

## 4.5. POLYMER CRYSTALLOGRAPHY

The selection rule therefore results in a region around the  $Z$  axis of reciprocal space that is devoid of diffraction, the shape of the region depending on the helix symmetry.

## 4.5.2.3.3. Approximate helix symmetry

In some cases the nature of the subunits and their interactions results in a structure that is not exactly periodic. Consider a helical structure with  $u + x$  subunits in  $v$  turns, where  $x$  is a small ( $x \ll 1$ ) real number; *i.e.* the structure has approximate, but not exact,  $u_v$  helix symmetry. Since the molecule has an *approximate* repeat distance  $c$ , only those layer planes close to those at  $Z = l/c$  show significant diffraction. Denoting by  $Z_{mn}$  the  $Z$  coordinate of the  $n$ th Bessel order and its associated value of  $m$ , and using the selection rule shows that

$$Z_{mn} = [(um + vn)/c] + (mx/c) = (l/c) + (mx/c), \quad (4.5.2.15)$$

so that the positions of the Bessel orders are shifted by  $mx/c$  from their positions if the helix symmetry is exactly  $u_v$ . At moderate resolution  $m$  is small so the shift is small. Hence Bessel orders that would have been coincident on a particular layer plane are now separated in reciprocal space. This is referred to as *layer-plane splitting* and was first observed in fibre diffraction patterns from tobacco mosaic virus (TMV) (Franklin & Klug, 1955). Splitting can be used to advantage in structure determination (Section 4.5.2.6.6).

As an example, TMV has approximately  $49_3$  helix symmetry with a  $c$  repeat of 69 Å. However, close inspection of diffraction patterns from TMV shows that there are actually about 49.02 subunits in three turns (Stubbs & Makowski, 1982). The virus is therefore more accurately described as a  $2451_{150}$  helix with a  $c$  repeat of 3450 Å. The layer lines corresponding to this larger repeat distance are not observed, but the effects of layer-plane splitting are detectable (Stubbs & Makowski, 1982).

## 4.5.2.4. Diffraction by fibres

The kind of diffraction pattern obtained from a fibre specimen made up of helical molecules depends on the kind of specimen as described in Section 4.5.2.2. This section is divided into four parts. The first two describe diffraction patterns obtained from noncrystalline and polycrystalline fibres (which are the most common kinds used for structural analysis), and the last two describe diffraction by partially crystalline fibres.

## 4.5.2.4.1. Noncrystalline fibres

A noncrystalline fibre is made up of a collection of helical molecules that are oriented parallel to each other, but are otherwise randomly positioned and rotated relative to each other. The recorded intensity,  $I_l(R)$ , is therefore that diffracted by a single molecule cylindrically averaged about the  $Z$  axis in reciprocal space *i.e.*

$$I_l(R) = (1/2\pi) \int_0^{2\pi} |F_l(R, \psi)|^2 d\psi; \quad (4.5.2.16)$$

using equation (4.5.2.12) shows that

$$I_l(R) = \sum_n |G_{nl}(R)|^2, \quad (4.5.2.17)$$

where, as usual, the sum is over the values of  $n$  that satisfy the helix selection rule. On the diffraction pattern, reciprocal space  $(R, \psi, Z)$  collapses to the two dimensions  $(R, Z)$ . The  $R$  axis is called the *equator* and the  $Z$  axis the *meridian*. The layer planes collapse to *layer lines*, at  $Z = l/c$ , which are indexed by  $l$ . Equation (4.5.2.17) gives a rather simple relationship between the recorded intensity and the Fourier–Bessel structure factors.

Coherence length and disorientation, as described in Section 4.5.2.2, also affect the form of the diffraction pattern. These effects are described here, although they also apply to other than noncrystalline fibres. A finite coherence length leads to smearing of the layer lines along the  $Z$  direction. If the average coherence length of the molecules is  $l_c$ , the intensity distribution  $I_l(R, Z)$  about the  $l$ th layer line can be approximated by

$$I_l(R, Z) = I_l(R) \exp(-\pi l_c^2 [Z - (l/c)]^2). \quad (4.5.2.18)$$

It is convenient to express the effects of disorientation on the intensity distribution of a fibre diffraction pattern by writing the latter as a function of the polar coordinates  $(\rho, \sigma)$  (where  $\sigma$  is the angle with the  $Z$  axis) in  $(R, Z)$  space. Assuming a Gaussian orientation density function [equation (4.5.2.1)], if  $\alpha_0$  is small and the effects of disorientation dominate over those of coherence length (which is usually the case except close to the meridian), then the distribution of intensity about one layer line can be approximated by (Holmes & Barrington Leigh, 1974; Stubbs, 1974)

$$I(\rho, \sigma) \simeq \frac{I_l(R)}{2\pi\alpha_0 l_c \rho} \exp\left[-\frac{(\sigma - \sigma_l)^2}{2\beta^2}\right], \quad (4.5.2.19)$$

where (Millane & Arnott, 1986; Millane, 1989c)

$$\beta^2 = \alpha_0^2 + (1/2\pi l_c^2 \rho^2 \sin^2 \sigma_l) \quad (4.5.2.20)$$

and  $\sigma_l$  is the polar angle at the centre of the layer line, *i.e.*  $R = \rho \sin \sigma_l$ . The effect of disorientation, therefore, is to smear each layer line about the origin of reciprocal space.

## 4.5.2.4.2. Polycrystalline fibres

A polycrystalline fibre is made up of crystallites that are oriented parallel to each other, but are randomly positioned and randomly rotated about their molecular axes. The recorded diffraction pattern is the intensity diffracted by a single crystallite, cylindrically averaged about the  $Z$  axis. On a fibre diffraction pattern, therefore, the Bragg reflections are cylindrically projected onto the  $(R, Z)$  plane and their positions are described by the cylindrically projected reciprocal lattice (Finkenstadt & Millane, 1998).

The molecules are periodic and are therefore usually aligned with one of the unit-cell vectors. Since the  $z$  axis is defined as the fibre axis, it is usual in fibre diffraction to take the  $\mathbf{c}$  lattice vector as the unique axis and as the lattice vector parallel to the molecular axes. It is almost always the case that the fibre is rotationally disordered about the molecular axes, *i.e.* about  $\mathbf{c}$ . Consider first the case of a monoclinic unit cell ( $\alpha = \beta = 90^\circ$ ) so that the reciprocal lattice is cylindrically projected about  $\mathbf{c}^*$ . The cylindrical coordinates of the projected reciprocal-lattice points are then given by

$$R_{hkl}^2 = h^2 a^{*2} + k^2 b^{*2} + 2hka^*b^* \cos \gamma^* \quad (4.5.2.21)$$

and

$$Z_{hkl} = lc^*, \quad (4.5.2.22)$$

so that  $R$  depends only on  $h$  and  $k$ , and  $Z$  depends only on  $l$ . Reflections with fixed  $h$  and  $k$  lie on straight *row lines*. Certain sets of distinct reciprocal-lattice points will have the same value of  $R_{hkl}$  and therefore superimpose in cylindrical projection. For example, for an orthorhombic system ( $\gamma = 90^\circ$ ) the reciprocal-lattice points  $(hkl)$ ,  $(\bar{h}kl)$ ,  $(h\bar{k}l)$  and  $(\bar{h}\bar{k}l)$  superimpose. Furthermore, the crystallites in a fibre specimen are usually oriented randomly up and down so that the reciprocal-lattice points  $(hkl)$  and  $(h\bar{k}l)$  superimpose, so that in the orthorhombic case eight reciprocal-lattice points superimpose. Also, as described below, reciprocal-lattice points that have similar values of  $R$  can effectively superimpose.