Novel Structures of C_{60} and C_{70}-Encapsulating Carbon Nanotubes

One of the interesting features of the single-wall carbon nanotube (SWNT) is its nanometer size inner hollow cavity [1,2]. This encourages researchers to study its use in industrial applications such as gas storage cylinders and one-dimensional nanometer molds. Recently, it was shown that bulk quantities of fullerene molecules can be encapsulated in SWNTs [3, 4]. This class of material is called "peapod". The reason for this can be clearly seen in Fig. 1.

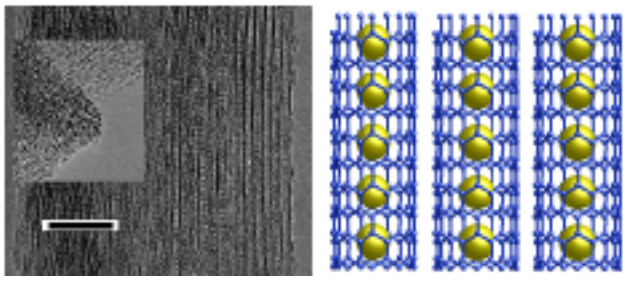

Fig. 1. The TEM image of C_{70}-peapods (left) and a schematic view of peapods (right). The scale is 10 nm. The inset shows a cross section of a bundle.

A theoretical calculation for C_{60}-peapods predicts new features in the band structure around the Fermi level [5], suggesting a possibility of high-temperature superconductivity without any doping. However, it must compete with instabilities such as the charge density wave (CDW) and the spin density wave (SDW), because the fullerene molecules form an one-dimensional crystal inside the tube. The C_{60} or C_{70} molecular orientation is another important freedom. In the case of solid C_{60}, it is known that the C_{60} exhibits quasi-free rotation at each lattice site; thus the solid C_{60} is a plastic crystal at room temperature (T). When T is lowered, an orientational ordering phase transition is shown at 261 K. On the other hand, the molecular rotation in solid C_{70} is very anisotropic, and the phase transition related to the molecular rotation occurs successively at 280 K and 340 K. The difference between the two molecules in the phase transition is ascribed to the molecular shape: the C_{60} is approximated to a sphere with a mean diameter of 0.71 nm while the C_{70} can be likened to a rugby ball with a short axis of 0.712 nm and a long axis of 0.796 nm.

In the present studies [6], we performed powder X-ray diffraction (XRD) measurements of the C_{60}- and C_{70}-peapods in a temperature range between 300 K and 1000 K to clarify the structural aspects. The XRD experiments were performed at **BL02B2** of SPring-8 and BL1B of PF. Figure 2 shows examples of the observed XRD patterns taken at room temperature (RT). Although the peaks are assigned to a two-dimensional triangular lattice in the bundles of SWNTs, each Bragg peak is significantly broadened due to the small coherent length, ~20 nm. For this reason, the XRD peak profiles are strongly modulated by the form factors of the tubes and fullerene molecules. We notice a large depression of 1 0 peak intensity around Q~6 (1/nm) on the encapsulation. This is a common feature associated with gas adsorption inside SWNTs [7].

The other important feature is the appearance of new peaks indicated by arrows in Fig. 2 in the encapsulation. These peaks are assigned to the one-dimensional crystals of fullerene molecules inside the tubes. The C_{60} intermolecular distance is estimated to be 0.97 nm. In the case of C_{70}, interestingly, there are two different intermolecular distances, 1.0 nm and 1.1 nm, which correspond to two molecular configurations of standing and lying alignments inside the tubes, respectively (Fig. 2).

Figure 3 shows the thermal expansion of intermolecular distances. Although the C_{60}-peapods showed complicated behavior depending on the sample treatment, careful measurements strongly suggested that the intrinsic thermal expansion is substantially smaller than those for the

solid C_{60} and for the C_{70}-peapods. Along with the rather short C_{60}-intermolecular distance of 0.97 nm, the inside of the tubes is found to be some novel environment for the C_{60} molecules. On the other hand, the C_{70}-peapods with the standing alignment show a large thermal expansion coefficient of the intermolecular distance, indicating that thermally activated C_{70}-stumbling occurs inside the tubes above 300 K. The absence of a clear phase transition in solid C_{70} is probably due to the one-dimensionality of the C_{70}-crystal.

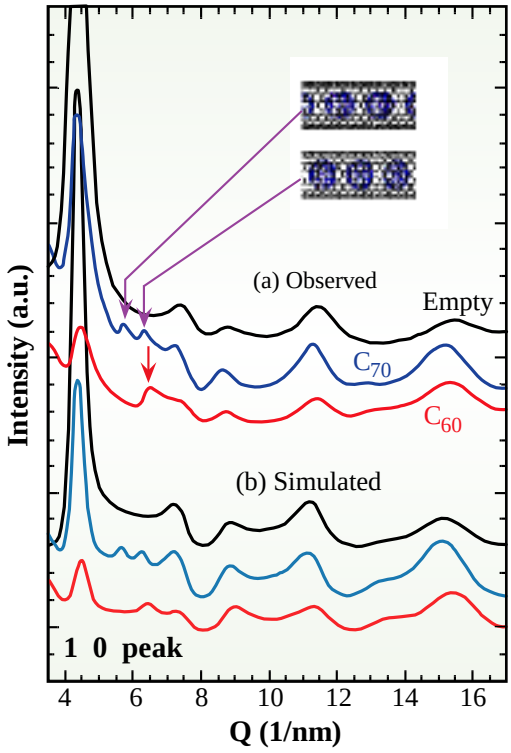

Fig. 2. The observed and simulated XRD patterns for empty SWNTs, C_{60}- and C_{70}-peapods.

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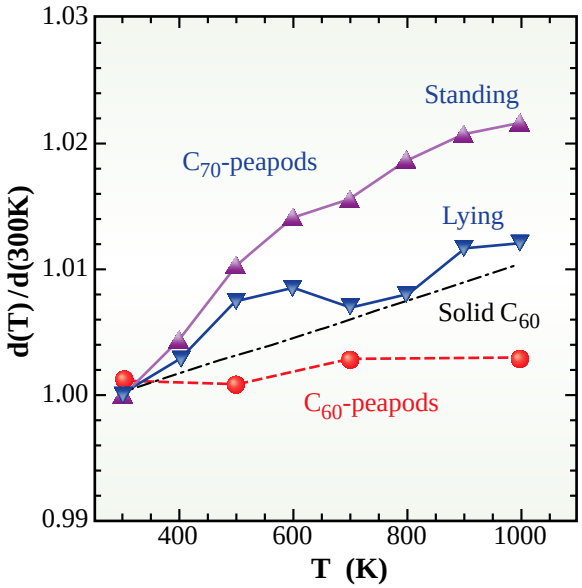

Fig. 3. Intermolecular distance of C_{60}- and C_{70}-peapods, normalized at 300 K, as a function of temperature.

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