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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

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