



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.