$$\rho = \frac{\Theta}{b(D\ell)^{1/2}}, \tag{6.4.3.1}$$

where ρ is the dislocation density, Θ is the total mosaic spread in radians, b is the Burgers vector of the dislocations, ℓ is the block size and D is the size of the irradiated region.

6.4.4. Radiation flow

The radiation flow is governed by the Hamilton–Darwin (H–D) equations (Darwin, 1922; Hamilton, 1957). These equations are

$$\frac{\partial P_i}{\partial t_i} = \tau P_i + \sigma P_f, \tag{6.4.4.1}$$

$$\frac{\partial P_f}{\partial t_f} = \tau P_f + \sigma P_i. \tag{6.4.4.2}$$

Here, P_i is the radiation current density ($m^{-2}\ s^{-1}$) in the incident ($i =$ initial) beam, P_f is the current density in the diffracted ($f =$ final) beam. The distances t_i and t_f are measured along the incident and diffracted beams, respectively. The coupling constant σ is the cross section per unit volume for scattering into a single Bragg reflection, while τ, which is always negative, is the cross section per unit volume for removal of radiation from the beams by any process. In what follows, it will be assumed that absorption is the only significant process, and τ is given by $\tau = -(\sigma + \mu)$, where μ is the linear absorption coefficient (absorption cross section per unit volume). This assumption may not be true for neutron diffraction, in which incoherent scattering may have a significant role in removing radiation. In those cases, τ should include the incoherent scattering cross section per unit volume.

The H–D equations have analytical solutions in the Laue case ($2\theta = 0$) and the Bragg case ($2\theta = \pi$). The solutions at the exit surface are, respectively,

$$P_f = \frac{P_i^0}{2}\exp(-\mu D)[1 - \exp(-2\sigma D)], \tag{6.4.4.3}$$

and

$$P_f = \frac{P_i^0 \sigma \sinh(aD)}{a\cosh(aD) - \tau\sinh(aD)}, \tag{6.4.4.4}$$

with $a^2 = \tau^2 - \sigma^2$. The path length of the diffracted beam through the crystal is D. The current density at the entrance surface is P_i^0.

To find formulae for the integrated intensity, it is necessary to express σ in terms of crystallographic quantities.

6.4.5. Primary extinction

Zachariasen (1967) introduced the concept of using the kinematic result in the small-crystal limit for σ, while Sabine (1985, 1988) showed that only the Lorentzian or Fresnellian forms of the small crystal intensity distribution are appropriate for calculations of the energy flow in the case of primary extinction. Thus,

$$\sigma(\Delta k) = \frac{Q_k T}{1 + (\pi T \Delta k)^2}, \tag{6.4.5.1}$$

where $Q_k V$ is the kinematic integrated intensity on the k scale ($k = 2\sin\theta/\lambda$), $Q_k = (N_c\lambda F)^2/\sin\theta$, and T is the volume average of the thickness of the crystal normal to the diffracting plane (Wilson, 1949). To include absorption effects, which modify the diffraction profile of the small crystal, it is necessary to replace T by TC, where

$$C = \frac{\tanh(\mu D/2)}{(\mu D/2)}. \tag{6.4.5.2}$$

To determine the extinction factor, E, the explicit expression for $\sigma(\Delta k)$ [equation (6.4.5.1)] is inserted into equations (6.4.4.3) and (6.4.4.4), and integration is carried out over Δk. The limits of integration are $+\infty$ and $-\infty$. The notation E_L and E_B is used for the extinction factors at $2\theta = 0$ and $2\theta = \pi$ rad, respectively.

After integration and division by $I^{\rm kin}$, it is found that

$$E_L = \exp(-y)\{[1 - (x/2) + (x^2/4) - (5x^3/48) + (7x^4/192)]\}, \quad x \le 1, \tag{6.4.5.3}$$

$$E_L = \exp(-y)[2/(\pi x)]^{1/2}\{1 - [1/(8x)] - [3/(128x^2)] - [15/(1024x^3)]\}, \quad x > 1, \tag{6.4.5.4}$$

$$E_B = A/(1 + Bx)^{1/2}, \tag{6.4.5.5}$$

$$A = \exp(-y)\sinh y/y, \tag{6.4.5.6}$$

and

$$B = (1/y) - \exp(-y)/\sinh y = A\frac{{\rm d}(A^{-1})}{{\rm d}y}. \tag{6.4.5.7}$$

In these equations, $x = Q_k TCD$ and $y = \mu D$.

6.4.6. The finite crystal

Exact application of the formulae above requires a knowledge of the shape of the crystal or mosaic block and the angular relation between the reflecting plane and the crystal surface. These are not usually known, but it can be assumed that the average block or crystal at each value of the scattering angle (2θ) has sides of equal length parallel to the incident- and diffracted-beam directions. For this crystal,

$$T = D\sin\theta, \ D = \langle L\rangle, \tag{6.4.6.1}$$

and

$$x = N_c{}^2\lambda^2F^2\langle L\rangle^2\tanh(\mu L^*/2)/(\mu L^*/2). \tag{6.4.6.2}$$

The quantity L^* is set equal to ℓ for the mosaic block and to L for the crystal.

6.4.7. Angular variation of E

Werner (1974) has given exact solutions to the transport equations in terms of tabulated functions. However, for the simple crystal described above, a sufficiently accurate expression is

$$E(2\theta) = E_L\cos^2\theta + E_B\sin^2\theta. \tag{6.4.7.1}$$

6.4.8. The value of x

For the single mosaic block, application of the relationship $T = D\sin\theta$ leads to

$$x = (N_c\lambda F\ell)^2, \tag{6.4.8.1}$$

where ℓ is the average path length through the block. In the correlated block model, x is also a function of the tilts between blocks and the size of the crystal.

It will be assumed for the discussion that follows in this section that the mosaic blocks are cubes of side ℓ, and the distribution of tilts will be assumed to be isotropic and Gaussian, given by

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

where Δ 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

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

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

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

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

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

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

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 $\sigma(\Delta\theta) = Q_\theta E_p W(\Delta\theta)$, where $Q_\theta = N_c^2\lambda^3F^2/\sin 2\theta$ for equatorial reflections in the neutron case, E_p is the correction for primary extinction evaluated at the angle θ, and $W(\Delta\theta)$ 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,

$$x = E_pQ_\theta GD, \qquad (6.4.9.1)$$

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, $W(\Delta\theta) = G$, for $|\Delta\theta| \le 1/2G$, $W(\Delta\theta) = 0$ 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, $W(\Delta\theta) = G(1-|\Delta\theta|G)$, for $|\Delta\theta| \le 1/G$, $W(\Delta\theta) = 0$ 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 $\cos 2\theta$

references