corresponding to the Patterson series in accordance with the following scheme:

$$\begin{pmatrix} F_0 & F_{\bar{n}} \\ F_n & F_0 \end{pmatrix} \rightarrow \begin{pmatrix} F_0+|F_n| & 0 \\ 0 & F_0-|F_n| \end{pmatrix} \rightarrow \begin{pmatrix} F_0^2+|F_n|^2 & 0 \\ 0 & F_0^2-|F_n|^2 \end{pmatrix} \rightarrow \begin{pmatrix} F_0^2 & |F_n|^2 \\ |F_n|^2 & F_0^2 \end{pmatrix}. \quad (50)$$

The first matrix represents the hermitian form

$$F_0 X_1 \bar{X}_1 + F_n X_1 \bar{X}_2 + F_{\bar{n}} X_2 \bar{X}_1 + F_0 X_2 \bar{X}_2$$

related to the original series, and the last matrix represents the hermitian form corresponding to the Patterson series. The second matrix is the diagonal form of the first and may be derived from it by a linear transformation. The third and fourth matrices are similarly related. Evidently a linear transformation relates the second and third matrices.

The practical significance of this type of transformation is that the inequalities associated with the Patterson series involve only the magnitudes of the Fourier coefficients. These inequalities have the obvious advantage that the quantities contained in them are directly derivable from experiment. Perhaps other intermediate cases occur in which inequalities arise that contain some complex coefficients and the magnitudes of others. Certainly, it is worth while investigating the further implications of linear transformation theory.

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Intensity of X-ray Reflexion from Perfect and Mosaic Absorbing Crystals

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The variation of the integrated Bragg reflexion of perfect absorbing crystals with the degree of asymmetry of the reflexion, structure factor and wave-length is studied theoretically and compared with that of ideally mosaic absorbing crystals. It is shown that the integrated reflexion of a perfect crystal is always less than that of a corresponding mosaic crystal. If absorption is very large, or if the reflexion is very asymmetric, the integrated reflexion of the perfect crystal approaches asymptotically that of the mosaic crystal. Approximate formulae are given for the integrated reflexion as a function of asymmetry of the reflexion, structure factor, and absorption coefficient. It is suggested that accurate determinations of structure factors may be made by the use of asymmetric reflexions for which the integrated reflexion becomes more nearly independent of the texture of the crystals.

1. Introduction

Recent experiments on the variation of the integrated reflexion of crystals with wave-length of the X-rays (Wooster & Macdonald, 1948) and asymmetry of the reflexion (Evans, Hirsch & Kellar, 1948) led the authors to a theoretical investigation of the integrated reflexion of perfect absorbing crystals as a function of the degree of asymmetry of the reflexion,* structure factor and absorption coefficient. For a mosaic crystal, expressions have been derived previously for the variation of integrated reflexion with these factors (see James, 1948). For a perfect crystal the dynamical theory of X-ray reflexions, as developed by Ewald (1918, 1924), Kohler (1933) and von Laue (1941), takes all these variables into account and leads to an expression for the intensity of the X-ray beam reflected by the crystal at a particular setting (e.g. Zachariasen, 1945). To obtain the integrated reflexion, it is necessary to integrate this expression over a range of settings of the crystal. Such an integration can be carried out analytically only in some special cases. Thus, when absorption is negligible, the well-known Darwin (1914) formula is obtained. When absorption is very large, it will be shown in a later section that the integrated reflexion tends to equal that for a mosaic crystal. In the general case the reflexion curves can be calculated and integrated graphically. Examples of such curves have been given by Prins (1930), Parratt (1932), Renninger (1934, 1937*a*) Zachariasen (1945), etc., and Renninger has also performed the graphical integration in a few special cases.

The present authors have attacked the problem in a general way. From Zachariasen's treatment of the dynamical theory, it follows that the effects of degree

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* A reflexion is asymmetric if the reflecting planes make an angle with the surface of the crystal.

of asymmetry, structure factor and absorption can all be described in terms of two parameters related to these factors. A number of reflexion curves for different values of these two parameters have been calculated and integrated graphically. The results of these calculations have then been used to discuss in general terms the variation of the integrated reflexion with the factors mentioned above. It must be emphasized here that the results of this paper have been obtained only for the 'Bragg' type of reflexions, in which the reflected beam emerges from the same crystal surface on which the X-ray beam is incident. Further, it has been assumed that the crystal possesses an inversion centre.

The results show that the integrated reflexion of a perfect crystal is always less than that of a mosaic crystal. If the structure factor is small or the absorption coefficient large, or if the reflexion is highly asymmetric, then the integrated reflexion for a perfect crystal approaches asymptotically the value for a mosaic crystal. Empirical formulae are given which describe the variation of integrated reflexion with these factors. It is pointed out that accurate structure factor determinations can be made either by using asymmetric reflexions or by choosing a wave-length for which the absorption is relatively heavy, for, under either of these conditions, the integrated reflexion becomes nearly independent of the texture of the crystal.

The paper is divided into two parts. The first part discusses the results obtained from the graphical integration. In this part the notation used is that commonly employed by most crystallographers. The second part contains the mathematical treatment of the problem leading to the graphical integration. It is also proved there analytically that when absorption is very strong the integrated reflexion of a perfect crystal equals that of a mosaic crystal. The notation used in Part II is that employed by Zachariasen (1945), on whose treatment these calculations are based.

PART I

Notation

θ	Grazing angle of incidence on crystal planes.
θ_B	Bragg angle.
ϕ	Acute angle between crystal surface and reflecting planes (positive if the reflected beam is concentrated).
b	Ratio of the direction cosines of incident and emergent beams $=\sin(\phi+\theta)/\sin(\phi-\theta)$.
β	Variable to represent asymmetry $(\equiv\tan\phi/\tan\theta_B)$.
H	Stands for *hkl*.
F_H	Structure factor of index H $(\equiv F'_H+iF''_H)$.
k	$\equiv F''_H/F'_H$.
g	$\equiv -\dfrac{1-b}{4K\sqrt{\lvert b\rvert}}\dfrac{mc^2}{e^2\lambda N}\dfrac{\mu\sqrt{(1+k^2)}}{\lvert F_H\rvert}$.
C	$\equiv\log_e(32/3\pi)$.
e	Electronic charge.
m	Electronic mass.
c	Velocity of light.
μ	Linear absorption coefficient.
N	Number of unit cells per cm.^{3}
λ	Wave-length of the X-rays *in vacuo*.
K	Polarization factor. $K=1$ for the normal component and $K=\lvert\cos 2\theta\rvert$ for the parallel component.
ρ_H	Integrated reflexion of a perfect crystal on the glancing-angle scale.
ρ'_H	Integrated reflexion of a mosaic crystal on the glancing-angle scale.
J	Integrated reflexion per unit area, called specific reflexion, for a perfect crystal.
J'	Integrated reflexion per unit area, called specific reflexion, for a mosaic crystal.

2. Integrated reflexion of perfect crystals

In Part II of this paper (equation (21)), it is shown that the integrated reflexion for a perfect crystal on the usual glancing-angle scale can be written in the form

$$\rho_H=\frac{1}{\sqrt{|b|}}\frac{K}{\sin 2\theta_B}\frac{e^2\lambda^2}{\pi mc^2}N\,|F'_H|\,R^y_H(g,k), \tag{1}$$

where $R^y_H(g,k)$ is a function only of two parameters g and k, which are given by

$$g=-\frac{1-b}{4K\sqrt{|b|}}\frac{mc^2}{e^2\lambda N}\frac{\mu\sqrt{(1+k^2)}}{|F_H|} \tag{2}$$

and $$k=F''_H/F'_H. \tag{3}$$

The considerations of this paper have been confined to 'Bragg reflexions', as mentioned earlier, and for these $|g|\geqslant|k|$ (see Part II, equation (20*a*)). The quantities b and g are negative or zero, and k may be either positive or negative.

The integrated reflexion ρ'_H for a mosaic crystal can also be written in a form similar to (1), viz.

$$\rho'_H=\frac{1}{\sqrt{|b|}}\frac{K}{\sin 2\theta_B}\frac{e^2\lambda^2}{\pi mc^2}N\,|F'_H|\,R'^y_H(g,k), \tag{4}$$

where $$R'^y_H(g,k)=\pi(1+k^2)/(4|g|). \tag{5}$$

Thus $$\frac{\rho_H}{\rho'_H}=\frac{R^y_H(g,k)}{R'^y_H(g,k)}, \tag{6}$$

so that the functions $R^y_H(g,k)$ and $R'^y_H(g,k)$ can be used to discuss the relative variation of ρ_H and ρ'_H respectively with the parameters g and k, and therefore their relative variation with asymmetry of reflexion, structure factor and absorption coefficient.

The values of R^y_H for different values of g and k have been obtained by calculation and graphical integration (see Part II).* Fig. 1 shows the variation of R^y_H and R'^y_H with $|g|$ for different values of k. It is shown in

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* The parameters g, k in $R^y_H(g,k)$, $R'^y_H(g,k)$ will be dropped hereafter unless required for a special reason.

Part II that the integrated reflexion is independent of the sign of k. Thus the three thin lines represent the values of R^y_H for a perfect crystal with $k=0$, $\pm 0{\cdot}1$ and $\pm 0{\cdot}2$, while the thick lines are the corresponding curves of R'^y_H for a mosaic crystal. Since $|g| \geqslant |k|$ for a Bragg reflexion, the curves for values of k other than zero do not start from the zero abscissa. The curves show that for a given value of k, R^y_H is less than R'^y_H for all values of g and that it tends to equal R'^y_H when $|g|$ is large. This is true for all three values of $|k|$ considered. Actually, the maximum difference between the two, viz. for $k=0$, is less than 10 % for $|g|=1{\cdot}0$ and less than 1 % for $|g|>2{\cdot}5$. The variation of integrated reflexion with $|k|$ is comparatively small. ρ'_H is proportional to $(1+k^2)$, and generally $|k|<0{\cdot}1$, so that ρ'_H is affected only by about 1 %. As shown in the curves, both ρ_H and ρ'_H are increasing functions of $|k|$. The variation with $|k|$ of ρ_H is larger than that of ρ'_H for small values of $|g|$, but is the same for large values of $|g|$. This is apparent from the curves if ordinates are compared for the same abscissae. It is to be noted that the three sets of curves have been displaced laterally to avoid overlapping.

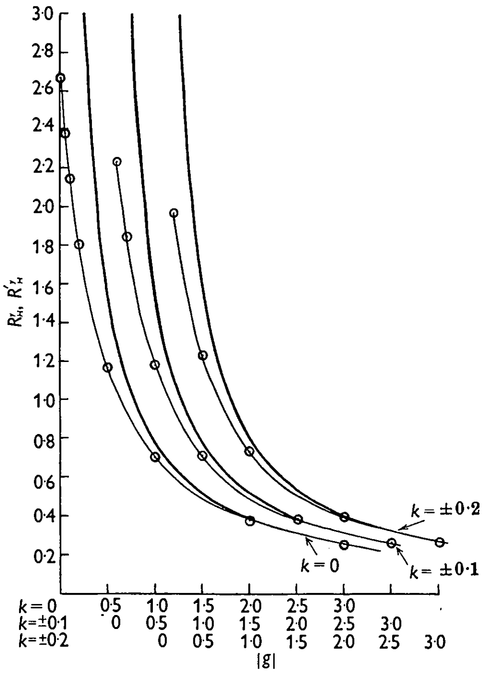

Fig. 1. Integrated reflexion in y-units as a function of $|g|$, for various values of k. Thin lines represent R^y_H for perfect crystals, based on the empirical formula. Circles represent the results of the numerical calculation. Thick lines represent R'^y_H for mosaic crystals.

Thus it appears that even if values of $|k|$ greater than 0·2 are encountered in practice, the general trend of the curves will be the same and that the curve for R^y_H will always be below that for R'^y_H (for the same value of k). Further, it is proved analytically in Part II that for any value of k, R^y_H is equal to R'^y_H for large values of $|g|$, i.e. $1 \ll |g| \gg |k|$. Thus it appears as a general result that the integrated reflexion of a perfect crystal is always less than that of a mosaic crystal, and that it approaches asymptotically the value for a mosaic crystal for large values of $|g|$.

The authors have developed an empirical formula which describes the variation of R^y_H with g and k. It is

$$R^y_H=\frac{\pi(1+k^2)}{4\{\exp[-(1+k^2)^2(|g|+C)]+|g|\}}, \quad C=\log_e\frac{32}{3\pi}. \tag{7}$$

This fits the actual values to within 2 %, which is about the accuracy of evaluation of R^y_H. In fact, in Fig. 1, the continuous lines have been drawn from the empirical formula, while the circles represent the calculated points. It may be noted that the empirical formula reduces to the mosaic formula (5) for large $|g|$ and to $R^y_H=\frac{8}{3}$ for $|g|=0$, which is the value given by Darwin's formula for a perfect, non-absorbing crystal. For small $|g|$ one obtains, for $k=0$,

$$R^y_H=\tfrac{8}{3}(1-2{\cdot}4|g|), \tag{8}$$

which is a good approximation for $|g|<0{\cdot}1$. This may be compared with the approximate formula

$$R^y_H=\tfrac{8}{3}(1-2|g|)$$

deduced by Zachariasen (1945) from purely general reasoning.

The empirical formula may be used for calculating the integrated reflexion of a perfect crystal when absorption is present and the reflexion is asymmetric. The complete formula for ρ_H corresponding to each of the polarized components is

$$\rho_H=\frac{1}{\sqrt{|b|}}\frac{K}{\sin 2\theta_B}\frac{e^2\lambda^2}{4mc^2} \times N|F_H|\frac{\sqrt{(1+k^2)}}{\{\exp[-(1+k^2)^2(|g|+C)]+|g|\}}. \tag{9}$$

If $|g|<0{\cdot}1$, we have the following approximate formula for unpolarized radiation

$$\rho_H=\frac{1}{\sqrt{|b|}}\frac{8}{3\pi}\frac{(1+|\cos 2\theta_B|)}{2\sin 2\theta_B}\frac{e^2\lambda^2}{mc^2}N|F_H| - \frac{1{\cdot}6}{\pi}\frac{(1-b)}{|b|}\frac{\lambda\mu}{\sin 2\theta_B}. \tag{10}$$

By these formulae, the structure factor, $|F_H|$, can be derived from the experimentally determined value of ρ_H.

3. Physical interpretation of the results

In an absorbing crystal, the penetration of the incident beam is determined by the energy which it loses owing to absorption and extinction. If absorption is supposed to be absent, then the penetration of the X-ray beam into the crystal is determined entirely by extinction. Then from equation (3·169) and Fig. 3·14 of Zachariasen (1945), it follows that most of the integrated reflexion is provided by a thickness of crystal, t_0, which is of the order of

$$t_0 \sim \frac{mc^2\sqrt{|\sin(\theta+\phi)\sin(\phi-\theta)|}}{Ke^2\lambda N|F'_H|}.$$

If, for the same crystal, we suppose extinction to be absent, but absorption to be present, then the depth, *t*, of the crystal which contributes effectively to most of the integrated reflexion is of the order of

$$t \sim \frac{1}{\mu\{\operatorname{cosec}(\theta+\phi)-\operatorname{cosec}(\phi-\theta)\}}.$$

Thus from (2)

$$\frac{t_0}{t} \sim +\frac{(1-b)}{K\sqrt{|b|}}\frac{mc^2}{e^2\lambda N}\frac{\mu\sqrt{(1+k^2)}}{|F_H|} \sim -4g. \tag{11}$$

Thus, $|g|$ then describes the relative importance of extinction and absorption in determining the intensity of reflexion, a small value of $|g|$ denoting a large extinction, and vice versa.

The numerical calculations described in the previous section show that ρ_H is always less than ρ'_H, and that the ratio ρ_H/ρ'_H increases with increasing magnitude of g, reaching the value unity asymptotically for large values of $|g|$. This means that the more the effective penetration of the beam into the crystal is limited by absorption rather than by extinction, the less is the difference between the integrated reflexions of a perfect and a mosaic crystal. For very large values of $|g|$, absorption controls the penetration completely and the integrated reflexions for the two types of crystal become equal. This result is to be expected on physical grounds. The difference between the intensity of reflexion of a mosaic and of a perfect crystal is due to the multiple interferences taking place in the latter. If these are in fact negligible, and the incident beam is extinguished by absorption before they become important, then the difference in reflexion between the two types of crystal should be small, as is borne out by the calculations.

So far the influence of the quantities g and k on the value of the integrated reflexion has been discussed; but g and k are functions of the various quantities that are of practical importance, such as b, F, μ, λ. In the sections that follow the variation of ρ_H and ρ'_H with asymmetry, structure factor and wave-length are discussed separately.

4. Asymmetric reflexions

For a reflexion from a given set of lattice planes, g is a function of b, and therefore varies with the degree of asymmetry of the reflexion with respect to the surface. Consequently, R^y_H also varies with the degree of asymmetry and, since $\rho_H \propto R^y_H/\sqrt{|b|}$, the integrated reflexion is a function of the degree of asymmetry. Suppose that the surface of the crystal makes an angle ϕ with the lattice planes. Then

$$b = -\frac{\sin(\theta_B+\phi)}{\sin(\theta_B-\phi)} = \left(\frac{\tan\phi}{\tan\theta_B}+1\right)\bigg/\left(\frac{\tan\phi}{\tan\theta_B}-1\right).$$

Let $\tan\phi/\tan\theta_B = \beta$. Then, as b varies from 0 to $-\infty$, β varies from -1 to $+1$ and ϕ varies from $-\theta_B$ to $+\theta_B$. The variable β can be chosen to represent the degree of asymmetry, where β is related to b by the equation

$$\beta = (b+1)/(b-1). \tag{12}$$

Then it follows that, for a mosaic crystal,*

$$\rho'(\beta)/\rho'(0) = 1-\beta. \tag{13}$$

Fig. 2 shows the variation of $\rho(\beta)/\rho'(0)$ with β for both mosaic and perfect crystals for different degrees of absorption, i.e. for different values of $|g(0)|$. All the curves have been calculated for $k=0$. For other values of k a slightly different set of curves will be obtained for perfect crystals, but the general features will remain the same. In any particular example the variation of ρ with asymmetry may be computed from equation (9).

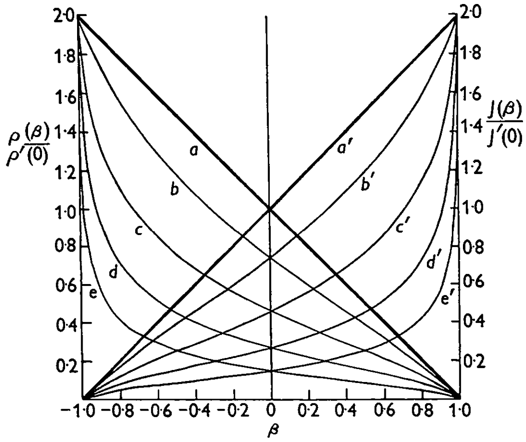

Fig. 2. Variation with asymmetry (β) of $\rho(\beta)/\rho'(0)$ and $J(\beta)/J'(0)$. Thick lines a, a' are for a mosaic crystal. Thin lines are for a perfect crystal with $k=0$ and with values of $|g(0)|=0{\cdot}5$ for b, b'; 0·2 for c, c'; 0·1 for d, d'; and 0·05 for e, e'.

In addition, one may consider the variation with asymmetry of the integrated reflexion per unit area, called 'specific reflexion', and denoted by the symbol J for a perfect crystal and J' for a mosaic crystal. It is clear that

$$J = |b|\rho \quad \text{and} \quad J'(\beta) = (1+\beta)\,J'(0). \tag{14), (15}$$

Fig. 2 also shows the variation of $J(\beta)/J'(0)$ with β for different values of $|g(0)|$ for $k=0$. It is to be noticed that these curves are the mirror-images of the curves for $\rho(\beta)/\rho'(0)$ with respect to the axis of ordinates.

By equations (13) and (15), the variation of both $\rho(\beta)/\rho'(0)$ and $J(\beta)/J'(0)$ with β for a mosaic crystal is independent of $g(0)$ and k, i.e. of absorption. On the other hand, for a perfect crystal, the variation is a function of $g(0)$ and k, and for a given value of k (viz. $k=0$) the curves are different for different values of $g(0)$. Now, for grazing incidence and grazing reflexion, i.e. for $b=0$ and $-\infty$, or $\beta=-1$ and $+1$, the penetration normal to the surface is small. Consequently, one should expect the perfect crystal to have the same characteristics as the mosaic crystal under these conditions; this is shown by the fact that the curves in Fig. 2 meet at a common point for $\beta=+1$ and

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* The subscript H will be dropped when there is no confusion.

-1. In particular, the specific reflexion attains a value $2J'(0)$ at grazing reflexion, irrespective of the degree of perfection.

This result has a bearing on the use of a perfect crystal as a concentrating monochromator (Fankuchen, 1937; Evans *et al.* 1948). It has been suggested (Fankuchen, 1938) that, because of extinction, a perfect crystal would give a better improvement in intensity when used as a concentrating monochromator than a mosaic crystal. It is now clear that, although $J(1)/J(0) > J'(1)/J'(0) = 2$, the absolute value of the specific reflexion can never be greater than for a mosaic crystal. If values of $J/J(0)$ and $J'/J'(0)$ are calculated from the curves shown in Fig. 2, then it is found that, starting from $\beta = 0$ and proceeding towards increasing values of β, $J/J(0)$ increases more rapidly than $J'/J'(0)$. This probably explains a slight deviation between theory and experiment found in one of the figures reproduced by Evans *et al.* (1948). In Fig. 4 of their paper, the experimental points for A lie significantly above the curve deduced from their equation (4); this is probably due to the fact that the polished crystal was not truly mosaic. Experiments are being carried out on perfect crystals to test the variation of $J(\beta)$, predicted by theory.

It must be pointed out that the discussion in this section holds only in so far as the effect of refraction can be neglected. At very small glancing angles of the order of 10^{-3}, i.e. 3′ of arc, refraction is appreciable and leads to complications.

5. Variation of integrated reflexion with structure factor

From (2), g is proportional to $1/|F|$, so that for a particular crystal the value of $|g|$ is larger for planes with smaller structure factors, even though the absorption coefficient is the same. Consequently, ρ/ρ' would be larger for the weaker reflexions than for the stronger ones. The variation of ρ and ρ' with $|F|$ is indicated in Fig. 3. To make the curves more general and applicable to crystals with different absorption coefficients, the abscissae and ordinates have been made equal to $1/|g|$ and $R^y/|g|$ respectively. They are therefore not equal to, but proportional to, $|F|$ and ρ respectively. The actual value of the structure factor corresponding to any particular value of the abscissa can be obtained from (2). The curves in Fig. 3 have been drawn for $k=0$. Since R^y and R'^y are functions of k, curves for other values of k will be slightly different, but the general features will remain the same. For any values of k the curves can be computed from (9). It will be noticed from Fig. 3 that ρ and ρ' are the same for small values of $|F|$, but for larger values, ρ' increases more rapidly than ρ. In fact, for very large values of $|F|$ the curve for ρ is asymptotically parallel to the straight line given by Darwin's formula for a non-absorbing crystal (also shown in Fig. 3), but displaced downwards by a constant amount. This fact has already been stated by Renninger (1937*b*). The asymptote to the perfect-crystal curve ($k=0$) in Fig. 3 is given by the equation

$$\frac{R^y}{|g|} = \frac{8}{3}\frac{1}{|g|} - 6{\cdot}4.$$

This means that the percentage deviation from the Darwin value decreases to zero asymptotically for very strong reflexions.

If, therefore, one studies the integrated reflexions of different planes of a crystal which is not ideally mosaic, then the weakest reflexions would be expected to agree with the mosaic-crystal value, while the stronger ones would progressively deviate from this. Therefore in the determination of $|F|$ values for a crystal from measurements of the integrated reflexion, weak reflexions will yield relatively accurate values of $|F|$, since the mosaic crystal formula can then be used irrespective of the texture of the crystal. Also, for a strong reflexion, it is an advantage to use an asymmetric reflexion, so that $|g|$ is made large and the disparity between the integrated reflexions for a perfect and a mosaic crystal is diminished. Alternatively, $|g|$ may be increased by using longer wave-lengths for which the absorption coefficient may be larger.

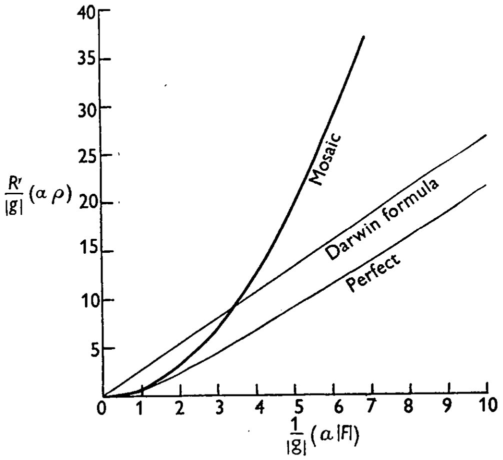

Fig. 3. Variation of integrated reflexion with F for absorbing perfect and mosaic crystals ($k=0$). Abscissae and ordinates are in units proportional to F and ρ respectively.

The results discussed above are strikingly illustrated by a comparison of the 111 and 222 reflexions of diamond. ρ'/ρ is expected to be much greater for the strong 111 reflexion than for the weak 222 reflexion. Renninger's experiments (1937*b*) indicate that this is the case. Using crystals of different degrees of perfection, he found a ratio of 1:13 for 111 while a ratio of only 1:1·5 for 222. Experiments made at Bangalore by one of the authors (G.N.R.) showed similarly that, with crystals varying from near perfect to highly mosaic ones, the integrated reflexion for 222 varied only by a factor of 2. This result cannot, however, be regarded as conclusive, as no precaution was taken to avoid double reflexions occurring simultaneously with the 222 reflexion (Renninger, 1937*b*).

6. Variation of integrated reflexion with wave-length

The absorption coefficient of a crystal varies with wave-length, so that g varies with wave-length for a particular reflexion. If no absorption edges intervene, μ increases towards longer wave-lengths, so that $|g|$ also increases correspondingly. Consequently, with increase of wave-length, the disparity between the integrated reflexions of a perfect and a mosaic crystal should diminish. This has in fact been shown to be the case in a number of crystals by Wooster & Macdonald (1948).

PART II

Notation

α	$\equiv 2(\theta_B-\theta)\sin 2\theta_B$.
ψ'_0, ψ''_0	Real and imaginary parts of the Fourier component of index zero of 4π times the polarizability.
ψ'_H, ψ''_H	Real and imaginary parts of the Fourier component of index H of 4π times the polarizability.
F_H	Structure factor of index H ($\equiv F'_H+iF''_H$). $=\dfrac{\pi mc^2}{e^2\lambda^2 N}(\psi'_H+i\psi''_H)$.
y	$\equiv\{\tfrac{1}{2}(1-b)\psi'_0+\tfrac{1}{2}b\alpha\}/(K\vert\psi'_H\vert\sqrt{\vert b\vert})$.
g	$\equiv\tfrac{1}{2}(1-b)\psi''_0/K\vert\psi'_H\vert\sqrt{\vert b\vert}$ $=-\dfrac{(1-b)}{4K\sqrt{\vert b\vert}}\dfrac{mc^2}{e^2\lambda N}\dfrac{\mu\sqrt{(1+k^2)}}{\vert F_H\vert}$.
k	$\equiv\psi''_H/\psi'_H=F''_H/F'_H$.
μ	Linear absorption coefficient ($=-2\pi\psi''_0/\lambda$).
I_0	Intensity (energy per unit area) of the incident parallel and monochromatic beam.
I_H	Intensity of the reflected beam of index H.
P_0	Power (total energy) of incident parallel and monochromatic beam.
P_H	Power of reflected beam of index H.
R^y_H	Integrated reflexion of index H in y units of angle.

7. Mathematical treatment

An account of the dynamical theory of X-ray diffraction has been given by Zachariasen (1945), whose notation we shall follow in this part of the paper. The supplementary notation and its relation to that used in Part I are set out above.

The intensity of the beam reflected by the crystal in a Bragg reflexion of index H is given by the exact formula of Zachariasen (1945, equation (3·189)) for a thick crystal possessing an inversion centre. This is

$$\frac{I_H}{I_0}=\frac{b^2K^2|\psi_H|^2}{\{|q+z^2|+|z|^2+\sqrt{[(|q+z^2|+|z|^2)^2-|q|^2]}\}},$$

where $q=bK^2\psi_H^2$ and $z=\tfrac{1}{2}(1-b)\psi_0+\tfrac{1}{2}b\alpha$.

It follows from this that

$$\frac{P_H}{P_0}=\frac{|q|}{\{|q+z^2|+|z|^2+\sqrt{[(|q+z^2|+|z|^2)^2-|q|^2]}\}}$$
$$=\frac{\{|q+z^2|+|z|^2-\sqrt{[(|q+z^2|+|z|^2)^2-|q|^2]}\}}{|q|}$$
$$=L-\sqrt{(L^2-1)}, \tag{16}$$

where

$$L=(|q+z^2|+|z|^2)/|q|. \tag{17}$$

Now, define

$$\left.\begin{aligned}y&=(\tfrac{1}{2}(1-b)\psi'_0+\tfrac{1}{2}b\alpha)/(K|\psi'_H|\sqrt{|b|}),\\ g&=\tfrac{1}{2}(1-b)\psi''_0/(K|\psi'_H|\sqrt{|b|}),\\ k&=\psi''_H/\psi'_H.\end{aligned}\right\} \tag{18}$$

Then
$$\frac{|z|^2}{|q|}=\frac{\{\tfrac{1}{2}(1-b)\psi'_0+\tfrac{1}{2}b\alpha\}^2+\{\tfrac{1}{2}(1-b)\psi''_0\}^2}{|b|K^2|\psi'_H|^2(1+k^2)}$$
$$=(y^2+g^2)/(1+k^2)$$

and

$$\frac{|q+z^2|}{|q|}$$
$$=\frac{|bK^2(\psi'_H+i\psi''_H)^2+\{\tfrac{1}{2}(1-b)\psi'_0+\tfrac{1}{2}b\alpha+i\tfrac{1}{2}(1-b)\psi''_0\}^2|}{|b|K^2|\psi'_H|^2(1+k^2)}.$$

Remembering that for a Bragg type of reflexion b is negative, so that $b=-|b|$, this may be written in the form

$$\frac{|q+z^2|}{|q|}=\frac{\begin{aligned}\sqrt{[}&\{(\tfrac{1}{2}(1-b)\psi'_0+\tfrac{1}{2}b\alpha)^2-(\tfrac{1}{2}(1-b)\psi''_0)^2\\&-|b|K^2\psi'^2_H+|b|K^2\psi''^2_H\}^2\\&+4\{-|b|K^2\psi'_H\psi''_H\\&+(\tfrac{1}{2}(1-b)\psi'_0+\tfrac{1}{2}b\alpha)(\tfrac{1}{2}(1-b)\psi''_0)\}^2]\end{aligned}}{|b|K^2(1+k^2)|\psi'_H|^2}$$
$$=\sqrt{[(y^2-g^2-1+k^2)^2+4(yg-k)^2]}/(1+k^2).$$

Thus

$$L=\{y^2+g^2+|\sqrt{[(y^2-g^2-1+k^2)^2+4(gy-k)^2]}|\}/(1+k^2). \tag{19}$$

Equations (16) and (19) may be compared with (3·190a) and (3·190) of Zachariasen (1945), which read

$$P_H/P_0=L-\sqrt{[L^2-(1+4k^2)]}$$

and $$L=y^2+g^2+|\sqrt{[(y^2-g^2-1)^2+4(gy-k)^2]}|.$$

These formulae of Zachariasen are approximations which hold only when $|k|\ll 1$, and under this condition they are equivalent to (16) and (19). The formulae (16) and (19) are, however, exact and apply quite generally to crystals which possess an inversion centre and whose thickness can be regarded as infinite compared with the penetration of the X-ray beam.

Miller (1935) has worked out similar formulae for symmetric reflexions using the theory of Prins (1930). It can be shown that for the special case of symmetric reflexions ($b=-1$), equations (16) and (19) reduce to those given by Miller.

The accurate formulae (16) and (19) have been numerically evaluated for values of g varying from 0 to $-3{\cdot}0$ and for values of $k=0{\cdot}0$, $0{\cdot}1$ and $0{\cdot}2$. The reflexion curves obtained in this way are plotted in Figs. 4, 5 and 6. Particular examples of such curves have been given by various authors, e.g. Renninger (1934) and Zachariasen (1945). For Bragg reflexions g is negative or zero, while k can assume both positive or negative values. From equation (19) it follows that for a given value of g the curves for equal and opposite values of k are mirror images about the axis of ordinates and that their areas are equal.

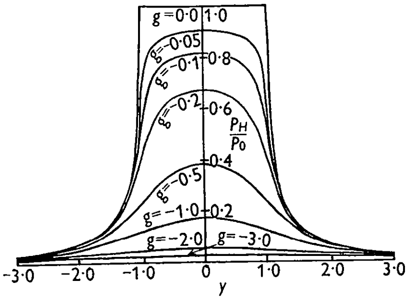

Fig. 4. Reflexion curve for a perfect crystal for various values of g ($k=0$).

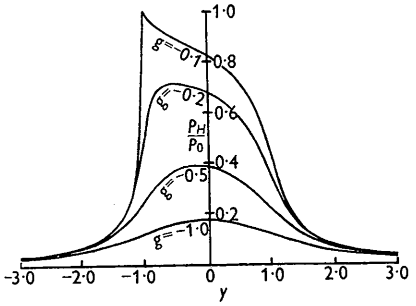

Fig. 5. Reflexion curve for a perfect crystal for various values of g ($k=+0{\cdot}1$)

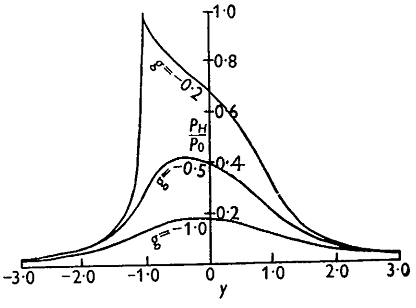

Fig. 6. Reflexion curve for a perfect crystal for various values of g ($k=+0{\cdot}2$).

The following features of the curves may be noted. First, they are symmetrical about $y=0$ only when $k=0$. Also, in every case, P_H/P_0 for all values of y decreases continuously with increasing magnitude of g. This can be proved quite generally as follows. For a Bragg reflexion g is negative, so that

$$\frac{d}{d|g|}\left(\frac{P_H}{P_0}\right)=-\frac{d}{dg}\left(\frac{P_H}{P_0}\right)=\left(1-\frac{L}{\sqrt{(L^2-1)}}\right)\left(-\frac{dL}{dg}\right).$$

The first factor is always negative, since $L\geqslant 1$. Now

$$\left(-\frac{dL}{dg}\right)=\frac{1}{(1+k^2)}\times\left[-2g+\frac{2g(y^2-g^2-1+k^2)-4y(gy-k)}{|\sqrt{[(y^2-g^2-1+k^2)^2+4(gy-k)^2]}|}\right].$$

Here again, $-2g$ is positive, and the second term can be shown to be positive or zero for all values of y if

$$k^2/g^2\leqslant(g^2-k^2+1). \tag{20}$$

Now $|k|=|\psi''_H|/|\psi'_H|$, and for a given set of reflecting planes the minimum value of $|g|$ for a Bragg reflexion is $|g|=|\psi''_0|/|\psi'_H|$. But

$$|\psi''_H|\leqslant|\psi''_0|, \tag{20a}$$

and therefore $k^2/g^2\leqslant 1$. Hence (20) is always satisfied. Thus $(d/d|g|)(P_H/P_0)$ is always negative, i.e. P_H/P_0 decreases with increasing $|g|$ for all values of y and k. The area under the curve should therefore be a monotonically decreasing function of $|g|$.

8. Integrated reflexion

The integrated reflexion on the glancing-angle scale is given by

$$\rho_H=\int\frac{P_H}{P_0}d\theta=\frac{d\theta}{dy}\int\frac{P_H}{P_0}dy=\frac{d\theta}{dy}R^y_H,$$

where R^y_H is the integrated reflexion on the y angle scale and is equal to the area under the reflexion curves shown in Figs. 4, 5 and 6. Since P_H/P_0 is a function of g, k and y only, R^y_H is a function of g and k only.

Now $$y=\frac{\frac{1}{2}(1-b)\,\psi'_0+b(\theta_B-\theta)\sin 2\theta_B}{K|\psi'_H|\sqrt{|b|}},$$

and therefore $$\frac{d\theta}{dy}=\frac{1}{\sqrt{|b|}}\frac{K|\psi'_H|}{\sin 2\theta_B}.$$

According to equation (3·95) of Zachariasen

$$|\psi_H|=\frac{e^2\lambda^2}{\pi mc^2}N|F_H|,$$

and hence

$$\rho_H=\frac{1}{\sqrt{|b|}}\frac{K}{\sin 2\theta_B}\frac{e^2\lambda^2}{\pi mc^2}N|F'_H|R^y_H(g,k). \tag{21}$$

Thus, to determine ρ_H it is necessary to evaluate $R^y_H(g,k)$. In the last section it was shown that for a given value of k the area under the curve, and therefore R^y_H, is a monotonically decreasing function of $|g|$. Also for a given value of g the areas under the curves for equal and opposite values of k are equal. Hence R^y_H is a function of $|k|$ only, and in the discussion of the variation of integrated reflexion with k, absolute values only of k need be considered.

The evaluation of R^y_H can be carried out analytically in some special cases. Thus, when absorption is negligible, the Darwin formula is obtained (see Zachariasen, 1945, p. 142, Table 3·2). This is

$$R_H^y = \tfrac{8}{3}.$$

Consider now the case of a reflexion for which $|g| \gg 1$ and $|k| \ll |g|$. Then

$$\begin{aligned} L &= \{(y^2+g^2) + |\sqrt{[(y^2-g^2)^2+4y^2g^2]}|\}/(1+k^2) \\ &= 2(y^2+g^2)/(1+k^2) \end{aligned}$$

so that $L \gg 1$. Consequently,

$$P_H/P_0 = L - \sqrt{(L^2-1)} = 1/2L = (1+k^2)/[4(y^2+g^2)].$$

This can be integrated and gives

$$R_H^y = \int_{-\infty}^{+\infty} \frac{P_H}{P_0}\, dy = \frac{\pi}{4} \frac{(1+k^2)}{|g|}. \tag{22}$$

Hence

$$\rho_H = \frac{1}{4\mu} \frac{N^2 e^4 \lambda^3}{m^2 c^4} \frac{K^2}{\sin\theta_B \cos\theta_B} |F_H|^2 \frac{1}{\frac{1}{2}(1-b)}, \tag{23}$$

which is exactly the expression for an asymmetric Bragg reflexion from a mosaic crystal.

The assumption made in the above derivation that $|g|$ is large may be secured in either of two possible ways: (i) if $|\psi_0''| \gg |\psi_H'|$; or (ii) if $(1-b)/\sqrt{|b|}$ is large, which happens if $b \to 0$ or $\to \infty$, i.e. when either the incident or reflected beam is very oblique to the surface. In such a case, a perfect crystal gives the same integrated reflexion as a mosaic crystal.

The integration was done graphically from the curves shown in Figs. 4, 5 and 6 for the range $-3{\cdot}0 < y < 3{\cdot}0$. Outside this range the value of the integral was found by using an approximate formula with a correction. The numerical values of R_H^y are probably correct to 2%. They are plotted in Fig. 1 together with the corresponding values for a mosaic crystal. These results are discussed in detail in § 2.

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The Crystal Structure of *p*-Dinitrobenzene

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The previous two reports on the crystal structure of *p*-dinitrobenzene are shown to be correct in essence, but to possess serious internal inconsistencies. The earlier of these investigations apparently ceased before the Fourier series was completely refined, while the later determination gives a set of atomic co-ordinates which is not in accord with the given description of the molecule. These co-ordinates show that the molecule is not coplanar, the plane of the nitro group making an angle of 11½° with the plane of the benzene ring. A further structure is proposed, based upon a new double Fourier series investigation, in which the molecule remains non-coplanar, the angle between the two planes being 9½°. The C–N distance is changed from 1·41 to 1·48 A.; the other bond distances and angles remain unaltered.

Introduction

The first complete crystal-structure investigation of *p*-dinitrobenzene was reported by James, King & Horrocks (1935), who employed the double Fourier series method, based upon the absolute intensities from the zonal planes, and using Mo $K\alpha$ radiation. The result was a very distorted molecule, which became the object of considerable criticism, especially by Pauling (1938,

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