International Tables for Crystallography (2006). Vol. C, Section 6.3.3.3, pp. 604–606.

where z and $T(z)$ are the path lengths for the incident and diffracted beams, respectively. τ is the radius, along the line of the incident beam, of the ellipse described by the cross section of the crystal in the plane of diffraction, shown in Fig. 6.3.3.2. The equation for the ellipse is

$$\tau = R(1 - \sin^2\theta \sin^2\chi)^{-1/2}. \tag{6.3.3.15}$$

The outgoing elliptical radius v satisfies

$$Av^4 + Bv^2 + C = 0, \tag{6.3.3.16}$$

where

$$\begin{aligned} A &= [1 - \sin^2\theta \sin^2\chi]^2 \\ B &= -2R^2[1 - \sin^2\theta \sin^2\chi] \\ &\quad - 2(\tau - z)^2[\cos^2\theta - \sin^2\theta\cos^2\chi]\sin^2 2\theta \sin^2\chi \\ C &= R^4 + 2R^2(\tau - z)^2 \sin^2 2\theta \sin^2\chi \cos 2\theta \\ &\quad + (\tau - z)^4 \sin^4 2\theta \sin^4\chi. \end{aligned}$$

In the case where the cylinder axis is inclined at an angle Γ to the φ axis, these equations become

$$\begin{aligned} A &= [1 - \sin^2(\theta + \beta)\sin^2\chi_1]^2 \\ B &= -2R^2[1 - \sin^2(\theta + \beta)\sin^2\chi_1] \\ &\quad - 2(\tau - z)^2[\cos^2(\theta + \beta) \\ &\quad - \sin^2(\theta + \beta)\cos^2\chi_1]\sin^2 2\theta \sin^2\chi_1 \\ C &= R^4 + 2R^2(\tau - z)^2 \sin^2 2\theta \sin^2\chi_1 \cos 2(\theta + \beta) \\ &\quad + (\tau - z)^4 \sin^4 2\theta \sin^4\chi_1, \end{aligned}$$

where

$$\tan\beta = \sin\Gamma \sin\varphi / [\sin\Gamma \cos\chi \cos\varphi + \sin\chi \cos\Gamma].$$

The roots of the quadratic equation (6.3.3.16) for v^2 are real and positive for reflection from within the crystal. The convergent path length T is given by the positive root of the triangle formula

$$T^2 - 2T(\tau - z)\cos 2\theta + (\tau - z)^2 - v^2 = 0. \tag{6.3.3.17}$$

It should be noted that the volume of the specimen irradiated changes with the angular settings of the diffractometer. Normalization to constant volume requires that the absorption correction be multiplied by the volume-correction factor $[1 - \sin^2(\theta - \beta)\sin^2\chi_1]^{-1/2}$.

The method readily extends to the case of a cylindrical window or sheath, such as used for mounting an unstable crystal of conventional size. The correction in this case is

$$\begin{aligned} &\exp[-\mu(\tau_2 - \tau_1 + v_2 - v_1)] \\ &\quad = \exp\Big(-\mu(R_2 - R_1)\{[1 - \sin^2(\theta - \beta)\sin^2\chi_1]^{-1/2} \\ &\qquad + [1 - \sin^2(\theta + \beta)\sin^2\chi_1]^{-1/2}\}\Big), \end{aligned} \tag{6.3.3.18}$$

where the subscripts 1 and 2 apply to the inner and outer radii, respectively.

The integral in equation (6.3.3.14) may be evaluated by Gaussian quadrature, *i.e.* by approximation as a weighted sum of the values of the function at the N zeros X_i of the Legendre polynomial of degree N in the interval $[-1, +1]$. The weights w_i for the points are tabulated by Abramowitz & Stegun (1964). Further details are given in Subsection 6.3.3.4. The emergent path lengths $T(z_1)$ and $T(z_2)$ for the case of the sheath are calculated as functions of the Gaussian variable X_i using the linear transformation

$$z_i = \tau_1 X_i + \tau_2, \quad i = 1, 2, \ldots, N. \tag{6.3.3.19}$$

This transformation converts the Gaussian variable X into the beam coordinate z for each i of the N summation points.

6.3.3.3. *Analytical method for crystals with regular faces*

For a crystal with regular faces, (6.3.3.1) may be integrated exactly, giving the correction in analytical form. In its simplest form, the analytical method applies to specimens with no re-entrant angles. It is efficient for crystals with a small number of faces. Its accuracy does not depend on the size of the absorption coefficient. The principles can be illustrated by reference to the two-dimensional case of a triangular crystal shown in Fig. 6.3.3.3.

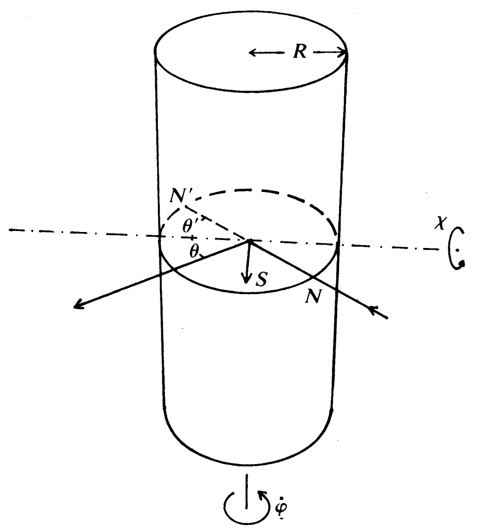

Fig. 6.3.3.1. Geometry of the Eulerian cradle with the axis of a cylindrical specimen coincident with the φ axis.

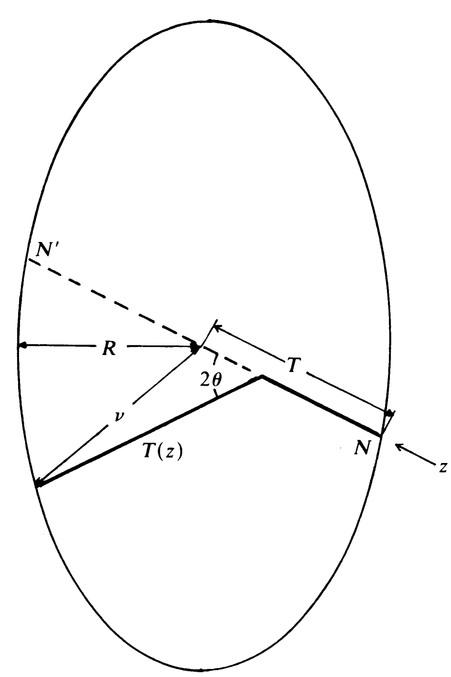

Fig. 6.3.3.2. Cross section of the plane of diffraction for a cylindrical specimen coincident with the φ axis.

The crystal is divided into polygons *ADC*, *AFD*, *CDE*, and *BEDF* as shown. The radiation incident on each polygon enters through one face of the crystal, and is either absorbed or emerges through another. Within each polygon, the loci of constant absorption are the straight lines dotted in Fig. 6.3.3.3. It is convenient to subdivide *BEDF* into the triangles *BEF* and *EDF*. By the derivation of an expression for the contribution of a triangular crystal to the scattering, including allowance for absorption, and with the sum taken over the component triangles *ADC*, *AFD*, *CDE*, *BEF*, and *EDF*, the correction for absorption can be calculated.

A three-dimensional crystal is divided into polyhedra, for each of which the radiation enters through one crystal face and leaves through another. Corners for the polyhedra are of five types, namely,

(1) Crystal vertex.

(2) An intersection of a ray through a lit vertex with an opposite face.

(3) An intersection of an incident ray through a lit (*i*) vertex with a plane of diffracted (*d*) rays through a lit (*d*) edge, and the corresponding intersection with incident and diffracted beams interchanged.

(4) An intersection of a plane of incident rays through a lit (*i*) edge with an opposite edge, and its equivalent.

(5) An intersection on a shaded face of planes of incident and diffracted rays through (*i*) and (*d*) edges.

For each vertex x, y, z, the sum of the path lengths to each of the crystal faces is calculated, and multiplied by the absorption coefficient μ to give the optical path length using the equation

$$\mu r_j = \mu(d_j - a_j x - b_j y - c_j z)/(a_j u + b_j v + c_j w),$$

where u, v, w are the direction cosines for the beam direction, and $a_j x + b_j y + c_j z = d_j$ is the equation for the crystal face. The minimum for all j is the path length to the surface.

The analytical expression for the scattering power for each polyhedron, including the effect of absorption, can be expressed in a convenient form by subdividing the polyhedra into tetrahedra. The auxiliary points define the corners of the tetrahedra.

The total diffracted intensity is proportional to the sum of contributions, one from each tetrahedron, of the form

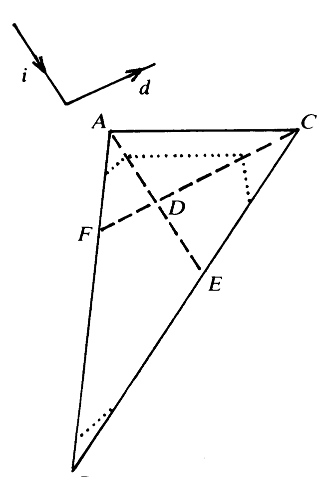

Fig. 6.3.3.3. The crystal *ABC* divided into polygons by the dashed lines *AE* and *CF* parallel to the incident (*i*) and diffracted (*d*) beams, respectively. A locus of constant absorption is shown dotted.

$$\begin{aligned} R_t &= 6V_t e^{-g} H(1) \\ &= \frac{6V_t}{(b+c)} e^{-g} \left\{ \frac{h(a) - h(a+b)}{b} - \frac{h(a+b) - h(a+b+c)}{c} \right\}, \end{aligned} \tag{6.3.3.20}$$

where

$$h(x) = \frac{1 - e^{-x}}{x}. \tag{6.3.3.21}$$

V_t is the volume of the tetrahedron. For a crystal with Cartesian coordinate vertices 1, 2, 3, and 4,

$$V_t = \tfrac{1}{6} \begin{vmatrix} x_1 - x_2 & x_1 - x_3 & x_1 - x_4 \\ y_1 - y_2 & y_1 - y_3 & y_1 - y_4 \\ z_1 - z_2 & z_1 - z_3 & z_1 - z_4 \end{vmatrix}. \tag{6.3.3.22}$$

The g_i are optical path lengths (*i.e.* path lengths rescaled by the absorption coefficient) ordered so that

$$g_1 < g_2 < g_3 < g_4$$

and

$$g = g_1, \quad a = g_2 - g_1, \quad b = g_3 - g_2, \quad c = g_4 - g_3. \tag{6.3.3.23}$$

The transmission factor for the crystal is the sum of the scattering powers for all the tetrahedra $\sum R_t$ divided by the volume $\sum V_t$. The equality of the total volume to the sum of the V_t values for the component tetrahedra provides a useful check on the accuracy of the calculations, since the total volume is independent of the beam directions, and must be the same for all reflections.

When any of a, b, and c are small, asymptotic forms are required for the expressions in (6.3.3.20). For $\varepsilon < 0.3 \times 10^{-2}$, and

$$\begin{aligned}
&a < \varepsilon && h(a) = 1 - a/2 + a^2/3! \\
& && h(b+a) = h(b) + ah_1(b) + a^2 h_2(b)/2; \\
&b < \varepsilon && h(a+b) = h(a) + bh_1(a) + b^2 h_2(a)/2 \\
& && [h(a) - h(a+b)]/b \\
& && \quad = -h_1(a) - bh_2(a)/2 - b^2 h_3(a)/3!; \\
&c < \varepsilon && [h(a+b) - h(a+b+c)]/c \\
& && \quad = -h_1(a+b) - ch_2(a+b)/2 \\
& && \qquad -c^2 h_3(a+b)/3!; \\
&b, c < \varepsilon && H(1) = h_2(a)/2 + (2b+c)h_3(a)/3! \\
& && \qquad + (3b^2 + 3bc + c^2)h_4(a)/4!; \\
&a, c < \varepsilon && h(a) = 1 - a/2 + a^2/3! \\
& && [h(a+b) - h(a+b+c)]/c \\
& && \quad = -h_1(a+b) - ch_2(a+b)/2 \\
& && \qquad -c^2 h_3(a+b)/3!; \\
&a, b < \varepsilon && h(a+b) = 1 - (a+b)/2 + (a+b)^2/3! \\
& && [h(a) - h(a+b)]/b \\
& && \quad = 1/2 - a/3 - b/3! + a^2/8 + ab/8 + b^2/4!; \\
&a, b, c < \varepsilon && H(1) = \frac{1}{3!} - \frac{a+b}{8} + (b-c)/4! \\
& && \qquad + [(a+b+c)(4a+3b) \\
& && \qquad + 2a^2 + ab + c^2]/5!;
\end{aligned} \tag{6.3.3.24}$$

where the nth derivative of $h(x)$ is

$$h_n(x) = (-)^n h(x) - \{(-)^n + n h_{n-1}(x)\}/x. \qquad (6.3.3.25)$$

An alternative method of calculating the scattering power of each Howells polyhedron is based on a subdivision into slices. Within each polyhedron, the loci of constant absorption are planes, equivalent to the dotted lines for the two-dimensional example in Fig. 6.3.3.3. The loci may be determined from the path lengths of rays diffracted at each vertex of the polyhedron. The sum of the path lengths in the incident and diffracted directions is found for each vertex, and the loci determined by interpolation. The slices into which each polyhedron is divided are bounded at the upper and lower faces by planes parallel to the loci of constant absorption, such that at least one vertex of the polyhedron lies on those planes.

The volume of the slice is determined from the coordinates of the vertices on each of the opposite faces. Dummy vertices are inserted if necessary to make the number of vertices on the top and bottom faces identical. For simplicity, an axis (z) is chosen perpendicular to the upper face. This locus of constant absorption with N_v vertices x_i, y_i, z_i has an area

$$D_U = 1/2 \sum_{i=1}^{N_v} (x_i y_{i+1} - y_i x_{i+1}) = E/2. \qquad (6.3.3.26)$$

The corresponding vertices on the lower face may be written $x_i + q\Delta x_i, y_i + q\Delta y_i, z_i + q\Delta z$, with $q = 1$. The lower face has an area

$$D_L = 1/2(E + qF + q^2 G), \quad q = 1, \qquad (6.3.3.27)$$

where

$$F = \sum_{i=1}^{N_v} \Delta x_i y_{i+1} + \Delta y_{i+1} x_i - \Delta x_{i+1} y_i - \Delta y_i x_{i+1}$$

and

$$G = \sum_{i=1}^{N_v} \Delta x_i \, \Delta y_{i+1} - \Delta y_i \, \Delta x_{i+1} \qquad (6.3.3.28)$$

so that the volume of the slice is

$$V_s = 1/2(z_L - z_U)(E + F/2 + G/3). \qquad (6.3.3.29)$$

The diffracting power of an element of the slice, allowing for absorption, is $D(q)\exp(-\mu T)\,\mathrm{d}z$, where T is the total path length of the rays diffracted from this plane. Because of the definition of the Howells polyhedron, the path length

$$T = T_U + q(T_L - T_U) = T_U + q\Delta T. \qquad (6.3.3.30)$$

Thus, the total diffracting power of the slice

$$\begin{aligned} R_s &= 1/2(z_L - z_U)\exp(-\mu T_U) \\ &\quad \times \int_0^1 (E + qF + q^2 G)\exp(-\mu q \Delta T)\,\mathrm{d}q \\ &= 1/2(z_L - z_U)\exp(-\mu T_L)\left\{\frac{-E}{\mu\Delta T} - \frac{F(\mu\Delta T + 1)}{(\mu\Delta T)^2} \right. \\ &\quad \left. - G\frac{(\mu\Delta T^2 + 2\mu\Delta T + 2)}{(\mu\Delta T)^3}\right\} \\ &\quad - 1/2(z_L - z_U)\exp(-\mu T_U)\left\{\frac{-E}{\mu\Delta T} - \frac{F}{(\mu\Delta T)^2} - \frac{2G}{(\mu\Delta T)^3}\right\}. \end{aligned} \qquad (6.3.3.31)$$

The transmission factor for the Howells polyhedron is obtained by summing over the slices, and that for the whole crystal is obtained by summing over the polyhedra, *i.e.*

$$A = \sum R_s \Big/ \sum V_s, \qquad (6.3.3.32)$$

where the crystal volume is $\sum V_s$.

$\mathrm{d}A/\mathrm{d}\mu$, required in calculating $\bar{T}$ for the extinction correction, can be obtained by differentiating R_s for each slice with respect to μ, summing the derivatives for each slice, and dividing by $\sum V_s$. To reduce rounding errors in calculation, it may be desirable to rescale the crystal dimensions so that the path lengths are of the order of unity, multiplying the absorption coefficient by the inverse of the scale factor. Further details are given by Alcock, Pawley, Rourke & Levine (1972).

The number of component tetrahedra or slices, which determines the time and precision required for calculation, is a rapidly increasing function of the number of crystal faces. The method may be computationally prohibitive for crystals with complex shapes.

6.3.3.4. *Gaussian integration*

The integral in the transmission factor in equation (6.3.3.1) may be approximated by a sum over grid points spaced at intervals through the crystal volume. It is usually convenient to orient the grid parallel to the crystallographic axes. The grid is non-isometric, the points being chosen weighted by Gaussian constants to minimize the difference between the weighted sum at those points and the exact value of the integral.

Thus, an integral such as $\int_a^b f(y)\,\mathrm{d}y$ may be approximated (Stroud & Secrest, 1966) by

$$\int_a^b f(y)\,\mathrm{d}y = \frac{b-a}{2}\sum_{i=1}^{n} w_i f(y_i) + R_n, \qquad (6.3.3.33)$$

where

$$y_i = \left(\frac{b-a}{2}\right)X_i + \left(\frac{b+a}{2}\right),$$

X_i is the ith zero of the Legendre polynomial $P_n(X)$,

$$w_i = \frac{2}{(1 - X_i^2)}[P_n'(X_i)]^2, \qquad (6.3.3.34)$$

and

$$R_n = \frac{(b-a)^{2n+1}(n!)^4}{(2n+1)[(2n!)]^3} 2^{2n+1} f^{(2n)}(\xi), \quad -1 < \xi < 1. \qquad (6.3.3.35)$$

When applying this to the calculation of a transmission coefficient (Coppens, 1970), we commence with the a-axis grid points x_i selected such that

$$x_i = x_{\min} + (x_{\max} - x_{\min})X_i, \qquad (6.3.3.36)$$

where the X_i are the Gaussian constants.

For each x_i, a line is drawn parallel to $\mathbf{b}$ and points are then selected such that

$$y_{ij} = y_{\min}(x_i) + [y_{\max}(x_i) - y_{\min}(x_i)]\,X_j. \qquad (6.3.3.37)$$

The procedure is repeated for the c direction, yielding

$$z_{ijk} = z_{\min}(x_i, y_j) + [z_{\max}(s_i, y_j) - z_{\min}(x_i, y_j)]\,X_k. \qquad (6.3.3.38)$$

To calculate the absorption corrections, the incident and diffracted wavevectors are determined. For each grid point, the sum T_{ijk} of the path lengths for the incident and diffracted beams is evaluated. The sum that approximates the transmission coefficient is then

$$A = 1/V \sum_{i,j,k} w_i w_j w_k \exp(-\mu T_{ijk}). \qquad (6.3.3.39)$$

references