

case of a wedge-shaped crystal the new correction is very small [up to 12% for the function $\varphi(\sigma)$] and is zero for the plane parallel plate. For spherical crystals the influence of the primary beam is more serious. If σr_0 becomes large compared to 1 the deviation from a crystal bathed in a constant beam increases. This case becomes important for small scattering angles and large crystals, *i.e.* when extinction effects become large. Under these circumstances, corrections for primary beam shapes might not be negligible.

In any case, before applying the uncorrected theory it is recommended that each specific experiment should be carefully investigated in order to establish whether

a treatment for the primary beam is necessary. With the use of high-speed computers this can be done for arbitrarily shaped crystals and primary beams by using equations (2a-c).

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Extinction in Neutron Diffraction

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This article re-analyses the extinction problem in diffraction. It has been proved that Hamilton's equations are valid only for mosaic crystals, type I. The solution of these equations has been found for any shape of crystal using general initial conditions.

Introduction

The extinction problem received considerable attention once it was found necessary to make corrections for extinction, when determining crystallographic structures. Later, the necessity of using monochromatic crystals more efficiently led to the same problem.

For an ideal crystal, the extinction factor is determined from the dynamic theory, but in practice its formula has been computed only for an infinite, plane parallel crystal plate (see Zachariasen, 1945). For a real crystal, however, Darwin's equations formulated for an infinite plane parallel plate, were generalized by Hamilton (1957) for a crystal of arbitrary shape and these were solved numerically by him. Werner & Arrott (1965) arranged Hamilton's equations into an integral form and solved them by successive approximations. This, in practice, is a tedious method which requires much calculation. But, as will be indicated below, there are regions in the crystal where it is possible to obtain a direct solution of Hamilton's equations by solving two initial-value problems. It should be mentioned that Werner, Arrott, King & Kendrick (1966) have proposed another method for solving Hamilton's equations for both finite and infinite plane parallel crystal plates. This method involves the expansion of the incident and diffracted intensities, in terms of modified Bessel functions. This method is not general because, when another crystal shape is considered,

another set of functions must be found from which the expansion may be performed.

Zachariasen (1967) has suggested a general extinction theory. Several authors have carried out a number of experimental tests and no experimental agreement has been found for Zachariasen's theory for strong extinction. It has been concluded that some approximations used by Zachariasen are not valid (see Cooper & Rouse, 1970). Werner (1969) also found fault with this theory. One criticism is that Hamilton's equations do not hold good for a perfect crystal. Zachariasen wrote Hamilton's equations using variables t_1 and t_2 to represent the depths below the surface measured along the two propagation directions. But for these variables the form of the equations is not always preserved. A new term appears, which contains the derivative of the function describing the boundary. This term disappears only if the crystal takes the form of a parallelepiped whose edges are oriented in the two propagation directions. Therefore, Zachariasen's theory is valid in this case only.

Consequently, it is necessary to reconsider the extinction problem. §1 of this article is devoted to a general discussion of the transport equations for Bragg diffraction. It will be demonstrated that the Hamilton equations are valid for type I mosaic crystals only. In the §2, these equations are solved for a crystal of any shape. An application of the formulae derived in §2 is given in §3.

1. Transport equations for Bragg diffraction

In a classic diffraction experiment, a slightly divergent, energetic narrow beam of neutrons (X-rays) is incident on a monocrystal at an angle approximately equal to the Bragg angle θ_B , such that a single diffracted beam is produced. For simplicity, it will be assumed that the incident beam is perfectly monochromatic. Passing on to the real case is a simple matter.

The spatial and angular distribution of the scattered neutrons needs to be determined. The starting point of the analysis is equation (1) from Vineyard's (1954) article. Let $I^{(n)}(\mathbf{r}, \mathbf{s})$ be the intensity at point \mathbf{r} of neutrons reflected n times and propagated along the direction \mathbf{s} . Let $\sigma_d(\mathbf{s}, \mathbf{s}')$ be the cross section per unit volume, describing Bragg scattering in direction \mathbf{s}' of neutrons propagated along direction \mathbf{s} . The cross section describing Bragg scattering of neutrons propagated in direction \mathbf{s} , is defined thus:

$$\sigma(\mathbf{s}) = \int d\mathbf{s}' \sigma_d(\mathbf{s}, \mathbf{s}') ; \quad (1)$$

σ_d corresponds to a sub-macroscopic part of the crystal, which is large enough to have a structure, but small enough to have only one scattering process. If the total absorption coefficient is denoted by μ , the equation governing the scattering is:

$$\mathbf{s} \nabla_{\mathbf{s}} I^{(n)}(\mathbf{r}, \mathbf{s}) = -[\mu + \sigma(\mathbf{s})] I^{(n)}(\mathbf{r}, \mathbf{s}) + \int d\mathbf{s}' \sigma_d(\mathbf{s}', \mathbf{s}) I^{(n-1)}(\mathbf{r}, \mathbf{s}') . \quad (2)$$

For convenience, the coordinate system is taken to have x and y axes along the incident and reflected direction respectively, thus satisfying the ideal Bragg relationship, and the z axis normal to the (x, y) horizontal plane (Fig. 1). Any direction \mathbf{s} in the incident and reflected beams will be given by the horizontal and vertical divergences γ_1, δ_1 and γ_2, δ_2 measured relative to the x, y axes. It will be assumed that these angles are small. When the neutrons are scattered n times it will be noticed that, if n is even, propagation is in the incident beam and, if n is odd, in the reflected beam. Therefore, from equation (2):

$$\frac{\partial I_0(\mathbf{r}\gamma_1\delta_1)}{\partial x} = -[\mu + \sigma(\gamma_1\delta_1)] I_0(\mathbf{r}\gamma_1\delta_1) + \iint \sigma_d(\gamma_2\delta_2\gamma_1\delta_1) I(\mathbf{r}\gamma_2\delta_2) d\gamma_2 d\delta_2 , \quad (3a)$$

$$\frac{\partial I(\mathbf{r}\gamma_2\delta_2)}{\partial y} = -[\mu + \sigma(\gamma_2\delta_2)] I(\mathbf{r}\gamma_2\delta_2) + \iint \sigma_d(\gamma_1\delta_1\gamma_2\delta_2) I_0(\mathbf{r}\gamma_1\delta_1) d\gamma_1 d\delta_1 , \quad (3b)$$

where

$$I_0(\mathbf{r}\gamma_1\delta_1) = \sum_{k=0}^{\infty} I^{(2k)}(\mathbf{r}, \mathbf{s}) , \quad (4a)$$

$$I(\mathbf{r}\gamma_2\delta_2) = \sum_{k=0}^{\infty} I^{(2k+1)}(\mathbf{r}, \mathbf{s}') . \quad (4b)$$

It is now necessary to calculate σ_d , which is defined as a differential cross section per unit volume in a kinematic approximation.

(i) Small perfect crystal

For a perfect crystal, the range of coherence is extended to the whole volume of the crystal. With this in mind, Zachariassen (1967) defines σ_d as the ratio of the kinematic cross section of the whole crystal to its volume. Thus:

$$\sigma_d(\gamma_1\delta_1\gamma_2\delta_2) = \frac{1}{u} \frac{d\sigma}{d\Omega} = \frac{1}{u} |F(\mathbf{\kappa})|^2 \sum_{\mathbf{l}} \exp(i\mathbf{\kappa}\mathbf{l})^2 \quad (5)$$

where $\mathbf{\kappa}$ is the momentum transfer, \mathbf{l} is the lattice vector and u is the volume of the crystal. When using equation (5) to determine σ_d it is assumed that its value does not depend on \mathbf{r} . For the parallelepiped shown in Fig. 1, the right-hand side of equation (5) becomes:

$$\begin{aligned} \sigma_d(\gamma_1\delta_1\gamma_2\delta_2) &= \sigma_{ah}(\gamma_1\gamma_2)\sigma_{av}(\delta_1\delta_2) \\ &= Q\alpha^3/\sin 2\theta \cdot \frac{\sin^2 \pi\alpha\gamma_1}{(\pi\alpha\gamma_1)^2} \cdot \frac{\sin^2 \pi\alpha\gamma_2}{(\pi\alpha\gamma_2)^2} \\ &\times \frac{\sin^2 [\pi\alpha(\delta_1+\delta_2)/\sin 2\theta]}{[\pi\alpha(\delta_1+\delta_2)/\sin 2\theta]^2} \end{aligned} \quad (6)$$

where

$$Q = \lambda^3 n_c^2 |F|^2 / \sin 2\theta ; \quad \alpha = t/\lambda . \quad (7)$$

In equation (6), h and v are the factors which exclusively depend upon the horizontal and vertical divergences respectively. For any shape of crystal σ_d becomes more complicated. But (6) may be used provided that t is replaced by \bar{t} the mean thickness measured normal to the incident direction (Zachariassen, 1967). By using (6) and (1):

$$\sigma(\gamma_1\delta_1) = \sigma_h(\gamma_1) = Q\alpha \frac{\sin^2 \pi\alpha\gamma_1}{(\pi\alpha\gamma_1)^2} . \quad (8)$$

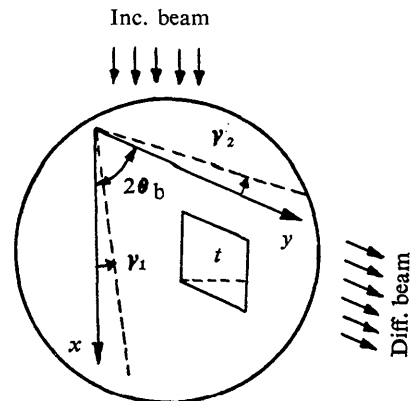


Fig. 1. Geometry of incident and diffraction directions. The axes x, y are taken along the incident and reflected directions satisfying the ideal Bragg relation.

(ii) *Real crystals*

It is assumed that a real crystal consists of a large number of small, perfect crystals whose misalignment obeys the isotropic Gaussian distribution law:

$$W(\Delta) = \sqrt{2g} \exp(-2\pi g^2 \Delta^2), \quad (9)$$

where Δ is the angular deviation measured from the mean orientation. It will also be assumed that these mosaic regions are almost identical and the primary extinction is weak. Therefore, for any such region, the cross section per unit volume is given by (6), where α depends on the mean size of that region. Consequently, a mean value $\bar{\sigma}_a$ may be defined:

$$\begin{aligned} \bar{\sigma}_a(\gamma_1 \delta_1 \gamma_2 \delta_2) &= \bar{\sigma}_{ah}(\gamma_1 \gamma_2) \bar{\sigma}_{ah}(\delta_1 \delta_2) \\ &= \int \sigma_{ah}(\gamma_1 - \Delta, \gamma_2 - \Delta) W(\Delta) d\Delta \\ &\times \int \sigma_{av}(\delta_1 - \Delta \sin \theta, \delta_2 - \Delta \sin \theta) W(\Delta) d\Delta. \end{aligned} \quad (10)$$

With the approximation:

$$\sin^2 \pi x / (\pi x)^2 \simeq \exp(-\pi x^2) \quad (11)$$

(10) becomes:

$$\begin{aligned} \bar{\sigma}_{ah}(\gamma_1 \gamma_2) &= Q \frac{g\alpha}{\sqrt{\alpha^2 + g^2}} \\ &\times \exp \left\{ -\pi \frac{\alpha^2}{2(\alpha^2 + g^2)} [(\alpha^2 + 2g^2)(\gamma_1^2 + \gamma_2^2) - 2\alpha^2 \gamma_1 \gamma_2] \right\} \end{aligned} \quad (12a)$$

$$\begin{aligned} \bar{\sigma}_{av}(\delta_1 \delta_2) &= \frac{\alpha g}{\sqrt{g^2 \sin^2 2\theta + 2\alpha^2 \sin^2 \theta}} \\ &\times \exp \left[-\pi \frac{\alpha^2 g^2}{g^2 \sin^2 2\theta + 2\alpha^2 \sin^2 \theta} (\delta_1 + \delta_2)^2 \right], \end{aligned} \quad (12b)$$

and therefore, from (1):

$$\begin{aligned} \bar{\sigma}(\gamma_1 \delta_1) = \bar{\sigma}_h(\gamma_1) &= \sqrt{2} Q \frac{g\alpha}{\sqrt{\alpha^2 + 2g^2}} \\ &\times \exp \left(-2\pi \frac{\alpha^2 g^2}{\alpha^2 + 2g^2} \gamma_1^2 \right). \end{aligned} \quad (13)$$

Now, using the theorem of the mean for the integrals over δ_2 and δ_1 respectively in the right hand side of (3a) and (3b) and integrating the resulting equations from δ_1 and δ_2 , then:

$$\begin{aligned} \frac{\partial P_0(\mathbf{r}\gamma_1)}{\partial x} &= -[\mu + \bar{\sigma}_h(\gamma_1)] P_0(\mathbf{r}\gamma_1) + \int \bar{\sigma}_{ah}(\gamma_1 \gamma_2) P(\mathbf{r}\gamma_2) d\gamma_2 \end{aligned} \quad (14a)$$

$$\begin{aligned} \frac{\partial P(\mathbf{r}\gamma_2)}{\partial y} &= -[\mu + \bar{\sigma}_h(\gamma_2)] P(\mathbf{r}\gamma_2) + \int \bar{\sigma}_{ah}(\gamma_2 \gamma_1) P_0(\mathbf{r}\gamma_1) d\gamma_1, \end{aligned} \quad (14b)$$

where:

$$P_0(\mathbf{r}\gamma_1) = \int I_0(\mathbf{r}\gamma_1 \delta_1) d\delta_1, \quad (15a)$$

$$P(\mathbf{r}\gamma_2) = \int I(\mathbf{r}\gamma_2 \delta_2) d\delta_2. \quad (15b)$$

Clearly, for a perfect crystal the values $\bar{\sigma}_{ah}$ and $\bar{\sigma}_h$ are replaced in (14a) and (14b) with σ_{ah} and σ_h respectively.

Zachariasen (1967) investigated two limiting cases for a real crystal.

(a) If $\alpha \gg g$ the crystal is of type I, and (12a) and (13) then become:

$$\bar{\sigma}_{ah}(\gamma_1 \gamma_2) = Q W(\gamma_1) \delta(\gamma_2 - \gamma_1), \quad (16)$$

$$\bar{\sigma}_h(\gamma_1) = Q W(\gamma_1), \quad (17)$$

and (14a) and (14b) become:

$$\frac{\partial P_0(\mathbf{r}\gamma)}{\partial x} = -[\mu + Q W(\gamma)] P_0(\mathbf{r}, \gamma) + Q W(\gamma) P(\mathbf{r}, \gamma), \quad (18a)$$

$$\frac{\partial P(\mathbf{r}, \gamma)}{\partial x} = -[\mu + Q W(\gamma)] P(\mathbf{r}, \gamma) + Q W(\gamma) P_0(\mathbf{r}, \gamma). \quad (18b)$$

These are the transport equations in the form given by Hamilton.

(b) If $\alpha \ll g$ the crystal is type II, and (12a) and (13) are written:

$$\bar{\sigma}_{ah}(\gamma_1 \gamma_2) = Q \alpha^2 \exp[-\pi \alpha^2 (\gamma_1^2 + \gamma_2^2)], \quad (19)$$

$$\bar{\sigma}_h(\gamma_1) = Q \alpha \exp(-\pi \alpha^2 \gamma_1^2), \quad (20)$$

and (14a) and (14b) are unaltered.

Thus, the transport equations for Bragg diffraction have the form given by Hamilton only for type I mosaic crystals.

2. The solution of the Hamilton equations

Equations (18) will be solved for any shape of crystal with any initial conditions. This means that the crystal may be totally or partially immersed in the incident beam, which may have a spatial variation at the boundary.

So, let us denote the quantity $QW(\gamma)$ from equations (18) by σ and by using the function transformation:

$$P_0 = \psi \exp[-(\mu + \sigma)(x + y)], \quad (23a)$$

$$P = \varphi \exp[-(\mu + \sigma)(x + y)], \quad (23b)$$

equations (18) become:

$$\frac{\partial \psi}{\partial x} = \sigma \varphi; \quad \frac{\partial \varphi}{\partial y} = \sigma \psi. \quad (24a, b)$$

The boundary conditions for the functions ψ and φ will be obtained from the boundary conditions for P_0 and P using (23). By differentiating (24):

$$\frac{\partial^2 \psi}{\partial x \partial y} = \sigma^2 \psi; \quad \frac{\partial^2 \varphi}{\partial x \partial y} = \sigma^2 \varphi. \quad (25a, b)$$

Equations (25) are partial differential second-order equations of hyperbolic type for which the correspond-

ing Riemann function is:

$$w(x, y, \xi, \eta) = j_0[2\sigma\sqrt{(\xi-x)(y-\eta)}] \quad (26)$$

where j_0 is the Bessel function of zero order. The characteristic curves are the straight lines $x=c_1$ and $y=c_2$.

There are three kinds of initial-value problems for this type of equations: Cauchy, characteristic initial value, and mixed. Depending upon the region within the crystal, one of these will be applicable.

As far as the first two are concerned, there are some general formulae from which the function ψ (or ϕ) may be deduced (see Morse & Feshbach, 1953). For the mixed problem, however, only the successive approximation method has up to now been available. Below, another method for solving the mixed problem is suggested. This, although it requires less computation than the successive approximation method, is not a general method, but it holds for the case of multiple Bragg diffraction.

(i) Cauchy problem

The function and one of its derivatives are given on a monotonic curve Γ . The solution at a given point $R(\xi, \eta)$ (Fig. 2) is:

$$\psi_R = \psi_A + \int_{AB} w \frac{\partial \psi}{\partial x} dx + \psi \frac{\partial w}{\partial y} dy \quad (27a)$$

when ψ and $\partial\psi/\partial x$ are on the curve Γ , or:

$$\psi_R = \psi_B - \int_{AB} \psi \frac{\partial w}{\partial x} dx + w \frac{\partial \psi}{\partial y} dy \quad (27b)$$

when ψ and $\partial\psi/\partial y$ are on the curve Γ . Here $\int_{AB} \dots$ is a curvilinear integral on Γ , between the points A and B and in the sense from A to B . w is the Riemann function given by (26).

(ii) Characteristic initial-value problem

Here the function is given on the characteristics $x=x_c$, $y=y_c$ (Fig. 3), or equally the function is given on one characteristic and the derivative (of the function) on the other. The solution at any point $R(\xi, \eta)$ is:

$$\begin{aligned} \psi_R &= \psi_A + \int_C^B w \frac{\partial \psi}{\partial x} dx - \int_C^A \psi \frac{\partial w}{\partial y} dy \\ &= \psi_B - \int_C^B \psi \frac{\partial w}{\partial x} dx + \int_C^A w \frac{\partial \psi}{\partial y} dy. \end{aligned} \quad (28a, b)$$

The function ψ , given by the formulae (27) and (28), may be expanded in a power series of σ because along the boundary this function and its derivatives, as well as w and its derivatives, may be expanded in such a series. Clearly, these formulae are also valid for the function ϕ .

(iii) Mixed problem

Generally, for this problem the function is defined on a monotonic curve Γ and on a characteristic

(Fig. 2). For the case under consideration the problem may be formulated using other similar methods because the functions ϕ and ψ are correlated by (24). The problems for two practical cases are presented. Let the curve Γ be described by equations $y=\alpha(x)$ or $x=\beta(y)$.

(iii*a*) In the mixed problem for ψ it is known that ψ is given on the curve Γ and ϕ on the characteristic $y=y_0$, namely

$$g(y) = \psi[\beta(y), y], \quad (29a)$$

$$f(x) = \phi(x, y_0). \quad (29b)$$

We use Φ to denote function ϕ on the curve Γ (which is the boundary of the crystal):

$$\Phi(x) = \phi[x, \alpha(x)]. \quad (30)$$

For Bragg diffraction, functions ψ and ϕ may be expanded thus:

$$\psi(x, y, \sigma) = \sum_{n=0}^{\infty} \psi_n(x, y) \sigma^n, \quad (31a)$$

$$\phi(x, y, \sigma) = \sigma \sum_{n=0}^{\infty} \phi_n(x, y) \sigma^n. \quad (31b)$$

This is a general expansion but for a particular case the coefficients ψ_n and ϕ_n may be zero, starting with a given value of n . Allowing for this, a recurrence formula is given in Appendix I, from which the coefficients Φ_n may be calculated. Hence, by solving the mixed problem for ψ , the function ϕ on the boundary may be derived.

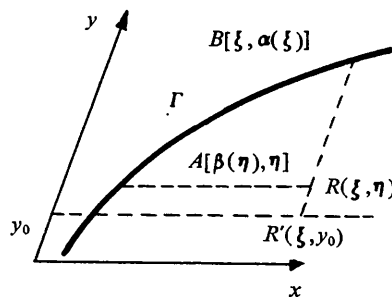


Fig. 2. Diagram for the Cauchy problem and the mixed problem. The curve Γ is a part of crystal boundary.

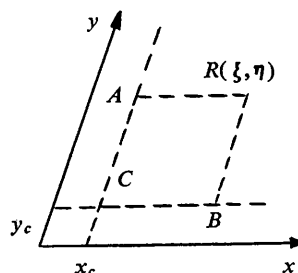


Fig. 3. Diagram for characteristic initial-value problem.

(iii**b**) In the mixed problem for φ the function φ is given on the curve Γ , and ψ on the characteristic $x = x_0$:

$$g(x) = \varphi[x, \alpha(x)] \tag{32a}$$

$$f(y) = \psi(x_0, y) . \tag{32b}$$

We use Ψ to denote the function ψ on the curve Γ :

$$\Psi(y) = \psi[\beta(y), y] . \tag{33}$$

Ψ_n is obtained in an analogous manner to the above.

One's attention should be drawn to the fact that the functions ψ and φ may be derived, if required, for any point in the region for which these mixed problems are solved (see Appendix I).

As has been mentioned previously, all three problems may occur in a real case. The solution of a problem on a certain straight line in the crystal represents an initial condition for another problem. For the example in Fig. 4, it is seen that the crystal is totally immersed in the incident beam. The crystal is divided into regions in accordance with the conditions required by the problems presented above. ψ is given on the arc ABC and φ on the arc DAB . Using (24), $\partial\psi/\partial x$ and $\partial\varphi/\partial y$ can be calculated on the arc CAB . Therefore, in the region $AMPQNB$ a Cauchy problem exists for both

functions ψ and φ . φ is calculated on the arc PQ and the segment BQ and ψ is calculated on the segment AP . In the region BNC a mixed problem exists for ψ from which is derived φ on the arc BC and ψ on the segment NC . A characteristic initial-value problem exists in the region NCQ . When this is solved φ is obtained on the arc CQ . In the region AMD , the function φ on the segment MD is deduced by solving a mixed problem for φ . In the region DMP , the solution to a characteristic initial-value problem gives φ on the arc DM . Therefore, the function φ is derived over the whole arc BCD . The function P is now deduced from (23b). For practical purposes it is enough to know only the function P on the arc BCD . But, if necessary, it may be derived for all the points in the crystal region.

It should be mentioned that the solution is not analytical for the whole crystal region. For example $\partial^2\varphi/\partial y^2$ and other higher derivatives have infinite values on AP . Also, $\partial^2\psi/\partial x^2$ is infinite on BQ , etc. Moreover, some discontinuities in the incident beam may lead to discontinuities even in the first-order derivatives of ψ and φ . A more detailed discussion may be found in Morse & Feshbach (1953).

3. Application of the mixed problem

Fig. 5 represents one example of the mixed problem for the reflexion of a δ -function beam on a plane parallel crystal plate. In regions I, III, V, etc., the mixed problem for ψ exists whilst in regions II, IV, etc., the mixed problem for φ is applicable. Let p and q be the depths in the plate along the incident and reflected beams respectively. The initial conditions for the first region are given by:

$$g(y) = \psi(\beta y, y) = \delta(y); \quad f(x) = \varphi(x, 0) = \delta(0) . \tag{34}$$

By applying formulae (42) from Appendix I:

$$\Phi(\xi) = \sigma \sum_{n=0}^{\infty} \frac{\alpha^n \xi^{2n}}{n!(n+1)!} \sigma^{2n} . \tag{35}$$

This result coincides with that of Werner (1965). Further, by using (43) the function ψ on BC may be expressed:

$$\begin{aligned} \psi(p, \eta) = & \delta(\eta) + \theta(\eta) (p - \beta\eta)\sigma^2 \\ & + (p - \beta\eta) \sum_{n=2}^{\infty} \frac{p^{n-1}\eta^{n-1}}{(n-1)!n!} \sigma^{2n}, \end{aligned} \tag{36}$$

where:

$$\theta(\eta) = \begin{cases} 1 & \text{for } \eta > \theta \\ 0 & \text{for } \eta = 0 . \end{cases} \tag{37}$$

For the second region, the initial conditions are:

$$g(x) = \varphi[x, \alpha(x-p)] = 0; \quad f(y) = \psi(p, y) . \tag{38}$$

By using (45) the function Ψ on BD becomes:

$$\begin{aligned} \Psi(\eta) = & \delta(\eta) + \theta(\eta) (p - \beta\eta)\sigma^2 \\ & + \sum_{n=2}^{\infty} \left[\sum_{l=0}^{\infty} a_l^{(n)} p^{n-l} \beta^l \eta^{n+l-1} \right] \sigma^{2n} \end{aligned} \tag{39}$$

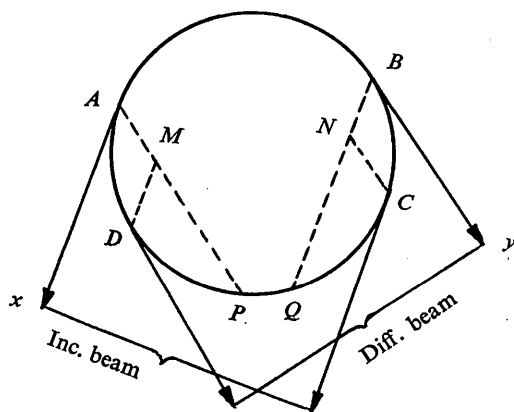


Fig. 4. Diagram of a subdivided, convex crystal totally immersed in incident beam, at a particular Bragg angle.

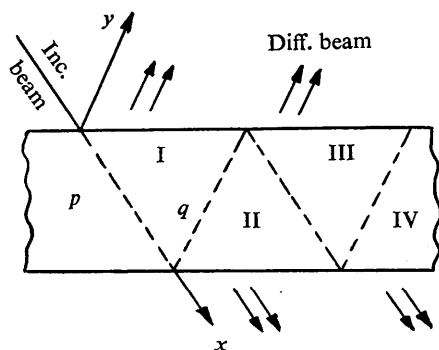


Fig. 5. Reflexion of a δ -beam on a plane parallel plate.

where the coefficients $a_i^{(n)}$ are given in Appendix II. This process may be continued for subsequent regions.

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APPENDIX I

Solution of the mixed problem

The solution of the mixed problem for ψ will be derived. Taking account Fig. 2 and the formulae (26, 29a, 30), (27a) becomes:

$$\begin{aligned} \psi(\xi, \eta) = & g(\eta) + \sigma \int_{\beta(\eta)}^{\xi} \Phi(x) j_0 \{ 2\sigma \sqrt{(\xi-x)(y-\eta)} \} \\ & - \sigma \int_{\eta}^{\alpha(\xi)} g(y) \sqrt{[\xi-\beta(y)](y-\eta)} \\ & \times j_1 \{ 2\sigma \sqrt{[\xi-\beta(y)](y-\eta)} \}. \end{aligned} \quad (40)$$

Let R be a point on a characteristic $y=y_0$ (point R'). Therefore, in equation (40), $\eta=y_0$. Further by differentiating with respect to ξ and by using (24a) and (29b):

$$\begin{aligned} \Phi(\xi) = & f(\xi) + \sigma \int_{\beta(y_0)}^{\xi} \Phi(x) \sqrt{[\alpha(x)-y_0]/(\xi-x)} \\ & \times j_1 \{ 2\sigma \sqrt{(\xi-x)[\alpha(x)-y_0]} \} dx \\ & + \sigma \int_{y_0}^{\alpha(\xi)} g(y) j_0 \{ 2\sigma \sqrt{[\xi-\beta(y)](y-y_0)} \} dy. \end{aligned} \quad (41)$$

This is a Volterra integral equation for the function Φ . Given that:

$$j_n(2t) = \sum_{k=0}^{\infty} \frac{(-1)^k}{k!(k+n)!} t^{2k+n},$$

and by consideration of the expansion (31), the equation (41) becomes:

$$\begin{aligned} \Phi_n(\xi) = & f_n(\xi) + \int_{y_0}^{\alpha(\xi)} g_n(y) dy \quad (\text{for } n=0, 1); \\ \Phi_n(\xi) = & f_n(\xi) \\ & + \int_{y_0}^{\alpha(\xi)} \sum_{k=0}^{[n/2]} \frac{(-1)^k}{(k!)^2} g_{n-2k}(y) [\xi-\beta(y)]^k (y-y_0)^k dy \\ & + \int_{\beta(y_0)}^{\xi} \sum_{k=0}^{[(n-2)/2]} \frac{(-1)^k}{k!(k+1)!} \Phi_{n-2-2k}(x) (\xi-x)^k \\ & \times [\alpha(x)-y_0]^{k+1} dx \quad (\text{for } n \geq 2), \end{aligned} \quad (42)$$

where $[n/2]$ represents the integer part of $n/2$.

Further, from (40) is obtained:

$$\psi_n(\xi, \eta) = g_n(\eta) \quad (\text{for } n=0, 1);$$

$$\begin{aligned} \psi_n(\xi, \eta) = & g_n(\eta) \\ & - \int_{\eta}^{\alpha(\xi)} \sum_{k=0}^{[(n-2)/2]} \frac{(-1)^k}{k!(k+1)!} g_{n-2-2k}(y) \\ & \times [\xi-\beta(y)]^{k+1} (y-\eta)^k dy \\ & + \int_{\beta(\eta)}^{\xi} \sum_{k=0}^{[(n-2)/2]} \frac{(-1)^k}{(k!)^2} \Phi_{n-2-2k}(x) (\xi-x)^k \\ & \times [\alpha(x)-\eta]^k dx \quad (\text{for } n \geq 2). \end{aligned} \quad (43)$$

$$\varphi_n(\xi, \eta) = \Phi_n(\xi) - \int_{\eta}^{\alpha(\xi)} g_n(y) dy \quad (\text{for } n=0, 1);$$

$$\begin{aligned} \varphi_n(\xi, \eta) = & \Phi_n(\xi) \\ & - \int_{\eta}^{\alpha(\xi)} \sum_{k=0}^{[n/2]} \frac{(-1)^k}{(k!)^2} g_{n-2k}(y) [\xi-\beta(y)]^k (y-\eta)^k dy \\ & - \int_{\beta(\eta)}^{\xi} \sum_{k=0}^{[(n-2)/2]} \frac{(-1)^k}{k!(k+1)!} \Phi_{n-2-2k}(x) (\xi-x)^k \\ & \times [\alpha(x)-\eta]^{k+1} dx \quad (\text{for } n \geq 2). \end{aligned} \quad (44)$$

The solution for the mixed problem for φ is obtained in the same manner. Only the results will be written:

$$\Psi_n(\eta) = f_n(\eta) \quad (\text{for } n=0, 1);$$

$$\begin{aligned} \Psi_n(\eta) = & f_n(\eta) \\ & + \int_{x_0}^{\beta(\eta)} \sum_{k=0}^{[(n-2)/2]} \frac{(-1)^k}{(k!)^2} g_{n-2-2k}(x) (x-x_0)^k \\ & \times [\eta-\alpha(x)]^k dx \\ & + \int_{\alpha(x_0)}^{\eta} \sum_{k=0}^{[(n-2)/2]} \frac{(-1)^k}{k!(k+1)!} \Psi_{n-2-2k}(y) \\ & \times [\beta(y)-x_0]^{k+1} (\eta-y)^k dy \quad (\text{for } n \geq 2). \end{aligned} \quad (45)$$

$$\varphi_n(\xi, \eta) = g_n(\eta) + \int_{\alpha(\xi)}^{\eta} \Psi_n(y) dy \quad (\text{for } n=0, 1);$$

$$\begin{aligned} \varphi_n(\xi, \eta) = & g_n(\eta) \\ & - \int_{\eta}^{\beta(\eta)} \sum_{k=0}^{[(n-2)/2]} \frac{(-1)^k}{(k+1)!k!} g_{n-2-2k}(x) (x-\xi)^k \\ & \times [\eta-\alpha(x)]^{k+1} dx \\ & + \int_{\alpha(\xi)}^{\eta} \sum_{k=0}^{[n/2]} \frac{(-1)^k}{(k!)^2} \Psi_{n-2k}(y) [\beta(y)-\xi]^k (\eta-y)^k dy \\ & \quad (\text{for } n \geq 2). \end{aligned} \quad (46)$$

$$\psi_n(\xi, \eta) = \Psi_n(\eta) \quad (\text{for } n=0, 1);$$

$$\begin{aligned} \psi_n(\xi, \eta) = & \Psi_n(\eta) \\ & - \int_{\xi}^{\beta(\eta)} \sum_{k=0}^{[(n-2)/2]} \frac{(-1)^k}{(k!)^2} g_{n-2-2k}(x) (x-\xi)^k \\ & \times [\eta-\alpha(x)]^k dx \\ & - \int_{\alpha(\xi)}^{\eta} \sum_{k=0}^{[(n-2)/2]} \frac{(-1)^k}{k!(k+1)!} \Psi_{n-2-2k}(y) \\ & \times [\beta(y)-\xi]^{k+1} (\eta-y)^k dy \quad (\text{for } n \geq 2). \end{aligned} \quad (47)$$

For a convex crystal region formulae (45,46,47) are simplified since $g(x) \equiv 0$.

APPENDIX II

The coefficients $a_l^{(n)}$ from (39) are:

$$a_0^{(2)} = \frac{1}{2} \quad a_1^{(2)} = 0 \quad a_2^{(2)} = -\frac{1}{3}.$$

For $n \geq 3$

$$a_0^{(n)} = \frac{1}{n!(n-1)!} \quad a_1^{(n)} = \frac{n-2}{n!(n-1)!};$$

$$a_l^{(n)} = \frac{1}{(n+l-1)!} \sum_{k=1}^l (-1)^{k-1} \frac{(n+l-k-1)!}{k!} a_{l-k}^{(n-k)} \quad (\text{for } 2 \leq l \leq n-2);$$

$$a_{n-1}^{(n)} = \frac{1}{(2n-2)!} \times \left[(-1)^{n-2} + \sum_{k=1}^{n-2} (-1)^{k-1} \frac{(2n-2-k)!}{k!} a_{n-k-1}^{(n-k)} \right];$$

$$a_n^{(n)} = \frac{1}{(2n-1)!} \times \left[n(-1)^{n-1} + \sum_{k=1}^{n-2} (-1)^{k-1} \frac{(2n-k-1)!}{k!} a_{n-k}^{(n-k)} \right].$$

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The Influence of Specimen Geometry on the Determination of X-ray Absorption Correction Factors for Spheres and Cylinders

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A simple numerical method of determining the absorption correction factors for spherical and cylindrical specimens is described. The construction of line profiles of the diffraction peaks for both types of specimen illustrates the origin of errors inherent in all numerical methods of this kind. The difference in line profiles, particularly the line shift, for spherical and cylindrical specimens could influence the choice of specimen geometry for accurate lattice parameter determinations.

1. Introduction

Recent numerical methods of calculating absorption correction factors for spheres and cylinders (Weber, 1967, 1969; Dwiggin, 1974, 1975) have revealed substantial discrepancies with *International Tables for X-ray Crystallography* (1959) of up to 2.5%. The largest errors are associated with low Bragg angles and large values of the product of the linear absorption coefficient and the radius of the specimen, μR , when the diffracted beam emerges from the 'skin' of the specimen only. It appears that these errors are due to inaccurate numerical integration in this region of the specimen. This paper describes the contribution of different regions of spherical and cylindrical specimens to the resultant line profile of the diffraction peaks in an attempt to establish the origin of these errors.

Several analytical and numerical methods (Claasen,

1930; Evans & Ekstein, 1952; Weber 1969; Dwiggin, 1975), whilst yielding the absorption factor do not afford a simple determination of the line profile. Taylor & Sinclair (1945) introduced a strip method for deriving the absorption factor for a cylinder in which the specimen was divided into strips parallel to the direction of the diffracted X-ray beam. From this construction line profiles for cylindrical specimens were determined. In this paper the strip method of Taylor & Sinclair is applied to both spherical and cylindrical specimens and automatic computing methods are used to eliminate time-consuming graphical integration.

2. Calculation of the absorption correction factor

For a non-absorbing medium the intensity of a diffracted X-ray beam is directly proportional to the