

A Simplification of Prins' Formula for Diffraction of X-Rays by a Perfect Crystal

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The intensity formula of Prins for diffraction of x-rays by a perfect crystal has been simplified so that $F(l)$ is a real, single-valued, algebraic function of l , the deviation of the glancing angle from the corrected Bragg angle. By neglecting absorption in the crystal, Darwin's formula is obtained in a new form. By differentiation the maximum ordinate of the diffraction pattern is obtained. To calculate percent reflection (i.e., maximum ordinate of the rocking curve of a double crystal spectrometer in the 1, -1 posi-

tion) $\int_{-\infty}^{+\infty} F(l)dl$ and $\int_{-\infty}^{+\infty} F^2(l)dl$ are needed, and these integrals have been evaluated analytically for Darwin's case of no absorption, leading to a value of 4/5 for $P(0)$. To include absorption $F(l)$ has been expanded into a series in powers of B/D and an approximate formula obtained for $P(0)$ in terms of the constants of the crystal. This formula agrees with the graphically determined values of $P(0)$ to within a few percent.

INTRODUCTION

THE shape of the x-ray diffraction of a crystal is of some interest, since a knowledge of the variation of reflected intensity with glancing angle is an essential part of the theory of the x-ray spectrometer. Unfortunately, as shown by v. Laue,¹ the shape of the diffraction pattern cannot be observed directly with the double crystal spectrometer. The method of Smith² for calibrating a double-crystal spectrometer cannot be applied to calculation of the diffraction pattern, although it gives³ the true shape of a spectrum line regardless of the diffraction pattern assumed. The method of checking any theoretical curve remains, therefore, to make observations upon related quantities such as half-width, percent reflection, etc., which can be calculated from the theory assumed, and hence obtain indirect evidence for or against the theory proposed.

In this manner Allison⁴ and Parratt⁵ have investigated the applicability of the Darwin-Ewald-Prins⁶ theory of x-ray reflection from a perfect crystal and have observed specimens of calcite approaching "perfection" in the sense that the predictions of the theory are fulfilled over certain wavelength ranges.

In order to carry through the analysis for any crystal, a great deal of laborious calculation must be done and many graphical integrations performed. It is the purpose of this paper to give a simplification of the algebraic form of Prins' formula, so that the labor of computation is greatly reduced, and to apply approximate methods to some of the integrals involved in order to obtain an approximate formula for percent reflection in terms of the constants of the crystal.

SIMPLIFICATION OF PRINS' FORMULA

Using the notation of Parratt,⁵ replacing his symbol A by the symbol D , we have for Prins' characteristic function

$$F(l) = I_l/I_0 = \left| \frac{(D+iB)/\delta}{l-i\beta/\delta \pm \{(l-i\beta/\delta)^2 - [(D+iB)/\delta]^2\}^{1/2}} \right|^2, \quad (1)$$

where l is the only variable and is the deviation of the glancing angle from the corrected Bragg angle ($\theta = \theta_0 + \delta \sec \theta_0 \csc \theta_0$) in units of $\delta \sec \theta_0 \csc \theta_0$. $F(l)$ is the ratio of intensity diffracted at an angular deviation l to the incident intensity. The constants of the crystal have been discussed in several places,^{5, 7} and we will only note that B and β are related to μ_l so that for no absorption both are equal to zero. The constants may be calculated for any crystal; for $\lambda 2.299\text{\AA}$ on calcite in the first order $\beta/\delta = 0.059$ and

¹ M. von Laue, *Zeits. f. Physik* **72**, 472 (1931).

² L. P. Smith, *Phys. Rev.* **46**, 343 (1934); L. P. Smith, paper at Pittsburgh meeting of the American Physical Society, 1934.

³ L. G. Parratt, *Phys. Rev.* **46**, 749 (1934).

⁴ S. K. Allison, *Phys. Rev.* **41**, 1 (1932).

⁵ L. G. Parratt, *Phys. Rev.* **41**, 561 (1932).

⁶ C. G. Darwin, *Phil. Mag.* **27**, 325 and 675 (1914); P. P. Ewald, *Ann. d. Physik* **54**, 519 (1917); P. P. Ewald, *Phys. Zeits.* **26**, 29 (1925); J. A. Prins, *Zeits. f. Physik* **63**, 477 (1930).

⁷ A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment*, D. Van Nostrand and Co., 1935, page 375. ($F(l)$ is there given the notation $I'(l)$.)

$B/D=0.084$, and are less for shorter wavelengths.⁸

In Eq. (1) the square of the absolute value of the complex quantity must be formed, and the ambiguity of sign is to be resolved so that $F(l) \leq 1$. Upon multiplying the two values of $F(l)$ together, we see that

$$F_1(l)F_2(l) \equiv 1, \quad (2)$$

a result to be used later. We may write Eq. (1) as

$$F(l) = \left| \frac{l - i\beta/\delta \mp \{(l - i\beta/\delta)^2 - [(D + iB)/\delta]^2\}^{1/2}}{(D + iB)/\delta} \right|^2, \quad (3)$$

and upon writing out the numerator and defining

$$\alpha^2 = (D^2 + \beta^2 - B^2)/\delta^2 \quad (3a)$$

Eq. (3) becomes

$$F(l) = \delta^2(D^2 + B^2)^{-1} |l - i\beta/\delta \mp \{(l^2 - \alpha^2) - 2i(\beta/\delta)(l + DB/\delta\beta)\}^{1/2}|^2. \quad (4)$$

We have

$$(A + iB)^{1/2} \equiv \pm \left[\pm \frac{1}{2}A + \frac{1}{2}(A^2 + B^2)^{1/2} \right]^{1/2} + i \left[-\frac{1}{2}A + \frac{1}{2}(A^2 + B^2)^{1/2} \right]^{1/2},$$

where the inner \pm has the sign of B , so that we may write

$$F(l) = \delta^2(D^2 + B^2)^{-1} |l - i\beta/\delta \pm \{\mp P^2 + iQ^2\}|, \quad (5)$$

where P and Q are real functions of l and

$$P + Q = \{(l^2 - \alpha^2)^2 + 4\beta^2(l + DB/\delta\beta)^2/\delta^2\}^{1/2}.$$

Thus, finally,

$$F(l) = \delta^2(D^2 + B^2)^{-1} [l^2 + \beta^2/\delta^2 + P + Q \mp \{\pm 2lP^2 - 2\beta Q^2/\delta\}]. \quad (6)$$

Eq. (6) may be simplified considerably by defining

$$G(l) = \delta^2(D^2 + B^2)^{-1} [l^2 + \beta^2/\delta^2 + \{(l^2 - \alpha^2)^2 + 4\beta^2(l + DB/\delta\beta)^2/\delta^2\}^{1/2}], \quad (7)$$

$$H(l) = \delta^2(D^2 + B^2)^{-1} [\pm 2lP^2 - 2\beta Q^2/\delta], \quad (8)$$

so that making use of Eq. (2) we must have

$$[G(l) + H(l)][G(l) - H(l)] \equiv 1. \quad (9)$$

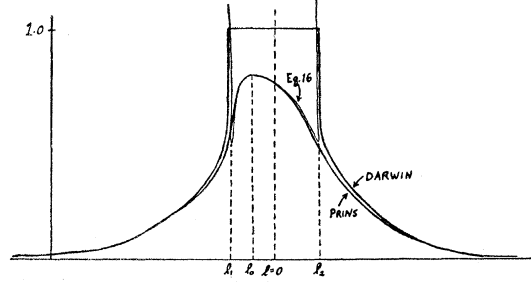


FIG. 1. Prins' function and Darwin's function (which neglects absorption) are plotted. Eq. (16) represents a series approximation to Prins' function which may be used between l_1 and l_2 .

Hence $H(l) = \{G^2(l) - 1\}^{1/2}$, and it may easily be shown that $G(l) \geq H(l) \geq 1$ for all values of l , so that for $F(l)$ we want $G(l) - H(l)$, or

$$F(l) = G(l) - [G^2(l) - 1]^{1/2}. \quad (10)$$

$G(l)$, defined by Eqs. (7) and (3a), is real, positive, single-valued, ≥ 1 for all values of l , and involves only the square-root of a real, positive polynomial in l .

An alternative form of Eq. (10), adapted to rapid calculation, may be written as

$$F(l) = e^{-\psi}, \quad (11)$$

where $\cosh \psi = G(l)$. (12)

Upon calculation of $G(l)$ for any angle, $F(l)$ may be found at once upon reference to ordinary tables of e^{-x} and $\cosh x$.

If $B = \beta = 0$, we have Darwin's case of no absorption, and $\alpha^2 = D^2/\delta^2$. For no absorption also $D/\delta = B/\beta = F/Z$, where F is the crystal structure factor and Z is the number of electrons per unit cell. Darwin's formula may therefore be written in the new form

$$F^D(l) = (F^2/Z^2) [l \mp \{l^2 - F^2/Z^2\}^{1/2}], \quad (13)$$

where the upper sign is for $l > F/Z$, the lower sign is for $l < -F/Z$, and for the region $-F/Z \leq l \leq +F/Z$ $F^D = 1$ is to be used. $F(l)$ and $F^D(l)$ are plotted in Fig. 1, and it will be seen that the two differ markedly only in the region for which Darwin's theory predicts $F^D(l) = 1$.

So far we have considered only σ -polarization of the incident beam, in which the electric vector is perpendicular to the plane of incidence. To obtain $F_\pi(l)$, D and B must be replaced by

⁸ In Parratt, Phys. Rev. **41**, 561 (1932), the fifth column in Table II on page 571 should be headed " B/δ " instead of " β/δ ."

$D \cos 2\theta_0$ and $B \cos 2\theta_0$, respectively, and for incident unpolarized radiation we will have $F(l) = \frac{1}{2}F_\sigma(l) + \frac{1}{2}F_\pi(l)$.

CALCULATION OF PERCENT REFLECTION

Of the various theoretical predictions based upon the shape of $F(l)$, the percent reflection is perhaps the easiest to calculate and to measure. Defined as the ratio of the maximum intensity obtainable from the second crystal of a double crystal spectrometer in an $(n, -n)$ position to the maximum intensity upon that crystal, it is given⁹ by

$$P(0) = \frac{\left(\int_{-\infty}^{+\infty} F_\sigma^2(l) dl + \int_{-\infty}^{+\infty} F_\pi^2(l) dl \right)}{\left(\int_{-\infty}^{+\infty} F_\sigma(l) dl + \int_{-\infty}^{+\infty} F_\pi(l) dl \right)}, \quad (14)$$

and for Darwin's case by

$$P(0) = \left(\int_{-\infty}^{+\infty} F_\sigma^2(l) dl \right) / \left(\int_{-\infty}^{+\infty} F_\sigma(l) dl \right). \quad (15)$$

Using Eq. (13), it is a simple matter to evaluate the integrals for Darwin's case analytically, with the result that

$$\int_{-\infty}^{+\infty} F_\sigma^2(l) dl = 32F/15Z;$$

the result

$$\int_{-\infty}^{+\infty} F_\sigma(l) dl = 8F/3Z$$

had been obtained in 1914 by Darwin.¹⁰ Dividing, we obtain $P(0) = 4/5$, a result to be compared with the value 0.798 obtained by graphical integration of the numerator by Allison.⁴

For Prins' case, which includes absorption, a similar analytic expression could not be obtained, and if an accurate value of $P(0)$, half-width of the rocking curve, or coefficient of reflection R_c , is desired, graphical integration, made easier by the new form of $F(l)$, must be used. However, an approximate expression for the predicted value of $P(0)$ may be derived as follows:

$F(l)$ is expanded into a power series in B/D , which vanishes with the absorption, using the binomial theorem and Eq. (10) or proceeding directly from Eqs. (11) and (12). The result is, for the region $-D/\delta < l < +D/\delta$, ($l^2 < a^2$),

$$F(l) = 1 - 2d \frac{l+k}{(a^2-l^2)^{1/2}} + 2d^2 \frac{(l+k)^2}{a^2-l^2} + \dots, \quad (16)$$

where for convenience we have written $d = B/D$, $a = D/\delta$, $k = \beta D/B\delta = a(\beta/B) > a$. Eq. (16) forms the first three terms of an exponential series, as might be expected from Eq. (12), and for Darwin's case $d=0$ and $k=1$, and $F(l)$ reduces to unity for this region, as it should.

For the outer regions, a similar series is obtained, lacking a term in d , accounting for the close agreement of Prins' function with Darwin's in these regions (see Fig. 1).

By differentiation of Eq. (16) is found that the series has minimum values equal to 0.5 for two values of l , $l_1 = -a + 2(k-a)^2 d^2/a$ and $l_2 = a - 2(k+a)^2 d^2/a$, and becomes infinite for $l = \pm a$. Thus the series may be used between these values of l , which are approximately at $\pm a$. Eq. (16) is plotted in Fig. 1.

To evaluate the integrals required in Eq. (14), series (16) is used between l_1 and l_2 , and Darwin's formula (13) is used for the other regions. The areas neglected are small, depending upon d^2 , and tend to compensate each other. In this manner the following expression is obtained:

$$P(0) = \frac{8N - 2(1 - 6d^2)P + 8QR - 4S - 11Q + U}{5(2 + 3d^2)N - P + 2QR - S - 4Q}, \quad (17)$$

where

$$N = 4a/15,$$

$$P = 2kd[\sin^{-1}(l_2/a) + \sin^{-1}(-l_1/a)],$$

$$Q = d^2(k^2 + a^2)/a,$$

$$R = \tanh^{-1}(l_2/a) + \tanh^{-1}(-l_1/a),$$

$$S = 4kd^2 \log_e[(k+a)/(k-a)],$$

$$U = 16k^2 d^4 \{3 + (k^2/a^2)\}/a;$$

$$-l_1/a = 1 - 2d^2(k-a)^2/a^2,$$

$$l_2/a = 1 - 2d^2(k+a)^2/a^2;$$

and

$$a_\sigma = D/\delta; \quad a_\pi = (D/\delta) \cos 2\theta_0,$$

$$d_\sigma = d_\pi = B/D; \quad k_\sigma = k_\pi = (\beta/B)a = \beta D/B\delta.$$

⁹ See reference 7, page 722, for a derivation of these expressions.

¹⁰ C. G. Darwin, Phil. Mag. 27, 675 (1914).

As given in Eq. (17) σ -polarization only is considered. To correct for this the numerator and denominator must be written as sums of two terms, one using a_σ , d , and k throughout, and the other using a_π , d , and k . However it probably is not worth the trouble, as Eq. (17) gives results to about 5 percent without making the correction.

For $\lambda 2.299$ on calcite, Parratt⁵ obtains for the calculated percent reflection $P(0) = 57.8$ percent, using graphical integration. Eq. (17) gives as an approximation to this calculated value $P(0) = 60.8$ percent without making the correction, and $P(0) = 60.5$ percent when polarization is considered. Series (16) represents Prins' function best for fairly soft x-rays, when $F(\pm a)$ is close to 0.5, and this is exactly the region where agreement of *experiments* with Prins' function seems best.⁵ Eq. (17) is therefore useful for checking rapidly the percent reflection according to Prins' theory, and as a test of the perfection of a particular crystal specimen referred to Prins' theory a fairly long wavelength should be used, not too close to a critical absorption limit of the crystal.

The experimental results of Parratt⁵ tend to show that the percent reflection is much more sensitive to slight imperfections of the crystal

than is the half-width of the rocking curve, so that the means of estimating the calculated percent reflection outlined above should be useful in judging the degree of perfection of a crystal specimen.

The method of computation given in Eqs. (10) to (12) is exact, and makes it very much easier to compute the curves, should graphical integrations be deemed necessary.

It is interesting to note that since $F(l)$ in the exact (Prins) form has been reduced to an ordinary real algebraic function of l , its derivative may be set equal to zero and the maximum ordinate calculated. It is readily found from Eq. (10) that the maximum ordinate of the diffraction pattern occurs for $l_0 = -BD/\beta\delta$ for σ -polarization and for $l_0 = -(BD/\beta\delta) \cos^2 2\theta_0$ for π -polarization. The maximum ordinate is $F_\sigma(l_0) = [(\beta^2 + D^2)^{\frac{1}{2}} - (\beta^2 - B^2)^{\frac{1}{2}}]^2 / (D^2 + B^2)$, with a corresponding expression for $F_\pi(l_0)$. These reduce to unity for no absorption, as they should, and serve to give a rapid estimate of the extent of deviation of Prins' function from Darwin's ideal case.

The author wishes to express his appreciation of stimulating and helpful discussions with Professor S. K. Allison concerning many of the concepts involved in this paper.