PRANDL, W., HOSER, A. & BRÜCKEL, T. (1988). *Mater. Sci. Forum*, **27/28**, 35-48.
PRINCE, E. & FINGER, L. W. (1973). *Acta Cryst.* B**29**, 179-183.
SAMATHIYAKANIT, V. & GLYDE, H. R. (1973). *J. Phys. C*, **6**, 1166-1180.
SCHERINGER, C. (1980). *Acta Cryst.* A**36**, 497-499.
SCHERINGER, C. (1985*a*). *Acta Cryst.* A**41**, 73-79.
SCHERINGER, C. (1985*b*). *Acta Cryst.* A**41**, 79-81.
SCHERINGER, C. (1987). *Acta Cryst.* A**43**, 703-706, 706-710.
SCHERINGER, C. (1988). *Acta Cryst.* A**44**, 343-349.
SHUKLA, R. C. (1981). *Phys. Rev. B*, **23**, 3087-3090.
SHUKLA, R. C. & HÜBSCHLE, H. (1989). *Phys. Rev. B*, **40**, 1555-1559.
SHUKLA, R. C. & MOUNTAIN, R. D. (1982). *Phys. Rev. B*, **25**, 3649-3657.
SHUKLA, R. C. & PLINT, C. A. (1989). *Phys. Rev. B*, **40**, 10337-10344.
TANAKA, K. & MARUMO, F. (1983). *Acta Cryst.* A**39**, 631-641.
TEWARY, W. K. (1973). *J. Phys. F*, **3**, 1515-1523.
WALLER, I. (1927). *Ann. Phys.* **83**, 153-183.
WILLIS, B. T. M. (1969). *Acta Cryst.* A**25**, 227-300.
WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.
WOLFE, G. A. & GOODMAN, B. (1969). *Phys. Rev.* **178**, 1171-1189.
YUDE, Y., BOYSEN, H. & SCHULZ, H. (1990). *Z. Kristallogr.* **191**, 79-91.
ZUCKER, U. H., PERENTHALER, E., KUHS, W. F., BACHMANN, R. & SCHULZ, H. (1983). *J. Appl. Cryst.* **16**, 358.
ZUCKER, U. H. & SCHULZ, H. (1982). *Acta Cryst.* A**38**, 568-576.

*Acta Cryst.* (1992). A**48**, 98-103

# The Ewald and Darwin Limits Obtained from the Hamilton–Darwin Energy Transfer Equations

BY T. M. SABINE* AND D. G. BLAIR†

*School of Physical Sciences, University of Technology, Sydney, NSW* 2007, *Australia*

(*Received* 4 *December* 1990; *accepted* 2 *July* 1991)

## Abstract

There are two classic limiting solutions for the diffraction profile and integrated intensity of Bragg reflections from semi-infinite perfect crystals. These are the Ewald and Darwin solutions for the symmetric Bragg case. It is shown that exact values of these limiting solutions can be obtained with the use of three concepts: (1) the kinematic scattering from a small absorbing crystal; (2) the Hamilton-Darwin energy transfer equations; (3) the dynamic refractive index of the crystal.

## 1. Introduction

In 1967 Zachariasen attempted to obtain a general solution for the extinction factor in a finite perfect crystal. He used the Darwin (1922) energy transfer equations to describe the flow of the incident and diffracted beams through the crystal and made the intuitive conjecture that the coupling coefficient between the beams could be represented by the kinematic scattering cross section per unit volume from a small and perfect crystal. He did not include absorption in the small crystal and he made the approximation that the wave vectors within the crystal were the same as the wave vectors in free space. His treatment did not reproduce the classical dynamical theory solutions for the flat plate of finite thickness, which is the only case for which exact solutions are available.

Sabine (1988, 1992) showed that, with the use of Hamilton's (1957) generalization of Darwin's equations this method led to the exact Ewald ($\mu \equiv 0$, $\mu D \equiv 0$) solution for the integrated intensity in the Bragg case, but that the solution obtained for the Darwin ($\mu \simeq 0$, $\mu D \gg 0$) case was in error by a factor of one-half.

In the present work it is shown that, with the inclusion of the dynamic refractive index of the crystal and explicit allowance for absorption in the calculation of the diffraction profile of the small crystal, the conjecture by Zachariasen (1967) leads to the exact solution for both limits.

The analysis is given for neutrons for which the polarization factor is unity and, by convention, the structure factor includes the scattering length.

## 2. Notation

$A$ $= \lambda N_c |F'_H| T/\sin\theta_B \equiv \lambda N_c |F'_H| D$.
$D$ Average path length of the diffracted beam in the crystal.
$F_H$ The structure factor of the reflection whose Miller indices are $HKL$ ($F_H = F'_H + iF''_H$).
$g$ $= -F''_0/|F''_H|$.
$\mathbf{k}$ Scattering vector in free space [$|\mathbf{k}| = 2(\sin\theta)/\lambda$].
$\mathbf{K}$ Scattering vector within the crystal.

* Present address: Advanced Materials Program, ANSTO, Private Mailbag 1, Menai, NSW 2234, Australia.
† Present address: Underwater Systems Division, DSTO, PO Box 44, Pyrmont, NSW 2009, Australia.

0108-7673/92/020098-06$03.00 

$\mathbf{k_B}$ The reciprocal-lattice vector for the reflection $HKL$.
$\Delta k$ $k - k_B$.
$n$ Static refractive index of the crystal.
$N_c$ Number of unit cells per unit volume.
$T$ Crystal thickness normal to the diffracting plane ($T = D \sin \theta_B$).
$y$ $= -F_0/|F'_H| + \pi \sin \theta_B \Delta k / N_c \lambda |F'_H|$.
$\lambda$ The wavelength of the incident radiation.
$\mu$ Linear absorption coefficient ($= -2gN_c\lambda|F'_H|$).
$\theta$ Glancing angle of incidence.
$\theta_B$ The exact Bragg angle.

### 3. The Hamilton–Darwin equations

These equations were introduced by Darwin (1922) to describe the energy interchange between the incident and diffracted beams as both beams travelled through the crystal. The equations were generalized by Hamilton (1957) to include removal processes other than Bragg scattering.

The Hamilton-Darwin equations are

$$\partial P_i/\partial t_i = \tau P_i + \sigma P_f \quad (1)$$

$$\partial P_f/\partial t_f = \tau P_f + \sigma P_i. \quad (2)$$

$P_i$ and $P_f$ are the power per unit area in the incident and diffracted beams respectively at the point in the crystal whose coordinates are $t_i$, $t_f$. The axis $t_i$ is parallel to the incident beam and the axis $t_f$ is parallel to the diffracted beam. The coupling constant $\sigma$ is the cross section per unit volume for Bragg scattering into the reflection under consideration, while $\tau$, which is always negative, is the cross section per unit volume for all removal processes (including Bragg scattering).

It will be assumed in this work that absorption and Bragg scattering are the only operative removal mechanisms. Then $\tau = -(\sigma + \mu)$, where $\mu$ is the absorption cross section per unit volume (the linear absorption coefficient).

For the following two cases in which the directions of $t_i$ and $t_f$ coincide the differential equations can be integrated to obtain the power in the diffracted beam at the exit surface.

(1) *The Laue case*, $2\theta_B = 0°$

$$P_f = \tfrac{1}{2}P_i^0 \exp(-\mu D)[1 - \exp(-2\sigma D)] \quad \mu \neq 0 \quad (3)$$

$$P_f = \tfrac{1}{2}P_i^0[1 - \exp(-2\sigma D)] \quad \mu = 0. \quad (4)$$

(2) *The Bragg case*, $2\theta_B = 180°$

$$P_f = \frac{\sigma P_i^0 \sinh(aD)}{a\cosh(aD) - \tau \sinh(aD)}, \quad \mu \neq 0 \quad (5)$$

with $a^2 = \tau^2 - \sigma^2$

$$P_f = \sigma P_i^0 D/(1 + \sigma D), \quad \mu = 0. \quad (6)$$

In (3) to (6) $D$ is the average path length of the diffracted beam in the crystal and $P_i^0$ is the power incident on the entrance surface.

In the infinite flat plate of finite thickness the Hamilton–Darwin equations lead to the same solutions for the symmetric Laue case, in which the diffracted beam exits from the opposite suface to the entrance surface, and for the symmetric Bragg case, in which the diffracted beam exits through the entrance surface. In each case both beams make equal angles with the normal to the plate and $D$ is related to the plate thickness, $T$, by $T = D \sin \theta_B$ for the Bragg case and $T = D \cos \theta_B$ in the Laue case.

### 4. The evaluation of $\sigma$

The coupling coefficient, $\sigma$, in the Hamilton–Darwin equations must be obtained in terms of crystallographic quantities. The starting point for doing this is the formula given by Marshall & Lovesey (1971) for the differential cross section per unit volume for elastic scattering into a single Bragg peak from a large defect-free crystal. In the notation of this paper this formula is

$$d\sigma/d\Omega = N_c^2|F_H|^2\delta(\mathbf{k} - \mathbf{k_B}). \quad (7)$$

$N_c$ is the number of unit cells per unit volume and $F_H$ is the structure factor per unit cell. The Debye–Waller factor is always included in $F_H$.

With the use of spherical polar coordinates and integration of the delta function over the angular variables (Weinstock, 1944) the total cross section for scattering into a single Bragg reflection becomes

$$\sigma(\Delta k) = Q_k \delta(\Delta k) \quad (8)$$

where $\delta$ is the Dirac delta function and

$$Q_k = N_c^2|F_H|^2\lambda^2/\sin\theta_B.$$

Thus the reciprocal-lattice point is scanned in the direction of increasing $k$ in slices of thickness $dk[= d(\Delta k)]$ where

$$\Delta k = k - k_B. \quad (9)$$

### 5. Kinematic scattering from a small crystal

This problem is solved for the non-absorbing crystal in most elementary text books on crystallography. Wilson (1949) considered the amplitude of scattering from a crystal in the shape of a parallelepiped. For one atom of unit scattering power per unit cell the amplitude of scattering in the neighbourhood of the reciprocal-lattice point $(H, 0, 0)$ is given by

$$A(h) = \sum_{n=0}^{N-1} \exp 2\pi i n h, \quad (10)$$

where $h = a\Delta k$. $N$ is the number of unit cells in the $a$ direction, in which the interplanar spacing is $a$.

To include absorption a damping factor $\exp(-\alpha)$ is introduced into (10) leading to

$$A(h) = \sum_{n=0}^{N-1} \exp n(2\pi i h - \alpha). \quad (11)$$

Summation of the geometric progression and multiplication of $A$ by its complex conjugate gives the intensity of scattered radiation as

$$I(h)=\frac{1-2\exp(-\alpha N)\cos(2\pi Nh)+\exp(-2\alpha N)}{1-2\exp(-\alpha)\cos(2\pi h)+\exp(-2\alpha)} \tag{12}$$

$$=\exp[-(N-1)\alpha]\times\left\{\frac{\sin^2(\pi Nh)+\sinh^2(N\alpha/2)}{\sin^2(\pi h)+\sinh^2(\alpha/2)}\right\}. \tag{13}$$

Equation (12) can be integrated (Gradshteyn & Ryzhik, 1980) to give

$$\int I(h)\,dh=[1-\exp(-2\alpha N)]/[1-\exp(-2\alpha)]$$
$$=\exp[-(N-1)\alpha](\sinh N\alpha)/(\sinh\alpha). \tag{14}$$

To relate (13) and (14) to (8) a normalized intensity $\beta(h)$ is defined by

$$\int\beta(h)\,dh=1.$$

Then, the division of (13) by (14) leads to

$$\beta(h)=\frac{\sinh\alpha}{\sinh(N\alpha)}\times\left\{\frac{\sin^2(\pi Nh)+\sinh^2(N\alpha/2)}{\sin^2(\pi h)+\sinh^2(\alpha/2)}\right\}. \tag{15}$$

It is an elementary step to show that $\alpha=\mu a\,\mathrm{cosec}\,\theta_B$ where $\mu$ is the linear absorption coefficient and $a$ is the interplanar spacing. Also, $Na$ is the thickness of the crystal normal to the diffracting plane ($T$) and $D=T\,\mathrm{cosec}\,\theta_B$, where $D$ is the average path length of the diffracted beam in the crystal. In the cases to be considered here the quantity $\mu a$ is very much less than unity, $h$ is small and, for glancing angles not close to zero,

$$\beta(h)=\frac{N^2\alpha}{\sinh(N\alpha)}\left\{\frac{\sin^2(\pi Nh)+\sinh^2(N\alpha/2)}{(\pi Nh)^2+(N\alpha/2)^2}\right\}.$$

In (8), the infinitely sharp distribution $\delta(\Delta k)$ must be replaced by the distribution function $a\beta(h)$ which satisfies the same normalization condition.

Then the relationships $T=Na$ and $h=a\Delta k$ lead to

$$\sigma(\Delta k)=\frac{Q_k\mu DT}{\sinh(\mu D)}\times\left\{\frac{\sin^2(\pi T\Delta k)+\sinh^2(\mu D/2)}{(\pi T\Delta k)^2+(\mu D/2)^2}\right\}. \tag{16}$$

It should be noted that in these equations refraction has been neglected and $k$ is the scattering vector *outside* the crystal.

As a check on the derivation of (16) the kinematic diffraction profile for a crystal of unit area corrected for absorption will be evaluated in the Bragg case. Then

$$\left(\frac{P_f}{P_i^0}\right)_{\text{kin}}=\sigma DA_B=Q_kDT\exp(-\mu D)\times\left\{\frac{\sin^2(\pi T\Delta k)+\sinh^2(\mu D/2)}{(\pi T\Delta k)^2+(\mu D/2)^2}\right\} \tag{17}$$

where $A_B$ is the standard absorption factor in the Bragg case, given by

$$A_B=\exp(-\mu D)\sinh(\mu D)/(\mu D),$$
$$A_B\to(2\mu D)^{-1}\text{ as }D\to\infty.$$

The result (17) is readily corrected for the static refractive index by including in $\Delta k$ a term proportional to $F_0'$.

Zachariasen (1945, equation 3.139) gives a general expression for the power ratio in the Bragg case. His kinematic result, which is obtained by allowing the reflected intensity to be vanishingly small, is identical with (17) corrected for the static refractive index. A detailed derivation is given in the Appendix.

### 6. The refractive index of the crystal

To this point it has been assumed that the scattering vector inside the crystal is the same as the scattering vector outside. The crystal, however, has a small but finite refractive index so this assumption is not valid and $\Delta k$ must be replaced by the real part of $\Delta K$, where **K** is the scattering vector within the crystal.

When no diffracted beam is present the refractive index is given by $n=n'+in''$ where

$$n'=1-N_cF_0'\lambda^2/2\pi\text{ and }n''=-N_cF_0''\lambda^2/2\pi.$$

When a diffracted beam is excited the concept of a definite refractive index must be discarded and replaced by refractive indices appropriate to the incident and the diffracted beams.

In this paper it will be assumed that

($a$) the crystal is centrosymmetric, so that $F_H=F_{\bar{H}}$;

($b$) absorption is a consequence of $F_0''$ only, so that $F_H$ is real. The linear absorption coefficient is related to $F_0''$ by

$$\mu=2\lambda F_0''N_c. \tag{18}$$

The quantity $\delta$, of magnitude $\simeq10^{-5}$, was introduced by Zachariasen (1945) such that the refractive index is $1+\delta$. In the notation of this paper

$$2\delta=-\lambda\sin\theta_B\Delta k+e_1e_2(\lambda^2N_c|F_H'|/\pi)\times[(y+ig)^2-1]^{1/2} \tag{19}$$

for the symmetric Bragg case. In (19) the square root having a positive real part is implied. The indicators $e_1$ and $e_2$ each take the values $\pm1$. For $y\neq0$ (or, in the case $g=0$, for $|y|>1$), $e_1$ is equal to sign ($y$) while $e_2$ is equal to $+1$ for the incident beam ($\delta_i$) and $-1$ for the diffracted beam ($\delta_f$).

The variables $y$ and $g$, which are also used by Zachariasen (1945), are given by

$$y = -\frac{F_0'}{|F_H'|} + \frac{\pi \sin\theta_B}{N_c\lambda|F_H'|}\Delta k, \qquad g = -F_0''/|F_H'|.$$

### 7. The relationship between $\Delta k$ and $\Delta K$

The incident and diffracted wave vectors within the crystal will be denoted by $\mathbf{K}_i$ and $\mathbf{K}_f$ respectively. Also,

$$K_i^2 = k_i^2(1+2\delta_i). \tag{20}$$

It will be assumed that the crystal is set in the symmetric Bragg position. A coordinate system is chosen such that the $x$ axis is in the plane defined by $\mathbf{k}_i$ and $\mathbf{k}_f$ and is parallel to the surface of the crystal. The $z$ axis is the outwardly directed normal to the crystal surface. The origin of coordinates is at the crystal surface.

The $x$ and $z$ components of $\mathbf{k}_i$ and $\mathbf{K}_i$ will be denoted by $k_{ix}$, $K_{ix}$ and $k_{iz}$, $K_{iz}$ respectively. In the symmetric Bragg setting the scattering vector within the crystal is defined by

$$\mathbf{K} = -2K_{iz}\hat{\mathbf{z}}.$$

Then

$$\Delta K = -2K_{iz} - k_B. \tag{21}$$

For continuity across the crystal surface the components of $\mathbf{k}$ and $\mathbf{K}$ parallel to the surface are equal. Then

$$K_{ix} = k_{ix}. \tag{22}$$

Squaring (22) and subtracting the result from (20) one gets

$$K_{iz}^2 = k_{iz}^2 + 2k_i^2\delta_i. \tag{23}$$

Now

$$\begin{aligned} k_{iz} &= -k_i \sin\theta_B \\ K_{iz}^2 &= k_{iz}^2(1+2\delta_i \operatorname{cosec}^2\theta_B). \end{aligned} \tag{24}$$

Upon taking the square root, which is justifiable for glancing angles not close to zero,

$$K_{iz} = k_{iz}(1+\delta_i \operatorname{cosec}^2\theta_B), \tag{25}$$

then applying (21)

$$\Delta K = \Delta k + 2k_i\delta_i \operatorname{cosec}\theta_B$$

and substituting for $\delta_i$ from (19), one gets

$$\Delta K = (\lambda N_c|F_H'|/\pi\sin\theta_B)e_1[(y+ig)^2-1]^{1/2}. \tag{26}$$

The quantity $\Delta K$ can be written as $\Delta K = \Delta K' + i\Delta K''$. Then, with the variables $Y$ and $G$ defined by

$$Y = [\pi(\sin\theta_B)/|F_H'|N_c\lambda]\Delta K' \tag{27}$$

$$G = [\pi(\sin\theta_B)/|F_H'|N_c\lambda]\Delta K'', \tag{28}$$

(26) becomes

$$(Y+iG)^2 = (y+ig)^2 - 1. \tag{29}$$

Upon equating the real and imaginary parts in equation (29) and solving for $Y$ and $G$, one obtains the relations

$$Y = e_1[\tfrac{1}{2}(L-2g^2-1)]^{1/2} \tag{30}$$

$$G = -[\tfrac{1}{2}(L-2y^2+1)]^{1/2} \tag{31}$$

where

$$L = |[(y^2-g^2-1)^2+4(gy)^2]|^{1/2} + y^2 + g^2. \tag{32}$$

This last quantity is the same as Zachariasen's (1945) quantity $L$ when $F_H'' = 0$. The desired quantity $\Delta K'$ is given by substituting (30) into (27).

The imaginary part, $\Delta K''$, proportional to $G$, represents exponential attenuation of the wave. It arises in part from absorption (through $g$) and in part from a second effect, which is present even when $\mu = 0$, namely Bragg reflection of neutrons that lie in the energy gap ($|y| < 1$) of the crystal.

### 8. The Ewald solution

For this case $\mu \equiv 0$, $\mu D \equiv 0$, $D \to \infty$ then (16) becomes

$$\sigma(\Delta k) = Q_k T \sin^2(\pi T\Delta K')/(\pi T\Delta K')^2. \tag{33}$$

The profile of the diffracted beam is obtained by inserting $\sigma(\Delta k)$, given by (33), into (6).

Development of the formulae is made clearer by adoption of the variable (also used by Zachariasen, 1945)

$$A = \lambda N_c|F_H'|T/\sin\theta_B = \lambda N_c|F_H'|D. \tag{34}$$

Then

$$\sigma(\Delta k) = \sin^2(AY)/DY^2 \tag{35}$$

and

$$P_f/P_i^0 = \sin^2(AY)/[Y^2+\sin^2(AY)]. \tag{36}$$

For $A$ large the trigonometric expressions oscillate rapidly and the individual oscillations usually cannot be resolved. Hence (36) may be replaced by its average over one cycle, centred on $Y$, which is

$$(A/\pi)\int_{Y-\pi/(2A)}^{Y+\pi/(2A)} \sin^2(Au)/(u^2+\sin^2 Au)\,\mathrm{d}u.$$

Under conditions where the first term in the denominator may be treated as a constant, equal to $Y^2$, the integral is readily evaluated *via* the identity $\sin^2 t = \frac{1}{2}(1-\cos 2t)$, the change of variable $x = 2Au$ and the standard integral (Speigel, 1968)

$$\int_0^{2\pi} (a+b\cos x)^{-1}\,\mathrm{d}x = 2\pi(a^2-b^2)^{-1/2}.$$

The 'constancy' assumption is valid provided $A|Y| \gg 1$ or, equivalently, $|y|-1 \gg A^{-2}$, from (28). Hence for

any $y$ outside the region of perfect reflection ($|y| \le 1$), the result holds for sufficiently large $A$.

The power ratio becomes

$$P_f/P_i^0 = 1-[Y^2/(Y^2+1)]^{1/2}. \quad (37)$$

The substitution $Y^2 = y^2-1$ then gives

$$P_f/P_0 = 1-(1-1/y^2)^{1/2} \quad (38)$$

which is the Ewald result.

For the earlier result, (36), which was derived without going to the limit $D \to \infty$, only the condition $\mu = 0$ was required. Thus, (36) gives the prediction of the present theory for the full evolution of the profile from the kinematic non-absorbing limit to the Ewald limit. For the case of a neutron in the energy gap ($|y| < 1$), (36) must be interpreted as the limit as $Y \to 0$, that is

$$P_f/P_i^0 = A^2/(1+A^2).$$

Thus, the predicted profile has a 'flat top' in the gap. Comparison with Zachariasen's (1945) equations [3.143], [3.144] shows exact agreement outside the gap but disagreement inside. The integrated intensities agree exactly in both the kinematic limit ($A \to 0$) and the Ewald limit ($A \to \infty$); the maximum disagreement in the integrated intensities occurs near $A = 1{\cdot}6$ and amounts to only 6%.

## 9. The Darwin solution

For this case, $\mu \to 0$, $\mu D \gg 1$ and, since $\mu D \gg 1$, (16) becomes

$$\sigma(\Delta k) = Q_k \mu DT/2\{(\mu D/2)^2 + (\pi T \Delta K')^2\} \quad (39)$$

and (5) becomes

$$P_f/P_i^0 = \{[2\mu/\sigma + (\mu/\sigma)^2]^{1/2} + \mu/\sigma + 1\}^{-1} \quad (40)$$

where, using (27) and (34) in (39)

$$\mu/\sigma = (2/A^2)[(\mu D/2)^2 + A^2 Y^2]. \quad (41)$$

Introduction of the quantity, also used by Zachariasen (1945),

$$g = -\mu/2\lambda N_c |F'_H| \quad (42)$$

means that, from (30) and (42), (41) becomes

$$\mu/\sigma = 2(g^2 + Y^2) = L-1 \quad (43)$$

and, from (40),

$$P_f/P_i^0 = 1+(\mu/\sigma)-\{[1+(\mu/\sigma)]^2-1\}^{1/2}$$
$$= L-(L^2-1)^{1/2}. \quad (44)$$

When the substitution $g = 0$ is made, this result reduces to the Darwin result. But the result (40) was derived without going to the limit $\mu \to 0$; only the condition $\mu D \gg 1$ was assumed. The corresponding result of Zachariasen (1945) is given by his equation [3.190]; the present result agrees exactly.

At this point a useful result can be derived, to which Zachariasen (1945) gave only a 'crude approximation'. For $|g| \ll 1$, by applying the binomial theorem to (32) and (44), the following power series in $g$ is obtained:

$$L = 1+2(1-y^2)^{-1}g^2+\ldots$$
$$P_f/P_0 = 1-2(1-y^2)^{-1/2}|g|+\ldots. \quad (45)$$

The two terms on each right-hand side dominate the remaining terms provided that $y$ is in the gap ($|y| < 1$) and not near either edge. By integrating (45) from $y = -1$ to $+1$ and ignoring $y$ outside the gap,

$$R = \tfrac{8}{3} - 2\pi|g| = \tfrac{8}{3}(1-2{\cdot}36|g|) \quad (46)$$

where $R$ is the integrated intensity on the $y$ scale. A closer analysis verifies that the second term in (46) correctly gives the leading term in the departure of $R$ from the Darwin value of 8/3. The first neglected term in $R$ is of the order of $|g|^{3/2}$ at most. The term in $|g|$ is in close agreement with the empirical result of Hirsch & Ramachandran (1950) who obtain $R = (8/3)(1-2{\cdot}4|g|)$.

## 10. Discussion

It has been demonstrated that the Hamilton-Darwin equations, the kinematic diffraction profile from a small absorbing crystal and inclusion of the dynamic refractive index of the crystal lead to the classic Ewald and Darwin solutions for both the diffraction profile and integrated intensity from the semi-infinite flat plate. Unlike the conventional dynamical theory spatial coherence between scattering centres over large volumes of crystal is not required explicitly in the present theory. However, the parameter $T$ on which $\sigma$ depends is sensitive to the size of the spatially coherent region and allows distinction between scattering from, for example, a monolithic block of perfect crystal and a scatterer consisting of slices of perfect crystal separated by random displacements but untilted with respect to each other.

The theoretical methods presented above will be used to examine the diffraction profiles and integrated intensities from finite crystals, mosaic and distorted crystals.

This work was supported by the Australian Research Council.

## APPENDIX

### The kinematic result

It is shown that, in two separate limiting cases, Zachariasen's equation reduces to the desired kinematic result. It is then shown that the case of vanishingly small reflected power always reduces to one or other of the above limits.

Zachariasen's equation [3.139] contains the quantities $\psi_0$, $\psi_H$, $q$, $z$, $a$, $v$ and $w$ defined by

$$\psi_0 = -\lambda^2 F_0 N_c/\pi \qquad (A\text{-}1)$$

$$\psi_H = -\lambda^2 F_H N_c/\pi. \qquad (A\text{-}2)$$

For the symmetric Bragg case

$$q = -\psi_H \psi_{\bar{H}} \qquad (A\text{-}3)$$

$$z = \psi_0 + (\lambda^2/2) k_B \Delta k \qquad (A\text{-}4)$$

$$a = \pi T/\lambda \sin\theta_B \qquad (A\text{-}5)$$

$$v + iw = (q + z^2)^{1/2} \qquad (A\text{-}6)$$

with $v$ and $w$ real.

First consider the limit $|z| \gg |q|^{1/2}$. Then (A-6) becomes $v + iw = \pm z$ whence, from $(A-4)$,

$$v = \lambda^2[-F_0' N_c/\pi + (k_B/2)\Delta k] \qquad (A\text{-}7)$$

$$w = -\lambda^2 F_0'' N_c/\pi \qquad (A\text{-}8)$$

where $F_0 = F_0' + iF_0''$, and $F_0''$ is related to the absorption coefficient $\mu$ by

$$\mu = 2\lambda F_0'' N_c. \qquad (A\text{-}9)$$

Then the numerator of [3.139] is readily evaluated. Throughout the five terms in the denominator, $q$ may be neglected; the third and fifth terms then vanish. The denominator then becomes

$$\begin{aligned} D &= |z|^2[1 + 2\sinh^2|aw| + \sinh|2aw|] \\ &= |z|^2 \exp|2aw| \\ &= (v^2 + w^2)\exp|2aw| \end{aligned}$$

and the power ratio [3.139] becomes (17) with the $F_0'$ correction for the static refractive index included.

Secondly, consider the limit in which $|aq^{1/2}| \ll 1$ and $|z| \lesssim |q|^{1/2}$ (*i.e.* $|z|$ is less than or of the same order of magnitude as $|q|^{1/2}$). Then

$$|az^2| \ll 1, \qquad |av| \ll 1, \qquad |aw| \ll 1.$$

Then it can be shown (the argument is simple in the subcase $|q + z^2| \sim |q|$ but very lengthy in the subcase $|q + z^2| \ll |q|$) that in the denominator of [3.139] the first term swamps each of the other four terms. Then the power ratio reduces to the value

$$Q_k T D \qquad (A\text{-}10)$$

to which (17) also reduces in this limit.

The condition for small reflected power is

$$A \ll 1 \quad \text{or} \quad A(\mu D)^{-1} \ll 1 \qquad (A\text{-}11)$$

where $A$ is given by (34). In the first case the scattered intensity is low because the crystal is thin; in the second case it is low because the absorption length ($\mu^{-1}$) is small.

In Zachariasen's notation (A-11) becomes

$$|aq^{1/2}| \ll 1 \quad \text{or} \quad |\Psi_H'/\Psi_0''| \ll 1. \qquad (A\text{-}12)$$

In the second of these cases, $|z| \gg |q|^{1/2}$ due to the large imaginary part of $z$. This case is therefore covered by the first of the limits already discussed in this Appendix.

In the first of the limits in (A-12) there are two subcases: first $|z| \gg |q|^{1/2}$ (*i.e.* $k$ far outside Ewald's region of perfect reflection) and, second, $|z| \lesssim |q|^{1/2}$. These subcases are covered respectively by the first and second limits already discussed in this Appendix, giving agreement with (17) under the respective conditions. Under conditions of small reflected power the profile has a width on the $z$ scale much greater than $|q|^{1/2}$, so that almost all the integrated intensity comes from values of $k$ to which the first limit applies.

It is worth noting that this paper eventually applies (17) to a non-thin crystal ($|aq^{1/2}| \gtrsim 1$). Then the profile sharpens and eventually becomes concentrated in the region $|z| \lesssim |q|^{1/2}$ where the first limit discussed above does not apply and the full conditions of the second limit are not met. This is why it becomes necessary to take into account the dynamic refractive index of the crystal.

## References


DARWIN, C. G. (1922). *Philos Mag.* **43**, 800-829.

GRADSHTEYN, I. S. & RYZHIK, I. M. (1980). *Table of Integrals, Series and Products.* New York: Academic Press.

HAMILTON, W. C. (1957). *Acta Cryst.* **10**, 629-634.

HIRSCH, P. B. & RAMACHANDRAN, G. N. (1950). *Acta Cryst.* **3**, 187-194.

MARSHALL, W. & LOVESEY, S. W. (1971). *Theory of Neutron Scattering.* Oxford: Clarendon Press.

SABINE, T. M. (1988). *Acta Cryst.* A**44**, 368-373.

SABINE, T. M. (1992). *International Tables for Crystallography*, Vol. C. Dordrecht: Kluwer. In the press.

SPEIGEL, M. R. (1968). *Mathematical Handbook of Formulas and Tables.* New York: McGraw-Hill.

WEINSTOCK, R. (1944). *Phys. Rev.* **65**, 1-20.

WILSON, A. J. C. (1949). *X-ray Optics.* London: Methuen.

ZACHARIASEN, W. H. (1945). *Theory of X-ray Diffraction in Crystals.* New York: John Wiley, Dover.

ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558-564.