup>R & D Group, NEC Corporation, 34 Miyukigaoka, Tsukuba 305-8501, Japan

<sup>4</sup>Department of Materials Science and Engineering, Meijo University, Tenpaku-ku, Nagoya 468-8502, Japan

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Single-walled carbon nanotubes show linear elasticity under hydrostatic pressure up to 1.5 GPa at room temperature. The volume compressibility, measured by *in situ* synchrotron x-ray diffraction, has been determined to be  $0.024 \text{ GPa}^{-1}$ . Theoretical calculations suggest that single-walled carbon nanotubes are polygonized when they form bundles of hexagonal close-packed structure and the intertubular gap is smaller than the equilibrium spacing of graphite (002) ( $d = 3.35 \text{ \AA}$ ). It has also been determined that the deformation of the trigonal nanotube lattice under hydrostatic pressure is reversible up to 4 GPa, beyond which the nanotube lattice is destroyed.

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Carbon nanotubes [1], due to their unique structure, exhibit many extraordinary physical properties, such as high stiffness, tunable electrical conduction between semi-conducting and metallic states, one-dimensional quantum wire effect, and electrical field-induced electron emission, etc. Of particular interest are their mechanical properties. While the multiwalled carbon nanotubes show the greatest values for the axial Young's modulus of about 2 TPa [2], the theoretical value of graphene, carbon nanotubes appear very soft in their radial directions. The van der Waals forces between neighboring carbon nanotubes can well induce flattening of the otherwise circular tubules. The softness of carbon nanotubes in radial directions has been observed experimentally. For example, when two nanotubes are brought close to each other, the contact area is flattened [3]; when its diameter is large, a nanotube assumes a flattened (collapsed) structure rather than maintains the cylindrical structure [4]. Single-walled carbon nanotubes are even softer than multiwalled nanotubes [5]. Molecular dynamics simulations have also demonstrated that large radial compressions could be induced by small force impact without C-C bond breakage [6]. However, though there have been many research results on the axial elasticity of carbon nanotubes, there is still no quantitative measurement of the radial elasticity of carbon nanotubes reported in the literature.

Hydrostatic high pressure provides an ideal condition to study the radial elasticity of carbon nanotubes. Since the C-C bond is strong, the axial deformation under moderate pressure can be largely ignored while substantial radial deformation is already induced. There have been several Raman spectroscopy studies reported on the electronic properties of single-walled carbon nanotubes under high pressure. Venkateswaran *et al.* [7] examined the pressure dependence of the radial and tangential vibrational modes and observed that the radial mode intensity vanished beyond 1.5 GPa, suggesting that the disappearance

of the radial mode intensity was due to polygonization of the nanotubes under pressure. Most recently, basing on Raman shifts, Peters *et al.* [8] reported that a structural phase transition had occurred at 1.7 GPa. In a separate paper, Chesnokov *et al.* [9] conducted a high pressure experiment up to 3 GPa and found that carbon nanotubes still undergo reversible deformation up to this pressure.

In this Letter, we report the measurement of mechanical deformation of single-walled carbon nanotubes (SWCNTs) under hydrostatic high pressure using a diamond anvil cell and *in situ* x-ray diffraction. Energetics calculations have also been carried out to establish the equilibrium intertubular gap and to simulate the morphological evolution under increased pressure in connection with the experimentally measured compressibility. It is suggested that polygonization of individual nanotubes must take place in order to lower the total energy when nanotubes are forming hexagonal closed-packing structure as observed experimentally.

SWCNTs were produced by single-beam laser evaporation of graphite powders catalyzed by Ni/Co fine particles. The pristine carbon nanotubes often aggregated to form raftlike bundles [10,11]. This material has been well characterized by both high-resolution electron microscopy and Raman spectroscopy [11]. Loosely tangled nanotube bundles were put into a gasketed diamond anvil cell and hydrostatic pressure was applied to the SWCNTs via a pressure medium made of ethanol-methanol. The applied pressure was measured using the *R*-line emission from the ruby crystals embedded in the pressure medium. Synchrotron x-ray diffraction data were collected using an imaging plate with sensitivity of 10 000 scales at the Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan using a selected wavelength of  $0.8000 \text{ \AA}$  to ensure that lattice reflections from the nanotube bundles were well preserved.

Carbon nanotubes form hexagonal close-packed structures as schematically illustrated in Fig. 1(a). As shown in

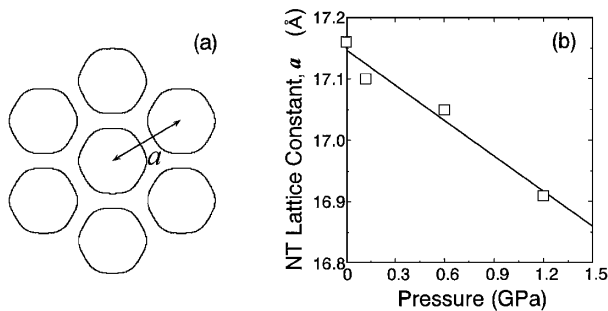


FIG. 1. (a) Single-walled carbon nanotubes form hexagonal close-packed structure. The lattice constant,  $a$ , equals the sum of the short nanotube diagonal and the intertubular gap. (b) Lattice constant of the trigonal nanotube lattice vs pressure as measured by *in situ* synchrotron x-ray diffraction. Compressibility of  $0.024 \text{ GPa}^{-1}$  is obtained.

the figure, the lattice constant,  $a$ , of the thus formed trigonal lattice equals the sum of the intertubular gap and the short diagonal of the nanotube cross section. At the ambient condition, the average lattice constant of the nanotube bundles was measured to be  $17.16 \text{ \AA}$  with a narrow distribution. The (1,0) reflection shifted to higher angles when pressure was increased, indicating that compaction of the nanotube material had occurred under pressure. Up to the pressure of 1.5 GPa, the nanotube lattice exhibited a linear behavior, as shown in Fig. 1(b). Since the Poisson ratio for graphite ( $= 0.012$ ) is so small due to the strong  $sp^2$  bonding [12], the lateral change in bonding length under pressure has been neglected for calculations of the radial elasticity parameters. The volume compressibility, defined by  $\nu = -\frac{1}{V} \frac{\partial V}{\partial P}$ , where  $V$  and  $P$  are the material volume and the applied pressure, respectively, is obtained to be  $0.024 \text{ GPa}^{-1}$  for the presently studied carbon nanotubes.

Given the lattice constant of the nanotube lattice, it is still undetermined what the exact nanotube diameter is, since the lattice constant equals the sum of the nanotube diameter and the intertubular gap, as illustrated in Fig. 1(a). On the other hand, although an SWCNT assumes a circular cross section when it is in an isolated state (except those of very large diameters [4]), it is not necessary to remain so when many SWCNTs form bundles. The morphology of the hexagonally stacked nanotube bundles of minimum energy has been analyzed by applying the continuum elastic theory proposed by Tersoff [13]. In this model, each nanotube is treated as an elastic sheet that is bent into a cylindrical form and each part of the cylindrical tube interacts with all the other cylindrical tubes with a potential of the Lennard-Jones type. The parameters for the Lennard-Jones type interaction potential and the elastic constants have been derived from the compressibility and the phonon frequencies of graphite. When the lattice constant at zero pressure was assumed to be  $a = 17.15 \text{ \AA}$  which is close to the experimentally observed value, it was obtained that the diameter of isolated SWCNTs was  $14.08 \text{ \AA}$  in the structure of minimum energy. It should be mentioned that the

cross section of each nanotube was found to be already faceted when they form a raftlike bundle. In other words, when the cylindrical nanotubes aggregate to form hexagonal close-packed bundles, the morphology of the nanotubes becomes prismatic instead of remaining cylindrical. Using the same potential, we have also performed calculations on the nanotubes of smaller diameters. The yielded results indicate that the nanotube lattice constant is smaller than the observed value and that the nanotubes are also slightly polygonized in the structure of minimum energy. For example, when the nanotube diameter assumes  $13.55 \text{ \AA}$ , the resultant lattice constant of the nanotube bundle is  $16.50 \text{ \AA}$ . Our calculations show that the intertubular separation at the state of minimum total energy is smaller than the value separating  $C_{60}$  molecules found in  $C_{60}$  crystals that was used to deduce the nanotube diameter by Thess *et al.* [14]. The calculated pressure dependence of the lattice constant is in excellent agreement with experiment as shown in Fig. 2(a). The figure also includes the pressure dependence calculated for rigid cylindrical tubes (dotted line) for reference, which showed a lower compressibility. Figure 2(b) shows the calculated structure of minimized formation energy at each pressure up to 4.2 GPa. It should be noted that, by applying pressure, the circular nanotube cross section is polygonized further to more faceted shapes. The polygonization of a nanotube can be quantified by the ratio  $\eta = r_S/r_L$ , where  $r_S$  and  $r_L$  are the short and the long radial dimensions of the cross section, respectively, as illustrated in Fig. 2(b). Our calculations have indicated that  $\eta$  deviates from unity (for isolated nanotubes) to 0.991 when the nanotubes forming bundles even at zero pressure, and that it reaches 0.982 at 1.5 GPa pressure when the diameter of the isolated SWCNTs was assumed to be  $14.08 \text{ \AA}$ . At higher pressures, the polygonization becomes more noticeable as expected. Details can be seen in Fig. 2(c), which is an enlarged portion of Fig. 2(b). Another interesting point is that the intertubular gap is much reduced from the equilibrium (002) spacing of graphite. For the present case, the equilibrium gap is  $3.12 \text{ \AA}$  at normal pressure, compared to  $3.35 \text{ \AA}$  for the (002) spacing of graphite. This is due to the fact that the large curvature of the nanotubes makes the area smaller on which the repulsive force between nanotubes is acting. The calculated intertubular gap vs pressure is shown in Fig. 2(d). For the purpose of comparison, the graphite (002) spacing, measured in the same experiment, is also plotted in the figure. It shows that, when such nanotube bundles are subject to pressure, further polygonization is necessary to accommodate the volume change.

We should mention that this compressibility value is valid only for nanotubes used in the present experiment. When the diameter of nanotubes changes, the compressibility would change accordingly. For thicker nanotubes, it is expected that their compressibility will be smaller than thinner nanotubes within the elastic limit.

We found that the trigonal nanotube lattice diminished beyond 1.5 GPa pressure as signified by the disappearance

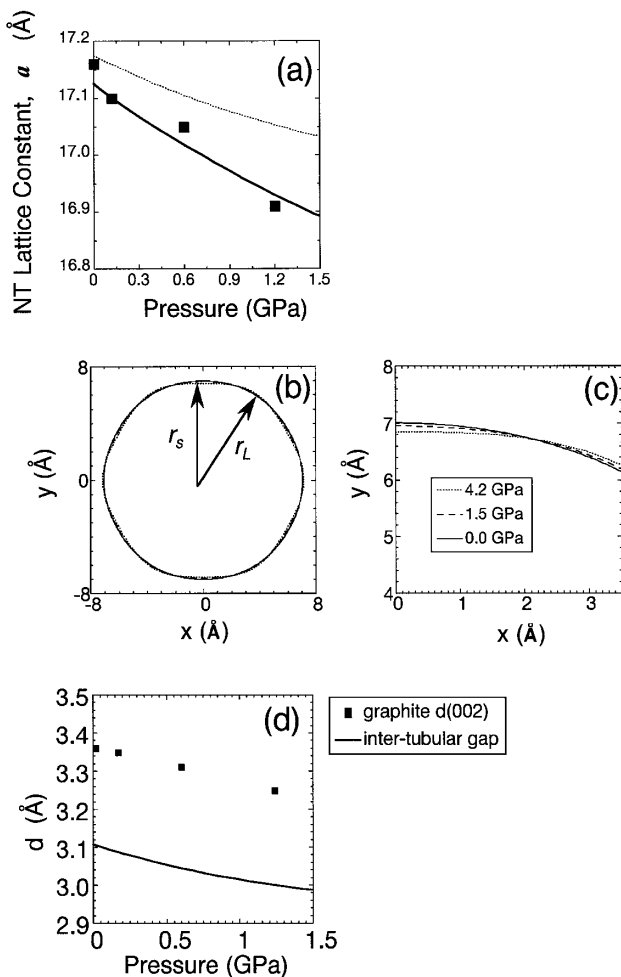


FIG. 2. (a) Calculated nanotube lattice constant (line curve) under pressure for 14.08 Å nanotubes in comparison with experimental data (filled squares). The dotted line is for rigid cylindrical carbon nanotubes. (b) Morphological evolution of nanotubes under increasing pressure. At the ambient condition, nanotubes of 14.08 Å diameter are already slightly polygonized when they form close-packed structure with  $\eta = 0.991$ . Further polygonization occurs when pressure is applied. At 1.5 GPa pressure,  $\eta = 0.982$ . (c) Enlarged portion of the nanotube cross sections at pressure 0, 1.5, and 4.2 GPa, respectively. (d) The intertubular gap vs pressure (line curve) is smaller than the graphite (002) spacing measured in the same experiment (filled squares).

of the characteristic nanotube lattice reflections. Therefore we could not confirm if the structural phase transition actually occurred as suggested by Peters *et al.* [8]. However, the individual nanotubes, though highly deformed, still exist, as shown by the reversal experiment. The deformation of the 14.08 Å nanotubes is found reversible up to 4 GPa. When the pressure was released, the diminished nanotube lattice reflections reappeared, indicating that the deformation was reversible. This demonstrates that the disappearance of the nanotube lattice reflection peaks was due to the structural distortions which occurred to the raft-like bundles, and the deformation is still elastic. However, beyond 5 GPa pressure, the diminished nanotube lattice re-

flections could not be recovered, indicating that the lattice structure had been totally destroyed.

It is interesting to note that the compressibility of graphite ( $\sim 0.028 \text{ GPa}^{-1}$ ) is actually larger than nanotubes. This is not surprising because much of the open space in SWCNTs is confined in the interior of nanotubes within the elastic limit.

The polygonization of carbon nanotubes has significant consequences on the physical properties of nanotubes. Raman spectroscopy measurements [7] showed disappearance of the characteristic breathing mode and that optical transitions were also altered, which indicated that the electronic band gap has been changed as predicted theoretically by Charlier *et al.* [15]. The faceting induces  $\sigma^*-\pi^*$  hybridization and lowers the symmetry of the otherwise cylindrical tubules.

The present results are a first experimental measurement of the compressibility of single-walled carbon nanotubes of diameter 14.08 Å. The upper limit of 4 GPa pressure for the stability of nanotube lattice establishes that the carbon nanotube lattice is rather fragile due to the weak van der Waals bonding forces. Further studies of the structural stability of individual nanotubes under pressure are underway and will be published separately.

- [1] S. Iijima, *Nature (London)* **354**, 56 (1991); S. Iijima and T. Ichihashi, *ibid* **363**, 603 (1993).
- [2] M.M.J. Treacy, T.W. Ebbesen, and J.M. Gibson, *Nature (London)* **381**, 678 (1996).
- [3] R.S. Ruoff, J. Tersoff, D.C. Lorents, S. Subramoney, and B. Chan, *Nature (London)* **364**, 514 (1993).
- [4] N.G. Chopra, L.X. Benedict, V.H. Crespi, M.L. Cohen, S.G. Louie, and A. Zettl, *Nature (London)* **377**, 135 (1995).
- [5] S. Iijima, C. Brabec, A. Maiti, and J. Bernholc, *J. Chem. Phys.* **104**, 2089 (1996).
- [6] V. Lordi and N. Yao, *J. Chem. Phys.* **109**, 2509 (1998).
- [7] U.D. Venkateswaran, A.M. Rao, E. Richter, M. Menon, A. Rinzler, R.E. Smalley, and P.C. Eklund, *Phys. Rev. B* **59**, 10928 (1999).
- [8] M. Peters, L.E. McNeil, J.P. Lu, and D. Kahn, *Phys. Rev. B* **61**, 5939 (2000).
- [9] S.A. Chesnokov, V.A. Nalimova, A.G. Rinzler, R.E. Smalley, and J.E. Fischer, *Phys. Rev. Lett.* **82**, 343 (1999).
- [10] L.-C. Qin and S. Iijima, *Chem. Phys. Lett.* **269**, 65 (1997).
- [11] M. Yudasaka, R. Yamada, N. Sensui, T. Ichihashi, and S. Iijima, *J. Phys. Chem. B* **103**, 6224 (1999).
- [12] O.L. Blaksee *et al.*, *J. Appl. Phys.* **41**, 3373 (1970); E.J. Seldin and C.W. Nezbeda, *J. Appl. Phys.* **41**, 3389 (1970).
- [13] J. Tersoff, *Phys. Rev. B* **46**, 15546 (1992); J. Tersoff and R.S. Ruoff, *Phys. Rev. Lett.* **73**, 676 (1994).
- [14] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tomanek, J.E. Fisher, and R.E. Smalley, *Science* **273**, 483 (1996).
- [15] J.-C. Charlier, Ph. Lambin, and T.W. Ebbesen, *Phys. Rev. B* **54**, R8377 (1996).