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SUPERLATTICE ORDERING IN GRAPHITE–IC1 SINGLE CRYSTALS AND FIBERS†

D. GHOSH,‡ R. GANGWAR§ and D. D. L. CHUNG‡
Carnegie–Mellon University, Pittsburgh, PA 15213, U.S.A.

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Abstract—By using X-ray diffraction, a 3-fold or 6-fold twinned monoclinic $\sqrt{(301)} \times 2$ $(-3.3°, 0°)$ superlattice ($a = 4.92$Å, $b = 42.68$Å, $c = 7.0$Å, $\gamma = 93.3°$) was observed in stage-1 graphite–IC1 single crystals intercalated in IC1 vapor. This in-plane superlattice was also observed in stage-1 and stage-2 graphite–IC1, which were based on Thornel P-100 graphite fibers and prepared by the two-bulb method, in which liquid IC1 was at 95°C while graphite was at 100°C for stage 1 and 130°C for stage 2. This work provides the first observation of in-plane intercalate ordering in intercalated graphite fibers and the first X-ray diffraction evidence of IC1 intercalation in graphite fibers. A different in-plane superlattice was observed in stage-1 graphite–IC1 single crystals intercalated in IC1 liquid.

1. INTRODUCTION

The in-plane superlattice in stage-1 graphite–IC1 single crystals prepared by exposure to iodine monochloride (IC1) vapor at 20–30°C was reported to have a six-fold twinned monoclinic unit cell with pseudocell dimensions of $a = 4.92$Å, $b = 19.2$Å and $\gamma = 93.5°$, as derived from X-ray oscillation photographs[1]. In this work, we obtained the same diffraction pattern by the precession method, but a three-fold or six-fold twinned monoclinic unit cell with $a = 4.92$Å, $b = 42.68$Å and $\gamma = 93.3°$ was found to fit the diffraction pattern better. Furthermore, this same in-plane unit cell was observed in IC1-intercalated fibers by the Transmission Laue method, and hence provided the first observation of in-plane intercalate ordering in intercalated graphite fibers.

Intercalated graphite fibers have recently received considerable attention because of their use in polymer–matrix composites for high electrical conductivity applications[2]. The intercalation of graphite fibers with HSO_3F, AsF_5 or SbF_5 gave an up to 50 times increase in the electrical conductivity[3]. X-Ray diffraction showed the formation of stage 2 graphite–AsF_5 in high modulus ex-PAN graphite fibers (e.g. Union Carbide TP 4104B)[4, 5]. Formation of stage 1 graphite–K in fibers was shown by X-ray diffraction[5] and the appearance of the gold color[5, 6]; the formation of mixed stages of graphite–K, graphite–Rb and graphite–Cs was also indicated by X-ray diffraction (Debye–Scherrer method)[7]. Absorption of Br_2 and IC1 in graphite fibers was indicated by weight uptake measurement[8, 9] but confirmation of intercalation by using X-ray diffraction has not been reported. Warner *et al.*[8] interpreted the absorption as not being intercalation, but rather plasticization, whereas Hooley and Deitz[9] interpreted the absorption as intercalation. Desorption of brominated graphite fibers resulted in a stable material having an electrical conductivity higher than that of pristine graphite fibers[5, 10]. Similar treatment with IC1 gave an even higher value of the electrical conductivity[5]. In this work, we have obtained the first X-ray diffraction evidence of intercalation of IC1 in graphite fibers.

Although the in-plane superlattice pattern of stage-1 graphite–IC1 prepared in IC1 vapor at room temperature (Type A) was the same as that of Ref. [1], the pattern of stage-1 graphite–IC1 prepared in IC1 liquid (Type B) was dramatically different and was observed for the first time in this work.

2. EXPERIMENTAL TECHNIQUES

The graphite crystals used in this work were typically 0.5–1.0 mm in diameter and ~0.05 mm thick. Intercalation to stage 1 was performed at room temperature by exposure to IC1 vapor (Type A) or IC1 liquid (Type B). The samples were sealed in glass capillaries while they were in contact with either IC1 vapor (Type A) or IC1 liquid (Type B). Single crystal X-ray diffraction was performed at room temperature by using a precession camera, with Zr filtered Mo$K\alpha$ radiation. All diffraction patterns were generated by 5° screenless precession, except that Type B photographs were generated using layer screens.

The graphite fibers used in this work are listed in Table 1. Intercalation was carried out by exposure of the fibers to IC1 vapor in equilibrium with IC1 liquid

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‡Department of Metallurgical Engineering and Materials Science.

§Department of Physics.

at 95°C; this temperature was chosen for the ICl liquid because ICl boils at 97.4°C. The purity of ICl was 95+%, as supplied by Alfa Products. While the ICl liquid was held at 95°C, the fibers (typically ~1.0 cm long) were held at a temperature ranging from 100 to 135°C. The reaction vessel was made of Pyrex glass and was sealed without evacuation. The intercalation time investigated ranged from 8 to 24 hr.

X-Ray diffraction was used to characterize the crystal structural effects of intercalation of the fibers. The Transmission Laue method was used, with Mo$K\alpha$ radiation and a specimen-to-film distance of 6 cm. The accuracy of visual measurement of the diameter of an observed ring on the film was ±0.5 mm, so that the maximum error in the measured d-spacing was ±1.7%. The set-up allowed d-values ranging from 0.8 to ~6Å to be measured. The intercalated fibers were removed from the reaction vessel, cut to a typical length of ~2 mm, and then sealed in a glass capillary of 1 mm I.D. and 0.01 mm wall thickness; this procedure took typically ~1 min. The fiber axes thus had a preferred orientation along the capillary axis. The exposure time was 6 hr for every sample.

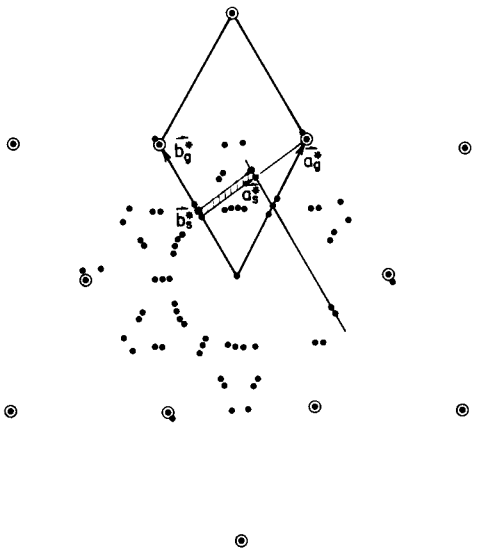

Fig. 1. The $hk0$ X-ray diffraction pattern (schematic) of a Type A graphite–ICl single crystal.

3. EXPERIMENTAL RESULTS

3.1 *Type A single crystals*

The $hk0$ diffraction pattern (precession photograph) of Type A (single crystal) represented in Fig. 1 appears to be the same as Figs. 2 and 4 of Ref. [1]. This pseudo-hexagonal pattern in Fig. 1 is the result of diffraction spots from a three-fold (or six-fold) twinned monoclinic lattice, having three (or six) possible in-plane orientations, rotated with respect to one another by 120° (or 60°) about the c-direction of the graphite lattice (Fig. 1 in reciprocal space, Fig. 2 in real space).

Designating the unique axis of the monoclinic cell as c (which is parallel to the c-axis of graphite), one can easily express the reciprocal lattice vectors $\mathbf{a}_s^*$ and $\mathbf{b}_s^*$ in terms of the graphite reciprocal lattice vectors $\mathbf{a}_g^*$ and $\mathbf{b}_g^*$ (thereby ensuring the commensurability of the superlattice "s") by the following simple relations:

$$\mathbf{a}_s^* = (1/2)\mathbf{a}_g^* - (9/40)\mathbf{b}_g^* \quad (1)$$

$$\mathbf{b}_s^* = (1/20)\mathbf{b}_g^* \quad (2)$$

With $|\mathbf{a}_g^*| = |\mathbf{b}_g^*| = 0.4694\text{Å}^{-1}$, eqns (1) and (2) yield the superlattice lattice parameters

$$|\mathbf{a}_s| = (\sqrt{(301}/40)|\mathbf{a}_g^*| = 4.92\text{Å}$$

$$|\mathbf{b}_s| = (1/20)|\mathbf{b}_g^*| = 42.68\text{Å}$$

and

$$\gamma_s = 93.3°,$$

where γ_s is the angle in real space between the $\mathbf{a}_s$ and $\mathbf{b}_s$ axes. We also directly calculated $|\mathbf{b}_s|$ by measuring the spot-to-spot separation in the Precession photograph, which yielded the value of 42.1 ± 1.0Å. This suggests that our geometrical interpretation of the diffraction patterns, as expressed in eqns (1) and (2), is correct. The c-axis length was determined from a $h0l$ photograph yielding $c = 7.0$Å, which agrees with the published c-axis periodicity of stage-1 graphite–ICl compound[1]. This cell is approximately double the size of the monoclinic cell given in Ref.[1], which is $a = 4.92$Å, $b = 1.92$Å and $\gamma = 93.5°$. The smaller cell in Ref. [1] could not explain the observed diffraction pattern as well as the one reported here, which we found to be the smallest

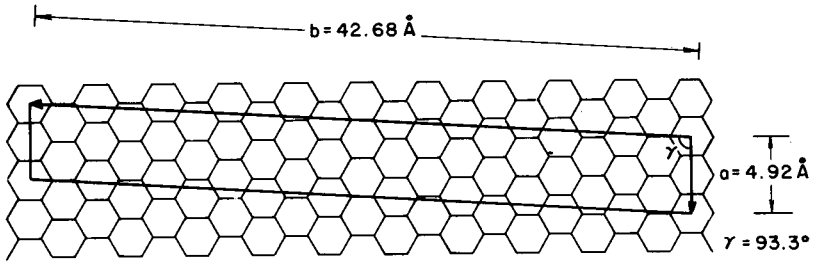

Fig. 2. In-plane unit cell of Type A graphite–ICl.

unit cell with the maximum symmetry, although it could be a pseudo-cell with the real cell being larger. In addition to their pseudo-cell, Turnbull and Eeles[1] mentioned about a real cell which is larger. However, in our diffraction pattern, we could not identify this larger unit cell.

The monoclinic in-plane unit cell of Type A is hence $\sqrt{(301)} \times 2(-3.3°, 0°)$. This convention is adapted for non-hexagonal cells. The graphite in-plane unit cell is $1 \times 1(30°, 0°)$. The angles are described by two in-plane orthogonal axes.

One important feature of the *hk*0 diffraction pattern is that some spots in Fig. 1 (denoted by circled dots) constitute a pattern identical to that of pure graphite. In other words, only the superlattice reflections exhibit the "twinning" effect. Thus, the effect is produced by the intercalate layers. Similar twinning was also noted in graphite–bromine[11].

3.2 *Type B single crystals*

Figure 3 shows the *hk*0 and *h*0*l* diffraction patterns (precession photographs) of Type B, which was intercalated in liquid ICl and photographed in contact with the liquid. The complicated *hk*0 pattern, characterized by sharp reflection spots, probably arises from two different orthorhombic systems. It is yet to be fully analyzed. The *h*0*l* diffraction pattern showed the diffraction spots along the c^* direction and gave an intercalate-carbon-intercalate sandwich thickness of 7.17Å; the axial repeat distance along this direction was either 7.17 or 14.34Å. This photograph does not show any streak at $h \neq 0$ positions, while a similar photograph for Type A exhibits streaks parallel to c^* at those positions (Fig. 4). This suggests that the Type B superlattice is more three-dimensionally ordered than that of Type A.

Figure 5 shows the X-ray diffraction photographs of the three types of pristine fibers listed in Table 1. The Thornel P-100 fibers gave the largest number of diffraction lines, as listed in Table 2. The Celion GY-70 fibers gave fewer lines, but they are as sharp as those of Thornel P-100. On the other hand, the Panex 30 fibers gave only a few relatively diffuse lines. Hence, the crystalline perfection of the graphite fibers decreased in the order (1) Thornel P-100, (2) Celion GY-70, and (3) Panex 30.

Figure 6 shows the X-ray diffraction photographs of (a) HOPG, (b) Thornel P-100, (c) Celion GY-70, and (d) Panex 30 after exposure to ICl. The HOPG sample was intercalated by exposure to ICl vapor at room temperature for 1 day, and resulted in a stage 1 compound (Fig. 6a); the indexing of the diffraction lines is shown in Table 3. All three types of fibers were treated identically by holding the fibers at 130°C and the ICl liquid at 95°C for 8 hr. After the treatment, the Thornel P-100 fibers (Fig. 6b) showed superlattice diffraction lines, which were absent in Fig. 5(a). Indexing of the pattern in Fig. 6(b) showed that the intercalated Thornel P-100 fibers were predominantly stage 2. (The indexing of the pattern for stage 2 Thornel P-100 fibers is given later in this paper.) The same treatment for Celion GY-70 and Panex 30 fibers did not yield any superlattice lines. It should be mentioned that *room temperature* exposure of any type of fibers to ICl did not yield any superlattice lines, although such treatment of HOPG resulted in stage 1. Thus, Fig. 6 shows that the ease of intercalation of the various graphite materials decreased in the order (1) HOPG, (2) Thornel P-100, (3) Celion GY-70, and (4) Panex 30. In fact, no diffraction evidence of ICl intercalation was obtained for Celion GY-70 nor Panex 30 fibers, although intercalation was clearly shown for Thornel P-100.

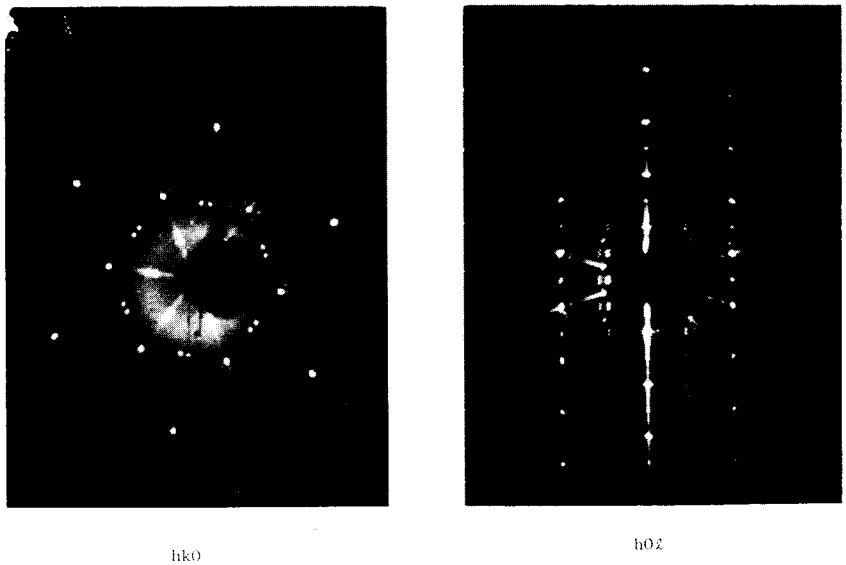

Fig. 3. The *hk*0 and *h*0*l* X-ray diffraction patterns of a Type B graphite–ICl single crystal.

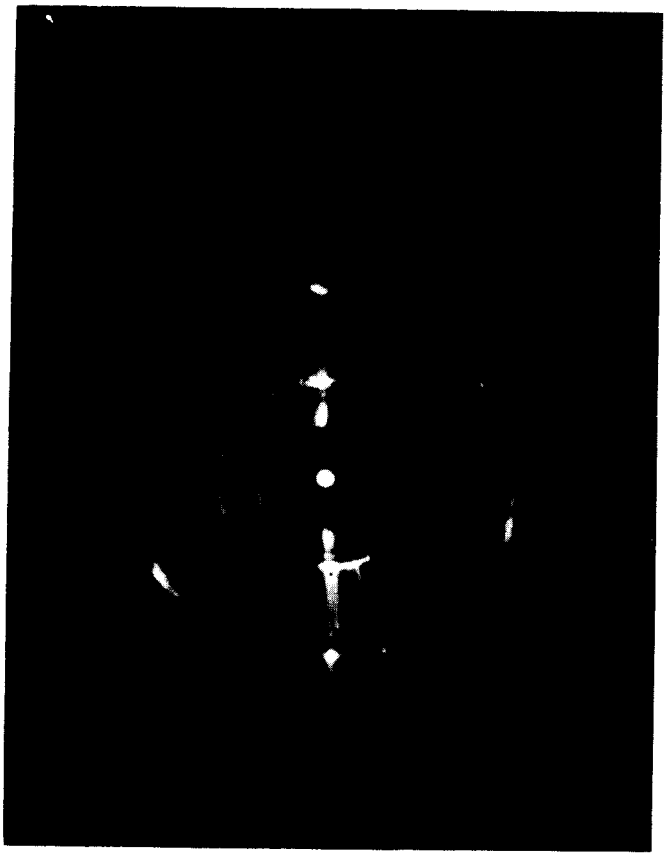

Fig. 4. The $h0l$ X-ray diffraction pattern of a Type A graphite–ICl single crystal.

Figure 7 shows X-ray diffraction patterns of intercalated Thornel P-100 fibers after various lengths of desorption time (0 min, 10 min, 2 hr, 1 week). Intercalation was performed by holding the fibers at 130°C and the ICl liquid at 95°C for 24 hr. Desorption was allowed to occur in air at room temperature. Figure 7(a) shows the pattern obtained after a negligible length of desorption time (0 min); the indexing of this pattern is shown in Table 4. Note that the second stage ($00l$) type lines were observed for $l = 2, 3, 5, 6, 8, 9$. The (001) line was not observed because its large d value caused it to be blocked by the beam stop. The absence of ($00l$) lines for $l = 4, 7$ is probably systematic due to the space group, which is presently not known since the positions of the intercalate molecules within a unit cell has not been determined. In addition to the ($00l$) lines, ($hk0$), ($h0l$) and ($0kl$) lines were observed. The in-plane superlattice was thus found to be the same as that of Type A single crystals. Desorption resulted in a gradual decrease of the intensities of the superlattice lines without shifting any line. This means that the initial stage (stage 2) was maintained during desorption. The presence of superlattice diffraction lines even after a week of desorption indicates that (1) desorption of intercalated fibers results in a material which is still intercalated, and (ii) desorption of intercalated fibers occurs over an appreciably long time.

By lowering the sample temperature to 100°C, with the ICl liquid maintained at 95°C, stage 1 graphite–ICl (mixed with small quantities of stages 2 and 3) was obtained in Thornel P-100 graphite fibers. Although we were able to obtain relatively pure stage 2, we have not been able to obtain pure stage 1. The in-plane superlattice of stage 1 was also found to be the same as that of Type A single crystals.

4. DISCUSSION

The large size of the in-plane unit cell makes it difficult to determine the positions of all the atoms in the unit cell. As guided by weight-gain results[2] and the in-plane atomic arrangement proposed by Turnbull and Eeles[1], one might assume that there are 9 ICl units in our in-plane unit cell, so that the stoichiometry of Type A is $C_{8.9}ICl$, which is close to the previously reported stage-1 stoichiometries of C_9ICl[1] and $C_{8.5}ICl$[12, 13].

The ICl chains in the model of Turnbull and Eeles[1] are approx. 4.26Å apart in the b-direction. Since our unit cell is 42.68Å long in the b-direction, it may be possible for our unit cell to contain 10 chains, which corresponds to 10 ICl units in our unit cell and a stoichiometry of C_8ICl. As weight measurement does not give an accurate determination of the stoichiometry, an intensity analysis using four-circle diffractometer results is needed to determine the

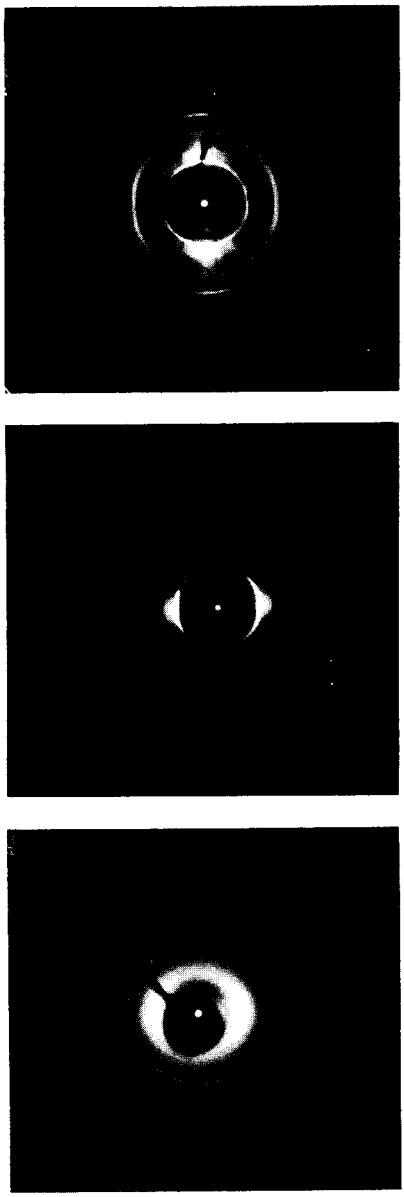

Fig. 5. X-Ray diffraction patterns of pristine graphite fibers. (a) Thornel P-100. (b) Celion GY-70. (c) Panex 30.

stoichiometry, which could be C_8IC1 (10 IC1 units per cell), $C_{8.9}IC1$ (9 IC1 units per cell) or $C_{10}IC1$ (8 IC1 units per cell).

The diffraction patterns from graphite–IC1, though seemingly indicative of more ordered structures than graphite–bromine, are complicated and difficult to interpret. This might stem from the fact that IC1 has two possible forms, α and β, both with melting points near room temperature. It might be noted that the Type A unit cell resembles that of β-IC1, which is monoclinic but pseudo-orthorhombic, with the angle being 91° 21′[14]. Furthermore, β-IC1 consists of nearly planar atomic layers, whereas α-IC1 does not[14].

The IC1 intercalation method used in this work is based on the two-bulb method developed for potassium intercalation[15]. In contrast, previous work on intercalation of IC1 in fibers involved exposure to IC1 vapor at room temperature[8, 9]. We have found that the two-bulb method used in this work gave graphite–IC1 of specific stages, whereas room temperature exposure to IC1 did not lead to superlattice formation.

The case of intercalation was found to increase with increasing crystal perfection of the graphite material, such that the crystal perfection decreases in the order (1) HOPG, (2) Thornel P-100, (3) Celion GY-70, and (4) Panex 30. In fact, Thornel P-100 was the only type of fibers which could be intercalated using our method, as indicated by the superlattice formation. Note that we consider superlattice formation to be conclusive evidence for intercalation. In this work, the first such evidence was obtained for the intercalation of IC1 in graphite fibers.

Of significance is that we have observed for the first time in-plane intercalate ordering in intercalated graphite fibers. Moreover, we have found that the in-plane unit cell of stage 1 and stage 2 IC1-intercalated fibers is the same as that of stage 1 graphite-IC1 single crystal graphite and that of stage 1 graphite–IC1 HOPG. In addition to the in-plane superlattice, staging was observed.

The Transmission Laue method used in this work was found to be more suitable for fiber material compared to the Debye–Scherrer method and the diffractometer method. This is because the preferred orientation of the fibers results in incomplete Debye rings, which might be missed by the film in the Debye–Scherrer method. Moreover, the need of a small sample quantity, the availability of thin-walled capillaries for sealed samples, and the possibility of a long exposure time make the Transmission Laue method more attractive than the diffractometer method.

Table 1. Specifications of graphite fibers used

Manufacturer	Union Carbide Corp.	Stackpole Fiber Co.	Celanese Corp.
Grade	Thornel P-100 Grade VS-0054	Panex 30	Celion GY-70
Precursor	Pitch	PAN	PAN
Tensile modulus (10^6 psi)	100	32	75
Tensile strength (10^3 psi)	0.325	0.375	0.27
Density (g/cm^3)	2.16	1.74	1.97
Electrical resistivity ($10^{-4}\Omega$-cm)	2.5		6.5

Table 2. X-Ray diffraction lines obtained from pristine graphite fibers (Thornel P-100)

Line No.	d_{obs} (Å)	d_{cal} (Å)	h	k	ℓ	Strength
1	3.38	3.35	0	0	2	S
2	2.11	2.13	1	0	0	M
3	1.69	1.68	0	0	4	S
4	1.23	1.23	1	1	0	Diffuse
5	1.17	1.15	1	1	2	Diffuse
6	1.13	1.12	0	0	6	M

Table 3. X-Ray diffraction lines obtained from stage 1 graphite–ICl based on HOPG flakes

Line No.	d_{obs} (Å)	d_{cal} (Å) (Stage 1)	hkℓ (Stage 1)			Strength
			h	k	ℓ	
1	5.32	5.33	0	8	0	W
2	4.86	4.89	1	0	0	VS
3	4.35	4.35	1	4	0	W
4	4.07	4.02	1	0	1	W
5	3.54	3.53	0	0	2	VS
6	3.38	3.42	0	3	2	W
7	3.19	3.16	0	6	2	W
8	3.09	--	--	--	--	VW
9	2.95	2.86	1	0	2	M
10 *	2.62	2.62	1	6	2	M
11	2.49	2.45	2	0	0	M
12	2.33	2.35	0	0	3	S
13	2.18	2.18	2	8	0	W
14	2.12	2.13	0	20	0	M
15 *	2.03	2.04	2	$\bar{1}$	1	W
16 *	1.93	1.94	2	5	2	VW
17 *	1.87	1.82	2	$\bar{1}$	2	W
18	1.78	1.76	0	0	4	W
19	1.65	1.63	3	0	0	M
20 *	1.56	1.58	2	$\bar{1}$	3	Diffuse
21	1.47	1.48	3	0	2	W
22 *	1.36	1.36	2	$\bar{1}$	4	Diffuse
23	1.32	1.34	3	0	3	W
24	1.18	1.18	0	0	6	S
25	1.14	1.14	1	0	6	M

* Tentative hkℓ assignment, since the streaks due to the two-dimensional character were not observed.

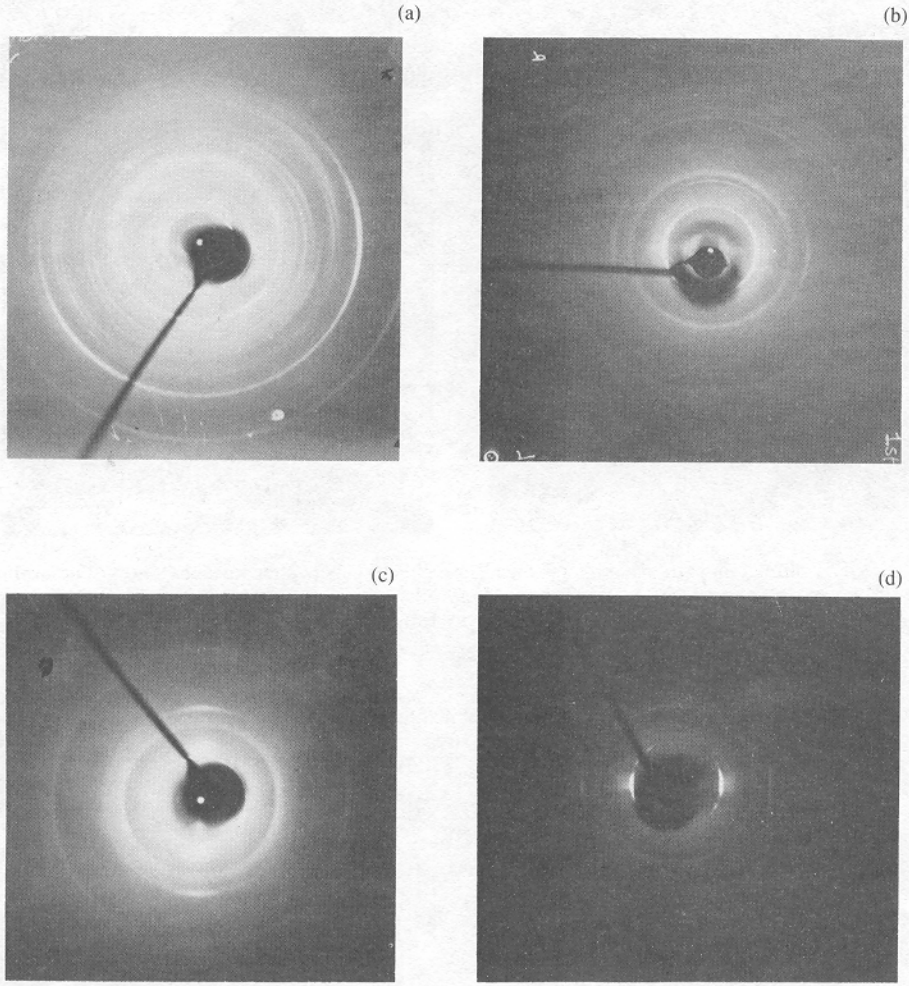

Fig. 6. X-Ray diffraction patterns. (a) HOPG. (b) Thornel P-100. (c) Celion GY-70. (d) Panex 30 after exposure to IC1.

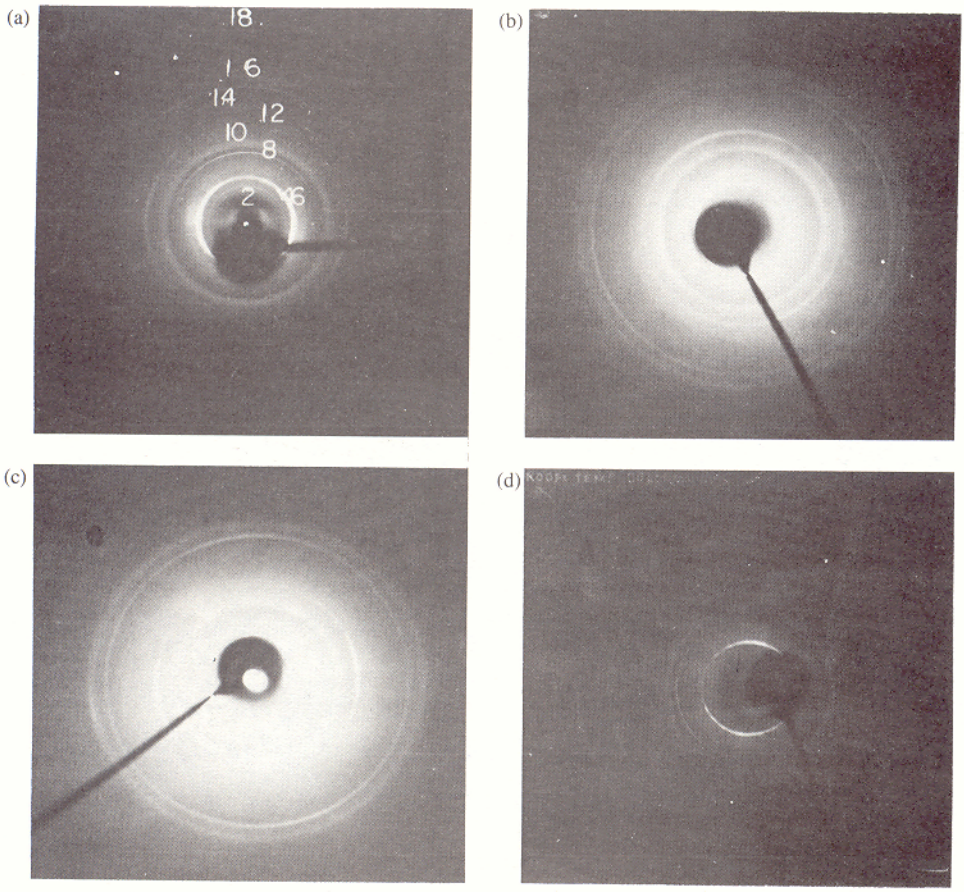

Fig. 7. X-Ray diffraction patterns of intercalated Thornel P-100 fibers after various lengths of desorption time. (a) 0 min. (b) 10 min. (c) 2 hr. (d) 1 week. Every other line in (a) is labeled by its Line No., which is defined in Table 4.

Table 4. X-Ray diffraction lines obtained from graphite fibers intercalated with IC1 by holding the fibers at 130°C

Line No.	d_{obs} (Å)	d_{cal} (Å) (Stage 2)	hkℓ (Stage 2)			Strength
			h	k	ℓ	
1	5.30	5.20	0	0	2	W
2	4.80	4.89	1	0	0	W
3	4.25	4.26	0	10	0	W
4	3.89	3.92	0	10	1	W
5	3.43	3.46	0	0	3	VVS
6	2.86	2.83	1	0	3	W
7	2.13	2.13	0	20	0	S
8	2.07	2.07	0	0	5	M
9	1.84	1.82	0	20	3	Diffuse
10	1.73	1.73	0	0	6	W
11 *	1.70	1.70	10	$\bar{5}$	6	W
12	1.63	1.63	3	0	0	W
13	1.31	1.30	0	0	8	W
14 *	1.26	1.26	2	$\bar{1}$	8	VW
15	1.23	1.23	4	$\bar{2}$	0	S
16	1.16	1.16	0	0	9	W
17 *	1.12	1.11	2	$\bar{1}$	4	W
18	0.99	0.99	4	0	4	W

* Tentative hkℓ assignment, since the streaks due to the two-dimensional character were not observed.

Note added in proof. Superlattice X-ray diffraction lines had been previously observed in Thornel Type P carbon fibers intercalated with Br_2 or HNO_3 (M. B. Dowell, *Mater. Sci. Eng.* **31**, 129 (1977)). However, identification of the in-plane superlattice unit cell has not previously been made in graphite fibers with any intercalate species. In this work, we have made this identification in graphite–ICl fibers.

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