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Bragg Reflection in Mosaic Crystals. I. General Solution of the Darwin Equations

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Abstract

The Darwin equations, which describe the multiple Bragg reflection of X-rays or neutrons in a mosaic crystal slab, have previously been solved only for special cases. Here, the complete and exact analytical solution of these equations is obtained for both the Bragg case (reflection geometry) and the Laue case (transmission geometry) with the help of a computer algebra program and it is shown that the resulting general expressions for both the reflectivity R and the transmissivity T can each be expressed in a compact form. It is found, for example, that for a mosaic crystal anomalous absorption occurs only in the Bragg case and not in the Laue case. This is in contrast to the dynamical theory of diffraction, which applies to an ideally perfect crystal, where anomalous absorption (due to the Borrmann effect) is found in both Laue and Bragg cases. With this new general expression for R, the Fankuchen gain is calculated for a crystal of finite thickness, taking correctly into account the effects of both absorption and secondary extinction. General expressions for the optimum crystal thickness are also obtained for both Bragg and Laue cases. In a companion paper, these general results are applied to a detailed numerical calculation of the reflecting properties of various neutron monochromator crystals.

1. Introduction

The Darwin equations (Darwin, 1922), which describe the multiple Bragg reflection of X-rays or neutrons in a mosaic crystal, are a coupled system of two linear homogeneous first-order differential equations with constant coefficients. If the crystal takes the form of a plane slab, these equations should be exactly solvable in terms of elementary functions. In fact, such a solution has previously been obtained only for special cases: *i.e.* for symmetrical reflections (Zachariasen, 1945), where the Bragg planes are either parallel or perpendicular to the surface, for a non-absorbing crystal (Sears, 1977) and for an infinitely thick crystal (Darwin, 1922).

That the general solution of the Darwin equations has not previously been obtained may be due to the algebraic complexities that arise. This is the kind of problem that is ideally suited to a computer algebra program. We have succeeded in obtaining the complete and exact analytical solution of these equations for both the Bragg case (reflection geometry) and the Laue case (transmission geometry) by using the program *Mathematica* (Wolfram, 1991) and the results are described in the present paper where we show that the resulting general formulas for both the reflectivity R and the transmissivity T can each be expressed in a compact form. Our general expressions for R reduce to those obtained by earlier authors for the special cases mentioned above.

The term 'anomalous absorption' refers to the change in the absorptivity of a crystal that occurs in the presence of a Bragg-reflected beam. We find that for a mosaic crystal such anomalous absorption occurs only in the Bragg case and not in the Laue case. This is in contrast to the dynamical theory of diffraction, which applies to an ideally perfect crystal, where the anomalous absorption is due to the Borrmann effect and occurs in both Laue and Bragg cases (Batterman & Cole, 1964; Sears, 1989).

The Fankuchen gain G is the ratio of the reflected flux when the Bragg planes make an angle α with the surface of the crystal to the flux when $\alpha = 0$. An oft-quoted result in the X-ray literature (Bozorth & Haworth, 1938) is that the maximum value of G is 2. However, this result is of quite limited validity. Firstly, it only includes the effect of absorption on the reflectivity and ignores the effect of secondary extinction, which is usually not negligible, especially for neutrons. Secondly, it is only valid for an infinitely thick crystal, which again is usually not a good approximation for neutrons. Using our new general expression for R, we can now calculate the Fankuchen gain for a crystal of finite thickness, taking correctly into account the effects of both absorption and secondary extinction. We then find that values of G larger than 2 are possible.

We also study the way in which the reflectivity behaves in the neighborhood of the Fankuchen position, *i.e.* the position where the transition from the Laue to the Bragg case occurs and the reflected beam is parallel to the surface of the crystal. We find that, for an absorbing crystal, there is a discontinuity in R at this position, but in a non-absorbing crystal there is only a cusp.

The question of optimum thickness is an important consideration in the design of monochromator crystals. In the Bragg case, this can be taken to be the thickness at which R reaches some specified fraction of its saturation value and, in the Laue case, it is the thickness at which R reaches its maximum value. We derive general expressions for the optimum thickness for both the Bragg and Laue cases.

There are four different ways in which a monoenergetic beam of neutrons can be reflected from a given set of Bragg planes. We show that these various ways are related by parity and time reversal, and calculate the way in which R and T transform under these symmetry operations.

The attenuation coefficient μ in the Darwin equations is the cross section per unit volume for all collision processes other than Bragg reflection. For neutrons, μ includes contributions not only from true absorption (*e.g.* radiative capture) but also from incoherent scattering and coherent inelastic scattering. At thermal-neutron wavelengths, the largest contribution to μ comes from coherent inelastic scattering in most materials at or above room temperature. Except in hydrogenous materials, the incoherent scattering term is usually very small and the absorption term is large only at long wavelengths in most materials. We derive a simple expression for the contribution to μ from coherent inelastic scattering that is based on the assumption that the motion of different atoms is statistically independent, while the distribution of vibrational frequencies is the same as in the actual crystal. With these assumptions, the coherent inelastic contribution to μ depends only on the root-mean-square displacement of an atom, which is the same parameter that determines the Debye–Waller factor.

In a companion paper (Sears, 1997, hereafter referred to as paper II), we apply the above-mentioned results to a detailed numerical calculation of the reflecting properties of various neutron monochromator crystals.

2. Darwin equations

The Darwin equations describe the Bragg reflection of X-rays or neutrons in a mosaic crystal. For simplicity, we shall formulate our discussion in terms of neutrons. Nevertheless, the results apply equally to X-rays, and we shall indicate where any minor differences in detail occur.

We consider a mosaic crystal in the form of a plane slab of thickness d and infinite lateral extent, and suppose that a collimated monoenergetic beam of neutrons is incident on this crystal such that Bragg's law is satisfied for only one set of reflection planes (hkl). Let $I(z)$ denote the incident-neutron current (neutrons s^{-1}) at a depth z inside the crystal and $I'(z)$ the corresponding reflected-neutron current. These quantities are then determined for $0 \le z \le d$ by the Darwin equations (Darwin, 1922):

$$\begin{aligned} [\mathrm{d}/\mathrm{d}z + (\alpha + \beta)]I(z) &= \beta' I'(z), \\ [\pm\mathrm{d}/\mathrm{d}z + (\alpha' + \beta')]I'(z) &= \beta I(z), \end{aligned} \tag{1}$$

where the plus sign is for the Laue case (transmission geometry) and the minus sign for the Bragg case (reflection geometry). These two cases are illustrated in Fig. 1, and the relations between the various angles in this figure are given in Appendix A1. The coefficients in (1) are given by

$$\begin{aligned} \alpha &= \mu/\sin\varphi, \quad & \beta &= \sigma/\sin\varphi, \\ \alpha' &= \mu/\sin\varphi', \quad & \beta' &= \sigma/\sin\varphi', \end{aligned} \tag{2}$$

in which φ is the angle that the incident beam makes with the surface of the crystal and φ' is the corresponding angle for the reflected beam. The quantity σ in (2) is called the Bragg reflection coefficient and μ the attenuation coefficient.

More precisely, σ is the cross section per unit volume for Bragg reflection. This quantity depends on both the incident-neutron wavelength λ and the Bragg angle θ and is different from zero only if λ and θ satisfy Bragg's law to within the range of values allowed by the mosaic spread in the crystal. In short,

$$\sigma = 0 \quad \text{unless} \quad \lambda \simeq \lambda_{\max} \sin\theta, \tag{3}$$

where $\lambda_{\max} = 4\pi/K_{hkl}$ and K_{hkl} denotes the magnitude of the reciprocal-lattice vector that corresponds to the Bragg planes (hkl).

The attenuation coefficient μ is the cross section per unit volume for all collision processes other than

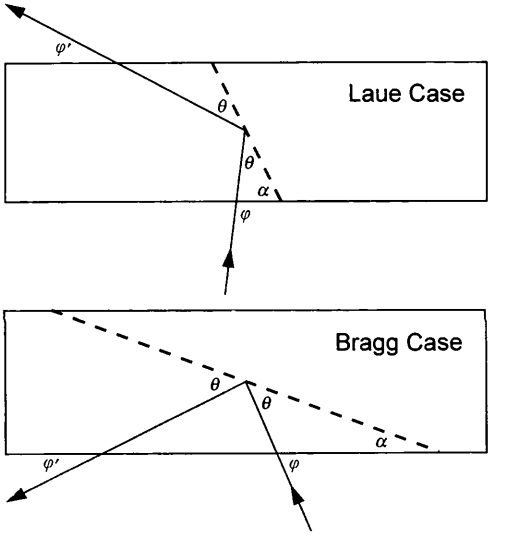

Fig. 1. Bragg reflection in a plane slab. Illustration of the Laue case (transmission geometry) and the Bragg case (reflection geometry). The dashed line represents a Bragg plane.

Bragg reflection. Thus, μ includes contribution not only from true absorption (*e.g.* radiative capture) but also from incoherent scattering and coherent inelastic scattering. For X-rays, the corresponding contributions to μ come from photoelectric absorption, Compton scattering and Rayleigh scattering. Explicit expressions for σ and μ for neutrons are given in Appendices *A*2 and *A*3. It will be noted that when Bragg's law is satisfied we usually have $\mu \ll \sigma$ for neutrons and $\mu \gg \sigma$ for X-rays.

The Darwin equations (1) describe multiple Bragg reflection within a mosaic crystal and can be derived either by simple heuristic considerations (Darwin, 1922) or, more rigorously, within the framework of neutron transport theory (Sears, 1977, 1989). In the derivation, it is assumed that multiple Bragg reflection within the individual mosaic blocks (and the associated primary extinction) can be neglected, so that only multiple Bragg reflection between different mosaic blocks (and the associated secondary extinction) need be taken into account. This requires that the linear dimensions of the mosaic blocks be small in comparison with the primary extinction length. In addition, it is assumed that σ and μ are constant throughout the crystal, which requires a homogeneous mosaic structure. These requirements are not always well satisfied for the small mosaic crystals that are used as samples in crystal structure determinations, and even less so for the large mosaic crystals that are used as monochromators. Nevertheless, they are convenient to ensure a mathematically tractable problem.

Before we can solve the differential equations (1), we must specify appropriate boundary conditions. If the incident-neutron current is normalized to unity then, for the Laue case, these conditions are

$$I(0) = 1, \quad I'(0) = 0, \tag{4}$$

and, for the Bragg case,

$$I(0) = 1, \quad I'(d) = 0. \tag{5}$$

Each neutron that is incident on the crystal is Bragg reflected, absorbed or transmitted. By 'absorption', we now mean all collision processes other than Bragg reflection, *i.e.* all processes that contribute to the attenuation coefficient μ. Then neutron conservation requires that

$$R + A + T = 1, \tag{6}$$

where R is the reflectivity, *i.e.* the fraction of incident neutrons that are Bragg reflected, A the absorptivity and T the transmissivity. For X-rays, the relation (6) expresses energy conservation. The reflectivity is given in the Laue case by

$$R = I'(d) \tag{7}$$

and in the Bragg case by

$$R = I'(0). \tag{8}$$

In both cases, the transmissivity is given by

$$T = I(d). \tag{9}$$

Thus, after we solve the Darwin equations (1) with the boundary conditions (4) and (5), the desired quantities R, A and T can be obtained from the preceding four relations.

Equations of the form (1) also occur in other areas. For example, Hamilton (1957) considered multiple Bragg reflection in a mosaic crystal of arbitrary size and shape, where the currents I and I' now depend on all three space coordinates (x, y, z), and showed that the currents obey a set of coupled equations that are formally the same as (1). These are now usually called the Hamilton–Darwin equations. Later, Takagi (1962, 1969) and Taupin (1964) considered, independently, the problem of dynamical diffraction in weakly deformed crystals, where the amplitudes of the Bloch waves vary only slightly over distances of the order of the lattice constant and showed that to a good approximation these amplitudes obey coupled equations that are formally identical to the Hamilton–Darwin equations except that the coefficients are now imaginary. Werner, Berliner & Arif (1986) have published a very elegant review of the Hamilton–Darwin and Takagi–Taupin equations in which they elucidate a number of formal properties of their solutions. They show, for example, that a general solution of the Hamilton–Darwin equations can be obtained as an infinite series of modified Bessel functions, while the corresponding solution of the Takagi–Taupin equations involves ordinary Bessel functions. Although this series solution also applies to the original Darwin equations (1), it is of less interest here because the exact solution of these latter equations can be obtained in closed form as we show in the next section.

3. Solution of the Darwin equations

The Darwin equations (1) are a coupled system of two linear homogeneous first-order differential equations with constant coefficients. As such, they should be exactly solvable in terms of elementary functions. That such a solution has previously been obtained only for special cases may be due to the algebraic complexities that arise. This is the kind of problem that is ideally suited to a computer algebra program and we have been able to obtain the complete and exact analytical solution of these equations for the neutron currents $I(z)$ and $I'(z)$ using the *DSolve* function in the program *Mathematica* (Wolfram, 1991).

Note, first of all, that it is evident from the form of the Darwin equations that the reflectivity, absorptivity and transmissivity are functions of three dimensionless variables:

$$\begin{aligned} R &= R(a, b, \zeta), \\ A &= A(a, b, \zeta), \\ T &= T(a, b, \zeta), \end{aligned} \tag{10}$$

in which

$$\begin{aligned} a &= \alpha d = \mu t, \\ b &= \beta d = \sigma t, \\ \zeta &= \sin\varphi / \sin\varphi' \end{aligned} \tag{11}$$

and $t = d/\sin\varphi$ is the thickness of the crystal in the direction of the incident beam. We find that the solution can be simplified by introducing the following auxiliary quantities:

$$\begin{aligned} p &= (a+b)(1+\zeta)/2, \quad r = (p^2 - \zeta b^2)^{1/2}, \\ q &= (a+b)(1-\zeta)/2, \quad s = (q^2 + \zeta b^2)^{1/2}. \end{aligned} \tag{12}$$

Then, for the Laue case, the general solution of the Darwin equations can be expressed as

$$\begin{aligned} I(z) &= \exp(-pz/d)[\cosh(sz/d) - (q/s)\sinh(sz/d)], \\ I'(z) &= \exp(-pz/d)(b/s)\sinh(sz/d), \end{aligned} \tag{13}$$

which then gives

$$\begin{aligned} R &= \exp(-p)(b/s)\sinh s, \\ T &= \exp(-p)[\cosh s - (q/s)\sinh s]. \end{aligned} \tag{14}$$

The corresponding solution for the Bragg case can be expressed as

$$\begin{aligned} I(z) &= \exp(-qz/d) \\ &\quad \times \left\{ \frac{r\cosh[r(1-z/d)] + p\sinh[r(1-z/d)]}{r\cosh r + p\sinh r} \right\}, \\ I'(z) &= \exp(-qz/d)\left\{ \frac{b\sinh[r(1-z/d)]}{r\cosh r + p\sinh r} \right\}, \end{aligned} \tag{15}$$

and this gives

$$\begin{aligned} R &= b/(r\coth r + p), \\ T &= r\exp(-q)/(r\cosh r + p\sinh r). \end{aligned} \tag{16}$$

In the Laue case, Darwin (1922) obtained an expression for R that is equivalent to (14). However, in the Bragg case, he only solved equations (1) for an infinitely thick crystal (see §5.2). Thus, the general expression (16) for R is a new result, as are also both the above expressions for T.

It is, of course, not necessary to use a computer to solve the Darwin equations (1). The solution can easily be obtained manually by the substitution method found in elementary text books. However, until one realizes that the parameters (12) are the natural quantities in terms of which to express the solution, one tends to get bogged down in the algebra, particularly in the Bragg case. This realization comes immediately when one inspects the solution generated by *Mathematica*, and this is the real advantage in using it. This may also explain why the general solution was not obtained by earlier authors who worked on this problem.

It will be noted in passing that the general solutions of both the Hamilton–Darwin equations and the Takagi–Taupin equations also contain exponential factors similar to those in (13) and (15) above (Werner, Berliner & Arif, 1986). For the Takagi–Taupin equations, these factors are, of course, complex exponentials.

Figs. 2–5 illustrate the way in which the reflectivity R varies with b for representative values of a and ζ for both the Laue and Bragg cases. We see that R is always a monotonically increasing function of b and a monotonically decreasing function of a and ζ. Note also that the reflectivity begins to saturate at much smaller values of b in the Laue case than in the Bragg case.

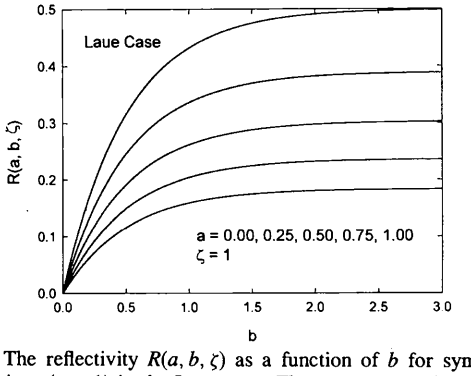

Fig. 2. The reflectivity $R(a, b, \zeta)$ as a function of b for symmetric reflections ($\zeta = 1$) in the Laue case. The curves are calculated for $a = 0.00$, 0.25, 0.50, 0.75 and 1.00 (reading from top to bottom).

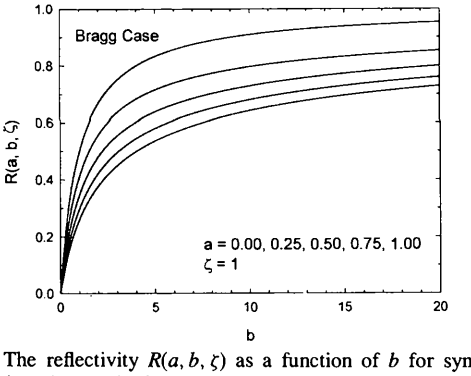

Fig. 3. The reflectivity $R(a, b, \zeta)$ as a function of b for symmetric reflections ($\zeta = 1$) in the Bragg case. The curves are calculated for $a = 0.00$, 0.25, 0.50, 0.75 and 1.00 (reading from top to bottom).

4. Special cases

We now demonstrate that the general results (14) and (16) reduce to those obtained by earlier authors in a number of special cases.

4.1. *Zero Bragg reflection*

Suppose we are well away from the Bragg position (3) so that $\sigma = 0$ and, hence, $b = 0$. We then find for both the Laue and Bragg cases that

$$\begin{aligned} R &= 0, \\ T &= \exp(-a), \\ A &= 1 - \exp(-a). \end{aligned} \tag{17}$$

Here, there is no Bragg-reflected beam and the incident beam is simply attenuated exponentially inside the crystal. In particular, for normal incidence ($\varphi = \pi/2$), we get

$$T = \exp(-\mu d), \tag{18}$$

which is the familiar Lambert law (Sears, 1989).

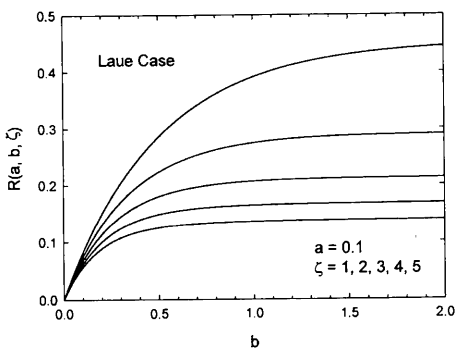

Fig. 4. The reflectivity $R(a, b, \zeta)$ as a function of b for $a = 0.1$ in the Laue case. The curves are calculated for $\zeta = 1$, 2, 3, 4 and 5 (reading from top to bottom).

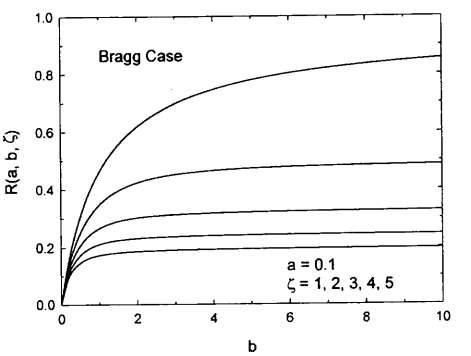

Fig. 5. The reflectivity $R(a, b, \zeta)$ as a function of b for $a = 0.1$ in the Bragg case. The curves are calculated for $\zeta = 1$, 2, 3, 4 and 5 (reading from top to bottom).

4.2. *Zero absorption*

Suppose, on the other hand, that $\mu = 0$ and, hence, $a = 0$. We then find, in agreement with Sears (1977, 1989), that, for the Laue case,

$$\begin{aligned} R &= \frac{1 - \exp[-b(1+\zeta)]}{1+\zeta}, \\ T &= \frac{\zeta + \exp[-b(1+\zeta)]}{1+\zeta} \end{aligned} \tag{19}$$

and, for the Bragg case,

$$\begin{aligned} R &= 2/\{(\zeta+1) + (\zeta-1)\coth[b(\zeta-1)/2]\}, \\ T &= (1-\zeta)/\{\exp[b(1-\zeta)] - \zeta\}. \end{aligned} \tag{20}$$

In both cases, $R + T = 1$ and $A = 0$ as it should.

4.3. *Symmetric reflection*

We now consider the case of a symmetric reflection where $\varphi' = \varphi$ and $\zeta = 1$. In the Laue case, this means that the Bragg planes are perpendicular to the surface of the crystal and, in the Bragg case, they are parallel to the surface.

For the Laue case, we then get

$$\begin{aligned} R &= \tfrac{1}{2}\exp(-a)[1 - \exp(-2b)], \\ T &= \tfrac{1}{2}\exp(-a)[1 + \exp(-2b)]. \end{aligned} \tag{21}$$

Note that $R + T = \exp(-a)$ and, hence, that $A = 1 - \exp(-a)$. This expression for A is the same as when there is no Bragg reflection (see §4.1). In other words, the presence of the Bragg-reflected beam does not affect the absorptivity in the Laue case.

For the Bragg case, we find that

$$\begin{aligned} R &= b/\{[a(a+2b)]^{1/2}\coth[a(a+2b)]^{1/2} + (a+b)\}, \\ T &= [a(a+2b)]^{1/2}/\{[a(a+2b)]^{1/2}\cosh[a(a+2b)]^{1/2} \\ &\quad + (a+b)\sinh[a(a+2b)]^{1/2}\}. \end{aligned} \tag{22}$$

In this case, $R + T \neq \exp(-a)$ and $A \neq 1 - \exp(-a)$. In other words, the presence of the Bragg-reflected beam changes the absorptivity of the crystal. This type of phenomenon is generally called 'anomalous absorption'.

In the dynamical theory of diffraction, which applies to an ideally perfect crystal, the anomalous absorption is due to the Borrmann effect, *i.e.* to the fact that under Bragg-reflecting conditions one component of the wave function has nodes at the atomic positions and, hence, is not attenuated by absorption (Batterman & Cole, 1964; Sears, 1989). In this case, one finds anomalous absorption in both Laue and Bragg cases. For a mosaic crystal, on the other hand, the anomalous absorption has nothing to do with the Borrmann effect. Its origin lies in the nature of the Darwin equations and it occurs only in the Bragg case as we have just seen.

Expressions for R equivalent to (21) and (22) were obtained by Zachariasen (1945) from a direct solution of the Darwin equations for symmetric reflections. The result for the Bragg case can be expressed alternatively as

$$R=\sigma/\{[\mu(\mu+2\sigma)]^{1/2}\coth\{t[\mu(\mu+2\sigma)]^{1/2}\}+(\mu+\sigma)\}. \tag{23}$$

Bacon & Lowde (1948) have asserted that the reflectivity for asymmetric reflections can be obtained simply by replacing μ by $\mu(1+\zeta)/2$ in (23). However, this prescription does not agree with our general result (16).

4.4. *Zero absorption and symmetric reflection*

Finally, we consider the case of a symmetric reflection with zero absorption. We then find, this time in agreement with Bacon & Lowde (1948), that, in the Laue case,

$$\begin{aligned} R&=\tfrac{1}{2}[1-\exp(-2b)],\\ T&=\tfrac{1}{2}[1+\exp(-2b)], \end{aligned} \tag{24}$$

and, in the Bragg case,

$$\begin{aligned} R&=b/(1+b),\\ T&=1/(1+b). \end{aligned} \tag{25}$$

In both cases, $R+T=1$ and $A=0$ as it should.

5. Limiting cases

In this section, we consider some limiting cases of the general expressions (14) and (16) and show that some of them also reduce to results obtained by earlier authors.

5.1. *Thin crystal*

We begin by considering the thin-crystal limit. Thus, we assume that $d\to 0$ in the sense that $a\ll 1$ and $b\ll 1$. We then find for both Laue and Bragg cases that, to first order in a and b,

$$\begin{aligned} R&=b,\\ T&=1-(a+b) \end{aligned} \tag{26}$$

and, hence, that

$$A=a. \tag{27}$$

Thus, the dimensionless variables a and b have a simple physical interpretation: a is the absorptivity in the thin-crystal limit and b is the corresponding reflectivity. Expression (26) for the reflectivity is the same as is found in the kinematical theory of diffraction (Sears, 1989). This is as it should be since the kinematical theory is valid only in the thin-crystal limit.

5.2. *Thick crystal*

Next, we consider the thick-crystal limit. In particular, we assume that $d\to\infty$ with $a>0$. We then find that, as we would expect, $T=0$ for both Laue and Bragg cases and, in addition, $R=0$ for the Laue case. For the Bragg case, we find, in agreement with Darwin (1922), that

$$R=2\gamma/\{(1+\gamma)(1+\zeta)+[(1+\gamma)^2(1+\zeta)^2-4\zeta\gamma^2]^{1/2}\}, \tag{28}$$

where $\gamma\equiv b/a=\sigma/\mu$. If $\gamma\ll 1$, which is usually true for X-rays, this expression reduces to $R=\gamma/(1+\zeta)$. If $\gamma\gg 1$, which is roughly the case for neutrons, it reduces to $R=1$.

5.3. *Fankuchen limit*

The Fankuchen limit, or Laue–Bragg transition as it is sometimes called, occurs when the Bragg angle θ equals the angle α that the Bragg planes make with the surface of the crystal (see Fig. 1 and Appendix A1). We then have the Laue case when $\theta<\alpha$ and the Bragg case when $\theta>\alpha$. When $\theta=\alpha$ exactly, the Bragg-reflected beam is parallel to the surface of the crystal and $\varphi'=0$. Hence, the quantity $\zeta\to\infty$ in the Fankuchen limit.

For the Laue case, it follows from (14) that

$$\lim_{\zeta\to\infty}\zeta R=[b/(a+b)]\exp\{-a[(a+2b)/(a+b)]\} \tag{29}$$

and, for the Bragg case, (16) gives

$$\lim_{\zeta\to\infty}\zeta R=b/(a+b). \tag{30}$$

In the case of zero absorption, where $a=0$, we see that (29) and (30) each reduce to

$$\lim_{\zeta\to\infty}\zeta R=1. \tag{31}$$

These results imply that, for an absorbing crystal, ζR has a discontinuity at the Laue–Bragg transition but, for a non-absorbing crystal, ζR has only a cusp at this point.

When the Bragg-reflected beam is almost parallel to the surface of the crystal (*i.e.* when φ' is of the order of a few minutes of arc, say), it is clear physically that the beam should be partially reflected and refracted at the surface. This effect is not allowed for in the Darwin equations where the neutrons are treated as classical particles as far as the multiple-scattering part of the problem is concerned (Sears, 1977, 1989). If necessary, the effect of specular reflection could, of course, be taken into account in an *ad hoc* way. In contrast, the effect of specular reflection and refraction at the surface can be taken into account in a rigorous and very natural way within the dynamical theory of diffraction because this is a wave theory at the outset (Kaganer, Indenbom, Vrána & Chalupa, 1982; Eichhorn, Kulda & Mikula, 1983).

6. Fankuchen gain

Let R denote the reflectivity in the Bragg case when the Bragg planes are at an angle to the surface of the crystal such that $\zeta > 1$ and let R_s be the corresponding reflectivity for a symmetric reflection where the Bragg planes are parallel to the surface and $\zeta = 1$. In paper II, it is shown that the reflected-neutron flux (neutrons cm^{-2}) is proportional to ζR. Hence, the reflected-flux ratio is given by the expression

$$G = \zeta R/R_s. \tag{32}$$

This ratio is then the gain in reflected flux that is obtained when the Bragg planes are at an angle to the surface and will be called the Fankuchen gain.

6.1. *Early work*

In his original paper, Fankuchen (1937) tacitly assumed that $R \simeq R_s$ and, hence, that $G \simeq \zeta$. As a result, he expected that a large gain in reflected flux would be obtained when $\zeta \gg 1$. However, if $\zeta \gg 1$, then the path length of the reflected beam inside the crystal is also large and the reflected beam is strongly attenuated by absorption and secondary extinction with the result that the value of R is reduced. In fact, it is clear from §5.3 that $\zeta R \leq 1$ in the limit $\zeta \to \infty$ and, hence, that $R \to 0$ in this limit while G remains finite.

It was later shown by Bozorth & Haworth (1938) that, when the effect of absorption is taken into account,

$$G = 2\zeta/(1 + \zeta) = 2 \sin\varphi/(\sin\varphi' + \sin\varphi) \tag{33}$$

and, hence, that the maximum value of G is 2. It is important to recognize that this oft-quoted expression is of quite limited validity. Firstly, it only includes the effect of absorption on the reflectivity and ignores the effect of secondary extinction, which is usually not negligible for neutrons. Secondly, it is only valid for an infinitely thick crystal, which again is usually not a good approximation for neutrons.

To overcome these limitations, one must calculate G using the general expression (16) for the reflectivity in the Bragg case. Extensive numerical calculations of this kind for crystals of arbitrary thickness are reported in paper II. In the meantime, we confine our attention to the two limiting cases that are discussed below.

6.2. *Thin crystal*

In the thin-crystal limit, where absorption and secondary extinction are both negligible, the reflectivity is given by (26), and (32) for the Fankuchen gain reduces to

$$G = \sin\theta/\sin\varphi' \tag{34}$$

so that $G \to \infty$ as $\varphi' \to 0$. While the gain can be arbitrarily large in this case, the reflected-neutron flux is also vanishingly small.

6.3. *Thick crystal*

When the thick-crystal limit is applicable, we can use (28) for R in which absorption and secondary extinction are both taken properly into account. In this case,

$$R_s = \gamma/[1 + \gamma + (1 + 2\gamma)^{1/2}] \tag{35}$$

and

$$G = 2\zeta[1 + \gamma + (1 + 2\gamma)^{1/2}]\{(1 + \gamma)(1 + \zeta) + [(1 + \gamma)^2(1 + \zeta)^2 - 4\zeta\gamma^2]^{1/2}\}^{-1}. \tag{36}$$

Expression (36) is illustrated in Fig. 6, which shows G as a function of ζ for $\gamma = 0, 1, 2, 3$ and 4 (reading from top to bottom). The parameter $\gamma = b/a$ and characterizes the relative importance of secondary extinction and absorption on G. In particular, when $\gamma \ll 1$, secondary extinction is negligible in comparison with absorption and (36) reduces to (33) as it should. The maximum value of G is 2 and this occurs when $\gamma \to 0$ and $\zeta \to \infty$.

In the limit of zero absorption, where $a \to 0$ and $\gamma \to \infty$, (36) reduces to

$$G = \begin{cases} 1, & \zeta \geq 1 \\ \zeta, & \zeta < 1. \end{cases} \tag{37}$$

Thus, for a non-absorbing thick crystal, there is no gain at all in using a Fankuchen geometry.

7. Optimum crystal thickness

The question of optimum thickness is an important consideration in the design of neutron monochromator crystals. In this section, we discuss this question on the basis of the exact solution of the Darwin equations that we presented in §3. The notion of optimum crystal thickness is very different in the Bragg case from what it is in the Laue case, so it is necessary to discuss these two cases separately.

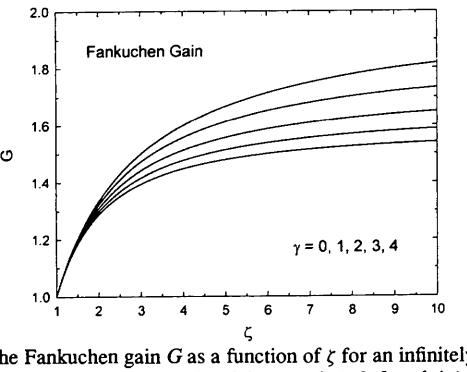

Fig. 6. The Fankuchen gain G as a function of ζ for an infinitely thick crystal. The curves are calculated for $\gamma = 0, 1, 2, 3$ and 4 (reading from top to bottom), where $\gamma = b/a$.

7.1. *Laue case*

It is evident from §5 that, if the crystal thickness $d \to 0$, then the reflectivity $R \to 0$ linearly with d. Also, in the Laue case, if $d \to \infty$ with $a > 0$ then $R \to 0$ again. Since R is a non-negative quantity, there must therefore be some intermediate thickness at which the reflectivity is a maximum. This can then be regarded as the optimum thickness for the particular reflection under consideration.

To calculate the optimum thickness, we begin by putting

$$\begin{aligned} p &= p_0 t, \quad r = r_0 t, \\ q &= q_0 t, \quad s = s_0 t, \end{aligned} \tag{38}$$

where $t = d/\sin\varphi$ as before and

$$\begin{aligned} p_0 &= (\mu+\sigma)(1+\zeta)/2, \quad r_0 = (p_0^2 - \zeta\sigma^2)^{1/2}, \\ q_0 &= (\mu+\sigma)(1-\zeta)/2, \quad s_0 = (q_0^2 + \zeta\sigma^2)^{1/2}. \end{aligned} \tag{39}$$

It then follows from (14) that the optimum thickness is given by

$$d_{\text{opt}} = [(\sin\varphi)/s_0]\coth^{-1}[p_0/s_0]. \tag{40}$$

7.2. *Bragg case*

According to (16), R is a monotonically increasing function of d in the Bragg case and approaches a saturation value R_∞, given by (28), as $d \to \infty$. In this case, the optimum value of d is not uniquely defined and will simply be taken to be the thickness at which $R = xR_\infty$, where x has some arbitrarily specified value ($x = 0.8$, say). We then find that

$$d_{\text{opt}} = [(\sin\varphi)/r_0]\coth^{-1}\{[r_0 + (1-x)p_0]/xr_0\}. \tag{41}$$

Note that $R \ll R_\infty$ if $d \ll d_{\text{opt}}$ but there is only a marginal increase in reflectivity if $d \gg d_{\text{opt}}$. In the latter case, the fast-neutron background and the order contamination will both continue to increase more or less linearly with d. Expression (41) therefore represents the optimum thickness in the sense that, roughly speaking, it gives a large reflectivity while keeping the fast-neutron background and the order contamination as small as possible.

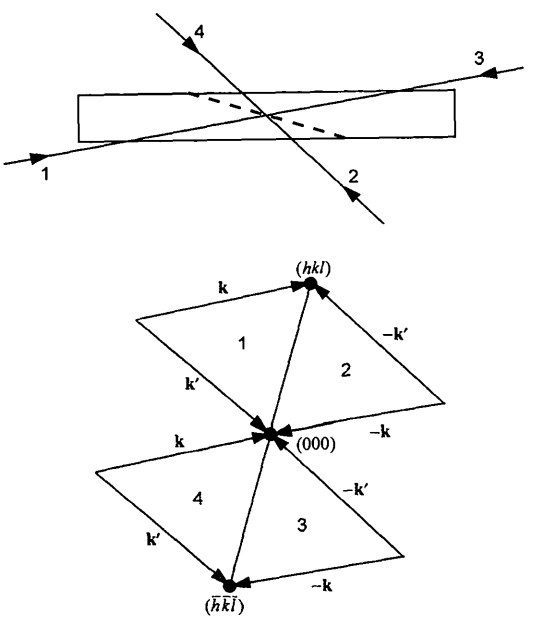

Fig. 7. Parity and time reversal in asymmetric Bragg reflections. The upper figure shows the incident-beam directions in **r** space, and the lower figure shows the corresponding wave-vector relationships in **k** space.

Table 1. *Transformation of quantities under parity ($\mathscr{P}$) and time reversal ($\mathscr{T}$)*

Quantity	$\mathscr{P}$	$\mathscr{T}$
$\mathbf{k}$	$-\mathbf{k}$	$-\mathbf{k}'$
$\mathbf{k}'$	$-\mathbf{k}'$	$-\mathbf{k}$
$\mathbf{K}_{hkl}$	$-\mathbf{K}_{hkl} = \mathbf{K}_{\bar{h}\bar{k}\bar{l}}$	$\mathbf{K}_{hkl}$
(hkl)	$(\bar{h}\bar{k}\bar{l})$	(hkl)
F_{hkl}	$F_{\bar{h}\bar{k}\bar{l}} = F_{hkl}^*$	F_{hkl}
φ	φ	φ'
φ'	φ'	φ
ζ	ζ	$1/\zeta$
t	t	ζt
μ	μ	μ
σ	σ	σ
a	a	ζa
b	b	ζb
R	R	ζR
T	T	See text

8. Parity and time reversal

As illustrated in Fig. 7, there are four different ways in which a monoenergetic beam of neutrons can be reflected from a given set of Bragg planes. In this final section, we show that these various ways are related by parity and time reversal and we calculate the way in which the reflectivity transforms under these symmetry operations.

We begin by noting that the condition for Bragg reflection is (Sears, 1989)

$$\mathbf{k} - \mathbf{k}' = \mathbf{K}_{hkl}, \tag{42}$$

where $\mathbf{k}$ and $\mathbf{k}'$ are the incident and reflected neutron wave vectors and $\mathbf{K}_{hkl}$ is the reciprocal-lattice vector corresponding to the particular Bragg planes (hkl) under consideration. Under the parity operation $\mathscr{P}$ (*i.e.* inversion in the origin),

$$\mathbf{k} \to -\mathbf{k}, \quad \mathbf{k}' \to -\mathbf{k}', \tag{43}$$

and under time reversal $\mathscr{T}$,

$$\mathbf{k} \to -\mathbf{k}', \quad \mathbf{k}' \to -\mathbf{k}. \tag{44}$$

These and other related transformation rules are summarized in Table 1.

With reference to Fig. 7, note that the incident wave vector always points to the reciprocal-lattice site and the reflected wave vector always points to the origin. Note also that under parity $1 \leftrightarrow 3$ and $2 \leftrightarrow 4$, and under time reversal $1 \leftrightarrow 2$ and $3 \leftrightarrow 4$.

The transformation of the unit-cell structure factor F_{hkl} under parity in Table 1 is, of course, just the neutron analog of Friedel's law (Friedel, 1913) and is valid if the bound coherent scattering lengths b_c in (54) are all real. Except for a few nuclides (such as ^{113}Cd) with absorption resonances at thermal-neutron energies, this is an excellent approximation. The fact that μ and σ are both invariant under parity and time reversal can be deduced from the expressions for these quantities that are given in Appendices *A*2 and *A*3.

The way in which the reflectivity R and transmissivity T transform under parity and time reversal can be obtained from the general solution of the Darwin equations given by (14) and (16). Thus, we find that for both the Bragg and Laue cases R and T are invariant under parity, while, under time reversal,

$$R(a, b, \zeta) \rightarrow R(\zeta a, \zeta b, \zeta^{-1}) = \zeta R(a, b, \zeta). \tag{45}$$

This result was originally obtained by Darwin (1922) from the way in which the thick-crystal expression (28) transforms when the source and the detector are interchanged. However, he apparently didn't realize that it was true quite generally, nor did he attribute it to time-reversal symmetry. Indeed, the concept of time reversal was not introduced until ten years later by Wigner (1932).

The transformation of the transmissivity under time reversal is more complicated. In the Bragg case, we find that

$$T \rightarrow \exp(2q)T \tag{46}$$

but there is no similar simple rule in the Laue case.

An important practical application of these results, which we make extensive use of in paper II, is that the reflectivity need only be calculated for compression geometry (see Appendix *A*1). The corresponding values for expansion geometry can then be obtained simply by using the time reversal symmetry (45).

APPENDIX *A*

The theoretical results presented in the body of the paper are of a rather formal nature. In this Appendix, we give the additional relations that are needed in order to apply the theory to actual numerical calculations of the reflectivity of specified crystals such as are given in paper II.

*A*1. Angular relations

As illustrated in Fig. 1, we let φ denote the angle that the incident beam makes with the surface of the crystal and φ' the corresponding angle for the reflected beam. The Fankuchen factor $\zeta = \sin\varphi/\sin\varphi'$ is then the ratio of the area of the incident beam to that of the reflected beam. We can now distinguish three kinds of reflection geometry:

$$\begin{aligned} &\text{compression geometry:} && \varphi' < \varphi, && \zeta > 1, \\ &\text{symmetric geometry:} && \varphi' = \varphi, && \zeta = 1, \\ &\text{expansion geometry:} && \varphi' > \varphi, && \zeta < 1. \end{aligned} \tag{47}$$

Let θ denote the Bragg angle ($0 < \theta < \pi/2$) and α the angle that the Bragg planes make with the surface of the crystal ($0 \leq \alpha \leq \pi/2$). If $[uvw]$ is the direction of the inward normal to the surface, then α is also equal to the angle between $[uvw]$ and the reciprocal-lattice vector $\mathbf{K}_{hkl}$ corresponding to the reflection planes (hkl). Thus, for example, for a cubic crystal,

$$\alpha = \cos^{-1}\{(hu + kv + lw)/[(h^2 + k^2 + l^2) \times (u^2 + v^2 + w^2)]^{1/2}\}. \tag{48}$$

For compression geometry,

$$\varphi = \alpha + \theta, \quad \varphi' = |\alpha - \theta|. \tag{49}$$

There are then three special cases:

$$\begin{aligned} &\text{Laue case:} && 0 < \theta < \alpha < \pi/2, \\ &\text{Fankuchen limit:} && 0 < \theta = \alpha < \pi/2, \\ &\text{Bragg case:} && 0 < \alpha < \theta < \pi/2. \end{aligned} \tag{50}$$

In the Laue case, the reflected beam is on the opposite side of the crystal to the incident beam (transmission geometry), and in the Bragg case the reflected beam is on the same side of the crystal as the incident beam (reflection geometry). In the Fankuchen limit, where $\varphi' \rightarrow 0$, the reflected beam is parallel to the surface and $\zeta \rightarrow \infty$. For expansion geometry, expressions (49) for φ and φ' are interchanged while (50) remains the same. For symmetric geometry, there are two cases:

$$\begin{aligned} &\text{symmetric Laue case:} && 0 < \theta < \alpha = \pi/2, \\ &\text{symmetric Bragg case:} && 0 = \alpha < \theta < \pi/2. \end{aligned} \tag{51}$$

In the symmetric Laue case, the Bragg planes are therefore perpendicular to the surface of the crystal and in the symmetric Bragg case they are parallel to the surface.

*A*2. Bragg reflection coefficient

The Bragg reflection coefficient σ is the cross section per unit volume for Bragg scattering and is the product of two factors (Sears, 1989):

$$\sigma = QW(\theta' - \theta). \tag{52}$$

The first factor is determined by the crystal structure and is given by the expression

$$Q = \lambda^3 |F_{hkl}|^2 / V_0^2 \sin 2\theta, \quad (53)$$

in which θ is the nominal Bragg angle corresponding to the neutron wavelength λ, V_0 is the volume of a unit cell and F_{hkl} is the unit-cell structure factor,

$$F_{hkl} = \sum b_c \exp(-W_{hkl}) \exp[2\pi i(hx + ky + lz)]. \quad (54)$$

Here, (x, y, z) denotes the position of an atom in the unit cell, b_c is its bound coherent scattering length, $\exp(-W_{hkl})$ is its Debye–Waller factor and the sum runs over all such atoms. The Debye–Waller exponent is given by $W_{hkl} = (K_{hkl} u_0)^2/2$, where K_{hkl} is the magnitude of the reciprocal-lattice vector, as before, and u_0 is the root-mean-square displacement of the atom perpendicular to the Bragg planes.

The second factor in (52) is the normalized rocking curve.

$$\int W(\theta' - \theta)\, d\theta' = 1, \quad (55)$$

in which θ' is the actual angle that the incident beam makes with the Bragg planes. The function $W(\theta' - \theta)$ is sharply peaked at $\theta' = \theta$ and its detailed shape is characteristic of the mosaic structure of the crystal. In particular, $W(\theta' - \theta)$ depends on the sizes and shapes of the individual mosaic blocks and on their degree of misorientation. This function is usually characterized by the parameter (Darwin, 1922)

$$g = \int W(\theta' - \theta)^2\, d\theta'. \quad (56)$$

The full width at half-maximum (FWHM) of $W(\theta' - \theta)$, which is often called the mosaic spread, is of the order of $1/g$. The function $W(\theta' - \theta)$ is sample dependent and often has a quite irregular shape (Schneider, 1974) that is nothing like the Gaussian model that is commonly assumed. In practice, it is, therefore, no less realistic to use the even simpler model

$$W(\theta' - \theta) = \begin{cases} g, & |\theta' - \theta| \le 1/(2g) \\ 0, & |\theta' - \theta| > 1/(2g). \end{cases} \quad (57)$$

In this case, the FWHM is exactly equal to $1/g$. This model is used in the calculations that are reported in paper II.

Finally, it will be noted that the X-ray expression for σ has the same form as (52) and is originally due to Bragg, James & Bosanquet (1921*a*,*b*). The main difference is that the quantity b_c in (54) is replaced by the corresponding X-ray scattering amplitude.

*A*3. Attenuation coefficient

The attenuation coefficient μ is the cross section per unit volume for all collision processes other than Bragg reflection. For neutrons, this quantity is given approximately by

$$\mu = (1/V_0) \sum [\sigma_c f(x) + \sigma_i + \sigma_a], \quad (58)$$

in which σ_c is the bound coherent scattering cross section of an atom in the unit cell, σ_i is the bound incoherent scattering cross section and σ_a is the absorption cross section. For most elements, the cross sections σ_c and σ_i are constant while σ_a is directly proportional to λ and, hence, to $\sin\theta$. The first term in (58) represents the contribution from coherent inelastic scattering and is based here on an Einstein-like model for the lattice vibrations for which we find

$$f(x) = 1 - \{[1 - \exp(-x)]/x\}, \quad (59)$$

in which

$$x = (4\pi u_0/\lambda)^2 = 2W_{hkl}/\sin^2\theta. \quad (60)$$

In deriving (59), we have assumed that the motion of different atoms is statistically independent but that the distribution of vibrational frequencies is the same as in the actual crystal. With these assumptions, the coherent inelastic scattering term depends only on the root-mean-square displacement of an atom u_0, which is the same parameter as determines the Debye–Waller factor.

The best current values for the cross sections in (58) have been tabulated by Sears (1992*a*,*b*). At thermal-neutron wavelengths, the largest contribution to μ comes from coherent inelastic scattering in most materials at or above room temperature. Except in hydrogenous materials, the incoherent scattering term is usually very small and the absorption term is usually large only at long wavelengths. We emphasize these points because *International Tables for Crystallography* only mention the contribution to μ from absorption (Willis, 1992).

Note added in proof: We have recently learned that expressions for R equivalent to (14) and (16) have also been obtained by H. C. Hu (unpublished).

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