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6.4. The flow of radiation in a real crystal

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6.4.1. Introduction

In a diffraction experiment, a beam of radiation passes into the interior of a crystal *via* an entrance surface. When the crystal is set for Bragg reflection, a diffracted beam passes out of the crystal through the exit surface. The scattering vector is allowed to sweep over a small region around the exact Bragg position, and the total intensity scattered into a detector is recorded. This record (called the integrated intensity) contains all the information available to the crystallographer, and includes the starting point for crystal structure analysis, which is the relative magnitude of the structure factor for the reflection under examination. In order to determine the relationship between the structure factor and the observed integrated intensity, it is necessary to take into account all processes that remove intensity from the incident and diffracted beams during their passage through the crystal.

The standard theory, which is called the kinematic theory, assumes that there is no attenuation of either the incident beam or the diffracted beam during the diffraction process. The fact that this is not so in a real crystal is expressed in the following way.

$$I^{\rm obs} = EI^{\rm kin}.$$

E is equal to unity for a crystal, called the ideally imperfect crystal, which scatters in accordance with the kinematical approximation. In kinematic theory, the integrated intensity is proportional to the square of the magnitude of the structure factor, $|F|^2$. The factor E has a value very much less than unity for a perfect crystal, to which the dynamical theory of diffraction applies. In the dynamical theory, the integrated intensity is proportional to the first power of the structure-factor magnitude, $|F|$. All crystals in nature lie between these limits, either because of the microstructure of the crystal, or because of the removal of photons or neutrons by electronic or nuclear processes. A real crystal may behave as a perfect crystal for some reflections and as an imperfect crystal for others. It is the purpose of this section to give formulae by which the value of $|F|$ can be extracted from the measured intensity of a reflection from a real crystal without resorting to mechanical methods of changing its state of perfection. Those methods, such as quenching or irradiation with fast neutrons, usually introduce problems that are more difficult than those that they were designed to solve.

The formulae are constructed so that they apply at all angles of scattering, and are either analytic or rapidly convergent for ease of use in least-squares methods.

It should be noted that whenever the symbol F subsequently appears it should be interpreted as the modulus of the structure factor, which **always** *includes the Debye–Waller factor.*

In common with all published theories of extinction, the theory presented here is phenomenological, in that the assumption is made that the wavevector within the crystal does not differ from the wavevector in vacuum whatever the strength of the interaction between the incident radiation and the crystal. The results will be compared with a solution in the symmetric Bragg case in which the dynamic refractive index of the crystal has been taken into account (Sabine & Blair, 1992).

6.4.2. The model of a real crystal

Following Darwin (1922), a crystal is assumed to consist of small blocks of perfect crystal (called mosaic blocks). These blocks are separated by small-angle boundaries formed by dislocations (Read, 1953), which introduce random tilts of the blocks with respect to each other. It is necessary to divide this model into two subclasses. In the first, the introduction of tilts does not destroy the spatial correlation between atoms in different blocks that have the same relative orientation. In this model (hereafter called the correlated block model), the removal of dislocations constituting the mosaic block boundaries by, for example, thermal annealing will recover a monolithic perfect single crystal. In the second subclass, which is the original Darwin model (hereafter called the uncorrelated block model), the introduction of tilts destroys spatial coherence between blocks. The weakness of the latter model is that removal of the tilts does not recover the monolithic single crystal, but leads to a brick-wall-type structure with parallel bricks but varying thicknesses of mortar between the bricks. In practice, thermal-annealing treatments at sufficiently high temperatures always regain the single crystal.

The existence of this problem for extinction theory has been recognized (Wilkins, 1981). Theories will be given in this article for both limits. For a more complete treatment, the introduction of a mixing parameter proportional to either the dislocation density in the crystal or the physical proximity of mosaic blocks may be necessary.

For a single incident ray, only those blocks whose orientation is within the natural width for Bragg scattering from a perfect crystal will contribute to Bragg diffraction processes. For these processes, the crystal presents a sponge- or honeycomb-like aspect, since blocks that are outside the angular range for scattering do not contribute to the diffraction pattern. During the scan used for measurement of the integrated intensity, all blocks will contribute. At any angular setting, the entire volume of the crystal contributes to absorption and other non-Bragg-type interactions.

6.4.3. Primary and secondary extinction

It is customary in the literature to distinguish between primary extinction, which is extinction within a single mosaic block, and secondary extinction, which occurs when a ray reflected by one mosaic block is subsequently reflected by another block with the same orientation. In the correlated block model, no distinction is made between the two types, and the problem reduces to that of primary extinction in the crystal as a whole. The angular distribution of blocks is an indicator of the extent of diffraction coupling between blocks during the passage of a single ray through the crystal.

In the uncorrelated block model, the problem must be separated into two regimes, with the input to the secondary-extinction system being the intensities from each mosaic block after allowance for primary extinction within each mosaic block.

In all theories, it is assumed that the primary-extinction parameter (the block size) and the secondary-extinction parameter (the mosaic spread) are physically independent quantities. If the dislocations in the crystal are concentrated in the small-angle boundaries, the two parameters can be combined to give the dislocation density. Qualitatively, the lower the dislocation density the larger the block size and the smaller the mosaic spread. Cottrell (1953) has given the relationship

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

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

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

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 $\sigma(\Delta\theta) = Q_\theta E_p W(\Delta\theta)$, 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 $W(\Delta\theta)$ 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,

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

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

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,

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

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,

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

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

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

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

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

For BCx large,

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

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 $\sigma(\Delta k)$:

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

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.

References

6.1.1

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