

The Structures of C₆₀ Films on Different Single-Crystal Substrates

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Received September 1, 1993; in revised form January 3, 1994; accepted January 5, 1994

The structures of C₆₀ films sublimated on the (001) surface of five substrates, LaAlO₃, SrTiO₃, ZrO₂, NaCl, and KBr, and an amorphous quartz substrate were studied by XRD and TEM. All films are of fcc structure with corresponding lattice parameters $a = 14.10, 14.10, 14.17, 14.16, 14.25,$ and 14.12 \AA , respectively. Various factors influencing the lattice constant are discussed. TEM was used to investigate two C₆₀ films prepared on NaCl(001) substrates with different temperatures and showed that in the initial growth stage of the film, it mainly contains microparticles with fcc structure; a few particles of hcp structure with $a = 1.02$ and $b = 1.64 \text{ nm}$ coexist in the film. With higher substrate temperature and growth of the film, the number of hcp phase particles was reduced. These results indicate that planar defects and hcp phase particles may contribute to the low-angle sawtooth feature on the (111) peak in the XRD patterns. The existence of an abnormal defect in fcc stacking with a sequence ABCAAAABC... in the (111) direction, which is normally impossible in fcc spherical packings, suggests that the adhesion forces between C₆₀ molecules are strong to some extent. © 1994 Academic Press, Inc.

INTRODUCTION

The extensive investigation of the physical and chemical properties of the new spherical carbon molecule C₆₀ has revealed new characteristics of the molecule and its potential application to the fields of superconductivity (1), magnetism (2), photoconductivity (3), photorefractivity (4), and optical nonlinearity (5). As a new member of the semiconductor family, the films of C₆₀ will present vast new vistas in the field of electronic devices (6). These films also have potential applications as new masks in X-ray lithography and as the quintessential micropore filter (7).

To date, the structure of C₆₀ films on different substrates has been studied by various techniques (8-11). It was found that the sublimation of this material *in vacuo* yields a solvent-free face-centered cubic (fcc) crystalline structure with a unit cell spacing of 14.2 \AA (12, 13). The hexagonal close-packed (hcp) phase can also be formed with the

aid of a solvent (14, 15). To our knowledge, the transition temperature T_c of superconductivity in alkali-metal-doped C₆₀ increases with the lattice constant of the fcc structure (16, 17). Recently Zhou *et al.* (18) have found that the reaction of ammonia with Na₂CsC₆₀ ($T_c = 10.5 \text{ K}$; lattice constant $a = 14.132 \text{ \AA}$) produces the compound (NH₃)₄Na₂CsC₆₀, which has an expanded unit cell ($a = 14.473 \text{ \AA}$) and an increased T_c of 29.6 K. Therefore the lattice constant of fcc C₆₀ may provide macroscopic information on the intrinsic properties of its compounds. We noted that though the stable crystal structure of pristine C₆₀ is fcc, its lattice parameter changes in different states of this molecule. Heiney reported two values of the C₆₀ lattice constant in his review article (19). One is 14.198 \AA for a C₆₀ single crystal grown by sublimation, reported by Fleming *et al.* (12). The other is 14.17 \AA for solvent-free C₆₀ powder, reported by Heiney's group (13). Luzzi *et al.* also reported a 14.12-\AA lattice constant of powder as well as of films on glass and amorphous SiO₂ (20). Williams' group found that the d -spacings of the pure C₆₀ film on CaF₂(111) substrate (9) were smaller than those of the film on Si(111) sublimated from 85% C₆₀ powder (21).

In this paper, we discuss two areas of interest. First, we studied the structures of films on different substrates by means of X-ray diffraction (XRD). Three kinds of (001)-faced single-crystal substrates, LaAlO₃, SrTiO₃, and ZrO₂, which are currently used as substrates for high- T_c oxide superconductor films, as well as cleaved NaCl(001), KBr(001), and amorphous quartz substrates were used. Second, because there is common interest in discovering the origin of the sawtooth feature which is always observed below the (111) peak in XRD spectra of C₆₀, and because there are two different proposed explanations for this feature (20, 22), we prepared two films sublimated onto substrates at different temperatures and studied their microstructure by transmission electron microscopy (TEM).

EXPERIMENTAL

Fullerene C₆₀ was produced and purified using the methods reported in Refs. (14, 23), resulting in better than

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99.9% pure C₆₀ powder in which no C₇₀ was found, as examined by mass spectroscopy. The C₆₀ thin films were grown by sublimating the pure C₆₀ powder onto five (001)-faced substrates, LaAlO₃, SrTiO₃, ZrO₂, NaCl, and KBr, and an amorphous quartz in a vacuum of 10⁻⁵ Torr at about 400–500°C. A pretreatment of C₆₀ powder in such a vacuum at 350°C for 40 min was carried out in order to remove residual solvent left over from the purification process. The typical sublimation rate was 4 nm/min, i.e., about five molecular layers/min. The initial temperature of substrates LaAlO₃, SrTiO₃, and ZrO₂ and quartz was kept at 300 K so that C₆₀ could easily adhere to them. After C₆₀ was sublimated for 5 min, the substrate temperature was raised to 400 K until the sublimation was finished. The source-to-substrate distance was 2.5 cm. The typical thickness of these films was 1 μm.

The measurement of XRD was performed on a Rigaku D/max-RB diffractometer. The specimens for TEM study were prepared by putting the substrates and C₆₀ thin films into distilled water. The films were separated from the substrates and mounted on copper grids. Conventional TEM was carried out on Philips EM420 and EM430 electron microscopes. High-resolution electron microscopy (HREM) was performed on a JEOL EM2010 electron microscope with an interpretable resolution of 0.19 nm. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the powder diffraction spectra of C₆₀ films on different substrates. The reflections in the spectra can be indexed as having fcc symmetry. We found that the lattice constant changes slightly with different substrates, as shown in Table 1. The film lattice constants which are close to the value of 14.17 Å reported in Refs. (13, 17) appear only on the ZrO₂ and NaCl substrates. For the films on substrates LaAlO₃ and SrTiO₃, the lattice constant is 14.10 Å, less than the previously reported value of 14.17 Å, while the value for the film on KBr is 14.25 Å, greater than 14.17 Å. The lattice constant of the film on quartz agrees with the value of 14.12 Å reported by Luzzi *et al.* (20). The causes of this difference have not been identified yet.

There are many factors possibly influencing the lattice parameter of C₆₀ besides temperature and pressure. Theoretical calculation has suggested that the room-temperature lattice parameter of this orientationally disordered fcc structure is 14.13 Å, and the lattice parameter should decrease as better quality crystals are produced (24). In C₆₀ alkali-metal-doped compounds, the lattice parameter changes from 14.025 Å in Na₂KC₆₀ to 14.555 Å in RbCs₂C₆₀, depending on the sizes of the intercalated ions (17). Their lattices can further expand through intercalation with NH₃ molecules (18). As shown in Ref. (18), the

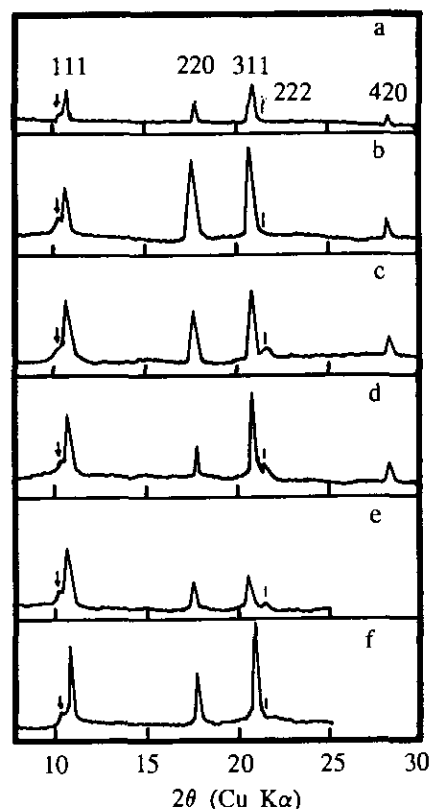


FIG. 1. X-ray powder diffraction patterns from C₆₀ films on (001)-faced substrates (a) SrTiO₃, (b) LaAlO₃, (c) ZrO₂, (d) NaCl, (e) KBr, and (f) an amorphous quartz. The peaks of substrates were subtracted.

lattice expands from 14.132 Å in Na₂CsC₆₀ to 14.473 Å in (NH₃)₄Na₂CsC₆₀ by forming larger Na(NH₃)₄⁺ cations on the octahedral site, and the ammonia intercalation is thermally reversible. These results indicate that the size of the unit cell of C₆₀ can be modified by changing the sizes of the octahedral and tetrahedral vacancies. On the other hand, the lattice can be contracted by phototransforming C₆₀ film. It was found that after the phototransformation, the lattice constant contracts about 0.1 Å (25). All these factors may influence the size of the C₆₀ lattice.

For the C₆₀ crystal and powder in Refs. (12, 13), because the samples are solvent-free and their purity is >99.5%, the influence of impurity is eliminated. Except for the factor of crystal quality, there may exist other causes of the difference in the lattice constants between the crystal and the powder. It was observed that during crystal growth by sublimation about one-third of the original material is hard to sublimate (26). This unclear factor may cause the difference in lattice constants between the crystal and the powder. For the sublimated films, Williams' group measured the lattice parameter *a* to be ~13.9 Å for the 99.9% pure C₆₀ film on CaF₂(111) (9), as shown in Table 1, and ~14.1 Å for the film on Si(111) sublimated

TABLE 1
Diffraction Data of C_{60} fcc Films on Different Substrates

Substrates	<i>d</i> -spacing (Å)				Lattice constant <i>a</i> (Å)
	(111)	(220)	(311)	(420)	
SrTiO ₃ (001) (cubic, <i>a</i> = 3.905 Å)	8.124	4.978	4.250	3.152	14.10
LaAlO ₃ (001) cubic, <i>a</i> = 3.793 Å)	8.124	4.984	4.250	3.157	14.10
ZrO ₂ (001) (cubic, <i>a</i> = 5.135 Å)	8.184	5.006	4.266	3.174	14.17
NaCl(001) (fcc, <i>a</i> = 5.640 Å)	8.18	5.006	4.258	3.168	14.16
KBr(001) (fcc, <i>a</i> = 6.597 Å)	8.215	5.040	4.303		14.25
Amorphous SiO ₂	8.124	4.995	4.262		14.12
CaF ₂ (111) (fcc, <i>a</i> = 5.464 Å) from Ref. (9)	7.98	4.90	4.22		13.9

from 85% C_{60} powder (21). They explained that the difference in unit cell size may arise from C_{70} contamination of the films (9). But this cannot explain their lattice constant for pure C_{60} film, which is smaller than those reported here and in, for example, Ref. (20). The difference between the lattice parameters may arise from the influence of the substrates, as suggested by our experiments in which all films were prepared under almost the same conditions, such as sublimation rate, substrate temperature, and the distance of substrate from source. The result of a study with C_{60} film on CaF₂(111) with highly stable

C_{60} fcc (311) free surfaces indicated that the size of the C_{60} unit cell is closely related to the substrate it sublimates (9). It was also found that the crystallinity of the films depends on that of the substrates (27). Because the films are not grown by epitaxy as reported in Refs. (28, 29), whether the substrate influences the size of the C_{60} unit cell needs to be investigated further (30). One possible explanation is that the lattice mismatch between C_{60} and the substrate may influence the quality of the crystalline film of C_{60} .

In Fig. 1, a sawtooth feature below the (111) peak is always observed. Luzzi, *et al.* attributed this feature to planar defects in the fcc structure (20). Li and Fagan assigned it to the hcp phase coexisting with the fcc phase (22). In order to discuss this question, we sublimated two films on NaCl(001) prepared at different substrate temperatures and studied their microstructure by TEM.

Film A was grown at 300 K on a NaCl(001) substrate with a thickness of about 200 Å. Film B was prepared at 400 K on a NaCl(001) substrate with a thickness 400 Å. Figure 2 shows their electron micrographs. The average particle sizes of film A and film B are about 50 and 300 nm, respectively. There are a few stacking faults in some particles of film A, as shown in Fig. 2a. In film B there exist planar defects of microtwins and stacking faults with high densities, as shown in Fig. 2b, where particles A, B, and C are multiply twinned particles with {111} stacking faults and microtwins.

Microdiffraction was utilized to study the crystallization of C_{60} thin film A and film B. It revealed that in film A, most particles are fcc; small numbers of hcp particles were found. In film B fcc particles predominate, but fewer hcp particles were observed than in film A. The microdiffraction patterns of fcc particles in film A are shown in

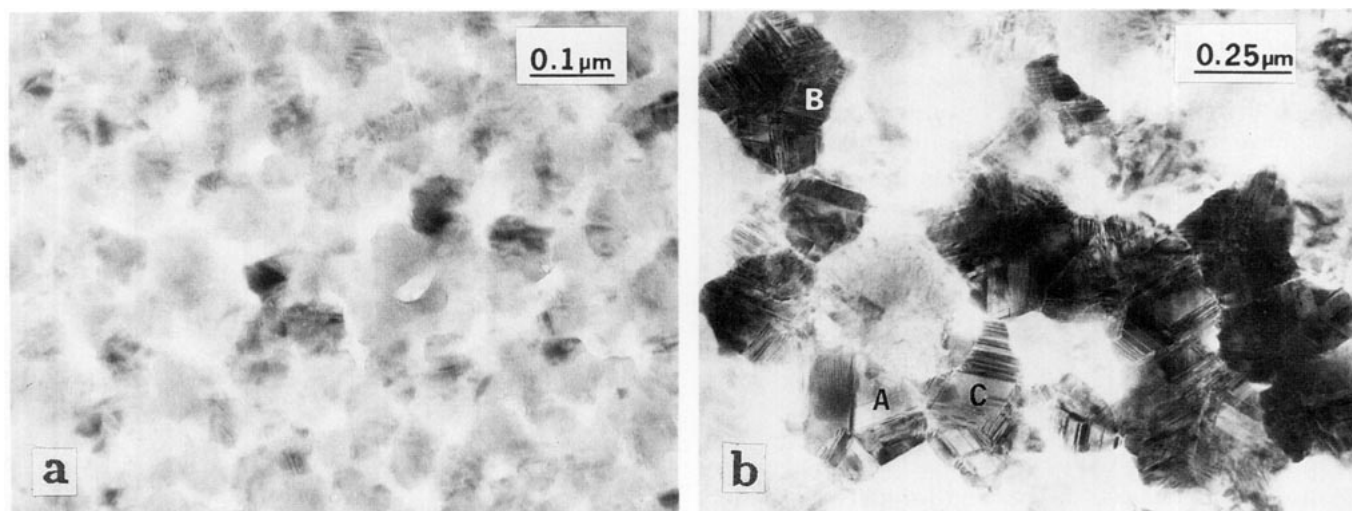


FIG. 2. Low-magnification electron micrographs of C_{60} (a) film A and (b) film B.

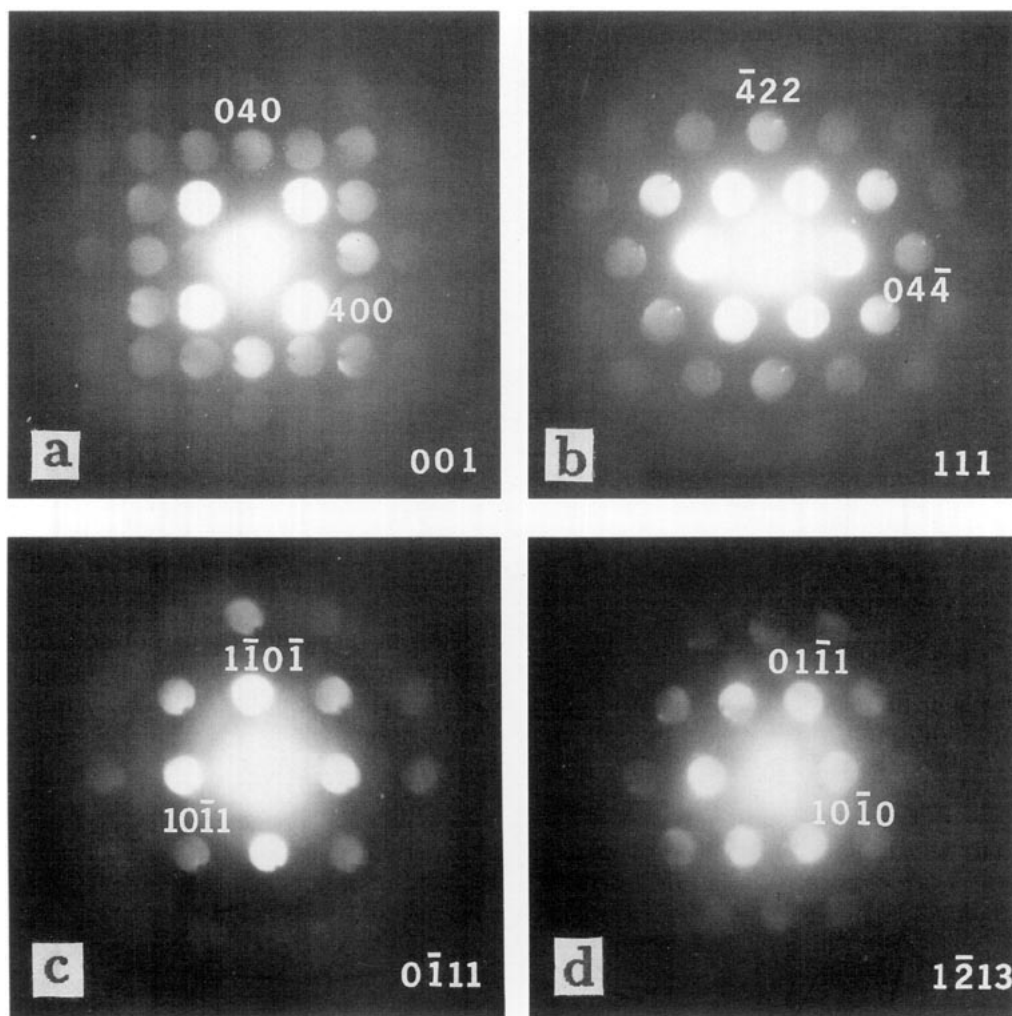


FIG. 3. Microdiffraction patterns of C_{60} fcc particles (a) [001] and (b) [111], and hcp particles (c) [0 $\bar{1}$ 11] and (d) [1 $\bar{2}$ 13].

Figs. 3a and 3b with lattice parameter $a = 1.42$ nm. Figures 3c and 3d show the microdiffraction patterns of hcp particles with lattice parameters $a = 1.02$ and $c \approx 1.64$ nm. Theoretical calculation indicated that fcc packing is more stable than hcp packing by 0.90 kcal/mole. However, because of the effects of solvent, powder-grain surface, crystal domain boundaries, the interaction of C_{60} with substrate, etc., the hcp phase can be stabilized, as found by Krättschmer *et al.* (14, 15), in thinner films (10) and in thicker films in which the hcp and fcc phases coexist as observed here and in Refs. (22, 27, 30, 31). Annealing is helpful for hcp conversion into fcc as shown in film B, but more defects are also found in this film. Therefore for thicker films, the origin of the sawtooth feature below the (111) peak in XRD spectra may be caused by both planar defects in the fcc phase, as suggested by Luzzi *et al.* (20), and hcp phase particles (22).

Careful examination of the fcc particles in film A by

microdiffraction shows that many particles are oriented along the $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 110 \rangle$ directions relative to the NaCl(001) substrate. Other orientations have also been observed. This means that there is a weak preference for the fcc C_{60} particles on NaCl(001) to grow along the $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 110 \rangle$ directions in film A, prepared at 300 K. When an electron beam was focused on the particles of the hcp phase, the diffraction patterns of particles became diffuse until the amorphous diffuse ring was formed. This implies that in our case the hcp to fcc phase transformation did not occur during electron beam irradiation. The result is in agreement with Banhart *et al.* (32). In light of hcp C_{70} conversion into the fcc structure at high temperature (33) and fewer hcp phase particles in film B, prepared at higher substrate temperatures, as discussed above, we cannot rule out the possibility of a hcp to fcc phase transformation with the aid of the heating effect of electron radiation, though there may also exist the possibility of

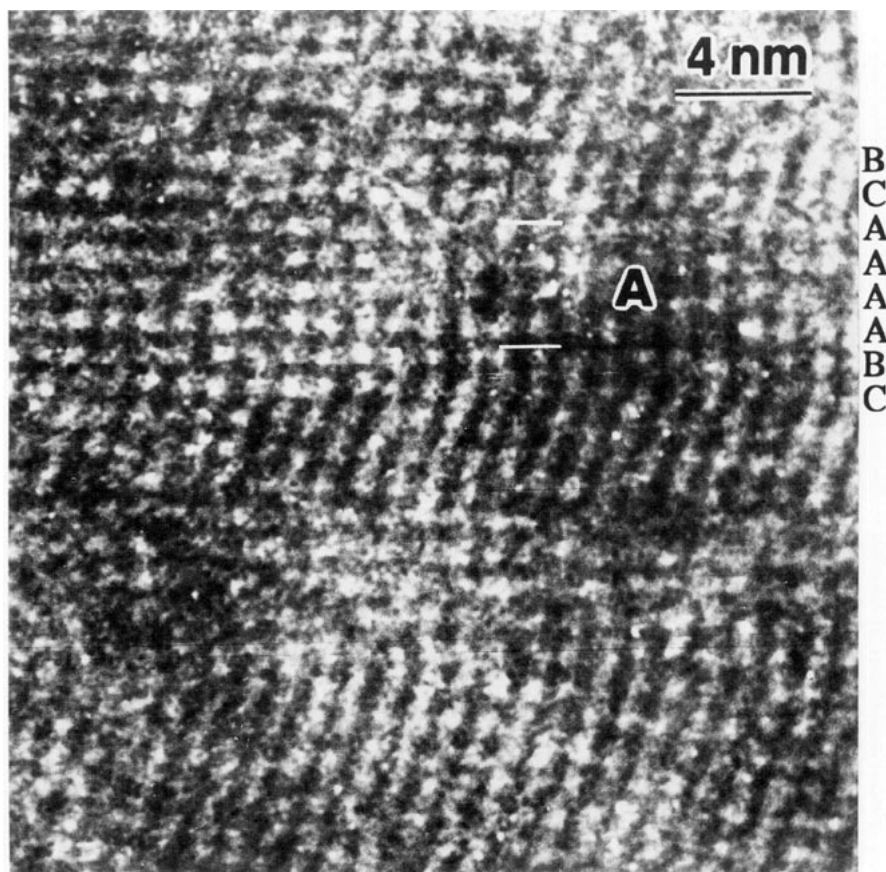


FIG. 4. A [110] HREM image of a fcc particle in C_{60} film B. The "abnormal" fcc sequence faults are indicated by area A.

C_{60} formation into higher fullerenes by electron beam irradiation as has occurred by ultraviolet laser radiation (34) as well as radiation damage of the molecule as observed in Refs. (32, 35). The result that hcp bulk crystals with residual solvent molecules can transform into the fcc structure with lattice defects during electron beam irradiation (36) has suggested a heating effect of the electron beam.

High-resolution images were used to investigate film B, which contains high-density defects. Figure 4 is a HREM image of a fcc particle in film B. In contrast to typical fcc structures, some abnormal defects in stacking of the close-packed planes were observed in region A, with a sequence ABCAAAABC . . . in the $\langle 111 \rangle$ direction. These defects can be better seen in Fig. 5. A similar structure has been observed in C_{60} crystal grown from benzene (22). Due to the solid-state interactions of solid C_{60} observed by infrared spectra, which suggest that besides van der Waals force there exists another attractive force between the adjacent molecules (37, 38), this high-energy stacking sequence in fcc spherical packings can be maintained in the solvent-free film. The existence of this high-energy stacking sequence, which is normally impossible in fcc

spherical packings, gives reciprocal information, i.e., the adhesion forces between C_{60} molecules are strong enough to support a free-standing C_{60} membrane as obtained by Eom *et al.* (7).

CONCLUSIONS

All C_{60} films on the (001) surface of five substrates, $LaAlO_3$, $SrTiO_3$, ZrO_2 , $NaCl$, and KBr , and an amorphous quartz substrate are of the fcc structure with corresponding lattice parameters of $a = 14.10, 14.10, 14.17, 14.16, 14.25,$ and 14.12 \AA , respectively. Various factors influencing the lattice constant have been discussed, and the cause of the lattice constant difference among these films was preliminarily attributed to the lattice mismatch between C_{60} and the substrates. Transmission electron microscopy shows that in the initial growth stage of the film on $NaCl(001)$, the film mainly contains microparticles of fcc structure. A few particles of the hcp structure with $a = 1.02$ and $b = 1.64 \text{ nm}$ coexist in the film. With higher substrate temperature and the growth of the film, i.e., increased film thickness, the number of hcp phase particles decreases. These results indicate that the planar de-

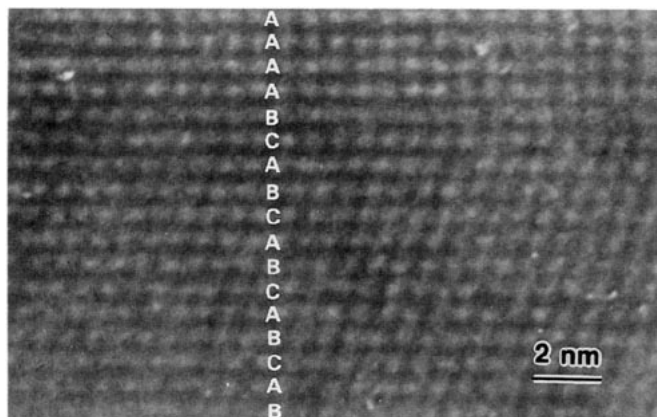


FIG. 5. A [110] HREM image of another fcc particle in C₆₀ film B.

fects and hcp phase particles may be the origins of the low-angle sawtooth feature on the (111) peak in the X-ray diffraction patterns. Defects such as microtwins and stacking faults are frequently seen in these films. The existence of an abnormal defect in fcc stacking with a sequence ABCAAAABC . . . in the $\langle 111 \rangle$ direction, which is normally impossible in fcc spherical packings due to the high energy of this stacking sequence, further suggests that the adhesion forces between C₆₀ molecules are strong to some extent.

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