PHYSICAL REVIEW B VOLUME 51, NUMBER 14 1 APRIL 1995-II

# Structural aspects of $C_{82}$ and $C_{76}$ crystals studied by x-ray diffraction

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(Received 7 November 1994)

A precession photograph of a $C_{82}$ single crystal cocrystallized with toluene shows a striking tenfold symmetry in the plane normal to its elongated ten-sided columnar axis. This pattern can be perfectly explained by superposition of ten domains systematically twinned and nearly equally distributed, each of which consists of a monoclinic lattice with $a=18.36$ Å, $b=11.36$ Å, $c=11.41$ Å $(a/c=1.609)$, and $\beta=108.07°$. Such extraordinary lattice parameters as its axial ratio $a/c$ nearly equal to the golden ratio $(\tau=1.61803\ldots)$ and monoclinic angle $\beta$ nearly equal to 108° result in a highly unusual twinning. A toluene-solvated $C_{76}$ is also found to have very similar structural features as $a=17.68$ Å, $b=11.08$ Å, $c=11.02$ Å $(a/c=1.604)$, and $\beta=108.10°$. Combining the previous results of pentane-solvated $C_{60}$ and $C_{70}$ by Fleming *et al.* which also crystallize into a monoclinic lattice, we have found that among all four fullerides the similarity with respect to the unit-cell shape, $a:b:c=\tau:1:1$ and $\beta=108°$, holds extraordinarily well within less than 1% accuracy regardless of kinds of fullerenes and solvents. We have also successfully analyzed these crystal structures with the space group $P2_1$ $(z=2)$ by assuming the $C_{82}$ or $C_{76}$ cage to be spherical, which can be driven from the "sphere packing model" previously proposed by Fleming *et al.* An *in situ* x-ray-diffraction experiment of the $C_{76}$ crystal upon heating reveals that the sublimation of toluene around 100 °C results in a fcc lattice formed purely by the $C_{76}$ molecules. This fact implies that the unusual monoclinic lattice of $C_{82}$ is also stabilized with intervening toluene molecules.

## I. INTRODUCTION

The closed-cage molecule characteristic of carbon fullerenes has stimulated considerable interest in its stable molecular as well as crystalline forms. Its dynamical rotations further provide a rich scheme of crystal structures and phase transitions. Extensive structural study has been carried out mainly on $C_{60}$ and its alkali fullerides[1] while the structure of other low-symmetry fullerenes is not well investigated. For the higher fullerenes $C_n$ with $n \geq 76$, it is not known even whether a stable crystalline state exists or what kind of structure is stabilized, because a producible pure sample is limited to an extremely small amount. From a structural point of view, the higher fullerenes provide excitement that unusual structures could be stabilized with the packing of their low-symmetry molecules and many isomers.

An unusual crystal system was reported even in the highly symmetric molecules $C_{60}$ and $C_{70}$ which were cocrystalized with *n*-pentane.[2] These single crystals exhibited remarkable tenfold symmetry recorded in an x-ray precession photograph reminiscent of the decagonal quasicrystal. The observed diffraction pattern could be explained by superposition of a twinned monoclinic lattice with its $a/c$ ratio and monoclinic angle nearly equal to the golden ratio and 108°, respectively. It is interesting to study why such a specially formed monoclinic lattice is stabilized and how the internal molecular symmetry affects the crystal symmetry. However, its crystal structure has not been well understood. Since the pure $C_{60}$ or $C_{70}$ crystal structure is known not to be monoclinic under any temperature or pressure conditions studied so far, the solvent molecule must play a role in stabilizing such a monoclinic structure. Therefore a crystal structure analysis is significantly needed to study the structural stability conditions.

In this paper we report observation of the similar, but more complete, tenfold symmetry resulting from the twinning of the monoclinic lattice of toluene-solvated $C_{82}$ and $C_{76}$. Also reported is finding of similarity with respect to the monoclinic unit cell among four fullerides, the previous $C_{70}$ and $C_{60}$ (Ref. 2) plus the present two cases. A crystal structure model of the present toluene-solvated $C_{82}$ and $C_{76}$ has been proposed to offer satisfactory agreement with the observed diffraction patterns. This study was carried out in the process of analyzing the crystal structure of La encapsulated in the $C_{82}$ cage as previously reported.[3]

0163-1829/95/51(14)/8723(8)/$06.00

## II. EXPERIMENT

Fullerenes containing $C_{82}$ and $C_{76}$ were extracted from carbon raw soot (type II VMC Ltd.) using $CS_2$. The isolation and purification was carried out by the recycled high-performance liquid-chromatography (HPLC) technique.[4] The purity was more than 99% for both $C_{82}$ and $C_{76}$. There are eight isomers of $C_{82}$ satisfying the isolated pentagon rule, but one of three isomers with the symmetry $C_2$ is found to be mainly produced.[5] In the case of $C_{76}$, only one isomer with the symmetry $D_2$ is produced among two isomers satisfying the isolated pentagon rule.[6] Both $C_2$-symmetry $C_{82}$ and $D_2$-symmetry $C_{76}$ have chirality with respect to the location of pentagons. in the present specimens no characterization was made of the chirality.

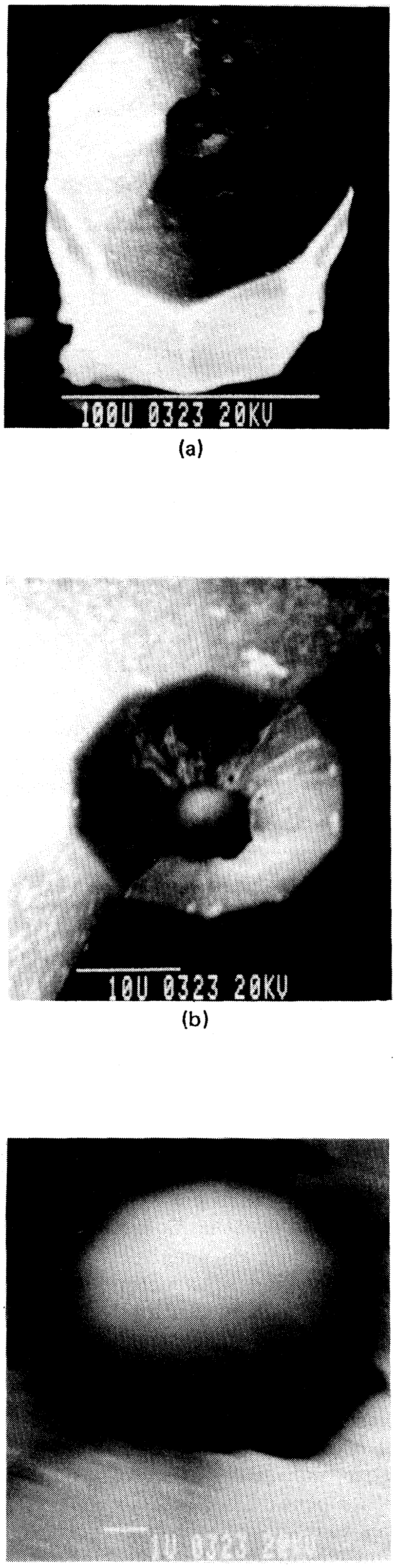
The powder sample of $C_{82}$ was further dissolved in toluene solution and slow evaporation successfully precipitated small cylindrically shaped single crystals. A close visual investigation of them revealed a remarkable ten-sided columnar structure as seen in the scanning electron microscope (SEM) photographs displayed in Figs. 1(a)–1(c) with different magnification. This crystal, whose size was about 100 $\mu$m in diameter and 300 $\mu$m in length, was used for an x-ray-diffraction experiment with a precession camera which was operated on an 18 kW rotating-anode station with a Cu target (MacScience MX-18). The Ni-filtered Cu-$K\alpha$ radiation (1.542 Å, 50 kV/200 mA) was collimated with a pinhole collimator 1.0 mm in diameter.

Fine powder samples of $C_{82}$ and $C_{76}$ prepared from toluene solution were used for synchrotron radiation x-ray experiments at the Photon Factory (2.5 GeV/350 mA, positron storage ring). We used a specially designed powder diffractometer for high-pressure research capable of detecting very weak signals from a tiny powder specimen efficiently with an imaging plate (IP).[7] Incident beams were monochromatized to the wavelength 1.100 Å with a sagitally focusing Si(111) double-crystal monochromator and collimated to 0.2 mm in diameter with a pinhole collimator on the beamline BL-6B. The powder sample, which was pressed to a disk shape 0.6 mm in diameter and 0.3 mm in thickness, was mounted either in a 10 K closed-cycle helium cryostat or in a furnace, depending on the temperature range investigated.

## III. EXPERIMENTAL RESULTS AND ANALYSIS

### A. $C_{82}$ single crystal

A precession photograph with a screen to select only the equatorial plane was taken for various geometries of the $C_{82}$ single crystal with the ten-sided column as shown in Fig. 1. Figure 2(a) displays a striking tenfold symmetry observed in the plane normal to its elongated columnar axis, which is assigned as the *b* axis, being parallel to its reciprocal axis $b^*$. Other principal reciprocal axes $a^*$ and $c^*$ are assigned to index the observed pattern as shown in the figure. In order to investigate periodicity along the *b* axis, we also took a similar photograph containing the *b* axis as shown in Fig. 2(b). One can see the



(a)

(b)

(c)

FIG. 1. SEM photographs of $C_{82}$ crystal grown from solutions in toluene. One can see its ten-sided columnar structure.

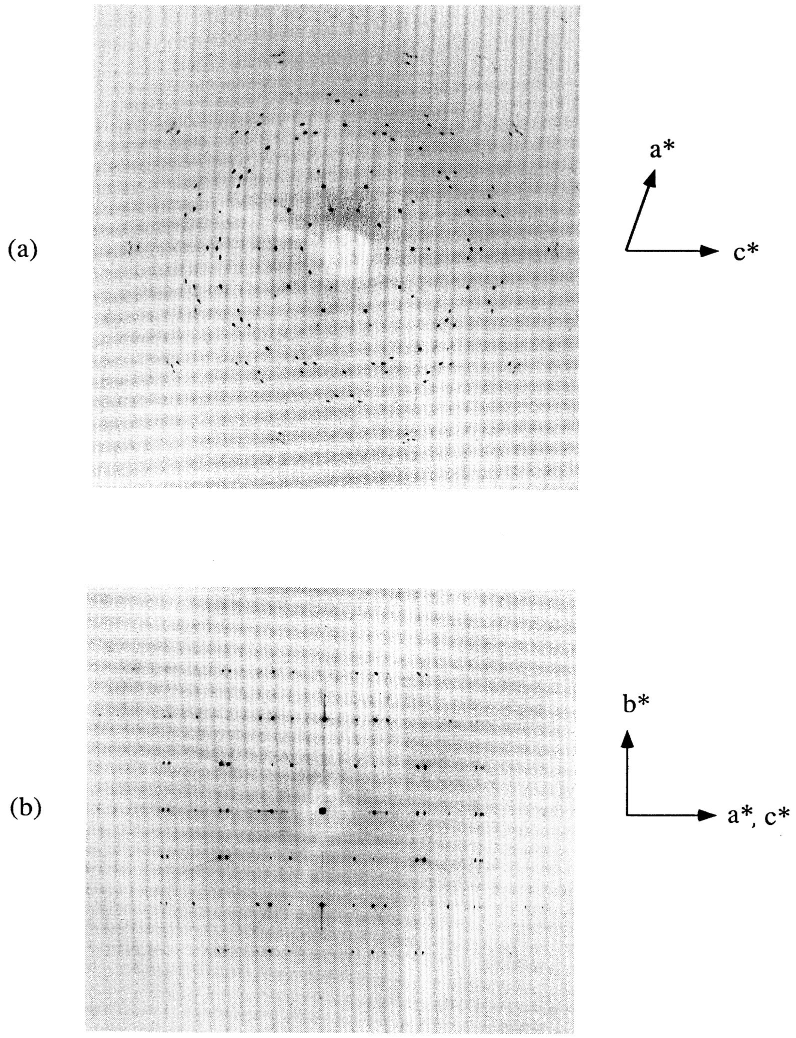


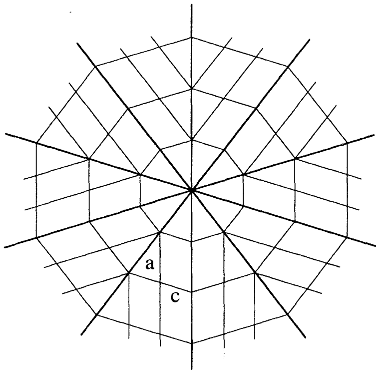
FIG. 2. Precession photographs of the $C_{82}$ crystal shown in Fig. 1. One can see (a) remarkable tenfold symmetry in the plane normal to its elongated, ten-sided columnar axis, along which the regular periodic spacing is observed as in (b).

twofold symmetry and a perfect periodicity along the $b^*$ axis. All diffraction spots are sharp enough to ensure the long-range order.

In Fig. 2(a) all diffraction spots lying on one of ten equivalent radially streaking principal axes can be classified into two series based on the distance measured from the origin, which is marked as the direct beam position. One group can be indexed as a multiple of $a^*$ and the other as a multiple of $c^*$ with the relation $c^*/a^*=1.618$. This fact directly leads to the formation of a two-dimensional monoclinic lattice with $a^*$ and $c^*$ making its monoclinic angle of $\beta^*=72°$ in reciprocal space. By rotating this monoclinic lattice every 36° around the origin, one can perfectly index all diffraction spots lying on any of ten domains. Thus the tenfold symmetry pattern can be understood by superposition of a twinned monoclinic lattice with its parameters as follows: $a^*=0.359$, $b^*=0.556$, $c^*=0.580$ Å$^{-1}$, and $\beta^*=72.0°$; $a=18.4$, $b=11.3$, $c=11.4$ Å, and $\beta=108.0°$. More accurate values are obtained from the present high-resolution powder diffraction experiment described in the following subsection. Figure 3(a) demonstrates schematic pieshaped domains formed by successive operation of twins which share the (100) twinning plane. Since the observed axial ratio $a/c=1.614$ and monoclinic angle $\beta=108.0°$ are close enough to the golden ratio ($\tau=1.61803\ldots$) and the inner angle of the pentagon ($3\pi/5$), respectively, such a successive operator for twin formation can be completed with satisfactory matching between the initial and final domains. This is also realized in the previously reported case of pentane-solvated $C_{60}$ and $C_{70}$ in which $\beta=107.7°$ and 107.70°, respectively.[2] Figure 3(b) is a superposition of ten reciprocal lattices connected with the twinning relation depicted in Fig. 3(a). Since the structure factor is not known, all reciprocal points are plotted without intensity variation. This pattern satisfactorily reproduces the observed one in Fig. 2(a). In particular, various clusters composed of several spots such as diamond-shaped and Y-shaped ones can be perfectly obtained.

In order to further check the reality of such a twinning formation, we successfully picked a major single domain (about 50 $\mu$m across and 100 $\mu$m in thickness) from the ten-sided column shown in Fig. 1(a) and took its precession photograph under exactly the same geometrical conditions as employed for Fig. 1(a). Figure 4 displays the

(a)



(b)

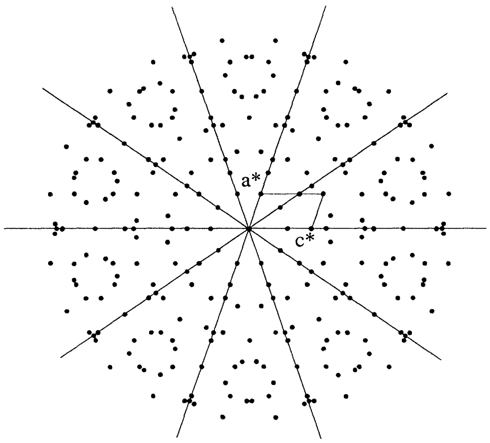


FIG. 3. (a) Ten monoclinic domains collected to form a ten-sided column. (b) The resultant reciprocal lattice equally contributed from them. This pattern is in very good agreement with the observed one shown in Fig. 2(a).

observed pattern in which the major diffraction spots come from a single domain, but some others from different minor domains not perfectly removed. This photograph clearly shows the $a^*$-$c^*$ monoclinic lattice as predicted. By using this crystal we found the extinction condition $(0k0)$ with $k$ odd. Therefore its space group is probably $P2_1$ or $P2_1/m$. A detailed structure analysis using a full set of intensity data is now under way on a four-circle diffractometer.[8]

### B. $C_{82}$ and $C_{76}$ powder

Debye-Scherrer photographs from powder samples were recorded on a flat IP. Figure 5 is raw data from the $C_{82}$ sample measured at room temperature. The exposure time was 28 min and the film distance was 254 mm for the wavelength 1.100 Å. One can see the intensity modulation in the radial direction due to the molecular form factor which is characteristic of a nearly spherically shaped macromolecule. The observed intensity along each ring is smooth enough to allow the following data processing of powder averaging. By using a computer program to integrate the intensity along rings,[7] we reduced this two-dimensional pattern into conventional one-dimensional data (intensity vs diffraction angle $2\theta$). The resultant data are plotted in Fig. 6(a). All diffraction peaks are well identified although the background is relatively high. By using the monoclinic lattice parameters tentatively obtained from the precession photographs as initial starting data, we carried out a least-squares fitting between the observed and calculated peak positions. The fitting with respect to the lattice spacing $d(hkl)$ was obtained extremely well as

$$R=\sum |d_{\text{cal}}(hkl)-d_{\text{obs}}(hkl)|/\sum d_{\text{obs}}(hkl)=0.0004$$

for a total of ten reflections when the set of lattice parameters tabulated in Table I was reached. The assigned diffraction indices are represented in Fig. 6(a).

We also carried out similar experiments for the $C_{76}$ powder sample. Its diffraction pattern observed at room temperature is shown in Fig. 6(b). One can see similarly between the two patterns (a) $C_{82}$ and (b) $C_{76}$ but the latter has the sharper peak width. The lattice parameters obtained by a least-squares fitting are also tabulated in Table I.

Since there was much more $C_{76}$ than $C_{82}$ available, we made an *in situ* x-ray-diffraction measurement by heating and cooling the $C_{76}$ sample to survey any phase transition and any effect of possible constituent solvent molecules. The temperature dependence of diffraction patterns in the process of heating from room temperature is shown in Fig. 7. A drastic change in the pattern is observed at 99 °C and further heating stabilizes a new structure giving a much simpler pattern. At 147 °C all diffraction peaks can be successfully assigned either to a major face-

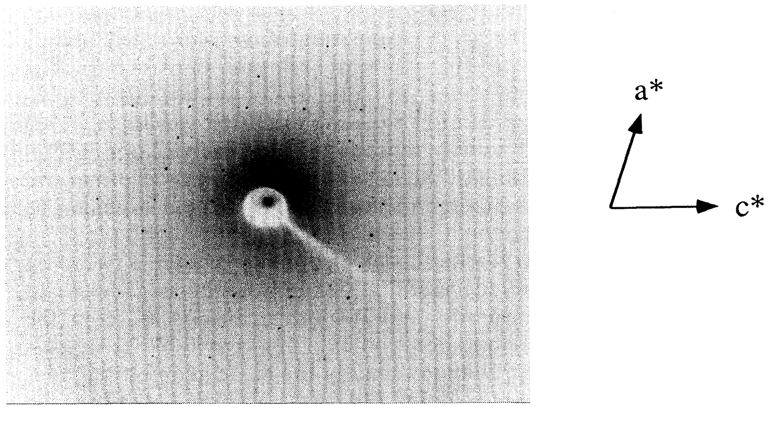


FIG. 4. Precession photograph of a single-domain $C_{82}$ crystal removed from the ten-sided columnarly structured crystal. One can clearly see a monoclinic reciprocal lattice as shown.

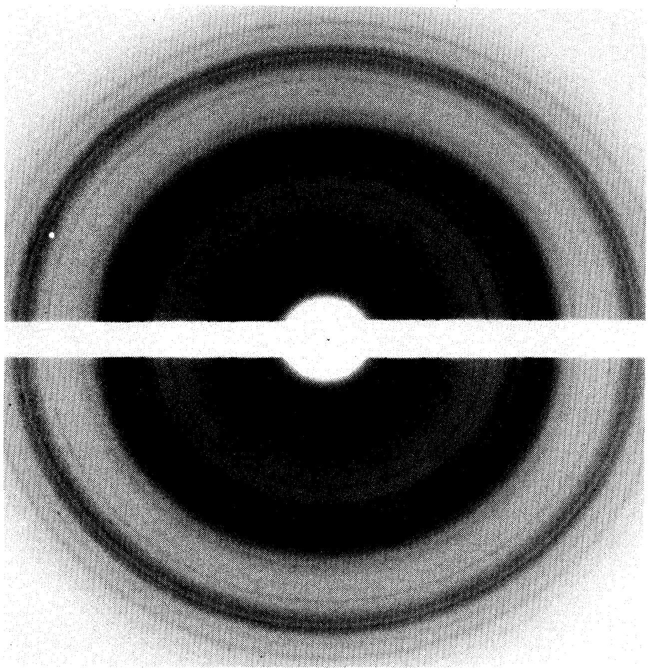


FIG. 5. Debye-Scherrer photograph of $C_{82}$ powder recorded with an imaging plate on the Photon Factory synchrotron source.

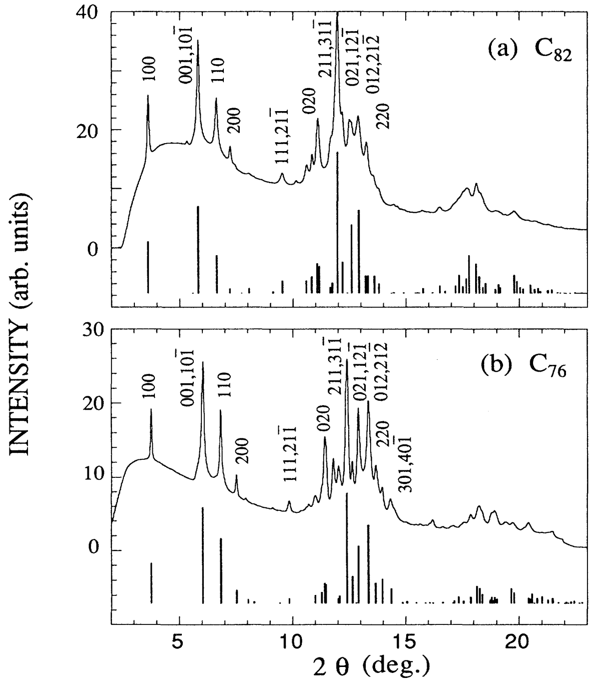


FIG. 6. Powder diffraction pattern indexed with monoclinic system of (a) $C_{82}$ and (b) $C_{76}$ grown from solutions with toluene. These patterns are obtained by integrating the Debye-Scherrer rings recorded with an imaging plate. One can see a remarkable resemblance between the two. Vertical bars represent the calculated intensity described in the text.

TABLE I. Monoclinic lattice parameters of fullerides forming unusual twins producing pseudotenfold symmetry. $\tau=(1+5^{1/2})/2=1.61803\ldots$ (golden ratio). The $a$ and $c$ axes in Ref. 2 are interchanged. Here we refer to the IUCr recommendation for $a > c$ and $b > 90°$ in a monoclinic system.

| Crystallographic data | Toluene-$C_{82}$ present | Toluene-$C_{76}$ present | Pentane-$C_{70}$ Ref. 2 | Pentane-$C_{60}$ Ref. 2 |
|---|---|---|---|---|
| $a$ (Å) | 18.355 | 17.684 | 17.33 | 16.5 |
| $b$ (Å) | 11.355 | 11.080 | 10.529 | 10.08 |
| $c$ (Å) | 11.410 | 11.018 | 10.618 | 10.14 |
| $\beta$ (deg) | 108.07 | 108.10 | 107.70 | 107.73 |
| $v$ (Å$^3$) | 2261 | 2052 | 1846 | 1606 |
| $a/c$ | 1.6086 | 1.6050 | 1.632 | 1.627 |
| $(a/c)/\tau$ | 0.9942 | 0.9919 | 1.009 | 1.006 |
| $b/c$ | 0.9952 | 1.0056 | 0.9916 | 0.9941 |
| $\Delta\beta=108°-\beta$ | −0.07 | −0.10 | 0.30 | 0.27 |

centered cubic (fcc) lattice or to a minor hexagonal close-packed (hcp) lattice, both of which coexist in this temperature range. This fcc-hcp mixed phase was found to be stable up to 300 °C. When the temperature decreased to room temperature, no transformation took place; therefore the structural change observed around 100 °C is irreversible, evidently due to the sublimation of toluene caught in the as-grown crystal. Therefore the present monoclinic lattice of both $C_{82}$ and $C_{76}$ must be stabilized with toluene molecules which are located at crystallographically regular positions. Figure 8(a) shows

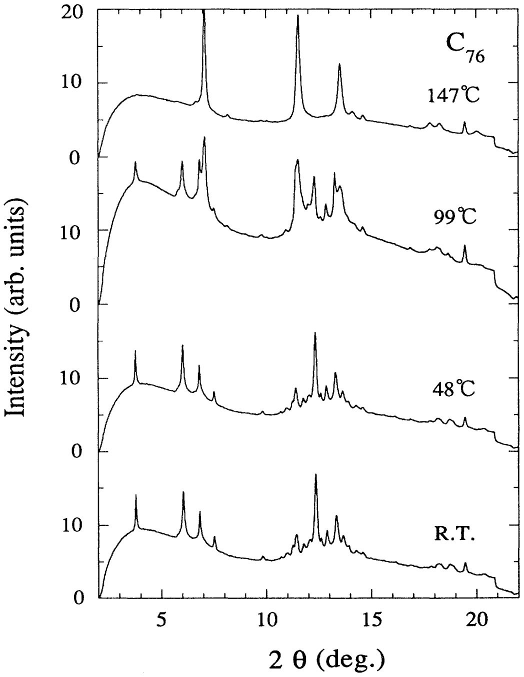


FIG. 7. Temperature dependence of powder diffraction patterns of $C_{76}$ in the process of heating. One can see a drastic change at 99 °C above which a fcc lattice is stabilized as observed at 147 °C.

the observed diffraction pattern from the fcc phase at room temperature after temperature decrease. Also shown in Fig. 8(b) is the calculated intensity assuming a dynamically rotating $C_{76}$ molecule at the fcc lattice sites with $a = 15.475$ Å. Its electron density is assumed to be uniformly distributed in a spherical shell with inner and outer radii of 3.47 and 4.47 Å, respectively. No contribution from toluene molecules is considered. The $R$ factor for the intensity fitting obtained is as good as 4.8% when the temperature factor is $B = 20$ Å$^2$, defined as intensity proportional to $\exp[-2B(\sin\theta/\lambda)^2]$. The curve in Fig. 8(c) is the molecular form factor calculated for the electron density distributed in a shell.

By using this fcc-hcp mixed sample, we also surveyed any change in diffraction pattern below room temperature down to 7.6 K. No appreciable change was detected except for the lattice contraction. Figure 9 summarizes the temperature dependence of the cubic lattice constant and the peak width of selected reflections both above and below room temperature in the whole temperature range presently investigated. By fitting a straight line to the data below about 450 K, we obtain the thermal expansion coefficient as $2.3 \times 10^{-5}$ K$^{-1}$, which is larger by a factor of 2 than that of the fcc $C_{60}$ crystal.[9]

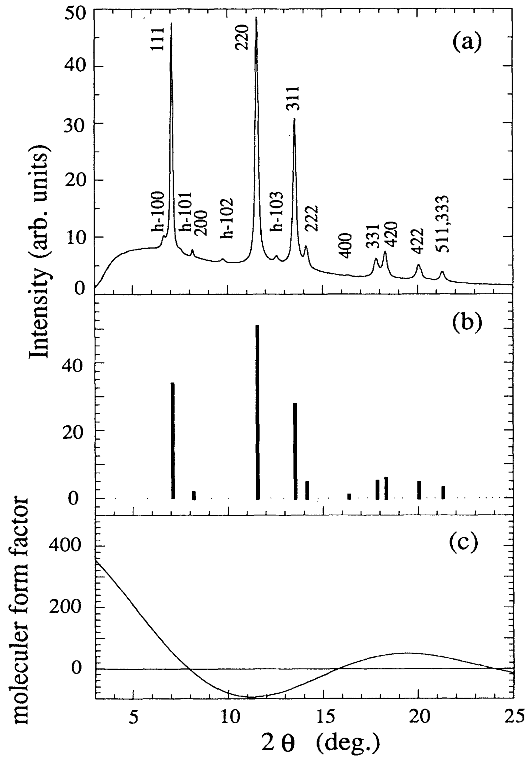


FIG. 8. (a) Diffraction pattern of the fcc $C_{76}$ at room temperature after it was cooled down from about 300 °C. A small portion of a hexagonal phase is also observed, as indexed with the symbol *h* preceding the diffraction index. The calculated intensity for the fcc phase is also shown in (b) by assuming a spherical shell of electron density which gives a molecular form factor as shown in (c).

## IV. DISCUSSION

### A. Monoclinic structure

In the present experimental study, we have determined the crystal lattice system (monoclinic) and lattice parameters of as-grown toluene-solvated $C_{82}$ and $C_{76}$, which form unusually systematic twins resulting in a remarkable tenfold symmetry in the diffraction pattern. In these fullerides as well as the previously reported pentane-solvated $C_{60}$ and $C_{70}$ that also form very similar twinning,[2] the internal molecular symmetry does not play a

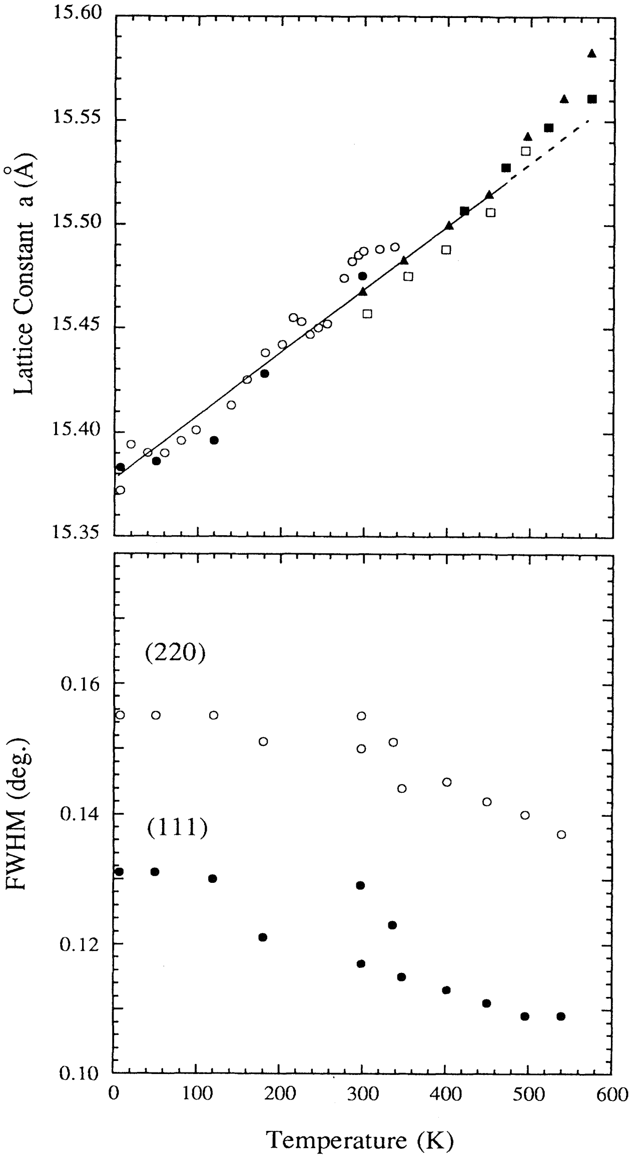


FIG. 9. Temperature dependence of lattice constant (top) and peak width of (220) and (111) reflections (bottom) in the fcc lattice of $C_{76}$. At the top the results obtained in several experimental runs are plotted. A straight line represents a least-squares fitting to data up to about 450 °C to evaluate the thermal expansion coefficient.

major role in crystallization because of the following facts evidenced in Table I. Among all four fullerides the similarity with respect to the monoclinic unit cell holds extraordinarily well within less than 1% accuracy. That is, $a:b:c=\tau$:1:1 and $\beta=108°$, where $\tau=(1+5^{1/2})/2=1.61803\ldots$ (golden ratio). Such a disappearance of each fullerene's character implies a dynamically rotating state so that it can be considered as an isotropic sphere. However, there is no experimental evidence for the dynamical rotation. On the other hand, such strongly elongated solvent molecules as toluene and *n*-pentane are unlikely to rotate freely.

According to the size of the molecules and the systematic change of unit-cell volume in Table I, there must be two fullerenes and probably two solvent molecules in a unit cell for all four fullerides. The present observation of diffraction conditions on the equatorial plane in precession photographs for toluene-$C_{82}$ suggests the space group $P2_1$ or $P2_1/m$. In the latter case, however, there are four molecules to be assigned in a unit cell. Therefore $P2_1(z=2)$ is most likely. It should be noted that this space group does not necessarily require spherical symmetry of the molecule. In the present experiment of toluene-$C_{76}$, we found that the sublimation of solvent molecules results in a completely different crystal lattice, fcc. Therefore the monoclinic structure must be stabilized by them as an intermolecular compound. It is extremely interesting to know how toluene or *n*-pentane, which are chemically and structurally quite different, coordinates the fullerene molecules around it and leads to the special monoclinic lattice.

Fleming *et al.*[2] proposed a sphere-packing model to explain how the monoclinic lattice can be made, but its structure has not been experimentally solved. The location of $C_{60}$ molecules in their model leads to the space group $C_2^2$-$P2_1$. In this space group the relevant atomic position is the 2*a* site having coordinates $(x,y,z;-x,y+\frac{1}{2},-z)$. By starting from their model, assuming the spherically shaped shell for the present $C_{82}$ fullerene, and assigning two toluene molecules in a unit cell, we carried out intensity calculations. The parameters assigned to present our simplified model are $(x_c,y_c,z_c)$ for the center of $C_{82}$ sphere with its inner $(r_i)$ and outer $(r_0)$ radii, $(x_t,y_t,z_t)$ for the center of the hexagon of toluene ($CH_3$- ⬡ ), and the orientation of the toluene molecule. Since we have not successfully subtracted the background from the observed patterns in Fig. 6, our present calculations offer a semiqualitative result. Figure 6(a) shows a comparison between the observed and calculated (vertical bars) intensities. The coordinates are obtained as follows:

$$x_c=0.28\ ,\quad y_c=0\ ,\quad z_c=0.14\ ,$$

$$x_t=0.11\ ,\quad y_t=0.44\ ,\quad z_t=0.57\ ,$$

$$r_i=3.95\ \text{Å}\ ,\quad r_0=4.45\ \text{Å}\ .$$

Regarding the orientation of toluene, we obtained good agreement when its hexagon surface lies on the *b* plane. Figure 10 displays the structure thus obtained projected on the *b* and *a* planes. This structure is surprisingly similar to that proposed by Fleming *et al.*[2] who however did not explicitly show the location of the solvent molecules. As they explained, this structure can be easily driven by alternately shifting the (001) basal plane of the fcc lattice (equivalent to the present *bc* plane) towards the [110] direction (equivalent to the present *c* axis) by one-half of its period. This operation results in the monoclinic lattice with $a:b:c=1.651$:1:1 and $\beta=107.63°$ and creates a channel extending along the *b* axis where the solvent molecules may be trapped. In the present preliminary structure analysis, the amount of shift is obtained as 0.5003, close enough to $\frac{1}{2}$ in the ideal sphere-packing model. By using a full set of intensity data collected from the single-domain crystal (Fig. 4), we are currently carrying out the structure refinement of this system in order to determine the molecular shape, i.e., the atomic coordinates of each carbon atom of both fullerene and toluene molecules. We also made similar intensity calculations for the present toluene-solvated $C_{76}$ as shown in Fig. 6(b).

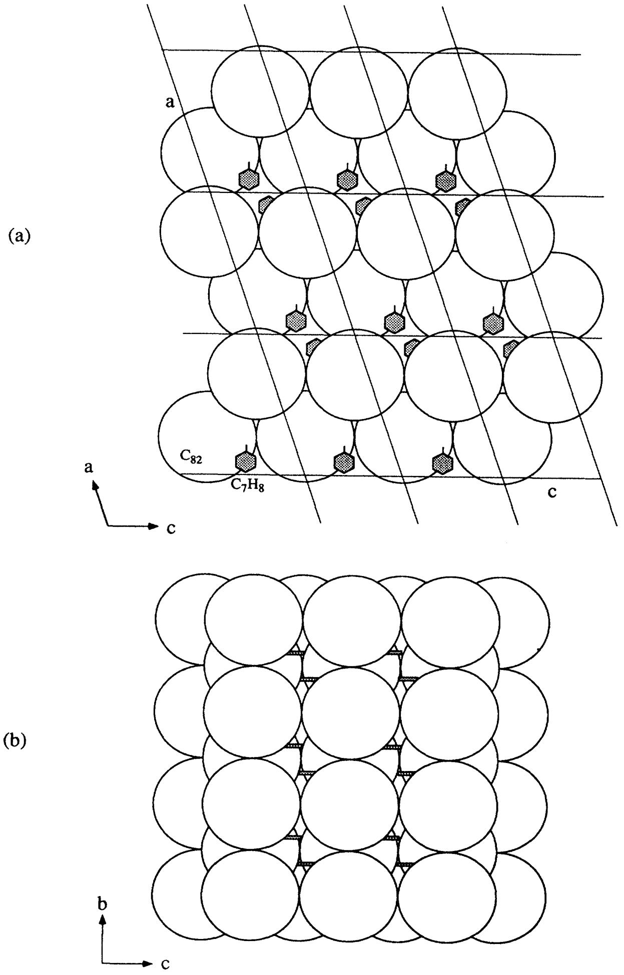


FIG. 10. Structural model obtained by the present preliminary analysis. Projection on (a) the *b* plane and (b) the *a* plane of the monoclinic system. This is very similar to the "sphere-packing model" previously proposed (Ref. 2).

In this case only the radii of the $C_{76}$ sphere are changed to $r_i = 3.75$ Å and $r_0 = 4.25$ Å. Reasonably good agreement between the observed and calculated intensities in both cases has led us to conclude that the "sphere-packing model" offers a key to understanding why a specially formed monoclinic lattice, resulting in the striking tenfold symmetry pattern due to twinning, is stabilized.

### B. fcc structure

The present study evidenced that pure $C_{76}$ molecules after toluene molecules are removed crystallize into a fcc lattice with $a = 15.475$ Å at room temperature. Such a structural change can be very reasonably explained by the sphere-packing model which is stabilized by intervening solvent molecules as described in the preceding subsection. The $C_{76}$ molecule has an approximately ellipsoidal form with its long and short axes 4.39, 3.79, and 3.32 Å, similar to $C_{70}$. Since a fcc lattice is highly isotropic, it is expected that the $C_{76}$ molecules are nearly freely rotating. However, we did not detect any significant change in diffraction patterns in the whole temperature range from 300 down to 7.6 K. All data can be completely analyzed by the fcc lattice. No extra peak appeared suggesting any lowering in symmetry. Even the internally highly symmetric $C_{60}$ undergoes a phase transition from fcc to the simple cubic system at 260 K. Therefore it is very unlikely that $C_{76}$ is in a rotational state at low temperatures. These facts imply that this fcc phase is realized as a statically orientationally disordered $C_{76}$ molecular arrangement at the fcc sites. According to a recent NMR study of the $C_{76}$ crystal after heat treatment at 200°C,[10] the molecule is rotating at room temperature and gradually slows down its rotation as the temperature decreases, without a drastic change suggesting any phase transition. This fact also implies a static disordered state with respect to the molecular orientation at low temperatures. If such a locally disordered state is realized, the lattice parameters must be significantly different per unit cell, which must lead to distribution of the lattice parameters through the crystal. As observed in Fig. 10, two typical reflections clearly show broadening of their peak width as the temperature decreases. This experimental fact implies the orientationally disordered state in the present case. More evidence might be further obtained by observation of diffuse scattering in x-ray scattering or residual heat capacity in specific-heat measurement.

## ACKNOWLEDGMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Area from the Ministry of Education, Science and Culture (No. 05233102).

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[1] See, for example, *The Fullerenes,* edited by H. W. Kroto, J. E. Fischer, and D. E. Cox (Pergamon, New York, 1993); J. Phys. Chem. Solids **54**, 1645 (1993), Special issue on physics and chemistry of fullerene-based solids II, edited by J. E. Fischer, Y. Maruyama, D. E. Cox, and R. N. Shelton.

[2] R. M. Fleming, A. R. Kortan, B. Hessen, T. Siegrist, F. A. Thiel, P. Marsh, R. C. Haddon, R. Tycko, G. Dabbagh, M. L. Kaplan, and A. M. Mujsce, Phys. Rev. B **44**, 888 (1991).

[3] H. Suematsu, Y. Murakami, H. Kawada, Y. Fujii, N. Hamaya, O. Shimomura, K. Kikuchi, Y. Achiba, and I. Ikemoto, *Novel Forms of Carbon II,* MRS Symposia Proceedings No. 349 (Materials Research Society, Pittsburgh, 1994), p. 213.

[4] K. Kikuchi, N. Nakahara, T. Wakabayashi, M. Honda, T. Moriwaki, S. Suzuki, H. Shiromaru, K. Saito, K. Yamauchi, I. Ikemoto, and Y. Achiba, Chem. Phys. Lett. **188**, 177 (1992).

[5] K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, and Y. Achiba, Nature **357**, 142 (1992).

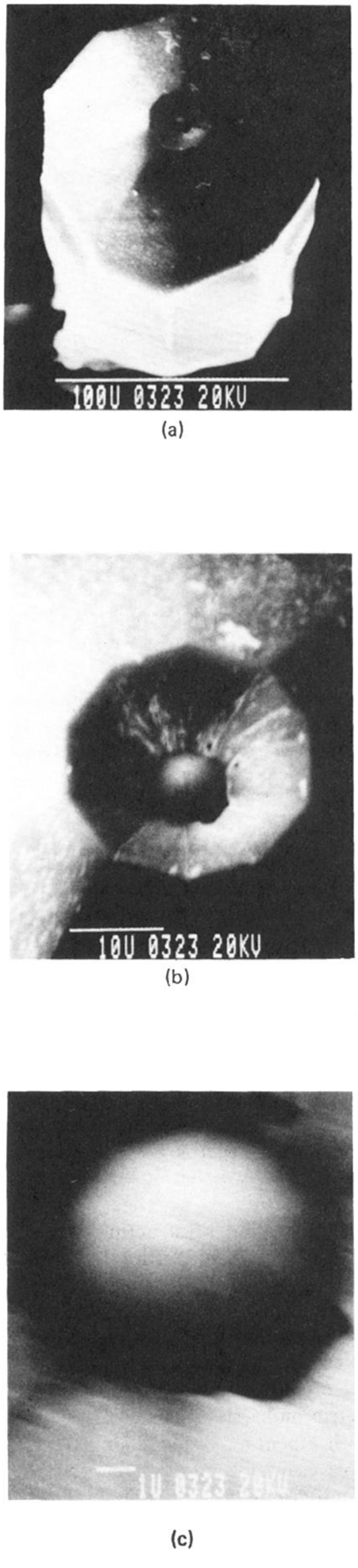
[6] R. Ettl, I. Cho, F. Diederich, and R. L. Whetten, Nature **353**, 149 (1991).

[7] O. Shimomura, K. Takemura, H. Fujihisa, Y. Fujii, Y. Ohishi, T. Kikegawa, Y. Amemiya, and T. Matsushita, Rev. Sci. Instrum. **63**, 967 (1992).

[8] H. Kawada, Y. Fujii, H. Nakao, K. Tanaka, Y. Murakami, T. Watanuki, H. Suematsu, K. Kikuchi, Y. Achiba, and I. Ikemoto (unpublished).

[9] Obtained from the $C_{60}$ data in W. I. F. David, R. M. Ibberson, T. J. S. Dennis, J. P. Hare, and K. Prassides, Europhys. Lett. **18**, 219 (1992).

[10] Y. Maniwa *et al.* (private communication).



(a)

(b)

(c)

FIG. 1. SEM photographs of $C_{82}$ crystal grown from solutions in toluene. One can see its ten-sided columnar structure.

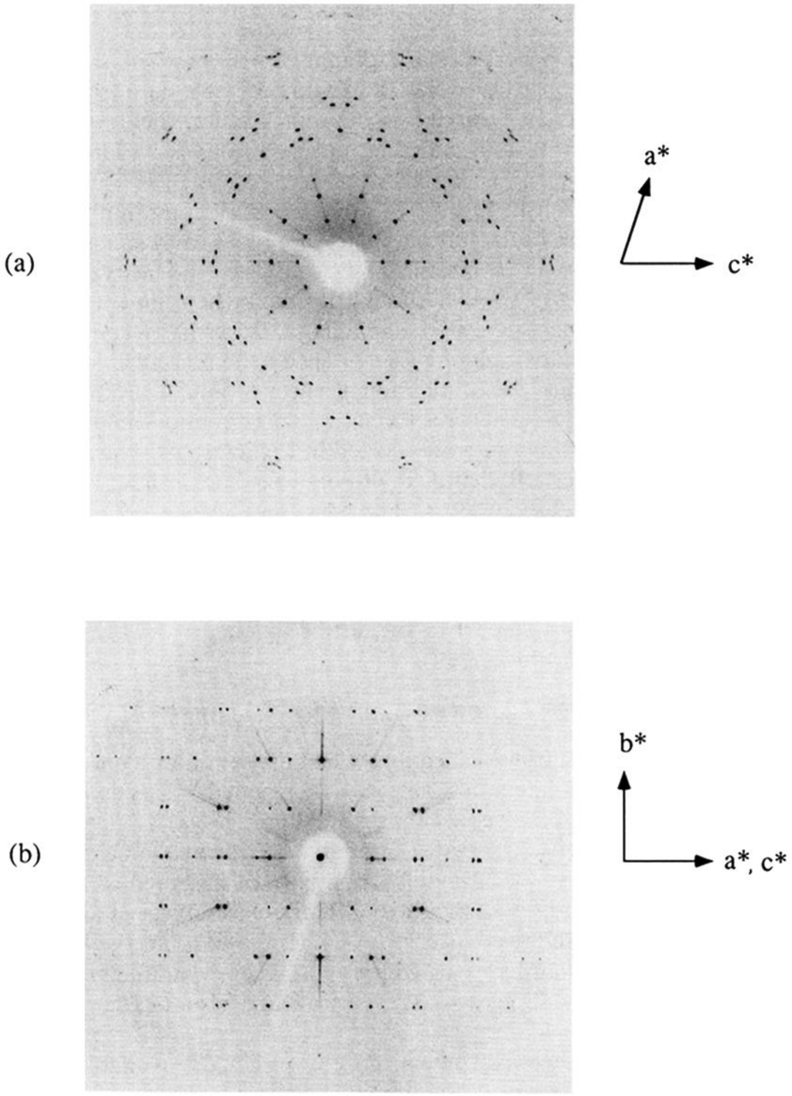


FIG. 2. Precession photographs of the $C_{82}$ crystal shown in Fig. 1. One can see (a) remarkable tenfold symmetry in the plane normal to its elongated, ten-sided columnar axis, along which the regular periodic spacing is observed as in (b).

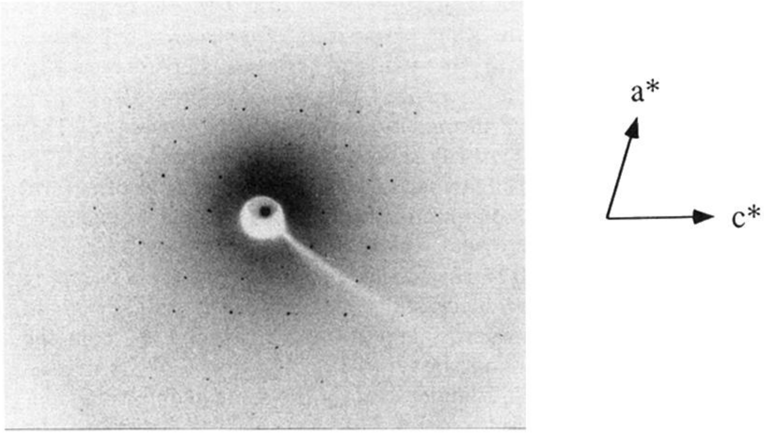


FIG. 4. Precession photograph of a single-domain $C_{82}$ crystal removed from the ten-sided columnarly structured crystal. One can clearly see a monoclinic reciprocal lattice as shown.

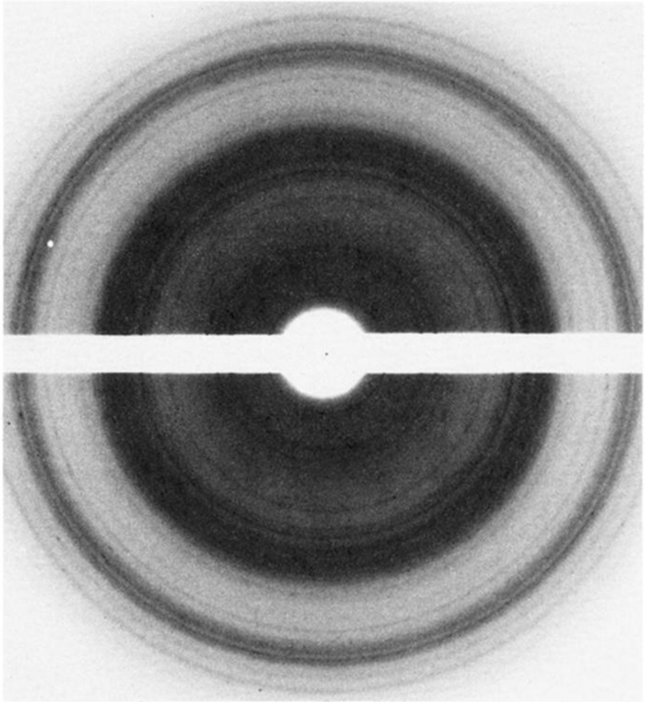


FIG. 5. Debye-Scherrer photograph of $C_{82}$ powder recorded with an imaging plate on the Photon Factory synchrotron source.