

Electron diffraction study of one-dimensional crystals of fullerenes

K. Hirahara,^{1,*} S. Bandow,¹ K. Suenaga,¹ H. Kato,² T. Okazaki,² H. Shinohara,² and S. Iijima^{1,3,4}

¹*Nanotubulites Project, Japan Science and Technology Corporation, c/o Department of Materials Science & Engineering, Meijo University, 1-501 Shiogamaguchi, Tenpaku-ku, Nagoya 468-8502, Japan*

²*Department of Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan*

³*NEC Corporation, 34 Miyukigaoka, Tukuba 305-8501, Japan*

⁴*Department of Materials Science & Engineering, Meijo University, Nagoya 468-8502, Japan*

(Received 9 April 2001; published 29 August 2001)

A variety of fullerene molecules are found to be fully packed in the interior space of a single-wall carbon nanotube (SWNT) and form a novel one-dimensional crystal with a regular intermolecular distance. Using electron diffraction, we have successfully measured the “lattice constants” for these crystals of various fullerenes and found that the intermolecular spacing of adjacent fullerenes in SWNTs is smaller than that of the three-dimensional bulk crystal but larger than that of polymerized crystal. It is also revealed that elongated fullerenes with a certain aspect ratio [such as C₇₀ and C₈₀(D_{5d})] exhibit polymorphic packing structures with different intermolecular distances due to their constrained orientations with respect to the tube axis. The packing orientations of elongated fullerenes strongly depend on the diameter of the host nanotube.

DOI: 10.1103/PhysRevB.64.115420

PACS number(s): 61.14.Lj, 61.48.+c, 81.05.Tp

INTRODUCTION

After finding the empty hollow carbon nanotubes,¹ filling of the interior space of a carbon nanotube has been reported by one of the present authors² and has been occasionally studied by others.^{3,4} More recently C₆₀ molecules and other materials were found to be engaged inside single-wall carbon nanotubes (SWNTs).⁵⁻⁷ Such a hybrid structure of fullerenes and SWNTs should be of dual interest in realizing truly a one-dimensional crystal of fullerenes in a limited nanometer-sized space. First, the molecular interaction between adjacent fullerene molecules can be affected by the interaction with the surrounding nanotube, and therefore specific arrangements of fullerene molecules are envisioned within SWNTs. Second, the regular arrangement of fullerene molecules inside a SWNT will modify the host SWNT electronically and mechanically. Therefore the hybrid structures may open up a new area of SWNTs in both science and industrial applications.

The low filling rate of fullerenes was an obstacle in characterizing the hybrid structures. This difficulty has been overcome recently by using the vapor-phase reaction by our group,⁹ and we have succeeded in preparing fullerene-encapsulated SWNTs with extremely high filling ratio.⁸⁻¹⁰ This allows us to make electron-optical measurements with enough statistics and therefore to discuss more detailed analysis on the nature of fullerene-encapsulated nanotubes. In the present study, we employ the electron diffraction method to characterize the one-dimensional fullerene crystals formed in the interior spaces of SWNTs. The experimental results are then analyzed in terms of a Fourier transform of a simple model for the linear arrangement of fullerene molecules. Our filling method is not limited to empty fullerenes such as C₆₀, C₇₀, and higher fullerenes C_n ($n=76, 78, 80, 82,$ and 84), but also endohedral metallofullerenes M₁@C_n [$M=\text{Gd}$ (Ref. 9), Sc, Sm, and La, etc.]. The present paper reports structural details of such hybrid structures.

EXPERIMENT

Fullerene-encapsulated SWNTs were prepared by doping fullerenes into the central hollows of SWNTs in the vapor-phase reaction. Various higher fullerenes and endohedral metallofullerenes were produced and purified by the method reported.¹¹ The purity of these fullerenes was more than 99.8% as revealed by LD time-of-flight (TOF) mass spectrometry. SWNTs used in this study were produced by pulsed Nd:YAG (YAG denotes yttrium aluminum garnet) laser vaporization of a graphite target containing Fe and Ni in pure Ar buffer gas at 1200 °C.¹² After purifying SWNTs by refluxing in HNO₃ for 8 h,¹³ they were heated in dry air at 420 °C for 20 min in order to open their tips. The treatment is essential for efficient filling of fullerene in SWNTs.⁹ Throughout the present experiments, care was taken with using the SWNTs from the same batch of the doped specimens, so that the size distribution of the SWNTs was kept constant. The average diameter of the SWNTs was about 1.43 nm.¹⁴ The SWNTs prepared in this way were vacuum-sealed together with fullerenes in a Pyrex glass tube and subsequently heated at 400–500 °C for more than 24 h.⁸ Here the temperature was set at slightly higher than the sublimation temperatures of fullerenes.¹⁵ The products were sonicated in hexane and collected on specimen grids for transmission electron microscope (TEM) observation. An electron microscopic study was performed with a JEM-2010F electron microscope at an acceleration voltage of 120 kV with the spatial resolution of about 0.14 nm.

RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show a high-resolution transmission electron microscope (HRTEM) image of a typical fullerene-encapsulated nanotube and its schematic illustration, respectively. The inside fullerenes are C₆₀, and therefore (C₆₀)_n@SWNT. Two parallel dark lines in Fig. 1(a) correspond to the wall of a SWNT parallel to the incoming

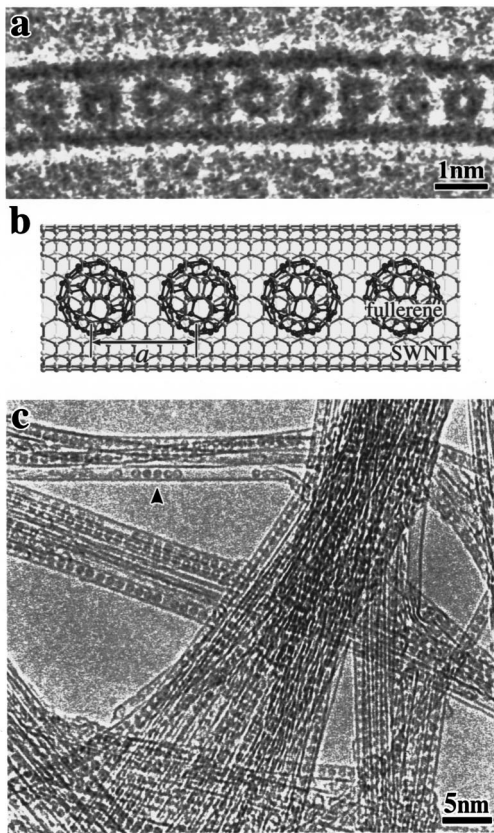


FIG. 1. (a) HRTEM image and (b) its schematic illustration of an individual fullerene-encapsulated single-walled carbon nanotube $[(C_{60})_n@SWNT]$, the so-called peapod. (c) A general view of the fullerene-encapsulated nanotubes of $(Sc_2C_{84})_n@SWNTs$.

electron-beam direction, and the space between the lines is an empty and hollow region. Ring-shaped objects are attributed to individual C_{60} molecules and they are aligned almost linearly along the tube axis. Figure 1(c) is a typical HRTEM image of $(Sc_2C_{84})_n@SWNTs$, demonstrating fully packed fullerene molecules inside the individual SWNTs even at the central portion of the bundle. Since the inside fullerenes seem to be spaced quite regularly with a certain distance, an average intermolecular distance can be measured by examining many such electron microscope images with a ruler.

Although the fullerene spacing seems quite regular in the HRTEM image, an alternative and more precise way to measure the intermolecular distance is to use the electron diffraction method, which is suitable for examining periodic microstructures in local areas. A HRTEM image from a part of a single bundle of $(C_{60})_n@SWNTs$ and its selected-area electron-diffraction pattern are shown, respectively, in Figs. 2(a) and 2(b). Several diffuse streaks (arrowhead positions) together with a typical electron diffraction pattern from the SWNT bundle are seen in the direction perpendicular to the bundle axis. It should be noted that the streaks are not present in the electron diffraction pattern taken from the bundle of empty SWNTs [see Fig. 2(d) for the image and 2(e) for the electron diffraction pattern in Fig. 2(b)]. Accordingly these streaks are caused undoubtedly by a regular arrangement of the fullerenes in individual SWNTs. Its validity

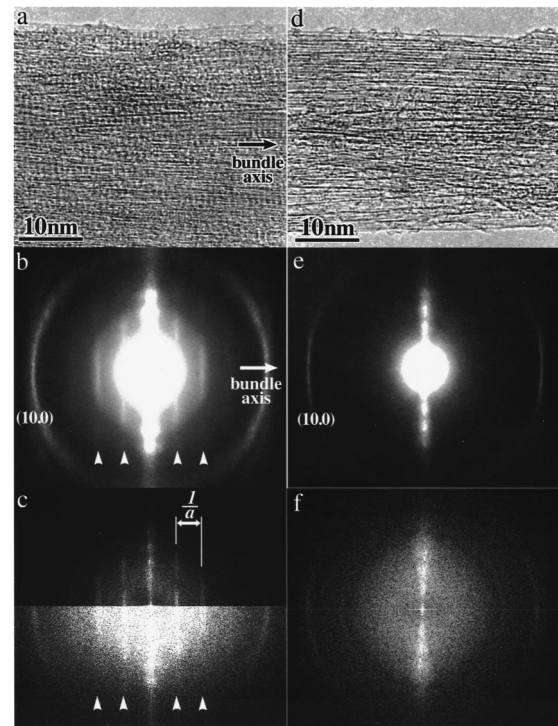


FIG. 2. (a) HRTEM image from a part of the $(C_{60})_n@SWNT$ bundle. Interior spaces of the SWNT are almost fully packed with fullerenes. (b) Electron diffraction pattern corresponding to the bundle shown in (a). In addition to a typical diffraction pattern of an empty SWNT bundle in (e), several streaks appear perpendicular to the bundle axis and align with regular spacing. These streaks are associated with the linear arrangement of fullerenes in individual SWNTs. (c) An optical diffraction pattern (Fourier transform) of (a). Some streaks also appear as seen in (b). (d) HRTEM image from a part of the empty SWNT bundle. (e) Electron-diffraction pattern corresponding to the bundle shown in (d). (f) An optical diffraction pattern (Fourier transform) of (d).

is proved by the similar streaks appearing in an optical diffraction pattern [Fourier transform of Fig. 2(a)] as shown in Fig. 2(c), but not in Fig. 2(f) [Fourier transform of Fig. 2(d)].

Following a simple diffraction theory describing that a linear array of points gives rise to a set of regularly spaced lines in its Fourier transformation, a set of streaks appearing periodically in the reciprocal space imply a regular arrangement of fullerene molecules. Namely, a set of fairly sharp streaks with a regular separation ($1/a$) in the diffraction pattern tell us that the fullerene molecules align periodically with a constant spacing a along the tubular axis. It is emphasized here that the linear array of the fullerene molecules can be considered as an almost ideal one-dimensional (1D) molecular crystal, which is suspended in a nearly free space with some interaction with a surrounding wall of the host SWNT. More structural details of the fullerene-encapsulated carbon nanotubes will be discussed in terms of electron diffraction analysis.

It should be remembered that the observed diffraction patterns also involve the contribution of fullerene cage shape. Since each lattice point of a 1D C_{60} crystal consists of a

TABLE I. Intermolecular spacings of various fullerenes in interior of the SWNT.

Fullerene (symmetry)	Intermolecular spacing of adjacent fullerenes (nm)		
	In 1D crystal inside SWNT	In bulk 3D crystal	In polymerized crystal
C ₆₀	0.97±0.02	1.002 ^a	0.91 ^b
C ₇₀	1.02±0.04	1.044 ^c	
C ₇₈ (C _{2v})	1.00±0.02		
C ₈₀ (D _{5d})	1.08±0.04		
C ₈₂ (C ₂)	1.10±0.03	1.14 ^d (toluene present)	
Gd@C ₈₂	1.10±0.03 ^e		
La@C ₈₂	1.11±0.03		
C ₈₄ (mixture of D ₂ +D _{2d})	1.10±0.03	1.12 ^f	
Sc ₂ @C ₈₄	1.10±0.03	1.12 ^g	

^aReference 16^bReference 21^cReference 17^dReference 18.^eReference 9.^fReference 19.^gReference 20.

spherical shell of fullerene, the feature of the streak is indeed modulated by the Bessel function.¹⁶ Caution should be taken because the discrete intensity distribution within the streak lines does not always imply the cross-talking among the tubes in a bundle (it is even misleading to the ordering of fullerenes along the direction perpendicular to the bundle axis) but is likely due to the convolution of the lattice points and the fullerene cage shape.

From the separation between adjacent streaks in electron-diffraction patterns recorded from single bundles of C₆₀ fullerene-encapsulated SWNTs, we estimate an average intermolecular distance a of inside fullerenes. Table I summarizes the intermolecular distances obtained experimentally from various fullerenes encapsulated into SWNTs, and the values are compared with known intermolecular distances for those corresponding to the bulk fullerene crystals. One can find that intermolecular distances for most of the fullerenes encapsulated in SWNTs are smaller than those in the bulk crystals. For example, the distances for (C₆₀)_n@SWNT and (C₇₀)_n@SWNT are 0.97±0.02 and 1.02±0.04 nm, respectively, which are about 3% smaller than those for the bulk crystals.^{17,18} Moreover, the intermolecular distance for 1D C₆₀ in a SWNT is about 4% larger than those reported for the polymerized C₆₀ crystal.²² Since the graphitic tube wall surrounds a chain of fullerenes, an interaction between fullerenes and the tube wall is expected in all of the (fullerene)_n@SWNT. The degree of the interaction will be dependent on the tubule diameters for a given a fullerene size. One of the reasons for smaller intermolecular distances in SWNTs would be some charge transfer from fullerene molecules to SWNT, which might cause small distortion to the host SWNTs. Detection of the distortion is beyond the capability of our electron optical technique. In this regard Raman spectroscopy on those hybrid nanotubes is now under way in our laboratory. For the higher fullerenes

of C₈₂ including its metallofullerenes, a measurable difference among their intermolecular distance was found and was constantly 1.10±0.03 nm except for the La@C₈₂ metallofullerene. The intermolecular distance for La@C₈₂ in SWNTs is slightly larger than those of others but it will be within the error.

The filling of fullerenes into SWNTs is restricted to some obvious reasons such as diameters of SWNTs and a degree of opening of tubes. Smaller nanotubes below the diameters of fullerene molecules are no way to encase the fullerenes but it is of interest to know what the threshold size is for a given diameter of a fullerene molecule. It is also essential for the fullerene molecules to be able to find in the entrance on the tube, which depends on the processing for the doping. Other reason is morphological defects of the SWNTs such as sharp kinks on the tubes and stuffed inclusions in the hollows of the tubes. Keeping those filling parameters in mind, we have tried to improve the filling rate as high as possible, and looked for those parameters on electron diffraction effects.

In the following section we examined packing morphologies of fullerene molecules in the SWNTs. The SWNT indicated by an arrow in Fig. 1(c) is not fully filled with fullerene molecules, but a few fullerene molecules appear to be clustering. This is one of common observations on partially filled fullerene molecules, which tend to coagulate and to form a cluster. It is noted that even in a short chain of fullerenes the intermolecular distance is similar to that of fully extended chains. This is not surprising because the intermolecular distance between the adjacent fullerenes can be reduced mainly by the total energy gain in the hybrid system due to the optimized interaction between fullerene and SWNT for individual fullerene molecules. Because of such interaction, the fullerene-packed region in SWNT shows a lower potential than the empty region; this potential barrier results in the

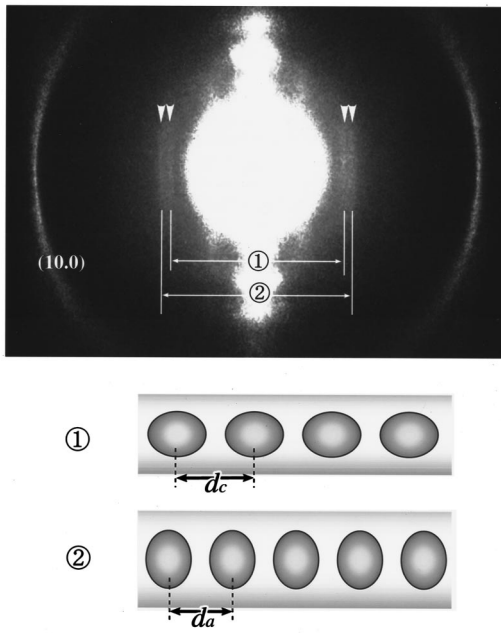


FIG. 3. An example of diffraction pattern of the bundle of $(C_{70})_n@SWNT$ and a schematic illustration for two kinds of dominant orientations of fullerene molecules in SWNTs, depending on the tubule diameter. In the diffraction pattern, streaks split to ① and ②, corresponding to the distances 1.10 and 1.01 nm, respectively.

attractive force between the adjacent fullerenes, working as pressure for individual fullerenes in any number of fullerene clusters.²³ Hence the electron diffraction pattern from such clusters does not affect much the positions of the diffuse lines corresponding to the intermolecular distance.

Broader diffraction streaks as compared with those observed for $(C_{60})_n@SWNT$ have been confirmed in the fullerenes with higher aspect ratio (namely, without a perfectly spherical shape) such as $C_{70}(D_{5h})$ or $C_{60}(D_{5d})$ (Ref. 24) (like rugby-ball-shaped fullerenes). This fact means that such elongated fullerenes align with random orientation in an entire bundle and therefore that their intermolecular distances slightly vary with the orientations of the adjacent molecules. However, in $(C_{70})_n@SWNT$, we often find in its diffraction pattern (Fig. 3) that the streaks split into two lines as indicated by the arrowhead, suggesting that there are two different dominant values for the intermolecular spacing, 1.10 and 1.01 nm. Here we note that the difference between the two spacings is almost equal to the difference between a - and c -axis diameters of C_{70} (0.086 nm). Therefore this splitting can be attributed to the difference between a - and c -axis diameters of C_{70} (shorter and longer diameters), proving that two types of preferred orientation exist for the C_{70} alignment in SWNTs. The distances of these two types of orientations correspond to d_a and d_c in Fig. 3, which are explained by taking into account the distribution of the tube diameter. Namely the tube diameter may restrict an inserting direction of rugby-ball-like molecule. Therefore, C_{70} molecules should take a certain orientation inside the specific SWNT. For example, in a smaller diameter tube, the c axis of C_{70} should be parallel to the tube axis.

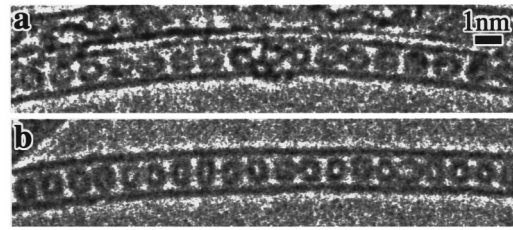


FIG. 4. HRTEM images of two kinds of individual $(C_{80})_n@SWNT$. In these SWNTs, the spacings between adjacent molecules are almost regular for each (~ 1.15 and 1.01 nm), and the diameters of these SWNTs were 1.29 and 1.43 nm, respectively. This suggests that C_{80} molecules have a preferred orientation, being the direction of smaller or longer diameter parallel to the tubule axis similar to ① and ② in Fig. 3.

For $(C_{80})_n@SWNT$, the anisotropy of the packing is also seen as shown in Fig. 4. In Fig. 4(a) the C_{80} molecules are aligned in the SWNT with the c (longer) axis parallel to the tube axis, while they are aligned with the c axis perpendicular to the tube axis in the Fig. 4(b). This variation must be due to the difference of the host nanotube diameter. The SWNT in Fig. 4(a) with 1.29 nm diameter, should be slightly small for the C_{60} longer diameter (c axis). Although, in a larger tube, each C_{80} molecule seems to be oriented randomly [in Fig. 4(b), with 1.43 nm diameter], the separations between adjacent molecules are 1.0 nm and almost constant, which is equal to d_a (1.01 nm) in Fig. 3 for both $C_{70}(D_{5h})$ and $C_{80}(D_{5d})$. This suggests that C_{80} molecules have also a preferred orientation being the direction of smaller diameter parallel to the tubule axis, and the fullerenes can only rotate on the tubule axis. Although d_a is slightly larger than C_{60} - C_{60} intermolecular distance in the SWNT, the diameters of $C_{70}(D_{5h})$ and $C_{80}(D_{5d})$ along the a axis are the same as that of C_{60} . This fact suggests the difference of intermolecular interaction between C_{60} molecules and C_{70} or C_{80} molecules.

The orientation anisotropy of fullerene molecules in SWNTs satisfied the close-packing arrangement. Moreover, a recent total energy calculation for the hybrid fullerene-SWNT system suggested an energetically stable state of fullerene molecule in the SWNT.²⁵ Therefore, we infer that a completely aligned fullerene crystal with a fixed orientational direction is possible by controlling the diameter of the host nanotube.

CONCLUSION

One-dimensional crystals of a variety of fullerenes encapsulated in the SWNT were characterized by HRTEM, optical method, and electron-diffraction pattern measurements. The electron diffraction pattern is interpreted as a mixture of an ordinary pattern from the “empty” SWNT bundle with a set of diffused streaks perpendicular to the bundle axis. These streaks originate from the linear alignment of fullerene molecules with the structure factor convolution associated with both the shape of a fullerene molecule and its linear arrangement in SWNTs. Therefore the streaks are direct evidence for periodically aligned fullerenes in individual SWNTs with a quite regular spacing. The results indicate that the intermolecular distances of fullerenes in SWNTs are considerably

smaller than those of the bulk crystal of fullerenes, suggesting a subtle competition between two kinds of interactions, namely, the fullerene-fullerene and fullerene-tube interactions. This is unique to the one-dimensional crystalline fullerenes in SWNTs and has never been found in the three-dimensional bulk crystals. Especially for the fullerenes with a nonspherical shape such as C_{70} and C_{80} , two kinds of orientations in individual SWNTs are clearly distinguished in the present study. This also reveals the substantial fullerene-

tube interaction, which determines the orientation of these elongated fullerenes in the SWNT.

ACKNOWLEDGMENTS

The authors are grateful to Professor D. Tománek for discussions about the energetic stability of the present hybrid fullerene-SWNT system. H.S. thanks the JSPS Future Program on New Carbon Nano-Materials for financial support.

*Author to whom correspondence should be addressed. Electronic address: kaori_h@meijo-u.ac.jp

¹S. Iijima, *Nature (London)* **354**, 56 (1991).

²P. M. Ajayan and S. Iijima, *Nature (London)* **361**, 333 (1993).

³Y. Murakami, T. Shibata, K. Okuyama, T. Arai, H. Suematsu, and Y. Yoshida, *J. Phys. Chem. Solids* **54**, 1861 (1993).

⁴Y. Zhang, K. Suenaga, C. Colliex, and S. Iijima, *Science* **281**, 973 (1998).

⁵B.W. Smith, M. Monthieux, and D.E. Luzzi, *Nature (London)* **396**, 323 (1998).

⁶Y. Zhang, S. Iijima, Z. Shi, and Z. Gu, *Philos. Mag. Lett.* **79**, 473 (1999).

⁷J. Sloan *et al.*, *Chem. Phys. Lett.* **316**, 191 (2000).

⁸T. Okazaki *et al.*, *Proceedings of the 19th Fullerene Symposium*, p. 13 (2000).

⁹K. Hirahara *et al.*, *Phys. Rev. Lett.* **85**, 5384 (2000).

¹⁰K. Suenaga *et al.*, *Science* **290**, 2280 (2000).

¹¹H. Shinohara, *Rep. Prog. Phys.* **63**, 843 (2000).

¹²A. Thess *et al.*, *Science* **273**, 483 (1996).

¹³It was found by electron spin resonance that this purification procedure could reduce the concentration of the remaining catalytic Fe-Ni particles in the sample to be less than 100 ppm.

¹⁴The diameter distribution of the host nanotube was measured by

examining TEM images with a ruler.

¹⁵ C_{60} and C_{70} are known to sublime in vacuum at ~ 350 and 460°C , respectively. M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996), Chap. 5, and references therein.

¹⁶K. Suenaga, Ph.D. thesis, University of Tokyo (1994).

¹⁷M.S. Dresselhaus, G. Dresselhaus and P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996), Chap. 7, and references therein.

¹⁸D.L. Dorset and J.R. Fryer, *J. Phys. Chem. B* **101**, 3968 (1997).

¹⁹H. Kawada *et al.*, *Phys. Rev. B* **51**, 8723 (1995).

²⁰Y. Saito, T. Yoshikawa, N. Fujimoto, and H. Shinohara, *Phys. Rev. B* **48**, 9182 (1993).

²¹R. Beyers *et al.*, *Nature (London)* **370**, 196 (1994).

²² C_{60} - C_{60} distance in a polymerized crystal varies with their preparation conditions; for example at a certain high pressure, ~ 0.91 nm: R. Moret *et al.*, *Europhys. Lett.* **40**, 55 (1997).

²³D. Tománek (private communication).

²⁴C-R. Wang, T. Sugai, T. Kai, T. Tomiyama, and H. Shinohara, *Chem. Commun. (Cambridge)*, 557 (2000).

²⁵T. Ishii *et al.*, *Proceedings of the 19th Fullerene Symposium*, 2000, p. 72, and the present study.