International Tables for Crystallography (2010). Vol. B, Section 4.5.2.4.2, pp. 570–571.

atom and $\rho = (R^2 + l^2/Z^2)^{1/2}$ is the spherical radius in reciprocal space. Equations (4.5.2.12) and (4.5.2.13) allow the complex diffracted amplitudes for a helical molecule to be calculated from the atomic coordinates, and are analogous to expressions for the structure factors in conventional crystallography.

The significance of the selection rule is now more apparent. On a particular layer plane l, not all Fourier–Bessel structure factors $G_{nl}(R)$ contribute; only those whose Bessel order n satisfies the selection rule for that value of l contribute. Since any molecule has a maximum radius, denoted here by $r_{\max}$, and since $J_n(x)$ is small for $x < |n| - 2$ and diffraction data are measured out to only a finite value of R, reference to equation (4.5.2.10) [or equation (4.5.2.13)] shows that there is a maximum Bessel order that contributes significant value to equation (4.5.2.12) (Crowther *et al.*, 1970; Makowski, 1982), so that the infinite sum over n in equation (4.5.2.12) can be replaced by a finite sum. On each layer plane there is also a minimum value of $|n|$, denoted by $n_{\min}$, that satisfies the helix selection rule, so that the region $R < R_{\min}$ is devoid of diffracted amplitude where

$$R_{\min} = \frac{n_{\min} - 2}{2\pi r_{\max}}. \qquad (4.5.2.14)$$

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 nth Bessel order and its associated value of m, and using the selection rule shows that

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

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.*

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

using equation (4.5.2.12) shows that

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

where, as usual, the sum is over the values of n that satisfy the helix selection rule. On the diffraction pattern, reciprocal space (R, ψ, 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 lth layer line can be approximated by

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

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 (ρ, σ) (where σ is the angle with the Z axis) in (R, Z) space. Assuming a Gaussian orientation density function [equation (4.5.2.1)], if α_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)

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

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

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

and σ_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

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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 **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 **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

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

and

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

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 $(hk\bar{l})$ 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.

If the unit cell is either triclinic, or is monoclinic with $\alpha \neq 90^\circ$ or $\beta \neq 90^\circ$, then $\mathbf{c}^*$ is inclined to **c** and the Z axis, and the reciprocal lattice is not cylindrically projected about $\mathbf{c}^*$. Equation (4.5.2.22) for Z_{hkl} still applies, but the cylindrical radius is given by

$$R_{hkl}^2 = h^2a^{*2} + k^2b^{*2} + l^2[c^{*2} - (1/c^2)] + 2hka^*b^*\cos\gamma^* + 2hla^*c^*\cos\beta^* + 2klb^*c^*\cos\alpha^* \qquad (4.5.2.23)$$

and the row lines are curved (Finkenstadt & Millane, 1998).

The most complicated situation arises if the crystallites are rotationally disordered about an axis that is inclined to **c**. Reciprocal space is then rotated about an axis that is inclined to the normal to the a^*b^* plane, R_{hkl} and Z_{hkl} are both functions of h, k and l, equation (4.5.2.23) does not apply, and reciprocal-lattice points for fixed l do not lie on layer lines of constant Z. Although this situation is rather unusual, it does occur (Daubeny *et al.*, 1954), and is described in detail by Finkenstadt & Millane (1998).

The observed fibre diffraction pattern consists of reflections at the projected reciprocal-lattice points whose intensities are equal to the sums of the intensities of the contributing structure factors. The observed intensity, denoted by $I_l(R_{hk})$, at a projected reciprocal-lattice point on the lth layer line and with $R = R_{hk}$ is therefore given by (assuming, for simplicity, a monoclinic system)

$$I_l(R_{hk}) = \sum_{h',\,k' \in \mathscr{S}(h,\,k)} |F_{h'k'l}|^2, \qquad (4.5.2.24)$$

where $\mathscr{S}(h, k)$ denotes the set of indices (h', k') such that $R_{h'k'} = R_{hk}$. The number of independent reflections contributing in equation (4.5.2.24) depends on the space-group symmetry of the crystallites, because of either systematic absences or structure factors whose values are related.

The effect of a finite crystallite size is to smear what would otherwise be infinitely sharp reflections into broadened reflections of a finite size. If the average crystallite dimensions normal and parallel to the z axis are $l_{\rm lat}$ (*i.e.* in the 'lateral' direction) and $l_{\rm axial}$ (*i.e.* in the 'axial' direction), respectively, the profile of the reflection centred at $(R_{hk}, Z = l/c)$ can be written as (Fraser *et al.*, 1984; Millane & Arnott, 1986; Millane, 1989*c*)

$$I(R, Z) = I_l(R_{hk})S(R - R_{hk}, Z - l/c), \qquad (4.5.2.25)$$

where the profile function $S(R, Z)$ can be approximated by

$$S(R, Z) = \exp[-\pi(l_{\rm lat}^2R^2 + l_{\rm axial}^2Z^2)]. \qquad (4.5.2.26)$$

The effect of crystallite disorientation is to smear the reflections given by equation (4.5.2.26) about the origin of the projected reciprocal space. If the effects of disorientation dominate over those of crystallite size, then the profile of a reflection can be approximated by (Fraser *et al.*, 1984; Millane & Arnott, 1986; Millane, 1989*c*)

$$I(\rho, \sigma) \simeq \frac{I_l(R_{hk})}{2\pi\alpha_0 l_{\rm lat} l_{\rm axial}\rho} \times \exp\left(-\left[\frac{(\rho - \rho_{hkl})^2}{2\beta_\rho^2} + \frac{(\sigma - \sigma_{hkl})^2}{2\beta_\sigma^2}\right]\right), \qquad (4.5.2.27)$$

where $(\rho_{hkl}, \sigma_{hkl})$ are the polar coordinates of the reflection,

$$\beta_\rho^2 = \frac{l_{\rm lat}^2 l_{\rm axial}^2}{2\pi(l_{\rm lat}^2\sin^2\sigma_{hkl} + l_{\rm axial}^2\cos^2\sigma_{hkl})} \qquad (4.5.2.28)$$

and

$$\beta_\sigma^2 = \alpha_0 + \frac{l_{\rm lat}^2 l_{\rm axial}^2}{2\pi\rho_{hkl}^2(l_{\rm axial}^2\sin^2\sigma_{hkl} + l_{\rm lat}^2\cos^2\sigma_{hkl})}. \qquad (4.5.2.29)$$

Reflections that have similar enough (R, Z) coordinates overlap severely with each other and are also included in the sum in equation (4.5.2.24). This is quite common in practice because a number of sets of reflections may have similar values of R_{hk}.

4.5.2.4.3. *Random copolymers*

Random copolymers are made up of a small number of different *kinds* of monomer, whose sequence along the polymer chain is not regular, but is random, or partially random. A particularly interesting class are synthetic polymers such as copolyesters that form a variety of liquid-crystalline phases and have useful mechanical properties (Biswas & Blackwell, 1988*a*). The structures of these materials have been studied quite extensively using X-ray fibre diffraction analysis. Because the molecules do not have an average c repeat, their diffraction patterns do not consist of equally spaced layer lines. However, as a result of the small number of distinct spacings associated with the monomers, diffracted intensity is concentrated about layer lines, but these are irregularly spaced (along Z) and are *aperiodic*. Since the molecule is not periodic, the basic theory of diffraction by helical molecules described in Section 4.5.2.3.2 does not apply in this case. Cylindrically averaged diffraction from random copolymers is described here. Related approaches have been described independently by Hendricks & Teller (1942) and Blackwell *et al.* (1984). Hendricks & Teller (1942) considered the rather general problem of diffraction by layered structures made up of different kinds of layers, the probability of a layer at a

references