International Tables for Crystallography (2006). Vol. C, Section 6.4.11, pp. 611–612.

$$W(\varDelta) = \frac{1}{\eta\sqrt{2\pi}} \exp\left(-\frac{\varDelta^2}{2\eta^2}\right), \qquad (6.4.8.2)$$

where $\varDelta$ is the angular deviation of the block from the mean orientation of all blocks in the crystal, and η is the standard deviation of the distribution. (The assumption of a Gaussian distribution is not critical to the argument that follows.)

Let the crystal be a cube of side L, and let α be the probability that a ray reflected by the first block is reflected again by a subsequent block. The effective size of the crystal for Bragg scattering of a single incident ray is then

$$\langle L \rangle = \ell + (L - \ell)\alpha, \qquad (6.4.8.3)$$

while the size of the crystal for all other attenuation processes is L, since, for them, the Bragg condition does not apply. The probability of re-scattering, α, can readily be expressed in terms of crystallographic quantities. The full width at half-maximum intensity of the Darwin reflection curve is given, after conversion to the glancing-angle (θ) scale, by Zachariasen (1945) as

$$\varDelta\theta = \frac{3\lambda^2 N_c F}{\pi\sqrt{2}\sin 2\theta} \text{ (radians)}. \qquad (6.4.8.4)$$

The full width at half-maximum (FWHM) of the mosaic-block distribution (6.4.8.2) is derived in the usual way, and the parameter g $(= 1/2\eta\sqrt{\pi})$ is introduced to clear (to 1%) numerical constants. Then α, which is equal to the ratio of the widths, is given by

$$\alpha = \frac{g N_c \lambda^2 F}{\sin 2\theta}. \qquad (6.4.8.5)$$

Insertion of $\langle L \rangle$ [equation (6.4.8.3)] in place of ℓ in equation (6.4.8.1) for x leads to

$$x = [N_c \lambda F \ell + g Q_\theta (L - \ell)]^2, \qquad (6.4.8.6)$$

where $Q_\theta = N_0^2 \lambda^3 F^2 / \sin 2\theta$.

6.4.9. Secondary extinction

A separate treatment of secondary extinction is required only in the uncorrelated block model, and the method given by Hamilton (1957) is used in this work. The coupling constant in the H–D equations is given by $\sigma(\varDelta\theta) = Q_\theta E_p W(\varDelta\theta)$, where $Q_\theta = N_c^2 \lambda^3 F^2 / \sin 2\theta$ for equatorial reflections in the neutron case, E_p is the correction for primary extinction evaluated at the angle θ, and $W(\varDelta\theta)$ is the distribution function for the tilts between mosaic blocks. The choice of this function has a significant influence on the final result (Sabine, 1985), and a rectangular or triangular form is suggested.

In the following equations for the secondary-extinction factor,

$$x = E_p Q_\theta G D, \qquad (6.4.9.1)$$

and A and B are given by equations (6.4.5.6) and (6.4.5.7). The average path length through the crystal for the reflection under consideration is D and G is the integral breadth of the angular distribution of mosaic blocks. It is important to note that A should be set equal to one if the data have been corrected for absorption, and B should be set equal to one if absorption-weighted values of D are used. If D for each reflection is not known, the average dimension of the crystal may be used for all reflections.

For a rectangular function, $W(\varDelta\theta) = G$, for $|\varDelta\theta| \le 1/2G$, $W(\varDelta\theta) = 0$ otherwise, and the secondary-extinction factor becomes

$$E_L = \frac{\exp(-\mu D)}{2x}[1 - \exp(-2x)], \qquad (6.4.9.2)$$

$$E_B = \frac{A}{1 + Bx}. \qquad (6.4.9.3)$$

For a triangular function, $W(\varDelta\theta) = G(1 - |\varDelta\theta|G)$, for $|\varDelta\theta| \le 1/G$, $W(\varDelta\theta) = 0$ otherwise, and the secondary-extinction factor becomes

$$E_L = \frac{\exp(-\mu D)}{x}\left\{1 - \frac{1}{2x}[1 - \exp(-2x)]\right\}, \qquad (6.4.9.4)$$

$$E_B = \frac{2A}{(Bx)^2}[Bx - \ln|1 + Bx|]. \qquad (6.4.9.5)$$

6.4.10. The extinction factor

6.4.10.1. *The correlated block model*

For this model of the real crystal, the variable x is given by equation (6.4.8.6), with ℓ and g the refinable variables. Extinction factors are then calculated from equations (6.4.5.3), (6.4.5.4), and (6.4.5.5). For a reflection at a scattering angle of 2θ from a reasonably equiaxial crystal, the appropriate extinction factor is given by (6.4.7.1) as $E(2\theta) = E_L \cos^2 2\theta + E_B \sin^2 2\theta$.

It is a meaningful procedure to refine both primary and secondary extinction in this model. The reason for the high correlation between ℓ and g that is found when other theories are applied, for example that of Becker & Coppens (1974), lies in the structure of the quantity x. In the theory presented here, x is proportional to F^2 for pure primary extinction and to Q_θ^2 for pure secondary extinction.

6.4.10.2. *The uncorrelated block model*

When this model is used, two values of x are required. These are designated x_p for primary extinction and x_s for secondary extinction. Equation (6.4.8.1) is used to obtain a value for x_p. The primary-extinction factors are then calculated from (6.4.5.3), (6.4.5.4) and (6.4.5.5), and $E_p(2\theta)$ is given by equation (6.4.7.1). In the second step, x_s is obtained from equation (6.4.9.1), and the secondary-extinction factors are calculated from either (6.4.9.2) and (6.4.9.3) or (6.4.9.4) and (6.4.9.5). The result of these calculations is then used in equation (6.4.7.1) to give $E_s(2\theta)$. It is emphasised that x_s includes the primary-extinction factor. Finally, $E(2\theta) = E_p(2\theta) E_s[E_p(2\theta), 2\theta]$.

Application of both models to the analysis of neutron diffraction data has been carried out by Kampermann, Sabine, Craven & McMullen (1995).

6.4.11. Polarization

The expressions for the extinction factor have been given, by default, for the σ-polarization state, in which the electric field vector of the incident radiation is perpendicular to the plane defined by the incident and diffracted beams. For this state, the polarization factor is unity. For the π-polarization state, in which the electric vector lies in the diffraction plane, the factor is $\cos 2\theta$. The appropriate values for the extinction factors for this state are given by multiplying F by $\cos 2\theta$ wherever F occurs.

For neutrons, which are matter waves, the polarization factor is always unity.

For an unpolarized beam from an X-ray tube, the observed integrated intensity is given by $I^{\rm obs} = \frac{1}{2} I_\theta^{\rm kin} \left(E_\sigma + E_\pi \cos^2 2\theta\right)$. In the kinematic limit, $E_\sigma = E_\pi = 1$, and the power to which $\cos 2\theta$

is raised (the polarization index n) is 2. In the pure primary-extinction limit, $E_\sigma = 1/(N_c \lambda F \ell)$, while $E_\pi = 1/(N_c \lambda F \ell \cos 2\theta)$. Hence, $n = 1$. In the pure secondary-extinction limit, $E_\sigma = 1/(gQL)$, where g is the mosaic-spread parameter, while $E_\pi = 1/(QgL \cos 2\theta)$. Hence, $n = 0$. In all real cases, n will lie between 0 and 2, and its value will reflect departures from kinematic behaviour.

6.4.12. Anisotropy

The parameters describing the microstructure of the crystal are the mosaic-block size and the angle between the mosaic blocks. These are not constrained in any way to be isotropic with respect to the crystal axes. In particular, they are not constrained by symmetry. For example, in a face-centred-cubic crystal under uniaxial stress, slip will occur on one set of {111} planes, leading to a dislocation array of non-cubic symmetry. In principle, anisotropy can be incorporated into the formal theory by allowing ℓ and g to depend on the Miller indices of the reflections. This has not been done in this work, but reference should be made to the work of Coppens & Hamilton (1970).

6.4.13. Asymptotic behaviour of the integrated intensity

From the definition of the extinction factor, the integrated intensity from a non-absorbing crystal in which the block size is sufficiently small, and the mosaic spread is sufficiently large, will approach the kinematic limit. It is instructive to examine the behaviour in the limit of large block size and low mosaic spread. The volume of the mosaic block is v and the volume of the crystal is V. The number of blocks in the crystal is V/v $(= L^3/\ell^3)$. The surface area of the block is $v^{2/3}$ and of the crystal is $V^{2/3}$. The subscripts L and B will again be used for the Laue and the Bragg case, respectively. The kinematic integrated intensity is given by

$$I^{\rm kin} = Q_\theta V = \lambda^3 N_c^2 F^2 V / \sin 2\theta. \qquad (6.4.13.1)$$

6.4.13.1. *Non-absorbing crystal, strong primary extinction*

(*a*) *Laue case*

The limiting value of E_L is $(2/\pi)^{1/2} x^{-1/2}$. Hence,

$$I_L = (4/5) N_c \lambda^2 F V v^{-1/3} / \sin 2\theta. \qquad (6.4.13.2)$$

The dynamical theory has a numerical constant of 1/2 instead of 4/5.

(*b*) *Bragg case*

The limiting value of E_B is $x^{-1/2}$. Hence,

$$I_B = N_c \lambda^2 F V v^{-1/3} / \sin 2\theta. \qquad (6.4.13.3)$$

This is in exact agreement with the dynamical theory (Ewald solution).

6.4.13.2. *Non-absorbing crystal, strong secondary extinction*

For this condition, the limiting values of the integrated intensity are $I_L = (4/5) g^{-1} V^{2/3}$, and $I_B = g^{-1} V^{2/3}$. In this limit, which was also noted by Bacon & Lowde (1948) and by Hamilton (1957), the intensity is proportional only to the mosaic spread and to the surface area of the crystal. No structural information is obtained from the experiment.

6.4.13.3. *The absorbing crystal*

Only the Bragg case for thick crystals will be considered here. The asymptotic values of A, B, and C are $1/(2\mu L^*)$, $1/(\mu L^*)$, and $2/(\mu L^*)$, respectively, so that

$$BCx = 2N_c^2 \lambda^2 F^2 / \mu^2. \qquad (6.4.13.4)$$

For BCx small, the integrated intensity, I_B, is given by

$$I_B = (Q_\theta / 2\mu)[1 - (N_c F/)2] V^{2/3}. \qquad (6.4.13.5)$$

For BCx large,

$$I_B = (1/2\sqrt{2})[1 - (\mu/2\lambda N_c F)^2] \lambda^2 N_c F V^{2/3} / \sin 2\theta. \qquad (6.4.13.6)$$

It can be shown that the parameter g (which has no relation to the parameter g used to describe the mosaic-block distribution) used by Zachariasen (1945) in discussing this case is equal to $-\mu/2NCF$. Hence, on his y scale,

$$I_B = (\pi/2\sqrt{2})[1 - g^2]. \qquad (6.4.13.7)$$

The value he obtained is $I_B = 8/3[1 - 2|g|]$, while Sabine & Blair (1992) found $I_B = 8/3[1 - 2.36|g|]$.

6.4.14. Relationship with the dynamical theory

Sabine & Blair have shown that the two classical limits for the integrated intensity in the symmetric Bragg case can be obtained from the Hamilton–Darwin equations when the dynamic refractive index of the crystal is explicitly taken into account. Their treatment is based on the following expression for $\sigma(\Delta k)$:

$$\sigma(\Delta k) = \frac{Q_k \mu D T}{\sinh(\mu D)} \left\{ \frac{\sin^2(\pi T \Delta K) + \sinh^2(\mu D/2)}{(\pi T \Delta K)^2 + (\mu D/2)^2} \right\},$$

where ΔK refers to the scattering vector within the crystal. Use of the relation $\Delta K \cong \Delta k$ and the replacement of the Fresnellian by a Lorentzian leads to equation (6.4.5.1) with the inclusion of C (6.4.5.2). The relationship between ΔK and Δk, which is a function of the dynamic refractive index of the crystal, is derived in the original publication. Insertion of this expression into equations (6.4.4.3) and (6.4.4.4) and integration over Δk, since the diffracted beam is observed outside the crystal, leads to a dynamic extinction factor, which can be compared with the values determined from the equations given in Section 6.4.5. The integrations cannot be carried out analytically and require numerical calculation in each case.

Olekhnovich & Olekhnovich (1978, 1980) have given limited expressions for primary extinction in the parallelepiped and the cylinder based on the equations of the dynamical theory in the non-absorbing case. Comparisons with the results of the present theory are given by Sabine (1988) and Sabine, Von Dreele & Jørgensen (1988).

6.4.15. Definitions

The quantity F used in these equations is the modulus of the structure factor per unit cell. It includes the Debye–Waller factor and the scattering length of each atom. (For X-ray diffraction, the scattering length of the electron is 2.8178×10^{-15} m.) λ is the wavelength of the incident radiation. 2θ is the angle of scattering. N_c is the number of unit cells per unit volume. The path length of the diffracted beam is D, while T is the thickness of the crystal normal to the diffracting plane. In practice, when the orientation of the crystal is unknown, D can be taken equal to ℓ or L, where these are average dimensions of the mosaic block or crystal.