

High-Pressure Phase of Polytetrafluoroethylene

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Synopsis

The effect of hydrostatic pressure on the crystal structure of PTFE has been studied up to pressures of ca. 25 kbar by x-ray diffraction. The experimental method uses opposed diamond anvils of small surface area as transmitters of pressure with $\text{MoK}\alpha$ x-radiation propagating through these anvils. A small specimen of oriented polymer is held in place with a molybdenum gasket. Pressures are measured by change in lattice spacing of sodium chloride included with some specimens. It is found that above 4.5 kbar the PTFE changes to a high-pressure phase in which the molecules have transformed from their normal helical arrangement to that of a planar zigzag and that the planes of the molecules all lie parallel to one another. Further changes in the diffraction pattern on increase in pressure are attributed to slip and twinning in the high-pressure phase rather than to another phase change.

Introduction

The exceptional frictional behavior of polytetrafluoroethylene (PTFE) still attracts interest. As a means of understanding the nature of the deformation in frictional processes, a study of the effects of high hydrostatic pressure and shear stresses on the structure and morphology of PTFE has been undertaken. In this paper the structure of a high-pressure phase of PTFE is described.

Previous volume measurements over a wide range of temperature and pressure have established a phase diagram consisting of four solid phases and one liquid phase.^{1,2} Figure 1 shows the phase diagram. In phases I, II, and IV the molecule exists in the form of a helix.³ This helix may be derived from the planar zigzag arrangement (shown by polyethylene) by giving the molecule a 180° twist every N CF_2 units, where $N = 15$ for phases I and IV, and $N = 13$ for phase II. The structure of phase III, which exists only at high pressures, is still largely unexplained. Brown⁴ found that the infrared spectrum of PTFE at pressures greater than 6 kbar was compatible with a planar zigzag conformation of the molecule. Hirakawa and Takemura,⁵ using an x-ray technique, have deduced, on the basis of extremely limited data, that the high pressure phase may be "closely packed but disordered with a 9 helical structure." Likewise, Newman and Pae⁶ have briefly reported a sharpening of lines and appearance of new lines

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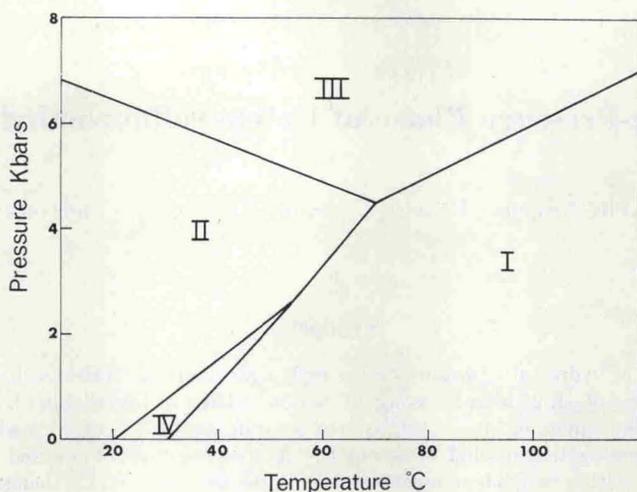


Fig. 1. Phase diagram for PTFE.

at pressures in excess of 20 kbar. Beecroft and Swenson¹ have also found some evidence of another transition above room temperature at pressures near 11 kbar.

Experimental Methods

A high-pressure x-ray camera was constructed to the design of Piermarini and Weir.⁷ This camera uses opposed diamond anvils, the surface area of the smaller diamond being ca. 0.25 mm². X-radiation from a molybdenum target (zirconium-filtered) propagates through the diamonds perpendicular to the anvil faces. The diffraction pattern is recorded on a flat-plate film. The apparatus is provided with two film holders with specimen-to-film distances of 13 and 36 mm, respectively. The first is used for exploratory photographs of low resolution and short exposure (40 kV, 25 mA; ca. 1 hr) and the second for higher resolution photographs (exposure times at 40 kV, 25 mA; ca. 8 hr). In front of the second film holder it is possible to insert a rotatable quadrant sector screen whereby the diffraction pattern of a specimen at two distinct pressures can be recorded separately on the same film. The maximum value of θ which is detectable with this apparatus is 16°.

Owing to the soft nature of the material studied, a gasket was necessary to retain a sufficient amount of sample between the diamond anvils. The gasket was constructed from molybdenum (thickness 0.25 mm with a hole 0.32 mm in diameter) following the technique of Weir, Block, and Piermarini.⁸ All high-pressure experiments were carried out at room temperature (21°C).

Oriented samples of polymer were used. These were produced by drawing PTFE at 300°C to an extension ratio of 350%. The specimens were mounted in the diamond cell with the direction of drawing parallel to the

face of the diamond anvils and thus perpendicular to the x-ray beam. These specimens were cylindrical with a diameter of 0.25 mm and a length of 0.30 mm and were prepared by using a hyperdermic needle as a punch. A specimen was loaded into the cell, pressure applied to bring the two diamonds into contact with the specimen and gasket, and then the pressure was released. However due to friction in the O-ring seals of the hydraulic system, the specimen was still under a slight excess pressure.

Some experiments have been performed to measure the pressure exerted on the sample at various stages of transformation. For this purpose PTFE, finely ground sodium chloride, and liquid glycerol were loaded into the cell. The presence of a liquid ensures that the stress on the PTFE and sodium chloride is equal. These experiments used the quadrant sector screen described above. The procedure was as follows. By means of exploratory photographs, the pressure on the specimen was adjusted to give a clearly recognizable diffraction pattern from the PTFE, e.g., a mixture of two phases or the disappearance of particular line(s). Two opposite quadrants of the large film were then exposed with the specimen at this pressure. The pressure was then released completely and the screen rotated so that the diffraction pattern at 1 bar was recorded on the other two quadrants of the film. Measurement of the change in spacing of the sodium chloride lines gives directly the value of the fractional change in volume $\Delta v/v$,

$$\Delta v/v = 3(1 - \sin \theta_1/\sin \theta_2)$$

where θ_1 , θ_2 are the Bragg angles at high and low pressure, respectively. By using the data of Decker⁹ for the compressibility of sodium chloride an estimate of the pressure is obtained.

For the structure analysis, values of interplanar spacing d were measured from the films. Intensities of reflections and structure factors were compared for general agreement. Structure factor calculations were carried out on the Titan computer of the University of Cambridge, with a set of crystallographic programs written by Matthewman.¹⁰ Atomic scattering factors for carbon and fluorine were taken from the *International Tables for X-ray Crystallography*.¹¹ Atomic coordinates were calculated by using the following values for bond lengths and angles: C—C, 1.541 Å; C—F, 1.344 Å; FCF 109.5°. The value of c and C—C necessitates bond angle CFC being 116.6°. Isotropic temperature factors B of 3 Å² were used for all atoms.

Results and Structure Analysis

The diffraction pattern shown in Figure 2 and obtained at 21°C is due to a mixture of phases II and IV. The pressure is just in excess of 1 bar and arises from the prestressing procedure described above. Around 4.5 kbar a new pattern had developed with loss of intensity of that due to phase II. This new pattern is shown in Figure 3. Further increase in pressure up to

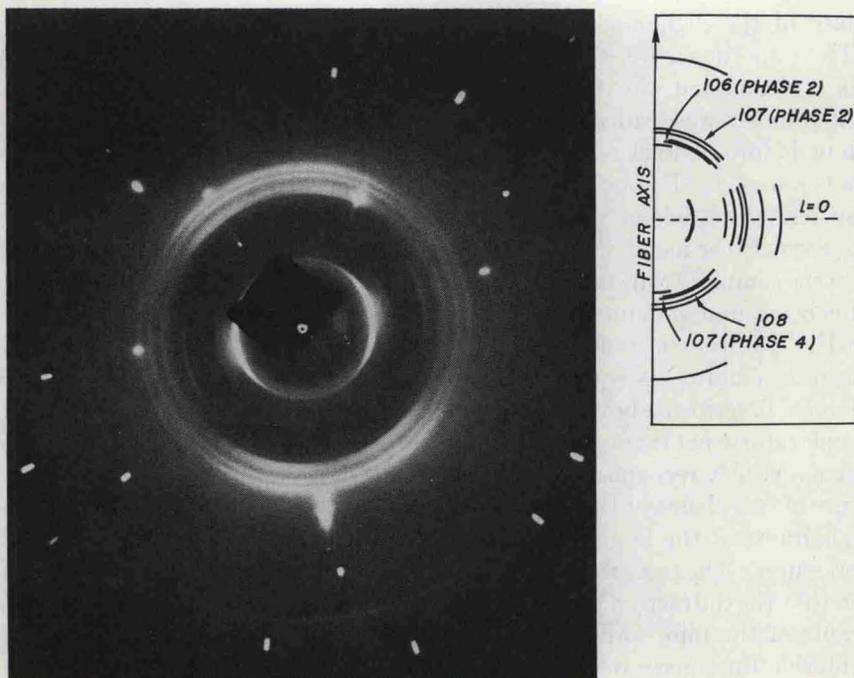


Fig. 2. X-Ray diffraction photograph of PTFE at ca. 1 bar MoK α radiation (Zr filter). The spots are Laue reflections due to the diamond anvils. Schematic diagram indicates orientation of specimen.

12 kbar caused the pattern to change gradually to that shown in Figure 4. (Figures 3 and 4 were taken from two different specimens which had different orientations of the fiber axis with respect to the diamonds.) From 12 kbar up to the maximum attainable (25 kbar) there was no further change in the pattern. All of the changes in the diffraction pattern were reversible on lowering the pressure. In Figure 5 the diffraction pattern is shown from the same specimen as that in Figure 2 but after the pressure had been raised to the maximum attainable and then back to ca. 1 bar. The pressures 4.5 ± 1 and 12 ± 1 kbar, were estimated on a different specimen containing sodium chloride and glycerol by adjusting the pressure so that for the change at 4.5 kbar the 106 and 107 reflections of phase II had just disappeared and so that for the 12 kbar measurement the 111 reflection of phase III did not increase further in intensity on increasing the pressure. In Table I the values of hkl , $\Delta v/v$, and pressure for those sodium chloride lines used in the two pressure determinations are given. In Figure 6 the diffraction pattern used to determine the 12-kbar change is presented.

Measurements from Figure 4 were used in the subsequent structure analysis. The diffraction photographs are interpreted to mean that phase III, which exists above 4.5 kbar at 21°C, is monoclinic, space group $B2/m$, with $a = 9.50 \text{ \AA}$, $b = 5.05 \text{ \AA}$, $c = 2.62 \text{ \AA}$, $\gamma = 105.5^\circ$ at 12 kbar. The molecule has changed from its helical to a planar zigzag arrangement. A projection

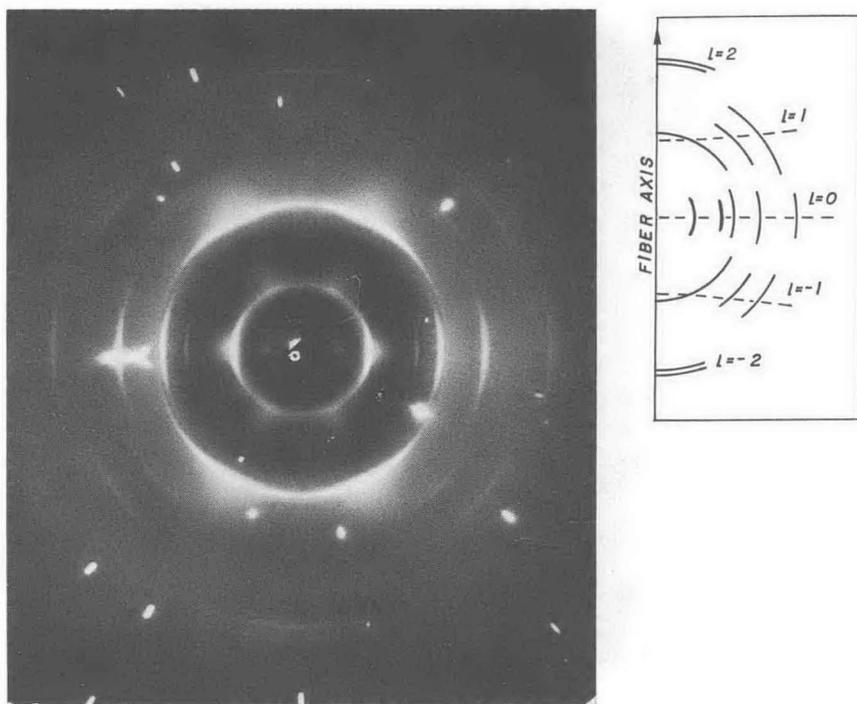


Fig. 3. X-Ray diffraction photograph of PTFE (as Fig. 2) at 4.5 kbar.

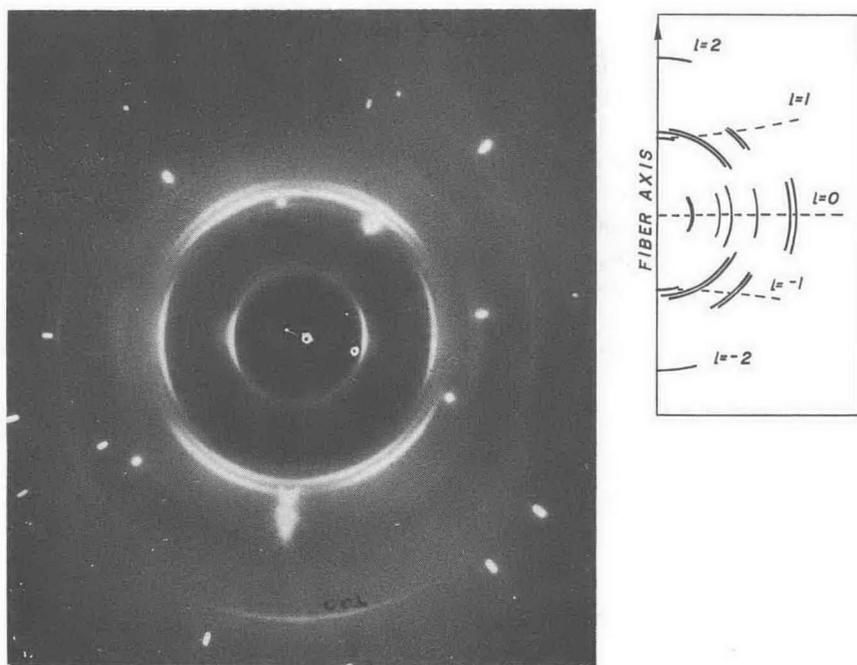


Fig. 4. X-Ray diffraction photograph of PTFE (as Fig. 2) but at 12 kbar.

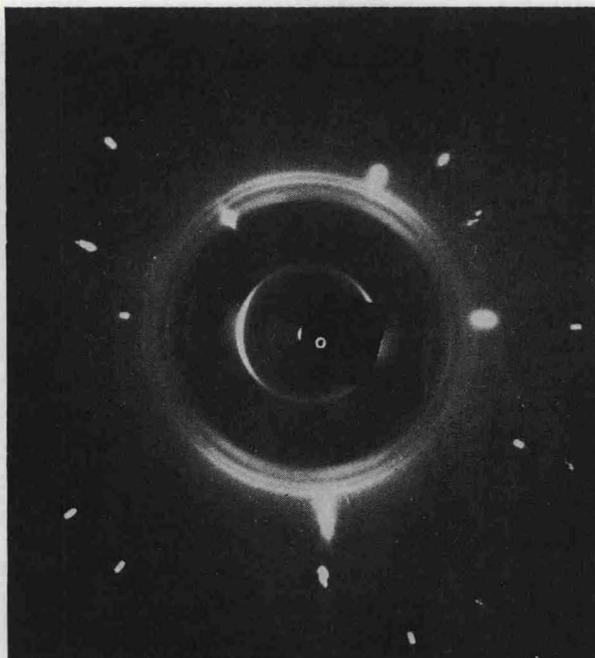


Fig. 5. X-Ray diffraction photograph of PTFE (as Fig. 2) but at 1 bar and after excursion to high pressure.

of the crystal structure onto (001) is shown in Figure 7 (the molecular axis and the monoclinic unique axis lie parallel to c). The molecule lies along one of the twofold screw axes, and the atoms are situated on mirror planes of symmetry at $z = 1/4$ ($Z = 4$ special position i Wyckoff notation¹¹). Atomic fractional coordinates are given in Table II. In Table III values of d observed, d calculated, $|F|$ calculated, and intensity observed are given for all reflections appearing on Figure 4. The observed intensities have been estimated very roughly by eye and have not been corrected for the Lorentz polarization, absorption, multiplicity, or preferred orientation effects. The x-ray density is 2.74 g/cc, and that derived from the data of Beecroft and Swenson¹ at 11 kbar is 2.70 g/cc. The distance of nearest approach

TABLE I
Values of hkl , $\Delta v/v$, and Pressure for Sodium Chloride Lines Used in Pressure Determinations

hkl	$\Delta v/v \times 10^2$	Pressure, kbar	Mean pressure, kbar
2 0 0	1.2	3.5	} 4.5 ± 1
2 2 0	2.1	5.5	
2 0 0	4.5	11.0	} 12 ± 1
2 2 0	5.6	13.0	

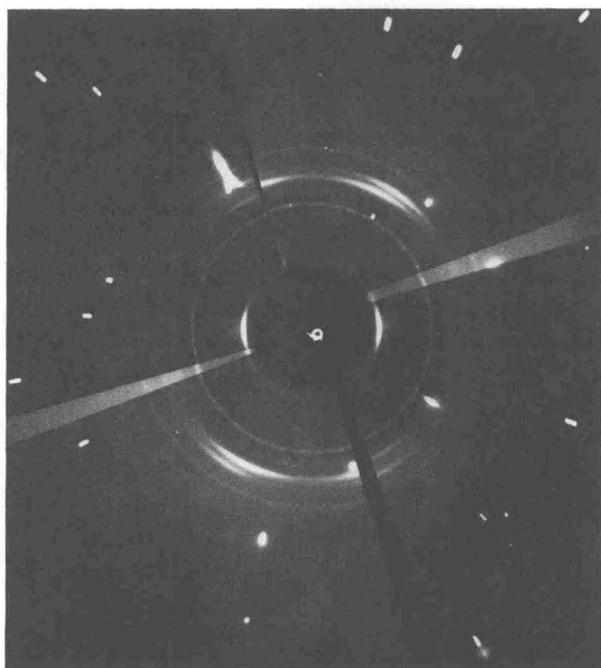


Fig. 6. X-Ray diffraction photograph of PTFE at 12 kbar and 1 bar with sodium chloride used to measure the pressure.

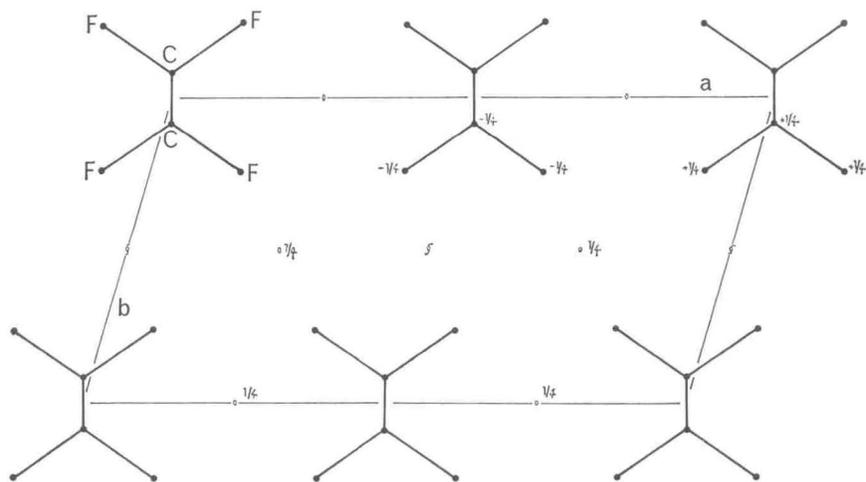


Fig. 7. (001) projection of phase III of PTFE.

between nonbonded atoms is 2.62 \AA for two fluorine atoms in the same molecule and 2.70 \AA for those in neighboring molecules.

The overwhelming evidence that the molecule has taken on a planar zigzag arrangement is seen in the position of the intense reflections $(\bar{1}11, 111)$ on the first layer lines of Figures 3 and 4. These reflections have re-

TABLE II
Atomic Fractional Coordinates for Atoms in the Asymmetric Unit of PTFE Phase III

	<i>x</i>	<i>y</i>	<i>z</i>
Carbon	0.0118	0.0832	0.2500
Fluorine	0.0150	0.2427	0.2500
Fluorine	-0.0810	0.2427	0.2500

TABLE III
Values of *hkl*, *D*_{obs}, *D*_{calc}, *F*_{calc}, *I*_{obs} for Reflections Appearing on Figure 4

<i>h</i>	<i>k</i>	<i>l</i>	<i>D</i> _{obs}	<i>D</i> _{calc}	<i>F</i> _{calc}	<i>I</i> _{obs} ^a
0	1	0	4.89	4.87	20	VS
2	1	0	2.97	2.96	9	W
0	2	0	2.45	2.43	40	VS
-4	2	0	1.94	1.95	28	M
4	1	0	1.90	1.89	32	M
4	2	0	1.48	1.48	19	S
1	0	1	2.52	2.52	9	W
-1	1	1	2.31	2.31	37	VS
1	1	1	2.17	2.17	37	S
-1	2	1	1.84	1.82	15	M
3	1	1	1.75	1.74	10	M
-5	2	1		1.42	16	
3	2	1	1.42	1.42	13	M
-1	3	1		1.41	11	
0	0	2	1.31	1.31	26	M
0	1	2	1.28	1.27	5	W

^a VS very strong, S strong, M medium, W weak.

placed the characteristic reflections of the helical structures (106, 107 of phase II and 107, 108 of phase IV; see Figure 2 or Clark and Muus³). Application of the theory of Cochran, Crick, and Vand¹² for diffraction from helical structures shows that unwinding the PTFE helix would cause the characteristic helical reflections to approach each other by movement parallel to the meridian and, in the limit of a planar zigzag arrangement, to become coincident. This has occurred in Figures 3 and 4.

Structure analysis was achieved by a trial-and-error method of solution. As there was only a fiber diagram with few reflections, it was not possible to index reflections from their value of *d* alone. It was necessary to postulate trial structures and then to compare both the position and intensity of each reflection on the photograph with that derived from the model structure. It was originally assumed that the specimen in the high pressure cell would have the same degree of preferred orientation as the drawn sample, i.e., with *c* parallel to the direction of drawing but with random orientation in the plane perpendicular to *c*. No model could be made to fit on this assumption. It was found possible, however, to fit a model by allowing preferred orientation in the plane perpendicular to *c*.

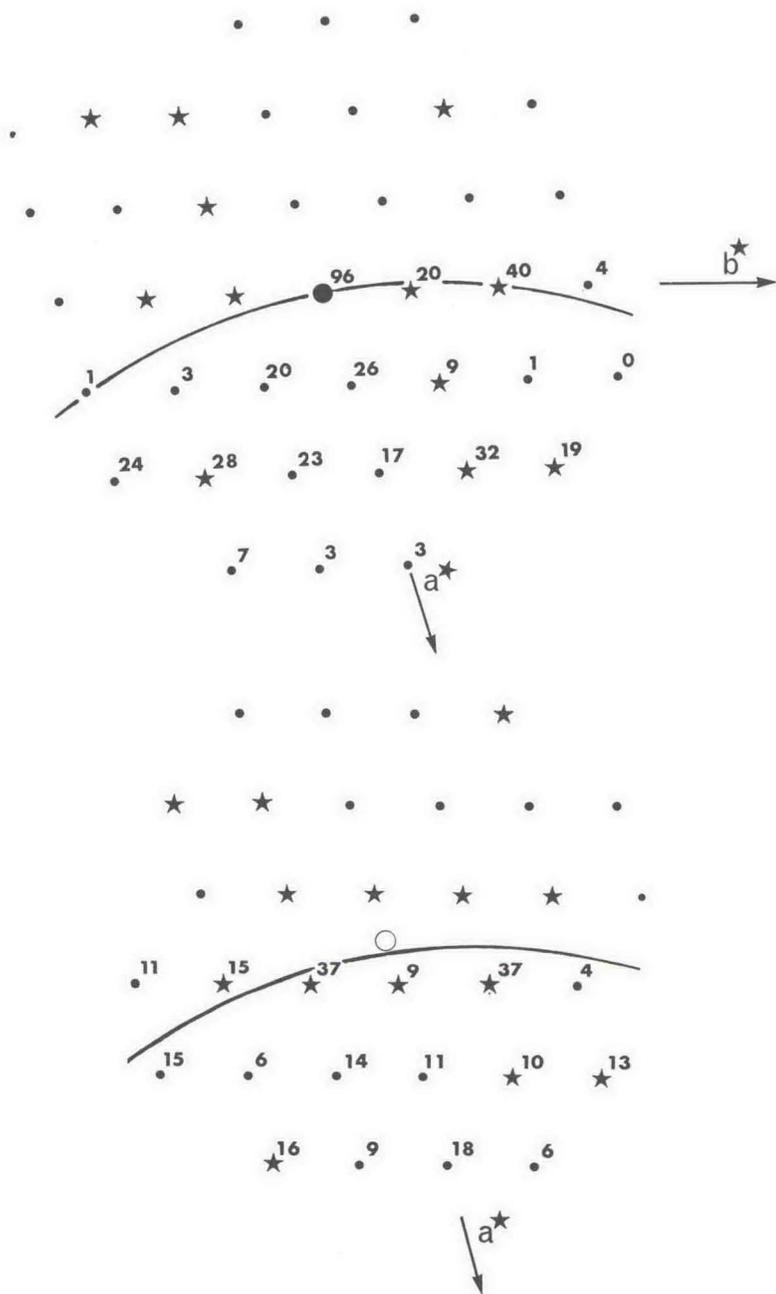


Fig. 8. Reciprocal lattice nets $hk0$, $hk1$. The reciprocal lattice nodes marked by the asterisk produce the reflections in Figure 4. Moduli of calculated structure factors and one possible position of the circle of reflection are marked.

Figure 8 shows the reciprocal lattice layers $hk0$ and $hk1$, with those reflections which appear in Figure 4 marked by asterisk. The calculated values of the structure factors and one possible position of the circle of reflection are also marked on this figure. It is clear that there is a non-random distribution of reciprocal lattice points which produce reflections on the x-ray photograph. Moreover, the $hk0$ and $hk1$ layers show the same distribution of reflections.

Rolling and transverse compression of drawn samples of phase-II or -IV PTFE¹³ with the direction of compressive stress perpendicular to the direction of drawing gradually move the $(10\bar{1}0)$ so that they lie parallel, at 60° and at 120° to the direction of compressive stress. Samples taken from the high-pressure experiments also show this orientation without regard to the pressure to which they have been subjected. Thus the sequence of deformation and phase change is as follows: the prestressing and release of pressure before the diffraction pattern at 1 bar is recorded results in the specimen being oriented in the plane perpendicular to c as described above. Further increase in pressure must cause more deformation of the specimen and consequently a slightly better defined orientation although no effect on the diffraction pattern in the high pressure apparatus is obvious. (A reduction in thickness of ca 100% occurs for experiments up to 20 kbar.) Around 4.5 kbar, phase transformation from phase II to phase III takes place sluggishly, and, as with polyethylene, there is presumably a geometric relationship between the transforming and transformed phases.¹⁴ From Figure 3 and from experiments of transverse compression on drawn samples of PTFE we have tried, without success, to determine the exact nature of this relationship. It is, however, clear from reciprocal lattice diagrams derived from Figure 3 that phase III is formed with a high degree of preferred orientation in the plane perpendicular to c . Increasing the stress further would cause slip or twinning of phase III with consequent change in the preferred orientation thus producing a change in the diffraction pattern. Since on lowering pressure Figure 4 changes back to Figure 3, it seems likely that a twinning mode is in operation. Seto, Hara, and Tamaka¹⁴ have found for the analogous phase of polyethylene that a reversible twinning mode exists. It has not been possible to prove this hypothesis for PTFE because of experimental difficulties. Complete removal of the pressure gives back an oriented sample of a mixture of phase II and IV similar to that after the initial prestressing.

An essential requirement for deformation by slip or twinning of a crystalline material is that the applied stress is not purely hydrostatic. It is certainly clear that in an opposed diamond anvil apparatus, even when using a gasket arrangement, that the stress applied to the polymer specimen has a significant shear component.

Discussion

One remarkable feature of this planar zigzag arrangement is the distance of 2.62 Å of one fluorine atom from another along the molecular chain.

The van der Waals radius for fluorine atoms is normally 1.4 Å, giving 2.8 Å for the F—F distance. Bates¹⁵ has carried out semiempirical calculations for the conformational energy for an isolated PTFE chain. Using "6-exp" terms for the interactions between nonbonded atoms, a dipole-dipole interaction term, and a threefold "intrinsic" torsion potential, he found that a helical arrangement has the least total energy. This helix was close to that experimentally observed from the room temperature x-ray observations and, at the very most, was only 530 cal/mole more stable than the planar zigzag conformation. As a more efficient side-by-side packing can be achieved with the molecule in the planar zigzag conformation, it is reasonable to find that high pressure forces the molecules into this conformation.

The pressure at which the change from helical to planar zigzag takes place is of the order of that occurring in frictional contacts and rolling. Consequently it is possible that some of the polymer is indeed in this planar form during the deformation. However, it has not been possible to observe the changes during deformation because of the reversible nature of the transformation.

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