

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  $\theta_1$ ,  $\theta_2$  are the Bragg angles at high and low pressure, respectively. By using the data of Decker<sup>9</sup> 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.<sup>10</sup> Atomic scattering factors for carbon and fluorine were taken from the *International Tables for X-ray Crystallography*.<sup>11</sup> 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 CĈC being 116.6°. Isotropic temperature factors  $B$  of 3 Å<sup>2</sup> 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

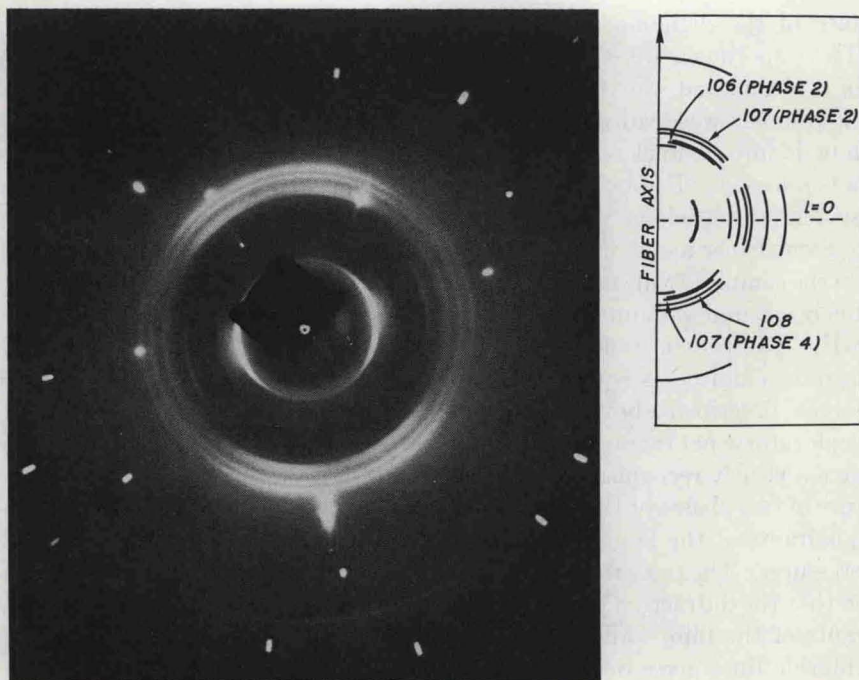


Fig. 2. X-Ray diffraction photograph of PTFE at ca. 1 bar  $\text{MoK}\alpha$  radiation (Zr filter). The spots are Laue reflections due to the diamond anvils. Schematic diagram indicates orientation of specimen.

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  $4.5 \pm 1$  and  $12 \pm 1$  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  $21^\circ\text{C}$ , 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