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A General Theory of X-Ray Diffraction in Crystals

BY W. H. ZACHARIASEN
Department of Physics, University of Chicago, Chicago, Illinois, U.S.A.

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A general theory of X-ray diffraction in a finite crystal is developed on the basis of an approximate treatment of the coupling between incident and diffracted beams. The theory leads to a universal formula for the integrated intensity of the diffracted beam, valid over the entire range from the perfect to the ideal mosaic crystal. The application of the theory to the mosaic model of a real crystal yields C. G. Darwin's theory of secondary extinction when the perfect domains are in poor alignment, in which case the half width of the distribution function for the orientation of the domains can be obtained experimentally. However, the general theory gives a new intensity formula if the domains are in good alignment. The intensity dependence upon wave length is different, and experiment will give the mean radius of a perfect domain.

1. Introduction

This paper describes the derivation of a universal intensity formula for X-ray diffraction in real crystals.

If $\mathscr{P}$ is the integrated intensity of a diffracted beam, one may set

$$\mathscr{P}=\mathscr{P}_k y \tag{1}$$

where $\mathscr{P}_k$ is the kinematical approximation and y the extinction factor. Thus the problem is that of finding the general expression for the quantity y.

The formula for $\mathscr{P}_k$ is the familiar one

$$\mathscr{P}_k=\mathscr{J}_0 v A(\mu) Q \tag{2a}$$

$$Q=\left|\frac{e^2FK}{mc^2V}\right|^2\lambda^3/\sin 2\theta \tag{2b}$$

where $\mathscr{J}_0$ is the incident intensity, v the irradiated crystal volume and $A(\mu)=v^{-1}\int \exp(-\mu T)dv$ the transmission factor with μ the linear absorption coefficient and T the path length through the crystal. $K=1$ for the normal and $K=\cos 2\theta$ for the parallel component of polarization. The other symbols of equation (2*b*) have their usual meanings.

Clearly the kinematical theory (for which $y=1$) on the one hand and the dynamical theory of Darwin (1914*a*, *b*) and Ewald (1916*a*, *b*, 1917) on the other must be contained in the general theory as limiting cases. However, the equations of the dynamical theory have been solved only for an infinite plane parallel crystal plate, and the expression for y is completely unknown for finite perfect crystals of any shape. The first important task of this paper is therefore the derivation of the general formula for the extinction factor of a finite perfect crystal. The account of this part of the investigation is presented in § 2.

The treatment of X-ray diffraction in a real crystal will be based on the mosaic model first introduced by Darwin (1922). The real crystal is assumed to be an aggregate of perfect crystal domains. The boundary between two domains represents a surface of discontinuity in respect to the periodicity, and in general there is a small relative rotation of the two domains. If the real crystal contains many domains, it is reasonable to suppose that the misalignment obeys an isotropic Gaussian distribution law, *i.e.*

$$W(\Delta)=\sqrt{2g}\exp(-2\pi g^2\Delta^2) \tag{3}$$

where Δ measures the angular deviation from the mean orientation. The derivation of the formulas for a real crystal is given in § 3. The assumed model of a real crystal is characterized by the mean radius of the perfect crystal domains, r, and the quantity g of the Gaussian distribution of equation (3). The intensity formulas for a real crystal will accordingly contain r and g as parameters.

Because of the complexity of the problem it has been necessary to introduce a number of approximations in the course of the derivations. Although these simplifications are believed to be theoretically justified, the ultimate test of the validity of the results must be agreement with experiment. A brief discussion of experimental tests of the theory is given in § 4.

2. The integrated intensity for a small perfect crystal

The basic equations

Let a plane wave of X-rays be incident on a perfect crystal of arbitrary shape near a Bragg angle such that a single diffracted beam is produced. It is convenient to assume that the reflecting lattice plane is vertical, and that all observations are made in the horizontal plane of incidence with a counter set to receive the total power associated with the diffracted beam. The crystal may be rotated about a vertical axis, and hence the direction of incidence is a function of a single parameter ε_1 which measures the deviation from the ideal Bragg angle. Refraction and ordinary absorption will be neglected.

At the crystal surface the incident intensity has a constant value $\mathscr{J}_0$. Upon entry into the crystal part of

the incident power will be transferred to the diffracted beam. However, the diffracted beam will again be diffracted and a fraction of the power will be retransferred to the incident beam. Thus the incident and the diffracted radiation form a coupled system within the crystal.

The internal beams are slightly divergent, but can be approximated as plane waves with intensities I_0 and I which are functions of position within the crystal. As shown in Fig. 1 the location of a volume element can be specified by two variables t_1 and t_2 representing the depth below the surface measured along the two propagation directions. The fundamental equations which I_0 and I must satisfy are

$$\frac{\partial I_0}{\partial t_1} = -\sigma I_0 + \sigma I \tag{4a}$$

$$\frac{\partial I}{\partial t_2} = -\sigma I + \sigma I_0 , \tag{4b}$$

with the boundary conditions

$$I_0 = \mathscr{I}_0 \text{ for } t_1 = 0$$
$$I = 0 \quad \text{for } t_2 = 0 . \tag{4c}$$

The quantity σ, the coupling constant, is the diffracting power and measures the diffracted power per unit volume and intensity. Clearly σ is a function of the incidence direction ε_1, and is different from zero only when ε_1 is very small. It will be assumed that σ is a constant for given ε_1, and that it can be evaluated from the kinematical theory of X-ray diffraction.

Addition of equations (4*a*) and (4*b*) gives

$$\frac{\partial I_0}{\partial t_1} + \frac{\partial I}{\partial t_2} = 0 \tag{5}$$

which expresses energy conservation.

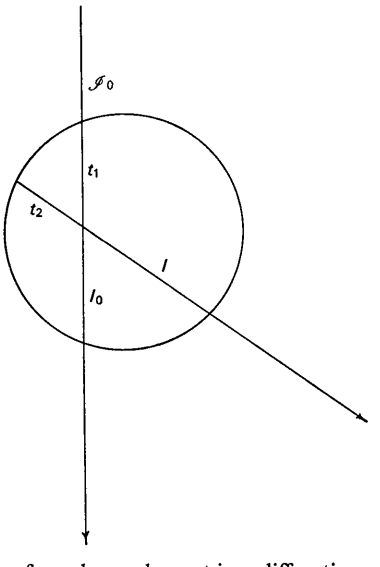

Fig. 1. The location of a volume element in a diffracting crystal by means of the path lengths t_1 and t_2 measured along the propagation directions.

If $I(t_1, t_2)$ is the solution for the diffracted beam, the corresponding solution for the incident beam is $I_0(t_1, t_2) = \mathscr{I}_0 - I(t_2, t_1)$. Hence, it will suffice in the following to specify only the function $I(t_1, t_2)$.

The total power of the diffracted beam, $P(\varepsilon_1)$, as recorded in the counter, the diffraction pattern in other words, is

$$P(\varepsilon_1) = \oint I\mathbf{u} \,.\, d\mathbf{S} = \int \frac{\partial I}{\partial t_2}\, dv , \tag{6}$$

where $\mathbf{u}$ is the diffraction direction and $d\mathbf{S}$ a surface element of the crystal. The volume integral form of equation (6) is obtained by application of the divergence theorem.

It is convenient to introduce a function $\varphi(\sigma)$ defined by the relation

$$P(\varepsilon_1) = \mathscr{I}_0 v \sigma \varphi(\sigma) . \tag{7}$$

Since the integrated intensity, $\mathscr{P}$, is given by the integral

$$\mathscr{P} = \int P(\varepsilon_1) d\varepsilon_1 , \tag{8}$$

the expression for the extinction factor y becomes

$$y = Q^{-1} \int \sigma \varphi(\sigma) d\varepsilon_1 . \tag{9}$$

In the kinematical (or zero order approximation) all extinction effects are neglected, and the system of equations (4) is radically simplified to

$$\frac{\partial I_0}{\partial t_1} \approx 0 \tag{10a}$$

$$\frac{\partial I}{\partial t_2} \approx \sigma I_0 . \tag{10b}$$

The solutions are $I_0 \approx \mathscr{I}_0$, $P(\varepsilon_1) \approx \sigma \mathscr{I}_0 v$, $\mathscr{P} \approx \mathscr{I}_0 v Q = \mathscr{P}_k$ and $y \approx 1$.

The first order approximation neglects only the 'feedback' term σI of equation (4*a*), and gives the solutions

$$I_0 \approx \mathscr{I}_0 \exp(-\sigma t_1)$$
$$I \approx \mathscr{I}_0 [1 - \exp(-\sigma t_2)] \exp(-\sigma t_1)$$
$$P \approx \mathscr{I}_0 v \sigma A(\sigma)$$
$$\varphi(\sigma) \approx A(\sigma) = 1 - \sigma \bar{t} + \tfrac{1}{2}\sigma^2 \overline{t^2} - \tfrac{1}{6}\sigma^3 \overline{t^3} + \ldots$$
$$\overline{t^n} = v^{-1} \int (t_1 + t_2)^n dv . \tag{11}$$

However, equation (5) is not satisfied by either approximation, and it is obvious that equations (11) can be used only if $\sigma \bar{t} \ll 1$.

Exact solutions of equations (4) are readily obtained for an infinite plane parallel crystal plate of thickness D_0.

For the symmetrical Laue case ($t_1 = t_2 = t$) one has

$$I = \mathscr{I}_0 [1 - \exp(-2\sigma t)]/2$$
$$\varphi(\sigma) = [1 - \exp(-2\sigma \bar{t})]/2\sigma \bar{t}$$
$$= 1 - \sigma \bar{t} + \tfrac{2}{3}(\sigma \bar{t})^2 - \tfrac{1}{3}(\sigma \bar{t})^3 + \ldots$$
$$\bar{t} = D_0 / \cos\theta . \tag{12}$$

The exact solution for the symmetrical Bragg case ($t_1=t, t_2=D-t$) is

$$I=\mathscr{J}_0\sigma(D-t)/(1+\sigma D)$$
$$\varphi(\sigma)=1/(1+\sigma\bar{t})=1-\sigma\bar{t}+(\sigma\bar{t})^2-(\sigma\bar{t})^3+\ \ldots$$
$$\bar{t}=D=D_0/\sin\theta\,. \tag{13}$$

Power series solution of equations (4) can be obtained for a perfect crystal of any shape totally immersed in the incident beam. (As shown in the Appendix the solution can be given in analytic form in terms of Riemann functions.) It is convenient to give the result for $\partial I/\partial t_2$:

$$\frac{\partial I}{\partial t_2}=\sigma\mathscr{J}_0\sum_n\frac{(-\sigma)^n}{n!}\,\overline{t^{(n)}} \tag{14a}$$

$$\overline{t^{(n)}}=\sum_j\binom{n}{j}\overline{t_1^{n-j}t_2^j}\,. \tag{14b}$$

Consider the special case of the parallelopiped shown in Fig. 2. Two of the edges are parallel to the incident and diffracted beams, the third is normal to the plane of incidence. For this shape the volume integral of equation (6) is readily evaluated. If all three edges t_1^0, t_2^0, t_3^0 are equal to t_0, one finds

$$\varphi(\sigma)=1-\sigma t_0+\tfrac{5}{6}(\sigma t_0)^2-\tfrac{7}{12}(\sigma t_0)^3+\ \ldots\,. \tag{15}$$

The general expression for arbitrary shape is

$$\varphi(\sigma)=\sum_n\frac{(-\sigma)^n}{n!}\,\overline{t^{(n)}} \tag{16}$$

where $\overline{t^{(n)}}=v^{-1}\int t^{(n)}dv$ with $t^{(n)}$ given by equation (14*b*).

Let the crystal be a sphere of radius r. For small scattering angles one has $t_1\approx t_2$ and

$$v^{-1}\int t_1^n dv=\frac{3(2r)^n}{(n+1)(n+3)}\,. \tag{17}$$

Hence, the formula for $\varphi(\sigma)$ for a sphere and small scattering angles becomes

$$\varphi(\sigma)=1-\sigma\bar{t}+\tfrac{16}{15}(\sigma\bar{t})^2-\tfrac{80}{81}(\sigma\bar{t})^3+\ \ldots\,. \tag{18}$$

with $\bar{t}=\frac{3}{2}r$. $\varphi(\sigma)$ can also be evaluated for the backward scattering direction with the result

$$\varphi(\sigma)=1-\sigma\bar{t}+\tfrac{64}{45}(\sigma\bar{t})^2+\ \ldots\,.$$

However, at large scattering angles it is normally true that $\sigma\bar{t}\ll 1$, and hence equation (18) will be used as a general expression.

The results given in equations (12), (13), (15), (18) show that the precise form of the function $\varphi(\sigma)$ does depend on the crystal shape. The formula

$$\varphi(\sigma)=\frac{1}{1+\sigma\bar{t}}\,, \tag{19}$$

where $\bar{t}$ is the mean path length through the crystal, is exact for a plane parallel plate in the symmetrical Bragg case and, as shown by equation (18), a very good approximation for a sphere. If $\sigma\bar{t}\gg 1$, one has $\varphi(\sigma)\approx(\sigma\bar{t})^{-1}$ which according to equation (7) implies total reflection. In the symmetric Laue case the power is equally divided between transmitted and diffracted beams for $\sigma\bar{t}\gg 1$, and equation (19) will be a poor approximation.

The diffracting power

As previously stated it is to be assumed that $\sigma(\varepsilon_1)$ will be correctly given by the kinematical theory, *i.e.*, that

$$\sigma(\varepsilon_1)=\mathscr{J}_0^{-1}v^{-1}P_k(\varepsilon_1)\,, \tag{20}$$

where $P_k(\varepsilon_1)$ is the power of the diffracted beam in the kinematical approximation for given direction of incidence.

The direction of incidence $\mathbf{u}_0=\mathbf{u}_0^0-\varepsilon_1\boldsymbol{\tau}_1$, where $\mathbf{u}_0^0$ is the ideal Bragg direction and $\boldsymbol{\tau}_1$ a unit vector in the plane of incidence normal to $\mathbf{u}_0^0$. Similarly, for the direction of diffraction one may set $\mathbf{u}=\mathbf{u}^0+\varepsilon_2\boldsymbol{\tau}_2+\varepsilon_3\boldsymbol{\tau}_3$, $\mathbf{u}^0$ being the ideal diffraction direction and $\boldsymbol{\tau}_2$ and $\boldsymbol{\tau}_3$ unit vectors normal to $\mathbf{u}^0$, $\boldsymbol{\tau}_2$ lying in the plane of incidence, $\boldsymbol{\tau}_3$ normal thereto. One has $\mathbf{u}^0-\mathbf{u}_0^0=\lambda\mathbf{H}$, where $\mathbf{H}$ is the reciprocal lattice vector associated with the diffracted beam. The diffraction vectors $\mathbf{s}=2\pi(\mathbf{u}-\mathbf{u}_0)/\lambda$ can be written as

$$\mathbf{s}=2\pi\mathbf{H}+\Delta\mathbf{s}\,,$$
$$\Delta\mathbf{s}=2\pi[\varepsilon_1\boldsymbol{\tau}_1+\varepsilon_2\boldsymbol{\tau}_2+\varepsilon_3\boldsymbol{\tau}_3]/\lambda\,. \tag{21}$$

The intensity of the radiation scattered in direction $\mathbf{u}$ is given by the familiar expression

$$I_k(\varepsilon_1,\varepsilon_2,\varepsilon_3)=\mathscr{J}_0\left|\frac{e^2FK}{mc^2R}\right|^2|\Sigma\exp(i\Delta\mathbf{s}\,.\,\mathbf{L})|^2\,, \tag{22}$$

where $\mathbf{L}$ is a lattice vector and R the distance from the crystal to the counter. The total power recorded in the counter, P_k of equation (20), is

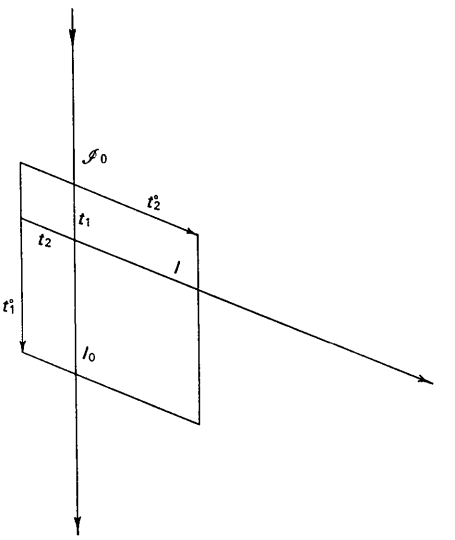

Fig. 2. A crystal parallelopiped with one edge, of length t_1^0, along the incident beam, a second edge, of length t_2^0, along the diffracted beam. The third edge, t_3^0, is normal to the plane of the Figure.

$$P_k(\varepsilon_1) = R^2 \iint I_k d\varepsilon_2 d\varepsilon_3 \,. \tag{23}$$

The summations and integrations of equations (22) and (23) represent a standard problem in diffraction theory and are readily carried out for the parallelopiped shown in Fig. 2. The expression for $\sigma(\varepsilon_1)$ becomes

$$\sigma(\varepsilon_1) = Q\alpha \frac{\sin^2 \pi\alpha\varepsilon_1}{(\pi\alpha\varepsilon_1)^2} \,, \tag{24}$$

where $\alpha = t_\perp/\lambda$. The meaning of the symbol $t_\perp$ is $t_\perp = |\mathbf{t}_2^0 \times \mathbf{u}_0| = t_0 \sin 2\theta$.

If one uses the series expansion for the function $\varphi(\sigma)$, the evaluation of y according to equation (9) will involve the integrals $\int \sigma^n d\varepsilon_1$. One has

$$\int \sigma d\varepsilon_1 = Q, \qquad \int \sigma^2 d\varepsilon_1 = \tfrac{2}{3} Q^2 \alpha$$

$$\int \sigma^3 d\varepsilon_1 = \tfrac{5}{9} Q^3 \alpha^2, \quad \int \sigma^4 d\varepsilon_1 = \tfrac{13}{27} Q^4 \alpha^3 \,. \tag{25}$$

The expression for $\sigma(\varepsilon_1)$ becomes very complicated for a crystal of arbitrary shape. However, for a symmetrically shaped crystal equations (24) and (25) will be approximately correct if everywhere $t_\perp{}^n$ is replaced by its mean value $\overline{t_\perp{}^n}$ over the crystal volume.

For the infinite plane parallel plate of thickness D_0 one must set $\mathbf{t}_2^0 = D_0\mathbf{n}$, $\mathbf{n}$ being the plate normal. Hence $t_\perp = D_0 \sin\theta$ for the symmetrical Laue case and $t_\perp = D_0 \cos\theta$ for the symmetrical Bragg case. If the crystal is a sphere of radius r, $\bar{t}_\perp$ is the mean thickness measured normal to the incident beam and parallel to the plane of incidence so that $\bar{t}_\perp = \frac{3}{2} r$.

It will be shown presently that equation (9) will give a very simple expression for y if the approximation of equation (19) is used and if the delta function of equation (24) is replaced by an equivalent expression of Poisson form. Let $\sigma = a/(1 + b^2\varepsilon_1^2)$ and let it be required that $\int \sigma d\varepsilon_1$ and $\int \sigma^2 d\varepsilon_1$ agree with the results of equations (25). The sought approximation to equation (24) becomes

$$\sigma(\varepsilon_1) \approx \frac{\frac{4}{3} Q\alpha}{1 + \left(\frac{4\pi}{3} \alpha\varepsilon_1\right)^2} \,. \tag{26}$$

The extinction factor

The results under the two preceding headings may now be combined to yield the formula for the extinction factor y.

The two approximate expressions of equations (19) and (26) substituted in equation (9) give

$$y = (1 + 2x)^{-\frac{1}{2}} = 1 - x + \tfrac{3}{2}x^2 - \tfrac{5}{2}x^3 + \ldots \,,$$
$$x = \tfrac{2}{3} Q\alpha \bar{t} \,. \tag{27}$$

It is useful to list the specific forms of x for various crystal shapes:

Symmetrical Laue case

$$x = \frac{\left|\frac{e^2 FK\lambda D_0}{mc^2 V}\right|^2}{3\cos^2\theta} \tag{28a}$$

Symmetrical Bragg case

$$x = \frac{\left|\frac{e^2 FK\lambda D_0}{mc^2 V}\right|^2}{3\sin^2\theta} \tag{28b}$$

Parallelopiped of Fig. 2

$$x = 2\frac{\left|\frac{e^2 FK\lambda t_0}{mc^2 V}\right|^2}{3} \tag{28c}$$

Sphere of radius r

$$x = 3\frac{\left|\frac{e^2 FK\lambda r}{mc^2 V}\right|^2}{2\sin 2\theta} \,. \tag{28d}$$

The exact results of the dynamical theory are known only for the infinite plane parallel plate (Zachariasen, 1945), and they are:

Laue case

$$y = \frac{\Sigma\, \mathscr{J}_{2n+1}(2\sqrt{3x})}{\sqrt{3x}} = 1 - x + \tfrac{9}{20}x^2 - \tfrac{3}{28}x^3 + \ldots \tag{29a}$$

Bragg case

$$y = \frac{\tanh \sqrt{3x}}{\sqrt{3x}} = 1 - x + \tfrac{6}{5}x^2 - \tfrac{51}{35}x^3 + \ldots \tag{29b}$$

with the same expressions for x as given in equations (28*a*) and (28*b*).

The asymptotic values at large x are $y = 1/2\sqrt{3x}$ and $y = 1/\sqrt{3x}$ respectively, whereas equation (27) gives $y = 1/\sqrt{2x}$. The agreement with the findings of the dynamical theory is not good for large x in the Laue case; but this was to be expected since equation (19) is a poor approximation to the correct form of equation (12).

The substitution of equation (26) for equation (24) does introduce a small error. If equation (24) is used, the series expansion of y for the Bragg case becomes

$$y = 1 - x + \tfrac{5}{4}x^2 - \tfrac{13}{8}x^3 + \ldots \,, \tag{30}$$

which is in excellent agreement with the exact solution of equation (29*b*).

The equations of the dynamical theory have not been solved for a perfect crystal sphere. Hence it is not possible to state precisely how well equations (27) and (28*d*) agree with the exact results for this shape. However, the satisfactory agreement for the Bragg case suggests that these equations are acceptable approximations.

If one assumes that the integrated intensity can be measured to an accuracy of two per cent, the applicability of the kinematical intensity formula ($y=1$) is restricted to the range $x<0{\cdot}02$. In a typical example, such as the strongest reflection of α-quartz for which $|F|/V=0{\cdot}348\times10^{24}$ cm^{-3}, the requirement $x<0{\cdot}02$ gives $r<0{\cdot}51\times10^{-4}$ cm for Cu $K\alpha$ radiation and $r<0{\cdot}76\times10^{-4}$ cm for Mo $K\alpha$ radiation.

3. The real crystal

As stated in § 1 it will be assumed that the mosaic model of C. G. Darwin correctly describes a real crystal. The domains will be imagined to be all of the same size and nearly spherical in shape. Hence, for the quantities $\bar{t}$ and $\bar{t}_\perp$ of the preceding sections one may set $\bar{t}=\bar{t}_\perp=\frac{3}{2}r$ where r is the mean domain radius.

For the present, ordinary absorption effects will be neglected, and it will be assumed that the linear dimension of the domain is small compared with that of the mosaic crystal. Thus the crystal will contain a great many domains, the orientations of which are governed by the distribution function $W(\Delta)$ of equation (3).

The half width of W is

$$\Delta_{\frac{1}{2}}=g^{-1}(\log 2/2\pi)^{\frac{1}{2}}=0{\cdot}332g^{-1}\,. \tag{31}$$

The quantity $\sigma(\varepsilon_1)$ of the preceding section represents the diffraction pattern of a single domain as function of the direction of incidence ε_1. According to equations (24) and (26) the half width of the diffraction pattern is given by:

$$\text{from equation (24), } (\varepsilon_1)_{\frac{1}{2}}=0{\cdot}295\lambda r^{-1}=0{\cdot}443\alpha^{-1}\,, \tag{32}$$

$$\text{from equation (26), } (\varepsilon_1)_{\frac{1}{2}}=1/2\pi\lambda r^{-1}=3/4\pi\alpha\,.$$

When $\alpha\gg g$ it implies that the distribution function W is much wider than the diffraction pattern of a single domain, while the situation is reversed when $\alpha\ll g$.

The diffraction in a mosaic crystal can be treated in precisely the same manner as was done for a perfect crystal. The basic equations will have the same form as equations (4), namely

$$\begin{aligned}\frac{\partial I_0}{\partial T_1}&=-\bar{\sigma}I_0+\bar{\sigma}I\,,\\ \frac{\partial I}{\partial T_2}&=-\bar{\sigma}I+\bar{\sigma}I_0\,,\\ I_0&=\mathscr{I}_0 \text{ at } T_1=0\,,\\ I_0&=\ 0 \text{ at } T_2=0\,.\end{aligned} \tag{33}$$

Instead of t_1 and t_2 the corresponding capital letters are used for the mosaic crystal, and because of the misalignment of the domains one has to use the expectation value $\bar{\sigma}$ for the diffraction power, where

$$\overline{\sigma(\varepsilon_1)}=\int W(\Delta)\sigma(\varepsilon_1+\Delta)d\Delta\,. \tag{34}$$

The integration of equation (34) can be carried out if one uses the approximation $\sigma(\varepsilon_1)\approx Q\alpha\exp(-\pi\alpha^2\varepsilon_1^2)$ with equation (24) and the result is

$$\bar{\sigma}\approx Q\alpha'\exp(-\pi\alpha'^2\varepsilon_1^2)\approx Q\alpha'\,\frac{\sin^2\pi\alpha'\varepsilon_1}{(\pi\alpha'\varepsilon_1)^2} \tag{35}$$

$$\alpha'=\sqrt{2}g\alpha/\sqrt{\alpha^2+2g^2}\,.$$

In using the Poisson form analogous to equation (26) it is convenient to use the approximate form for α' obtained by replacing $\sqrt{2}g$ with $3g/2$. Hence, the following expression for $\bar{\sigma}$ results:

$$\begin{aligned}\bar{\sigma}&\approx\frac{(4/3)Q\alpha'}{1+[(4\pi/3)\alpha'\varepsilon_1]^2}\\ \alpha'&\approx\alpha/\sqrt{1+(2\alpha/3g)^2}\,.\end{aligned} \tag{36}$$

When $\alpha\gg g$ one has accordingly $\alpha'=\frac{3}{2}g$, and when $\alpha\ll g$ $\alpha'=\alpha$.

The process for solving equations (33) is precisely analogous to that used for equations (4) except for the replacement of t_1,t_2,σ by $T_1,T_2,\bar{\sigma}$. For real crystals of symmetrical shape one may accordingly adopt the approximation equivalent to equation (19), *i.e.*

$$\varphi(\bar{\sigma})\approx\frac{1}{1+\bar{\sigma}\bar{T}}\,, \tag{37}$$

$\bar{T}$ being the mean path length through the crystal. Hence, with equation (36) and (37) the formulas for the diffraction pattern, $P(\varepsilon_1)$, and for $y=Q^{-1}\int\bar{\sigma}\varphi(\bar{\sigma})\,d(\sigma)$, become

$$P(\varepsilon_1)=\mathscr{I}_0Qv\,\frac{4\alpha'/3}{1+2x+(4\pi\alpha'\varepsilon_1/3)^2}\,, \tag{38a}$$

$$y=(1+2x)^{-\frac{1}{2}}\,, \tag{38b}$$

$$x=\tfrac{2}{3}Q\alpha'\bar{T}\,. \tag{38c}$$

It has been assumed so far that $\bar{t}$ is negligible compared with $\bar{T}$; but this is not necessarily true. Consider the diffraction by a single domain for which Δ is zero. The diffracting power within the domain is $\sigma(\varepsilon_1)$, while outside the domain it is $\bar{\sigma}(\varepsilon_1)$. The mean path length through the single domain under consideration is $\bar{t}$, and $\bar{T}-\bar{t}$ is the path length through other domains. Thus, x in equation (38c) should be replaced by its mean value $\bar{x}$ given by

$$\bar{x}=\tfrac{2}{3}Q\alpha[\bar{t}+(\bar{T}-\bar{t})/\sqrt{1+(2\alpha/3g)^2}]\,. \tag{39}$$

If ordinary absorption is taken into account, the intensities I_0' and I' of incident and diffracted beams must satisfy the equations

$$\begin{aligned}\frac{\partial I_0'}{\partial T_1}&=-(\mu+\sigma)I_0'+\sigma I'\\ \frac{\partial I'}{\partial T_2}&=-(\mu+\sigma)I'+\sigma I_0'\,.\end{aligned} \tag{40}$$

The solutions are $I_0'=I_0\exp[-\mu(T_1+T_2]$ and $I'=I\exp[-\mu(T_1+T_2)]$, where I_0 and I are the solutions of equations (33).

The approximation

$$I' \approx I\overline{\exp[-\mu(T_1+T_2)]} = IA(\mu) \qquad (41)$$

is justifiable unless the absorption effects are large. The integrated intensity will accordingly be reduced by the transmission factor $A(\mu)$. The only effect on the results obtained for the extinction factor y relates to the evaluation of the mean path length $\bar{T}$ which must be weighted with the absorption term $\exp[-\mu(T_1+T_2)]$. Accordingly

$$\bar{T} = -A^{-1}dA/d\mu\,. \qquad (42)$$

It remains to consider the effect of polarization. Let it be assumed that the incident radiation is unpolarized. If $\bar{x}_0$ be the value of $\bar{x}$ for $K=1$, the corresponding value for the parallel component of polarization is $K^2\bar{x}_0$. Thus the expression for y with polarization effect included is

$$y = \frac{(1+2\bar{x}_0)^{-\frac{1}{2}} + K^2(1+2K^2\bar{x}_0)^{-\frac{1}{2}}}{1+K^2}\,. \qquad (43)$$

In the limiting case when $\bar{x}_0 \gg 1$ one has

$$y \approx (1+|K|)/\sqrt{2}\bar{x}_0(1+K^2)\,. \qquad (44)$$

For $\bar{x}_0 < 5$ the following expression for y can be used instead of equation (43), and without introducing perceptible error,

$$y = \left(1+2\frac{p_2}{p_1}\bar{x}_0\right)^{-\frac{1}{2}}, \qquad (45)$$

where $p_n = (1+K^{2n})/2$ so that $p_2/p_1 = (1+K^4)/(1+K^2)$. The function p_2/p_1 does not vary much over the observational range. The maximum value of unity occurs at $2\theta = 0, 90°$ and $180°$, the minimum value of $2(\sqrt{2}-1)$ at $2\theta = 49{\cdot}9°$ and $130{\cdot}1°$.

It may be useful to summarize the findings for the general case:

$$\mathscr{P} = \mathscr{P}_k y = \mathscr{J}_0 Q_0 p_1 v A(\mu) y \qquad (46a)$$

$$y = (1+2p_2\bar{x}_0/p_1)^{-\frac{1}{2}} \qquad (46b)$$

$$\bar{x}_0 = \beta Q_0[\bar{t} + (\bar{T}-\bar{t})/\sqrt{1+(\beta/g)^2}] \qquad (46c)$$

$$\beta = 2\bar{t}_\perp/3\lambda\,, \qquad (46d)$$

where Q_0 is given by equation (2*b*) with $K=1$ and $\bar{T}$ by equation (42). One has $\bar{t} = 3r/2$ and $\beta = \lambda^{-1}r$ for a spherical domain of radius r.

It should be kept in mind that equations (19) and (37) for $\varphi(\sigma)$ and $\varphi(\bar{\sigma})$ as well as equations (26) and (36) for σ and $\bar{\sigma}$ are approximations, but that equation (46*b*) is a direct consequence of these simplifications. A careful analysis of the series solutions for spherical domains shows that equations (19) and (37) tend to underestimate $\varphi(\sigma)$ and $\varphi(\bar{\sigma})$ while the Poisson approximations of equations (26) and (36) may give over-estimations for σ and $\bar{\sigma}$. On theoretical grounds it is therefore difficult to tell which of the following three forms of the function y is to be preferred.

$$y = \tanh\sqrt{3x}/\sqrt{3x} = 1 - x + \tfrac{6}{5}x^2 - \tfrac{51}{35}x^3 + \ldots \qquad (47a)$$

$$y = (1+2x)^{-\frac{1}{2}} = 1 - x + \tfrac{3}{2}x^2 - \tfrac{5}{2}x^3 + \ldots \qquad (47b)$$

$$y = \tan^{-1}\sqrt{3x}/\sqrt{3x} = 1 - x + \tfrac{9}{5}x^2 - \tfrac{27}{7}x^3 + \ldots \qquad (47c)$$

The three proposed equations for y cannot be distinguished when x is small. However, for $x \gg 1$ there are significant differences. Thus when $x=10$, one finds $y = 0{\cdot}183$, $0{\cdot}218$, $0{\cdot}254$ for equations (47*a*), (47*b*), (47*c*) respectively.

4. Discussion

The two terms of equation (46*c*), $\beta Q_0\bar{t}$ and $\beta Q_0(\bar{T}-\bar{t})/\sqrt{1+(\beta/g)^2}$, correspond to the concepts of primary and secondary extinction as introduced by Darwin (1922). As mentioned at the end of § 2, primary extinction becomes negligible if $\beta Q_0\bar{t} < 0{\cdot}02$, and experiments show that this condition is fulfilled even for the strongest reflections of most crystal specimens.

When primary extinction can be neglected, equation (46*c*) reduces to

$$x_0 = r\lambda^{-1}Q_0\bar{T}/\sqrt{1+(r/\lambda g)^2}\,, \qquad (48)$$

which consequently becomes the basic equation for secondary extinction.

There are two important types of real crystals:

Type I, $r/\lambda g \gg 1$

$$x_0 = gQ_0\bar{T} \qquad (49a)$$

Type II, $r/\lambda g \ll 1$

$$x_0 = r\lambda^{-1}Q_0\bar{T}\,, \qquad (49b)$$

with equation (48) covering the intermediate type. In type I crystals the distribution function W is much wider than the diffraction pattern from a single domain, whereas the reverse situation is true in type II crystals.

The theoretical study of secondary extinction by Darwin (1922) and recent work (Zachariasen, 1963, 1965) have been confined to crystals of type I. It seems that the possible existence of type II crystals and of secondary extinction governed by equation (49*b*) has not been considered before.

It is interesting to note that the integrated intensity for type I crystals depends upon g, but is independent of r. For crystals of type II on the other hand the intensity depends on r and not on g.

The presumed absence of primary extinction implies $r < 10^{-4}$ cm for a strong reflection and hence that g for type I crystals is of the order of 10^{+3} or smaller. The quantity $Q_0 \approx 10^{-2} - 10^{-1}$ cm^{-1} for the strongest reflection. Hence, if $\bar{T} \approx 10^{-2}$ cm, $x_0 < 1$ and $y > 0{\cdot}5$. In other words, very large extinction effects cannot occur in type I crystals.

It is seen that values $x_0 \gg 1$ are possible for type II crystals even if r is as small as $0{\cdot}5 \times 10^{-4}$ cm.

Equations (48), (49*a*) and (49*b*) have the same dependence on scattering angle. If a single wavelength is used, it is accordingly impossible to tell from experiment whether the crystal is of type I or II or intermediate type. However, the dilemma is readily resolved if the intensities are measured for two different wavelengths. The procedure can be illustrated by an example: results reported for α-quartz (Zachariasen &

Plettinger, 1965) gave $y=0{\cdot}33$ for the reflection $10\bar{1}$ and Cu $K\alpha$ radiation. Measurements with Mo $K\alpha$ radiation and the same crystal sphere gave $y=0{\cdot}41$. The corresponding values for x_0 according to equation (46*b*) are 4·5 and 2·5 respectively with a ratio of 1·8 for the two x_0 values. The calculated ratio is 3·84 according to equation (49*a*) and 1·77 according to equation (49*b*). Thus experiments prove conclusively that the quartz specimen is of type II, the Cu $K\alpha$ result giving $r=0{\cdot}50\times10^{-4}$ cm, the Mo $K\alpha$ result $r=0{\cdot}49\times10^{-4}$ cm.

Many writers over the past forty years have reported experimental determinations of the parameter 'g' for various crystal specimens on the assumption that all real crystals are of type I. According to the results of this paper some, and possibly all, of the crystals investigated may have been of type II, in which case the reported 'g' values are the quantities $r\lambda^{-1}$.

If $r\lambda^{-1}$ and g are of the same magnitude, one must use equation (48) rather than equation (49*a*) or (49*b*). Experiments with two different wavelengths will then give both parameters r and g.

With the aid of a well collimated incident X-ray beam it is possible to measure the diffraction pattern $P(\varepsilon_1)$. An examination of equation (38*a*) shows that the determination of the half width of this pattern will not provide any new information.

The approximations of this paper led to the formula $y=(1+2x)^{-\frac{1}{4}}$. However, as mentioned earlier, one cannot exclude from consideration the hyperbolic or arc tangent forms given in equations (47*a*) and (47*c*). Measurements on α-quartz performed with both Cu $K\alpha$ and Mo $K\alpha$ radiations (to be reported in detail in a forthcoming article) indicate that equation (47*a*)is unsatisfactory, and that equation (47*c*) may be slightly preferable to equation (47*b*).

The writer recommends that the new intensity formula, rather than the crude kinematical approximation, be used in the analysis of crystal structure data. This recommendation implies the modification of least-square refinement programs so that the mosaic crystal parameters r and g as well as scale factor, positional and thermal parameters are varied. In this manner the extinction correction $y^{\frac{1}{4}}$ will be included in the calculated structure factor. Indeed, D. Cromer and A. Larsen (according to private communication) have adopted this logical procedure at Los Alamos Scientific Laboratory.

The general intensity formula presented in this paper provides a theoretical basis for the interpretation of experimental data involving large extinction effects. It is likely therefore that the structure parameters (in particular the thermal ones) can be found with greater precision than has been possible hitherto, and that more reliable determinations can be made of experimental f curves. The new result, that the domain radius can be found from experiment for crystals of type II and intermediate type, has interest and possible usefulness.

This paper deals specifically with X-ray diffraction. It is trivial to extend the results to electron and neutron diffraction. The general formulas of equations (46) remain valid; but one has $p_1=p_2=1$, and the expression for the quantity Q_0 must be appropriately modified.

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A preliminary account of the results of this paper was given in *Physical Review Letters*.

APPENDIX

Professor S. Chandrasekhar, to whom the series solution of equation (4) [given in equation (14)] was shown, has succeeded in finding the exact solution in terms of Riemann functions.

The Chandrasekhar solution is (with $\xi=\sigma t_1$ and $\eta=\sigma t_2$)

$$I_0=\mathscr{J}_0\exp\{-(\xi+\eta)\}\left[\mathscr{J}_0(i2\sqrt{\xi\eta})+\int_0^{\eta}e^{y}\mathscr{J}_0(i2\sqrt{\xi(\eta-y)}\,dy\right]$$

from which $I(\xi,\eta)=\mathscr{J}_0-I_0(\eta,\xi)$ can be found by interchange of variables.

The exact formula for $\varphi(\sigma)$, for the parallelopiped of Fig. 2, becomes (with $\xi_0=\sigma t_1^0=\eta_0=\sigma t_2^0$)

$$\varphi(\sigma)=\frac{\xi_0-\left[G(\xi_0)+\int_0^{\xi_0}G(\xi)d\xi\right]}{\xi_0^2}$$

$$G(\xi)=\int_0^{\xi}\exp-(x+\xi_0)\mathscr{J}_0(i2\sqrt{x\xi_0})dx\,.$$

The asymptotic form for $\xi_0\gg1$ is $\varphi=\xi_0^{-1}$ implying total reflection.

Unfortunately no tabulation of the function $G(\xi)$ is available.

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