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Description	

## **C<sub>70</sub> Molecular Stumbling inside Single-Walled Carbon Nanotubes**

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We report the structural study of C<sub>70</sub>-one-dimensional (1D) crystal formed inside single-walled carbon nanotubes (SWNTs). X-ray diffraction measurements were performed between 100 K and 999 K on C<sub>70</sub>-encapsulated SWNTs with an average diameter of 1.37 nm. Two different domains, where the dominant alignment of C<sub>70</sub> molecular long axis is standing or lying with respect to the tube axis, were observed; the ratio of the standing to the lying C<sub>70</sub>-domains is roughly 7:3. Thermal expansion of interfullerene distance gave no evidence for orientational phase transitions, not as in the 3D crystals. Instead, the long-range order of the standing C<sub>70</sub>-alignment was thermally destroyed with an activation energy of  $39 \pm 4$  meV. The results imply the importance of either the 1D fluctuation or the tube-C<sub>70</sub> interaction at finite temperatures.

**KEYWORDS:** thermal expansion, carbon nanotube, SWNT, peapod, C<sub>70</sub>, phase transition, structure, XRD, fullerene

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Existence of nanometer-size inner hollow cavities<sup>1, 2</sup> in single-walled carbon nanotubes (SWNTs) encourages us to form one-dimensional (1D) system. Recent efforts actually led to successful synthesis of high-quality fullerene crystals<sup>3, 4</sup> inside SWNTs, the so called "peapods". Although several interesting properties<sup>5-10</sup> have been predicted or observed in this system, order-disorder transition related to the orientation of fullerene molecule inside SWNTs has not yet been clarified. In the case of C<sub>60</sub>-peapods, the theoretical calculation predicted that the electronic states near the Fermi level are substantially modified by the C<sub>60</sub>-SWNT interaction<sup>5</sup>. Thus, in general, the issue of how the electronic state of peapods is affected by the fullerene orientation is an interesting one, and information on this is important for basic understanding of the physical properties of peapods. In the present paper, we report the structural study of C<sub>70</sub>-peapods by means of X-ray diffraction (XRD) in a temperature range between 100 K and 999 K.

The peapods were prepared by a vapor reaction method<sup>4, 6</sup> using purified SWNTs. The starting raw materials were generated by a pulsed laser vaporization method using a carbon rod with Ni and Co catalysts<sup>11</sup>. Transmission electron microscopy confirmed that the parallel-aligned carbon nanotubes were packed into bundles with a triangular lattice (Fig.1a). We also compared the results of C<sub>70</sub>-peapods with those of double-walled carbon nanotubes (DWNTs) and C<sub>60</sub>-peapods. Here, the DWNTs were converted from C<sub>60</sub>-peapods by heating at ~1470 K (ref. 12). The C<sub>70</sub> peapods and DWNTs are schematically illustrated in Figs. 1(b)-1(d).

Figure 2(a) shows the typical powder XRD patterns of C<sub>60</sub>- and C<sub>70</sub>-peapods and the pristine SWNTs at RT. The data were collected using synchrotron radiation with a wavelength of 0.1000 nm at beam lines BL02B2 of SPring-8 and BL1B of KEK PF. Samples were sealed in a quartz capillary after being evacuated at ~800 K to remove adsorbed gases<sup>13-15</sup>. The observed peaks are basically indexed on the basis of the 2D triangular lattice<sup>11</sup> formed by 1D SWNTs. In Fig. 2(a), we observed marked changes in the XRD profiles on

encapsulation: the 10 peak around  $Q \sim 4.5$  (1/nm) is strongly depressed, and its onset shifts to the high- $Q$  side, consistent with earlier works on molecular encapsulation inside SWNTs (refs. 13-15). We also observed new peaks around  $Q=6$  (1/nm), indicated by arrows. The lack of the corresponding peaks in the DWNTs (Fig. 2(c)) shows that they are assigned to diffraction peaks due to the 1D array of fullerene molecules inside. The estimated lattice constant,  $a$ , of the 1D fullerene crystals, which corresponds to the interfullerene distance, is shown in Table I, along with the interfullerene gap defined by  $g=a-M$ , where  $M$  is the mean diameter of the fullerene molecule.

The observed features mentioned above were well reproduced by a simulation (Fig. 2(b)), in which the SWNTs and fullerene molecules are approximated to homogeneously charged shells<sup>11</sup>. Within the framework of this model, we cannot discuss the structures in detail, such as the carbon coordinates within a graphene sheet. However, we could obtain the average triangular lattice constant  $L$  and tube diameters  $D$ , and found that  $L$  and  $D$  almost retain on encapsulation:  $L=1.649 \pm 0.010$  nm and  $D=1.352 \pm 0.002$  nm for the  $C_{60}$ -peapods, and  $L=1.683 \pm 0.010$  nm and  $D=1.373 \pm 0.002$  nm for the  $C_{70}$ -peapods.

In the case of  $C_{70}$  peapods, the two types of interfullerene distances, corresponding to the two peaks shown by arrows in Fig. 2(a), were observed:  $1.00 \pm 0.01$  nm and  $1.10 \pm 0.01$  nm at RT. These distances nearly correspond to those for the so-called "standing" and "lying" alignments<sup>4</sup> of the  $C_{70}$  molecules with an elongated "rugby-ball" shape, as schematically shown in Figs. 1(b) and 1(c), respectively. The observed clear double-peaked structure implies that there are two different domains; in one of them, the long molecular axes of  $C_{70}$  tend to align perpendicular to the tube axis at RT, but in the other, most  $C_{70}$  molecules align parallel to the tube axis. The simulation results indicate that the SWNTs for the standing alignment are dominant compared to those for the lying

alignment in the present sample, and the ratio of these domains is 7:3.

Because the SWNTs studied have a diameter distribution that peaks around  $\sim 1.37$  nm (the mean diameter estimated from the present XRD profile), the mean gaps between the tube wall and  $C_{70}$  molecule is 0.29 nm for the standing alignment and 0.33 nm for the lying alignment. Interestingly, the former gap is nearly equal to 0.292 nm in the bulk crystal of solid  $C_{60}$  and to 0.29-0.31 nm in SWNT bundles. These findings suggest the importance of tube- $C_{70}$  interaction in the stabilization of the standing alignment. The lying alignment may be favorable for thicker SWNTs, because the  $C_{70}$  molecules may tend to lie in order to gain the contact area between the tube wall and fullerene molecule. In thinner tubes, where the tube wall must be substantially deformed to insert the standing  $C_{70}$ , accommodation of the standing  $C_{70}$  is also difficult. Thus, the tube diameter is one of the important factors for determining the orientation of fullerene molecules inside the SWNTs. SWNTs with a different diameter actually gave a different standing alignment.

Now we discuss the thermal expansion of the  $C_{70}$  crystal. Figure 3 shows the temperature dependence of the interfullerene distance normalized at RT, along with that of solid  $C_{60}$  (shown by a solid straight line). We observed that the thermal expansion for the standing alignment is substantially larger, while that for the lying alignment is comparable to that of the bulk  $C_{60}$  crystal. This is unusual if the thermal expansion coefficient for the lattice constant,  $\alpha_L$ , is dominated by that of the intermolecular gap,  $\alpha_g$ . Assuming that the thermal expansion of the molecular axis is ignored, the  $\alpha_g$  in the standing alignment is estimated to be  $\sim 11 \times 10^{-5}$  (1/K) from the observed  $\alpha_L$  as an average value between 300 K and 999 K, which is much larger than  $2.6 \times 10^{-5}$  (1/K) for the graphite interlayer gap,  $\sim 5.4 \times 10^{-5}$  (1/K) for the solid  $C_{60}$  (ref. 16) and  $\sim 4.2 \times 10^{-5}$  (1/K) for the SWNT bundles<sup>15</sup>.

Such a large thermal expansion of the standing alignment must be due to a reorientation of C<sub>70</sub> molecules inside the tubes. In the case of 3D solid C<sub>70</sub>, it has been known<sup>1,17</sup> that the structural phase transition successively occurs at ~340 K and ~280 K: the C<sub>70</sub> molecules exhibit a quasi-free rotation above ~340 K, below which the molecular long axis freezes but the short axis is still dynamically disordered, and finally the complete freezing occurs below ~280 K. These orientational ordering transitions accompany a change in the lattice constant. In the present standing C<sub>70</sub>-peapods, almost all the molecules are aligned perpendicular to the tube axis at RT, so that when the  $T$  is raised from RT a jump of 2~3% in the lattice constant is expected at a transition into the "free-rotational state". The data, however, did not show such a sudden change. Instead, the lattice constant gradually increases with increasing  $T$ , indicating that the C<sub>70</sub> molecular stumbling is thermally activated<sup>18</sup>.

Assuming the simplest model for a quantitative discussion, the lattice constant is given by

$$a = M_S + (1 + \alpha_g T)g(0) + (M_L - M_S) \frac{\exp(-E_0/k_B T)}{[2 + \exp(-E_0/k_B T)]} \quad (1),$$

where  $M_S$ ,  $M_L$ ,  $g(0)$ , and  $E_0$  are the mean lengths of molecular short and long axes, intermolecular gap at  $T=0$  K, and activation energy for molecular stumbling, respectively. The second term describes the thermal expansion of the intermolecular gap and the coefficient  $\alpha_g$  is taken to be  $\sim 5.4 \times 10^{-5}$  (1/K), the value for the solid C<sub>60</sub>. The third term is due to the C<sub>70</sub> stumbling, where  $E_0$  is the energy required to make a C<sub>70</sub> molecule lie in the standing "ferromagnetic" array of molecules. (Note that the standing C<sub>70</sub> molecule can take two possible orientations perpendicular to the tube axis.) The least-squares fit with this equation leads to a good reproduction of the data, as shown by the thick solid curve in Fig. 3, using the parameters,  $E_0 = 39 \pm 4$  meV and  $g(0) = 0.276 \pm 0.08$  nm.

Why is the long-range order of standing alignment gradually destroyed with increasing temperature? One possibility is the case that the  $C_{70}$ -intermolecular interaction is negligibly small and the standing alignment is stabilized solely by the tube- $C_{70}$  interaction. In this case, the lying  $C_{70}$  should be thermally excited as observed. However, the fact that the transition temperatures ( $\sim 280$  K and  $\sim 340$  K) in the bulk 3D crystals are comparable in magnitude to the observed  $E_0/k_B \sim 449$  K suggests that the intermolecular interaction can not be ignored, because the transition temperature for the bulk materials is taken as a tentative magnitude for the intermolecular interaction. Thus, alternatively, the one dimensionality (1D) of the crystal must be considered. In 1D system with a short-range interaction<sup>19</sup>, it is known that the long-range order is destroyed by 1D fluctuation at finite temperatures. In 1D ising model with a ferromagnetic ground state, it is known that the domain-wall excitation is described by a similar formula to eq. (1). In the present case, however, since the lying and standing domains may have different energies, the situation is slightly different from the case of the above ising model. Here, we encounter a new situation where not only anisotropic  $C_{70}$ - $C_{70}$  interaction but also anisotropic  $C_{70}$ -SWNT interaction must be taken into account, and we need more sophisticated analysis for the lattice expansion.

Anyway, the present studies clarified that the standing alignment is dominant and stable at the low temperature in  $C_{70}$ -peapods with typical SWNTs with a mean diameter of 1.37 nm. With increasing temperature,  $C_{70}$  stumbling is thermally activated with a rather small activation energy of 39 meV. Thus, in a broad temperature region including room temperature, the  $C_{70}$  molecular reorientation cannot be ignored, because it affects many basic physical properties of  $C_{70}$ -peapods. In the future, however, the molecular dynamics should be investigated as a function of the  $C_{70}$ -filling inside the SWNTs, as well as a function of the diameter of SWNTs.

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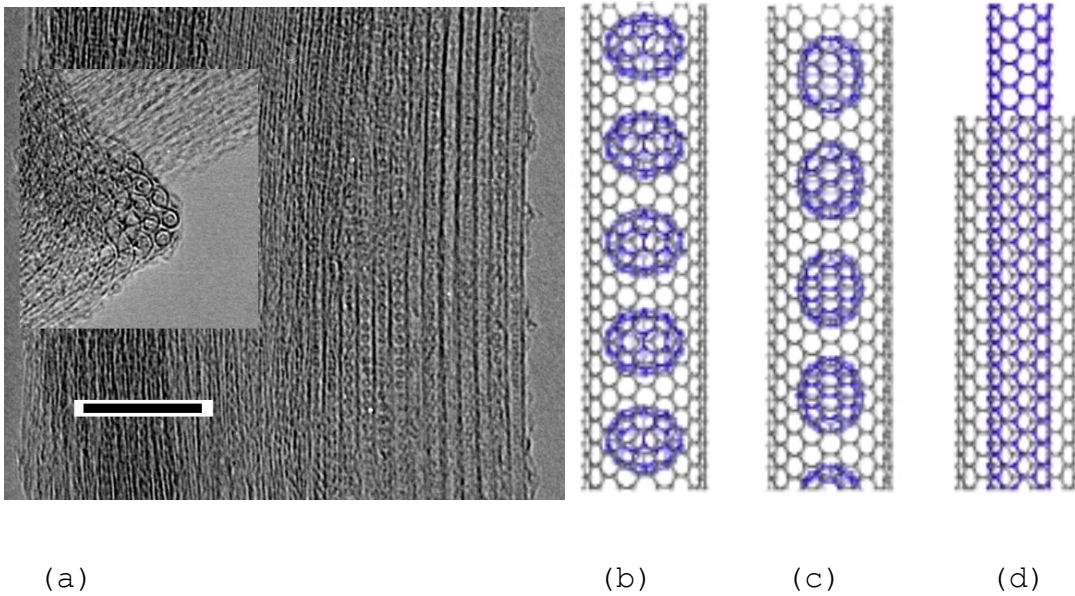
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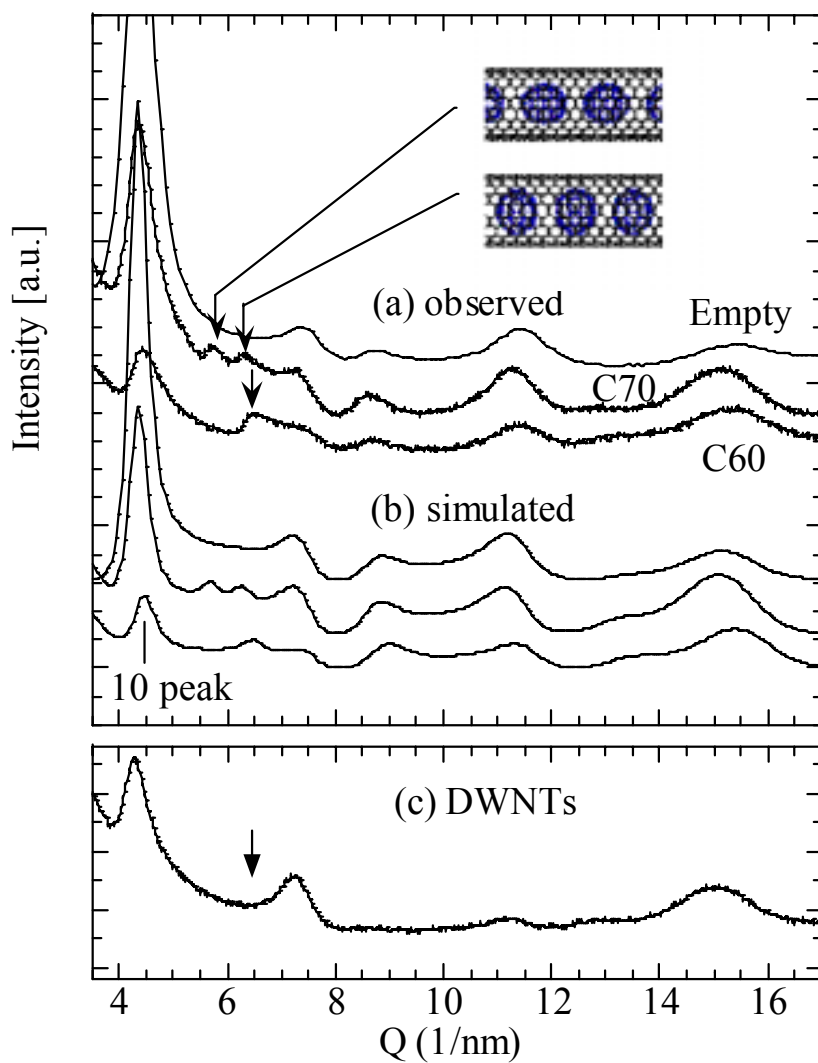
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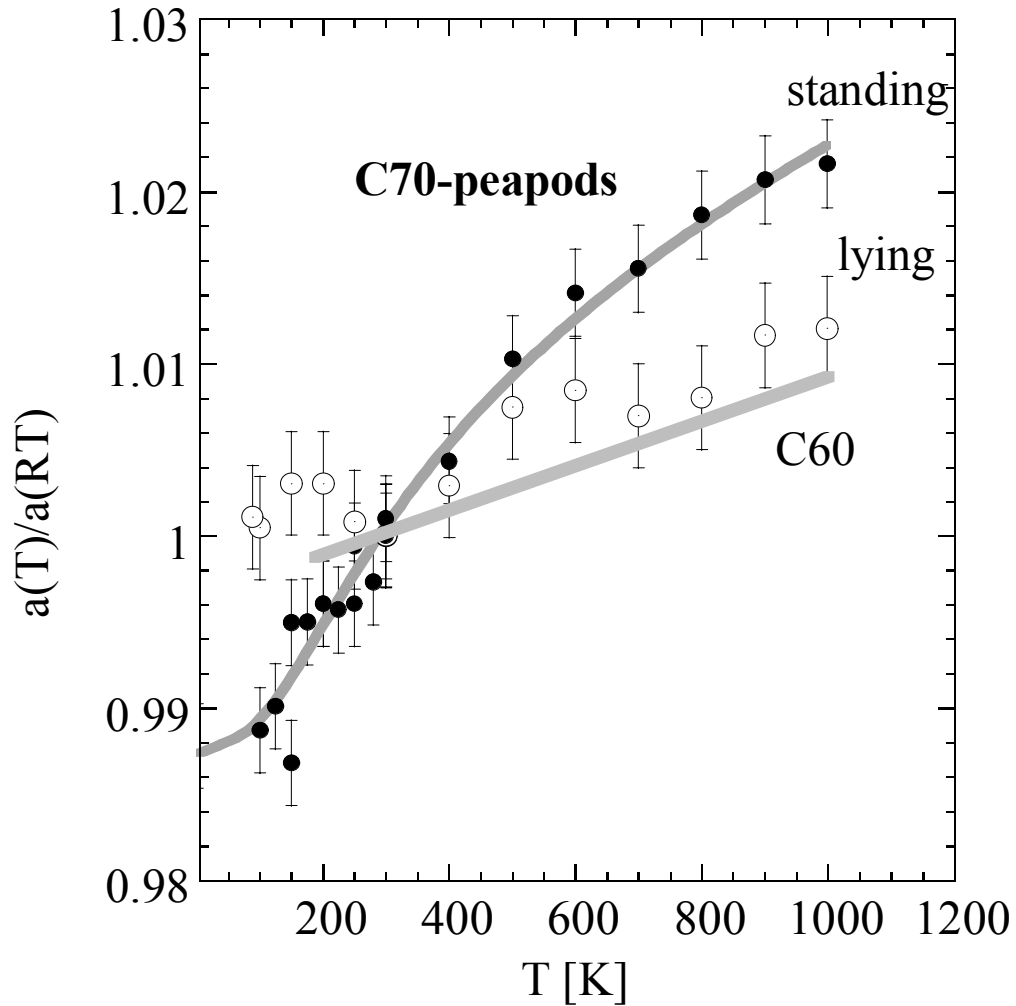
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**Figure 1.** (a) An example of transmission electron microscopy (TEM) image of C<sub>70</sub>-peapods. (b), (c) and (d) Schematic illustrations of C<sub>70</sub> standing alignment, lying alignment, and double-wall carbon nanotube (DWNT), respectively. The DWNT has a (10, 10) index for the outer tube, and (5, 5) for the inner tube. The inset shows a cross section of a bundle. The scale is 10 nm.



**Figure 2.** XRD profiles of pristine (empty) SWNTs,  $C_{70}$ -peapods and  $C_{60}$ -peapods: (a) observed and (b) simulated. In the simulations, a small amount of bundles of empty SWNTs was assumed to be included: 15 wt% for the  $C_{60}$ -peapods and 30 wt% for the  $C_{70}$ -peapods. (c) Observed XRD profile of DWNTs. The arrow shows the lack of the peak due to 1D  $C_{60}$  crystal observed in  $C_{60}$ -peapods.



**Figure 3.** Normalized interfullerene distance (1D lattice constant) as a function of temperature. The solid straight line shows that of solid  $C_{60}$ . The solid curve is the least-squares fit with eq. (1) in the text.

**Table I.** Interfullerene distance (lattice constant), interfullerene gap and tube-fullerene gap estimated by XRD analysis.

	Interfullerene distance, $a$	Interfullerene gap*, $g$	fullerene-tube gap**
C <sub>60</sub> -peapod (#1)	0.97	0.26	0.321
(#2)	0.95 (0.95 <sup>***</sup> )	0.24	0.321
C <sub>70</sub> -peapod	1.00 (1.00 <sup>***</sup> )	0.290	0.289
	1.10 (1.10 <sup>***</sup> )	0.304	0.332
C <sub>60</sub> solid <sup>****</sup>	1.002		0.292

\*The molecular shape is assumed to be spherical with a mean diameter of 0.710 nm for C<sub>60</sub> and that of a rugby ball with a mean short (a-b) axis of 0.712 nm and a mean long (c-) axis of 0.796 nm for C<sub>70</sub> (ref. 1).

\*\*The gap between the tube wall and fullerene molecules estimated using the average tube diameter.

\*\*\* From electron diffraction measurements (ref. 4).

\*\*\*\* Reference 1.