according to Wislicenus (1915). The absorption spectra of these compounds in benzene solution were determined with a Beckman spectrophotometer. The spectral examination of the pleochroism of the solid was carried out on a Bausch and Lomb high-dispersion grating spectrograph and involved a comparison, by the rotating-sector method, of the transmission of plane polarized light through a single crystal held in different orientations. Light was polarized by transmission through polaroid. The crystal was prepared by melting dibiphenylene-ethylene on a microscope slide, pushing a cover down on to the melt to obtain a thin section, allowing the melt to crystallize, and painting with black paint over all but a small area of a single acicular crystal. The pleochroism of the crystal allowed orienting the *c* axis in the desired manner.

Cu radiation filtered through nickel was used for all X-ray work. Intensities were estimated by visual comparison with a prepared scale running from 1 to 4000 in arbitrary units. Intensities were corrected by Lorentz and polarization factors. The empirical scattering power of carbon in hydrocarbons (Robertson, 1935) was used in calculating the structure amplitudes and the Fourier series were summed by the method of Patterson & Tunell (1942).

The author wishes to express his deep gratitude to Prof. J. D. H. Donnay for proposing this problem and for the many suggestions and conversations that accompanied the work on it.

References

BROOKER, L. G. S. (1942). *Rev. Mod. Phys.* **14**, 275.

BUNN, C. W. (1945). *Chemical Crystallography.* Oxford: Clarendon Press.

DONNAY, J. D. H. & HARKER, D. (1937). *Amer. Min.* **22**, 446.

FUSON, R. C. & PORTER, H. D. (1948). *J. Amer. Chem. Soc.* **70**, 895.

GROTH, P. (1906–19). *Chemische Krystallographie.* Leipzig: Engelmann.

HARKER, D. (1936). *J. Chem. Phys.* **4**, 381.

LONSDALE, K. (1929). *Proc. Roy. Soc.* A, **123**, 494.

MCLAIN, J. H. (1946). Thesis, The Johns Hopkins University.

PATTERSON, A. L. & TUNELL, G (1942). *Amer. Min.* **27**, 655.

ROBERTSON, J. M. (1935). *Proc. Roy. Soc.* A, **150**, 110.

ROBERTSON, J. M. & WHITE, J. G. (1945). *J. Chem. Soc.* p. 607.

RODEBUSH, W. H. (1947). *Chem. Rev.* **41**, 318.

SCHIEBE, G., HARTWIG, S. & MÜLLER, R. (1943). *Z. Elektrochem.* **49**, 372.

WAWZONEK, S. & FAN, J. W. (1946). *J. Amer. Chem. Soc.* **68**, 2541.

WELLS, A. F. (1946). *Phil. Mag.* **37**, 221.

WISLICENUS, W. (1915). *Ber. dtsch. chem. Ges.* **48**, 617.

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Secondary Extinction and Neutron Crystallography

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A detailed study of the effects of secondary extinction is made, with particular stress on the behaviour of the virtually non-absorbing crystals introduced by the advent of neutron diffraction. The penetration of a beam into a mosaic crystal of this kind will always be complete, and the relative importance of absorption and extinction is the reverse of that familiar in X-ray techniques. It is found that with increasing thickness the integrated reflexion of mosaic crystals falls away from proportionality to F^2 and, for normal thicknesses, has values of the order of the mosaic spread of the crystal expressed in radians. There is a useful range where the integrated reflexion is proportional to F, as with the perfect crystal. The discussion leads to an illuminating comparison between primary and secondary extinction. Criteria for 'thin', 'thick', 'non-absorbing' and 'absorbing' crystals are given. The importance of these results for neutron crystallography is discussed; if a technique similar to X-ray goniometry is to be developed, then crystals even smaller than those conventional with X-ray technique will be required. For this work the best crystals are those of the greatest mosaic spread.

1. INTRODUCTION

In a recent paper, Bacon & Thewlis (in the Press) discuss neutron diffraction from the point of view of the crystallographer. They point out that the very low value of true absorption coefficient for neutrons which most substances present entirely alters the problem of measuring structure factors, and leads to different results for the integrated reflexions measured in structure-analysis work. For strongly absorbing materials, the integrated reflexion from mosaic crystals is always proportional to the square of the structure factor for the reflexion; but with non-absorbing crystals, unless they are exceedingly thin, the integrated reflexion takes a value very much less dependent on the structure factor, and of the order of the angular spread of the mosaic blocks expressed in radians.

The theory of secondary extinction as so far developed appears to cover only the approximation for the case of highly absorbing crystals. In the present paper the theory is generalized to supplement the treatment given by Zachariasen (1944). The influences of structure factor, absorption coefficient and mosaic spread are examined in detail, and the consequences for neutron crystallography are worked out.

For a general introduction to the subject of extinction in mosaic crystals, the reader is referred to an article by Lonsdale (1947). We may state an essential fact: for the reflected intensity to be proportional to F^2, where F is the structure factor, the depth of crystal contributing to the reflected beam must be small. Now this can come about in two different ways: either the crystal itself is thin; or, if it is thick, true absorption may reduce the incident intensity so drastically that only a surface layer of crystal contributes to the reflexion. In X-ray diffraction the latter case applies almost invariably, and the crystal does not need to be excessively thin, for it is impossible for the beam to traverse a distance sufficient for secondary extinction to be serious. The formula for the integrated reflecting power under these conditions is the well-known expression $Q/2\mu$, μ being the true absorption coefficient, so that the proportionality to Q and hence to F^2 is assured.

The linear absorption coefficients of crystals to neutrons, however, are generally of the order of 10^{-1} cm.$^{-1}$ as compared with 10^2 cm.$^{-1}$ for X-rays, and the range of a neutron beam in the crystal will in general be very much greater than for X-rays. Severe extinction is therefore bound to occur unless the thickness of the specimen is reduced to a very small value. Zachariasen has given the relation between integrated reflexion and thickness of a mosaic crystal in a rather general case, and followed up the argument for highly absorbing materials. The discussion which follows is largely an elaboration and development of his equations in a more general way to cover the cases introduced by the advent of neutron diffraction.

We shall find it useful to approach the problem of secondary extinction with the close analogy to primary extinction in mind. For this reason the next section will be devoted to a statement of the standard results for integrated reflexion from perfect crystals. Throughout this paper the integrated reflexions considered are for the rotating-crystal method and are denoted by R^θ and $\mathscr{R}^\theta$ for perfect and mosaic crystals respectively; it may be remarked that these differ from the similar quantities R^λ and $\mathscr{R}^\lambda$ in the Laue method only by a factor of $2d\cos\theta_B$, so that $\mathscr{R}^\lambda = \mathscr{R}^\theta\, 2d\cos\theta_B$. In these expressions d is the interplanar spacing and θ_B the Bragg angle.

2. PERFECT CRYSTALS

A crystal whose structure is perfectly uniform and regular throughout is said to be 'perfect'. The manner in which radiation is reflected from it is examined by considering first the intensity of reflexion from a very small element of perfect crystal of volume δV. This element is taken so small that only a few per cent of the incident energy can be reflected by it. With this understanding it can be shown by diffraction theory that the integrated reflexion for the rotating crystal method from the small element is $Q\,\delta V$, where

$$Q = \frac{\lambda^3 N^2}{\sin 2\theta_B} K F^2,$$

with

$$F \equiv F_X = \sum_{\text{atoms}} \left(\frac{e^2}{mc^2}\right) f e^{2\pi i(hx/a+ky/b+lz/c)} \quad \text{for X-rays,}$$

and $$F \equiv F_N = \sum_{\text{atoms}} \sqrt{\left(\frac{\sigma_{\text{Bragg}}}{4\pi}\right)}\, e^{2\pi i(hx/a+ky/b+lz/c)} \quad \text{for neutrons.}$$

K, the polarization factor, is $\frac{1}{2}(1+\cos^2 2\theta_B)$ for X-rays and unity for neutrons. N is the reciprocal of the unit-cell volume, σ_{Bragg} the neutron cross-section for coherent scattering. The crystal structure factor F_X is that of Bacon & Thewlis (1948) and contains the term e^2/mc^2.

As an incident beam of X-rays or neutrons proceeds through a larger crystal at the Bragg angle, its amplitude is reduced both by actual absorption of the quanta (by photoelectric or nuclear capture processes, for example) and also by the very fact that some intensity is being diffracted and is escaping from the crystal as a reflected beam. Thus, even after allowing for the effect of true absorption, the deeper parts of the crystal contribute less than the upper parts, because energy which is incident at the correct angle for diffraction has been removed before it reaches them. Hence, quite apart from absorption, the simple expression QV will not apply over the extended volume, because the strength of the incident beam diminishes appreciably with penetration. This reduction of the incident intensity is the phenomenon of 'extinction'.

In a perfect crystal, the extinction of the forward-travelling wave may be regarded as due to repeatedly reflected components thrown into the same direction with opposite phase. At the Bragg angle it is so marked that reflexion effectively takes place in a very thin surface layer, the penetration distance being of the order of 10^{-4} cm. for both X-rays and neutrons. Extinction in this form, due to a perfectly ordered structure of scattering units, is called 'primary'.

True absorption in such a thin layer is negligible, and was assumed to be zero in the classical derivation of the diffraction curve by Darwin and Ewald. The diffraction curve is the one showing the variation of total diffracted energy with angle of incidence, and for a non-absorbing crystal of infinite thickness takes the familiar form shown by Zachariasen (1944, p. 129). Total reflexion takes place over an angular range of 2s, where

$$s=\frac{\lambda^2 N}{\pi \sin 2\theta_B} F \sqrt{\frac{|\gamma_H|}{\gamma_0}},$$

which usually amounts to a few seconds of arc, and γ_0, γ_H are the direction cosines of the incident and diffracted beams with respect to the inward normal to the plate. The integrated reflexion is

$$\frac{\lambda^2 N}{\sin 2\theta_B} F \sqrt{\frac{|\gamma_H|}{\gamma_0}}.$$

The effect of extinction is exhibited most clearly by the function which shows the dependence of the integrated reflexion on the thickness for Bragg reflexion from the face of a finitely thick crystal plate. It is given (Zachariasen, 1944, equations 3.167 and 3.143) for each component of polarization by

$$\begin{aligned} R^\theta &= s\int_{-\infty}^{\infty}\frac{dy}{y^2+(1-y^2)\coth^2[A(1-y^2)]} \\ &= \pi s \tanh A. \qquad (1) \end{aligned}$$

A is equal to $s't_0/\pi\gamma_0$, where $ss'=Q$ and t_0 is the thickness of the crystal plate. Both s and s' are directly proportional to the structure factor F.

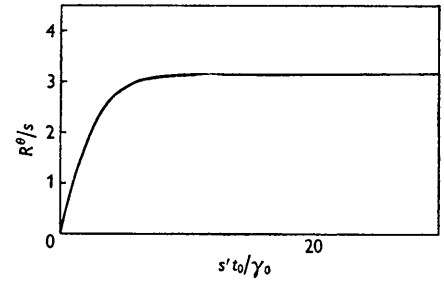


Fig. 1. Dependence of the integrated reflexion R^θ from a finitely thick non-absorbing perfect crystal plate on the thickness and structure factor.

The variation of R^θ/s with πA is shown in Fig. 1. t_0/γ_0 is the effective ray path through the crystal, and the figure shows clearly how the integrated reflexion depends upon this quantity and upon the structure factor. The part of the curve close to $y=x$ is the region where $R^\theta/s=s't_0/\gamma_0$, i.e. where the formula QV applies; at thicknesses corresponding to the knee of the curve primary extinction begins to set in, and where the curve approaches the horizontal, extinction is virtually complete and the crystal is effectively infinite. Since s' is proportional to F the penetration distance into a thick perfect crystal can be seen to be inversely proportional to the structure factor.

3. MOSAIC CRYSTALS

Most crystals are very far from perfect, and the ideal lattice regularity is restricted in them to very small regions, the boundaries of which are fixed by distortions and displacements in the structure. These crystals are called 'mosaic', and the reduction of the beam in their interior will be controlled by the type of mosaic structure, including the orientation function of the mosaic 'blocks'. Screening of a lower block by an identically oriented block nearer the surface will still occur, but the effect will be much less marked in the mosaic crystal, since intervening blocks will have different orientations and will not reflect at the same inclination of the incident beam. Moreover, since reflexions from the blocks at different depths are not coherent, the limitation of the forward-travelling wave to such a thin surface layer no longer occurs; and while extinction of the incident beam must take place, it may be expected on this account to be far less severe than in the perfect crystal. It will be shown below that the thickness of mosaic crystal for which the formula QV holds may be more than a hundred times that for a perfect specimen. Extinction in this form is said to be 'secondary'.

Naturally, if the mosaic blocks are large enough, primary extinction will occur within them, and if both forms of extinction are present simultaneously it will be very difficult to estimate the proper correction to the apparent structure factor. If secondary extinction alone is to take place, as is desirable, then the mosaic blocks must be small compared with the penetration distance for primary extinction. The crystal is then said to be 'ideally imperfect'.

To arrive at the law relating the integrated reflexion from an ideally imperfect crystal plate to the thickness and structure factor, the penetration of the crystal by the incident beam will be discussed. The diffraction curve for a crystal plate of thickness t_0 is next obtained, from which the integrated reflexion follows. We shall first treat substances having zero absorption at some length so as to fix attention on the phenomenon of secondary extinction alone, and to bring out the physical principles concerned.

Crystals of zero absorption

Solution of the equations governing reflexion

Before setting up the equations governing the intensity of the radiation within a mosaic crystal, Zachariasen obtains an expression for the reflectivity σ, which, owing to the mosaic disorientation, is a function of the mean glancing angle θ. The mosaic block angular distribution function W is defined so that $W(\Delta)\,d\Delta$ is the fraction of mosaic blocks having their normals between the angles Δ and $\Delta+d\Delta$ to the normal to the crystal surface. If now σdt is the reflecting power of a layer of mosaic blocks, the thickness of the layer being dt, then (Zachariasen, 1944, equations 4.20 and 4·33)

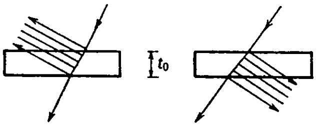
$$\sigma = \frac{Q}{\gamma_0} W(\theta - \theta_B). \tag{2}$$

γ_0 is the direction cosine of the incident beam relative to the inward normal to the crystal face, and is equal to $\sin \theta_B$ in the case of symmetrical reflexion. For want of a better assumption, $W(\Delta)$ is taken to be gaussian with cylindrical symmetry and is written

$$W(\Delta) = \frac{1}{\eta \sqrt{(2\pi)}} e^{-\Delta^2/2\eta^2}, \tag{3}$$

η being the standard deviation. Formula (2) above assumes that $\eta \gg s$.

The equations governing Bragg reflexion from an ideally imperfect crystal plate having zero absorption may now be written down for the case where the reflected beam emerges from the face of incidence as in Fig. 2 (*a*). It will be seen that there is no implication that the reflecting planes are parallel to the face of the crystal. Let $\mathscr{P}_0$ and $\mathscr{P}_H$ represent the power of the incident and diffracted beams respectively at a depth t below the surface of the crystal of thickness t_0. Then



(*a*) Reflexion method (*b*) Transmission method

Fig. 2. Diagrams to illustrate the reflexion and transmission methods referred to in the text.

$$\left.\begin{aligned} d\mathscr{P}_0 &= \mathscr{P}_H \sigma dt - \mathscr{P}_0 \sigma dt, \\ d\mathscr{P}_H &= \mathscr{P}_H \sigma dt - \mathscr{P}_0 \sigma dt. \end{aligned}\right\} \tag{4}$$

The boundary conditions are that $\mathscr{P}_0$ assumes the value of the incident intensity $\mathscr{P}_0(0)$ at $t=0$, and that $\mathscr{P}_H$ is zero at $t=t_0$. It follows that

$$\mathscr{P}_0(t) = \mathscr{P}_0(0) \frac{1+\sigma(t_0 - t)}{1+\sigma t_0} \tag{5}$$

controls the strength of the forward-going beam at the depth t from the crystal surface; and that the reflecting power is given by the function

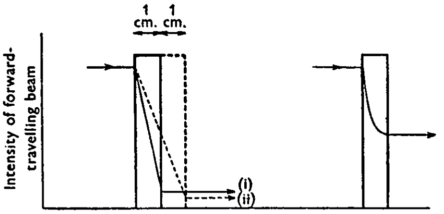
$$\frac{\mathscr{P}_H(0)}{\mathscr{P}_0(0)} = \frac{\sigma t_0}{1+\sigma t_0}. \tag{6}$$

These two results will now be discussed separately.

Penetration of the beam into the crystal

Equation (5) shows that the reduction of the intensity of the beam within the ideally imperfect crystal is linear with distance, and depends upon the total thickness of the crystal. The effect is illustrated for crystals of two different thicknesses in curves (i) and (ii) of Fig. 3 (*a*). The figure shows that if a mosaic crystal slab, say 1 cm. thick, is set up for Bragg reflexion of neutrons, the reflected beam will be very intense and will spring from all depths of the specimen; if an extra 1 cm. slab is brought up behind the first, it too will be a source of appreciable reflected power, even though the first crystal was already giving nearly 100% reflexion. The ingoing beam therefore ranges throughout the mosaic crystal, in contradistinction to the case of the perfect structure.

The physical meaning of this result is interesting. Suppose that the second crystal in Fig. 3 (*a*) is removed some arbitrary distance behind the first, and to begin with is turned away from the Bragg angle. Then the incident beam follows the line (i) and the beam incident on the second crystal will be transmitted completely. If the second crystal is now adjusted for Bragg reflexion, the beam previously transmitted through it will undergo multiple reflexion between the two crystals. Owing to the absence of phase relationship between the beams, however, the intensities of the components travelling between the two crystals all add, so that the intensity actually builds up to the appropriate height given by curve (ii). The phenomenon is therefore analogous to resonance, but without dependence on phase. On the other hand, if thin perfect crystals could be used for this experiment, the precise separation between the two crystals would be of vital importance, just as in the optical analogue of reflexion between half-silvered mirrors.



(*a*) Thickness of crystal traversed by beam → (*b*) Thickness of crystal traversed →

Fig. 3. The intensity of the incident beam: (*a*) within ideally imperfect crystals of two different thicknesses, having zero absorption, under conditions of Bragg reflexion; and (*b*) within a similar crystal when the diffracted beam emerges from the back.

From equations (2) and (5) together the transmitted intensity can be seen to be reduced by the factor

$$\left[1 + \frac{Q t_0}{\gamma_0} W(\theta - \theta_B)\right]^{-1}, \tag{7}$$

evaluated for the particular angle of incidence θ.

The case of the transmission method, in which the diffracted beam emerges from the back of the crystal plate, can be treated in an exactly similar way (Fig. 2 (*b*)). We shall merely remark that the incident beam behaves within the crystal according to

$$\mathscr{P}_0(t) = \tfrac{1}{2}\mathscr{P}_0(0)\,(1+e^{-2\sigma t}), \tag{8}$$

as shown in Fig. 3 (*b*). The complete penetration of the beam is even more noticeable than in the reflexion method of Fig. 3 (*a*).

The diffraction curve

Equations (6) and (2) give the diffraction curve as the variation, with angle of incidence, of the expression

$$Q\frac{t_0}{\gamma_0}W\Big/\left(1+Q\frac{t_0}{\gamma_0}W\right). \tag{9}$$

According to this, the width of the diffraction curve for a mosaic crystal depends primarily upon the angular spread of the mosaic blocks, which in practice is usually between ten and some two hundred times the angular width of the diffraction curve for the perfect crystal. If the maximum amplitude reflected from the crystal is small, the denominator of (9) is effectively unity, and the curve takes the gaussian form of the mosaic block angular distribution function.

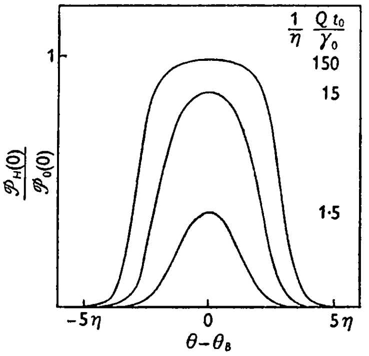


Fig. 4. Diffraction curves swept out by the beam reflected from the face of a non-absorbing ideally imperfect crystal plate as the crystal is rotated.

With a powerfully reflecting crystal, however, the diffraction curve is flattened off preferentially over the range of intense reflexion. Fig. 4 shows the curves for both weak and strong reflexions. Over any angular range of incidence for which the two terms in the denominator become comparable, owing to a sufficiently great t_0, Q, or small η, the ordinates fall below those appropriate to a gaussian form and the curve is noticeably flattened. Where this occurs, secondary extinction is prevailing; and this distortion of the curve is the essential characteristic of the extinction.

The integrated reflexion

The integrated reflecting power $\mathscr{R}^\theta$ from a rotating crystal is obtained by integrating the above reflecting power (9) over the whole extent of the diffraction curve. Thus

$$\mathscr{R}^\theta=\int_{-\infty}^{\infty}\left[Q\frac{t_0}{\gamma_0}W(\Delta)\Big/\left\{1+Q\frac{t_0}{\gamma_0}W(\Delta)\right\}\right]d\Delta. \tag{10}$$

If the peak (per cent) reflexion is small, the variable term in the denominator may be ignored; and since $\int_{-\infty}^{\infty}W(\Delta)\,d\Delta=1$ the integrated reflexion reduces to the normal formula QV and is consequently proportional to F^2. Where extinction prevails, however, the integrand is reduced below the value which gives QV and the integral falls away from that value.

The dependence of the integrated reflecting power on the various parameters can be shown most simply by plotting $\mathscr{R}^\theta$ against Qt_0/γ_0 for crystals of different mosaic spread, it being noted that Q and t_0 are always associated in the form of their product in (10). The resulting curves are given in Fig. 5. As expected, the curves show that as Qt_0/γ_0 is increased $\mathscr{R}^\theta$ departs from linear proportionality at values determined by the degree of the mosaic spread. The departure is greatest for crystals with the best oriented blocks, because, over the diminished range in which reflexion occurs in such a crystal, extinction will be correspondingly more marked. With increasing thickness the integrated reflexion calculated from (10) rises slowly to infinity, the crystal being non-absorbing.

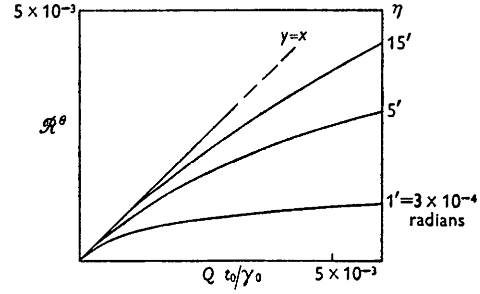


Fig. 5. Dependence of the integrated reflexion $\mathscr{R}^\theta$ on the thickness and structure factor, for reflexion from the face of finitely thick non-absorbing ideally imperfect crystal plates of different mosaic spread.

Criterion for a thin crystal

A 'thin' crystal may be defined as one for which the integrated reflexion is within 5 % of the value QV. It is found numerically that this happens when the value of the term QWt_0/γ_0 is less than 0·1 at the peak of W. Thus for a 'thin' crystal

$$\frac{t_0}{\gamma_0}<\frac{\eta}{4Q}. \tag{11}$$

The criterion brings out the well-known point that extinction is greatest for the stronger reflexions, and that the same crystal may be 'thin' for some reflexions and 'thick' for others.

The order of magnitude for t_0 for a thin crystal in practice may be illustrated by the example of the (200) reflexion of magnesium oxide, whose true absorption coefficient for neutrons is only 0·02 cm.$^{-1}$. For $\lambda=1\cdot5$ A., $Q=0\cdot02$; and we shall suppose η to be 5′, i.e. $1\cdot5\times10^{-3}$ radians, and $\gamma_0=0\cdot4$, say. Inserting these figures in (11), we have that for a 'thin' crystal, $t_0<0\cdot1$ mm. which would be exceedingly small for goniometric work.

Behaviour of a thick crystal of zero absorption and the possibility of structure analysis

It was shown above that the integrated reflexion increases without limit with Qt_0/γ_0. The physical meaning of this is easily understood. As thicker and thicker crystals are considered, the second term in the denominator of (9) becomes appreciable over an ever-increasing range of Δ; that is to say, there will be enough mosaic blocks at orientations further and further from the peak of the angular distribution to reflect all the beam. With increasing thickness there will eventually be found sufficient blocks even at relatively large angles away from the peak. Therefore, over a range of thicknesses well past the region of the QV law, the amplitude of the diffraction curve will tend to approach unity over the whole of the angle within which the mosaic blocks predominantly lie. The integrated reflecting power will then depend primarily on η, and comparatively little on Q, a circumstance under which structure analysis would be impossible.

Criterion for a thick crystal

We may also obtain from the above equations the criterion for an 'effectively infinite' crystal. Since with zero absorption there is no limit to the integrated reflecting power, a thick crystal cannot be defined as one whose integrated reflexion is close to the limiting value for infinite thickness. Instead, we take the arbitrary definition that the peak reflexion (i.e. the maximum value of the integrand in (10)) is to be greater than 0·95; it follows that

$$\frac{t_0}{\gamma_0} > \frac{50\eta}{Q}. \tag{12}$$

In the practical example of magnesium oxide this means that $t_0 > 1\frac{1}{2}$ cm. Evidently in a large number of practical cases in which Bragg reflexion might be required, a crystal of practical size may be expected to be of intermediate value with regard to thickness.

Criteria for non-absorbing and absorbing crystals

Before passing on to the completely general case it will be valuable to see what orders of magnitude would be implied in applying to practical cases the distinction we made between absorbing and non-absorbing crystals. The criteria for thickness above were obtained by considering the integrated reflecting power of crystals having zero absorption; the influence of true absorption may conveniently be examined in a preliminary fashion by taking another extreme case, the infinitely thick crystal. The strongly absorbing crystal will then be the one in which the beam is greatly reduced before penetrating the critical distance for extinction, the weakly absorbing one that in which secondary extinction invalidates the QV law before the beam has been absorbed.

The effective absorption coefficient for the reduction of a beam in which both true absorption and diffraction processes take part is $\mu + QW$ (Zachariasen, 1944, equations 4.31 and 4.33). The two terms in the coefficient separately represent the two processes, and their magnitudes express the relative importance of the separate effects in extinguishing the beam. Strongly and weakly absorbing crystals as defined by our above argument will therefore be those for which μ is respectively greater and less than the peak value of QW, namely $Q/\eta\sqrt{(2\pi)}$.

Absorbing crystals

The diffraction curve for symmetrical reflexion from the face of an infinitely thick absorbing crystal has been given by Zachariasen (1944, equation 4.27). Manipulating his result into a more convenient form, and taking the integral, we have

$$\mathscr{R}^\theta = \int_{-\infty}^{\infty} \tanh \tfrac{1}{4} \log_e\left(1 + \frac{2Q}{\mu} W\right) d\Delta, \tag{13}$$

or
$$\mathscr{R}^\theta = \int_{-\infty}^{\infty} \left\{\frac{Q}{2\mu} W - \frac{1}{2}\left(\frac{Q}{\mu}\right)^2 W^2 + \frac{17}{24}\left(\frac{Q}{\mu}\right)^3 W^3 - \dots\right\} d\Delta. \tag{14}$$

If μ is large, both the logarithmic and hyperbolic functions behave in a nearly linear manner and, as can be seen directly from the series expansion, the integrand is equal to $QW/2\mu$; the integrated reflexion is then the familiar $Q/2\mu$. This is the normal X-ray case where true absorption predominates over secondary extinction and prevents the beam from penetrating a distance large compared with the 'thin crystal' distance of $\eta/4Q$. For X-rays a typical value of μ is 100 cm.$^{-1}$, which would cause a reduction of beam intensity to $\frac{1}{3}$ after a distance of 0·1 mm.

A reasonable definition of an 'absorbing' crystal is one for which $\mathscr{R}^\theta$ is within 5% of the value $Q/2\mu$. Calculation from equation (13) shows that this holds if

$$\mu > 4Q/\eta. \tag{15}$$

It is to be noticed that the minimum absorption coefficient allowed by (15) is just the reciprocal of the thin-crystal distance (11). This is because only a truly thin surface layer can be permitted to take part in the reflexion if the integrated reflecting power is to remain proportional to Q.

'Non-absorbing' crystals

A set of diffraction curves very similar to those of Fig. 4 could be drawn for thick mosaic crystals of different absorption, the highly absorbing ones having diffraction curves similar to the thin non-absorbing crystals of the previous discussion. As μ is decreased the diffracted amplitude increases everywhere and the curve changes from one having the gaussian shape to the larger curve with the flattened top. This flattening occurs, mathematically, since the two functions in (13) fall off progressively from linear proportionality as their arguments are increased.

The attempt to define a 'non-absorbing' crystal from considerations of the thick model encounters the same difficulty as the thickness criterion for crystals of zero absorption given in (12). It is not possible to say that a non-absorbing, infinitely thick crystal is one in which the integrated reflexion approaches the limiting value as μ is decreased. The assumption of an infinitely thick crystal, however, destroys any connexion between the proposed criterion and the definitions of thin and thick crystals, whereas the practical need is for a criterion of non-absorption in finite crystals which will ensure that the criteria (11) and (12) are close to the truth. Since an arbitrary definition must be made, we choose to describe a 'non-absorbing' crystal as one having an absorption coefficient less than the reciprocal of the thick-crystal distance (12). Such a low absorption will certainly permit the radiation to enter sufficiently far to undergo the severe extinction essential to the concept of the 'thick' crystal. Thus for a non-absorbing crystal,

$$\mu < Q/50\eta. \tag{16}$$

Taking, as before, $Q=0{\cdot}02$ cm.$^{-1}$ and $\eta=5'$, we obtain for the two extremes: 'non-absorbing' crystal, $\mu<0{\cdot}3$ cm.$^{-1}$, 'absorbing' crystal $\mu>50$ cm.$^{-1}$. A typical value of μ for neutrons is 0·3 cm.$^{-1}$, which is the value for copper; very weak absorbers such as MgO have $\mu=0{\cdot}02$ cm.$^{-1}$; while a substance such as LiF (which contains the highly absorbing element lithium) has a μ of about 4 cm.$^{-1}$. Compounds containing cadmium and certain other substances have absorption coefficients of 100 cm.$^{-1}$ or more.

It follows from the limits given above that many practical cases in neutron crystallography will be intermediate in absorption as well as thickness, and the most useful information will be that obtained from the general solutions now to be examined.

General treatment of ideally imperfect crystals

Zachariasen (1944, pp. 162–3) has solved equations similar to (4) containing an absorbing term, assuming plane parallel plates for both the crystal and the mosaic blocks. He distinguishes between what he calls the Bragg case and the Laue case, which we shall continue to call the reflexion method and the transmission method respectively, to avoid any suggestion that white radiation is being used in the latter. The two methods give different diffraction curves, owing to the fact that in the transmission case all rays traverse the same thickness of crystal, unlike the reflexion case in which some of the diffracted beam does not have to pass through very much material. These diffraction curves are similar only when μt_0 and Qt_0 are both small, that is, when the total diminution of the beam in the sample is small.

If the crystal is absorbing, the integrated reflexion obtained will depend on the angle between the reflecting planes and the surface of the slab. Zachariasen works out his results for the symmetrical disposition in which the incident and diffracted beams make the same angle to the face of the crystal plate. The generalization to the case of reflecting planes not parallel to the surface will be discussed at a later stage.

Once more recasting the formulae of Zachariasen (1944, equations 4.24 and 4.25), the integrated reflexions for an ideally imperfect crystal can be written in the form of integrals over the diffraction curves:
Reflexion method:

$$\mathscr{R}^\theta=\int_{-\infty}^{\infty}\frac{a\,d\Delta}{(1+a)+\sqrt{(1+2a)}\coth\left[A\sqrt{(1+2a)}\right]}, \tag{17}$$

Transmission method:

$$\mathscr{R}^\theta=\int_{-\infty}^{\infty}\sinh\,(Aa)\,e^{-A(1+a)}\,d\Delta, \tag{18}$$

where A now equals $\mu t_0/\gamma_0$, and

$$a=\frac{Q}{\mu}W=\frac{Q}{\mu}\frac{1}{\eta\sqrt{(2\pi)}}e^{-\Delta^2/2\eta^2}.$$

The expression for $\mathscr{R}^\theta$ in the reflexion case may be compared with R^θ, the same quantity for a perfect crystal which was given in (1).

Now we may write the integrand in either case as

$$\mathscr{P}^\theta=\phi\left(\frac{\mu t_0}{\gamma_0},\frac{1}{\eta}\frac{Q}{\mu},\frac{\Delta}{\eta}\right); \tag{19}$$

and $$\mathscr{R}^\theta=\int_{-\infty}^{\infty}\phi\,d\Delta=\eta\int_{-\infty}^{\infty}\phi\,d\left(\frac{\Delta}{\eta}\right),$$

since η is constant over the integration. Therefore

$$\frac{1}{\eta}\mathscr{R}^\theta=\psi\left(\frac{\mu t_0}{\gamma_0},\frac{1}{\eta}\frac{Q}{\mu}\right). \tag{20}$$

Calling this $\psi(A, B)$ it is possible to plot $\mathscr{R}^\theta/\eta$ for various values of $A=\mu t_0/\gamma_0$ against $AB=\frac{1}{\eta}Q\frac{t_0}{\gamma_0}$. Q and t_0 being thus once more associated in the abscissa, these curves may be expected to possess a common part in the region of small secondary extinction.

The $\mathscr{R}^\theta$ curves obtained in this way appear in Fig. 6(a) for both the reflexion method (full lines) and the transmission method (broken lines). As Qt_0/γ_0 is increased, the integrated reflexion increases according to the simple law QV and then begins to fall off under the joint influences of secondary extinction and absorption. (In the lowest curves the common part close to $y=x$ is too small to be seen.) The effect of varying the mosaic spread of the crystal is simply to alter the scale of the axes in such a way that, for a given Qt_0/γ_0 value, the line $y=x$ corresponding to the thin crystal approximation is held more closely, and for stronger reflexions, the greater the disalignment of the mosaic blocks. The first practical conclusion from the general argument is therefore that in single-crystal work specimens of the widest mosaic spread are advised.

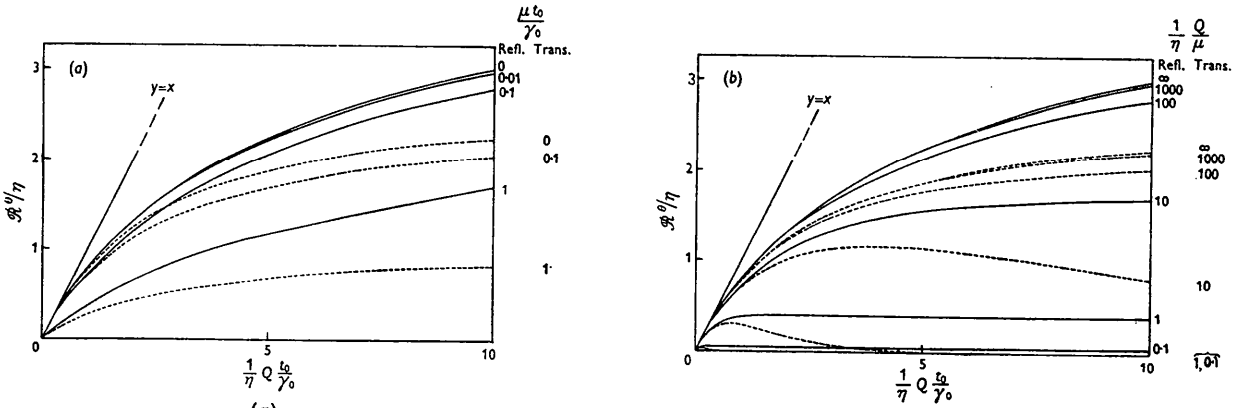
The intrinsically higher reflectivity of the reflexion method results in the curve for a given $\mu t_0/\gamma_0$ value always lying above the corresponding curve for the transmission method. For thin crystals, however, with the total diminution of the beam small, the solutions are very close. In the case of zero absorption we can compare the series expansions for the reflectivity in the two cases. For transmission, the integrand in (18) gives

$$\text{reflectivity} = (\sigma t_0) - (\sigma t_0)^2 + \tfrac{2}{3}(\sigma t_0)^3 - \ldots. \qquad (21)$$

For reflexion we have from (6)

$$\text{reflectivity} = (\sigma t_0) - (\sigma t_0)^2 + (\sigma t_0)^3 - \ldots. \qquad (22)$$

These expressions result in the divergence between the two types of integrated reflexion measurement being less than 5% at a thickness of eight times the 'thin crystal' distance of (11).



(a) (b)

Fig. 6. The integrated reflexion $\mathscr{R}^\theta$ from ideally imperfect crystal plates as a function of thickness, structure factor, absorption coefficient and mosaic spread. Full lines, symmetrical reflexion method, $\gamma_0 = \sin\theta_B$; broken lines, symmetrical transmission method, $\gamma_0 = \cos\theta_B$. Unsymmetrical methods are discussed in the text.

Use of the curves

In examining Fig. 6 (*a*) and later figures, Table 1 will be found useful. This gives values of $\frac{1}{\eta} Q \frac{t_0}{\gamma_0}$ for various combinations of η and t_0, for the particular values $Q = 0{\cdot}02$ cm.$^{-1}$ and $\gamma_0 = 0{\cdot}4$. It will be seen that practical cases cover a very wide range of values of $\frac{1}{\eta} Q \frac{t_0}{\gamma_0}$. The curves of Fig. 6 (*a*) are drawn only for the range 0–10 where the dependence of integrated reflexion on Q is fairly strong. At the abscissa 10, $\mathscr{R}^\theta$ has attained a value of a few times η as already predicted in a previous section. With further increase of $\frac{1}{\eta} Q \frac{t_0}{\gamma_0}$, $\mathscr{R}^\theta$ rises more and more slowly; in the case of the curve for $\mu = 0$, $\mathscr{R}^\theta$ is multiplied by a factor of only 2 when the abscissa is increased from 10 to 200.

The curves of Fig. 6 (*a*) could, in theory, be used for deriving Q values from measured reflexions, since in any given experiment the other factors are fixed. However, given the measured absolute value of the integrated reflexion, the exact determination of Q from the appropriate $\mu t_0/\gamma_0$ curve involves a knowledge of η, a not easily measured quantity. For this reason, practical use of the curves for accurate determination of Q beyond the linear portion is rather restricted. However, it may be noted that if the extinction is not too severe, the fractional error in Q, as read from the curves, will be very considerably less than the fractional error in η; so that even a rough value of η can be better than a total disregard of the extinction effect. A possible way of making a measurement of η in a minute crystal may be described in a later communication.

A major practical application of the curves is that of deciding upon the maximum thickness of crystal which can be permitted in a proposed investigation of a crystal which is not strongly absorbing. For this purpose they are recast into the form of Fig. 6 (*b*), where $\mathscr{R}^\theta/\eta$ is plotted against $\frac{1}{\eta} Q \frac{t_0}{\gamma_0}$ for various values of $\frac{1}{\eta}\frac{Q}{\mu}$. If the maximum Q value expected in a crystal analysis is fixed upon, the curves provide the greatest value of t_0 which does not incur an intolerable amount of extinction.

Table 1. *Values of* $\frac{1}{\eta} Q \frac{t_0}{\gamma_0}$ *when* $Q = 0{\cdot}02$ *and* $\gamma_0 = 0{\cdot}4$, *for various values of* t_0 *and* η

	Value of η		
Value of t_0	1′	5′	15′
0·1 mm.	1·6	0·3	0·1
1 mm.	16	3·2	1·1
1 cm.	160	32	11

As an example of the use of Fig. 6 (*b*), the criterion of 'thinness' for non-absorbing substances, equation (11), can be checked with it. Selecting the curve $\frac{1}{\eta}\frac{Q}{\mu}=\infty$, the abscissa at which the integrated reflexion departs from $y=x$ by 5 % can be read off at once. It can also be seen that there is negligible increase in this 5 % departure if the criterion of 'non-absorption' made in (16) is satisfied.

Travelling outwards along the curves in Fig. 6 (*b*) corresponds to taking a thicker and thicker crystal of fixed Q, μ and η. The lower curves for the reflexion method, which have small values of $\frac{1}{\eta}\frac{Q}{\mu}$, rise quickly to the limiting value $Q/2\mu$. This point is brought out in Fig. 7, where $\frac{1}{\eta}\mathscr{R}^\theta$ is plotted against $\frac{1}{\eta}\frac{Q}{2\mu}$ for an infinitely thick crystal. For small values of $Q/2\mu$ (as in the X-ray case) $\mathscr{R}^\theta=Q/2\mu$, whereas for larger values of $Q/2\mu$, as frequently in the neutron case, the integrated reflexion falls away from that quantity, and remains a small multiple of η over a wide range of values. It may be pointed out that for a limitingly large crystal, such as is assumed in Fig. 7, decreasing μ is equivalent to increasing the effective thickness of crystal taking part in the reflexion, so that the shape of the curve in Fig. 7 is similar to that of the topmost curve of Fig. 6 (*b*).

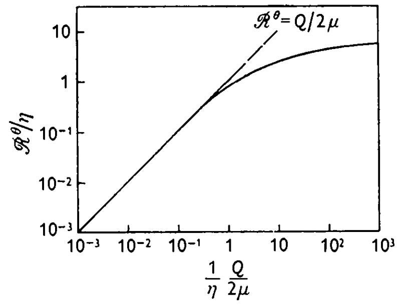


Fig. 7. The relation between $Q/2\mu$ and the integrated reflexion $\mathscr{R}^\theta$ for symmetrical reflexion from an ideally imperfect crystal of infinite thickness.

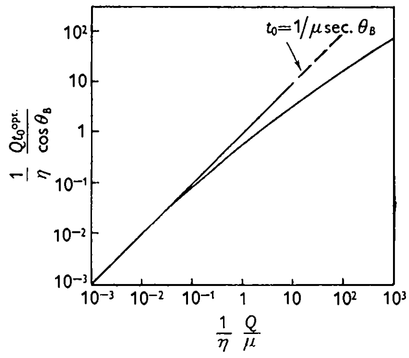


Fig. 8. Curve giving the thickness $t_0^{\text{opt.}}$ for maximum integrated reflexion from an ideally imperfect crystal plate by the symmetrical transmission method, taking account of secondary extinction.

For the transmission method, Fig. 6 (*b*) shows how the integrated reflexion eventually falls to zero with increasing t_0 in all cases where the true absorption is finite. The locus of the maxima is a curve giving the optimum thickness of mosaic slab for a crystal of given Q, μ and η. A calculation of this thickness ignoring secondary extinction is already familiar (Compton & Allison, 1935, pp. 418 and 422), and gives the value t_0 (optimum) $=1/\mu \sec\theta_B$. In Fig. 8 the $\frac{1}{\eta}Q\frac{t_0}{\gamma_0}$ value of the maximum integrated reflexion is shown according to the general theory; past the region of the thin-crystal law the optimum thickness of slab is reduced below $1/\mu \sec\theta_B$ by the added consideration of secondary extinction.

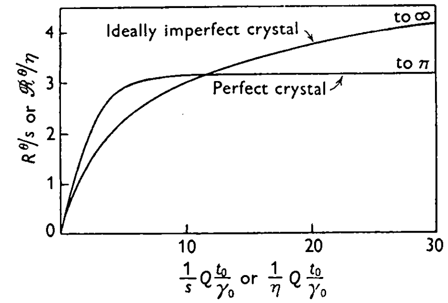


Fig. 9. Curves showing the effects of primary and secondary extinction on the integrated reflexion, by the reflexion method, from perfect (Ewald approximation) and ideally imperfect crystal plates.

Unsymmetrical diffraction from plane parallel plates

The general treatment given so far has been restricted to the symmetrical case, in which the reflecting planes are either parallel or perpendicular to the surface of the crystal plate. If the planes are obliquely inclined, it is obvious that the average path length within the crystal will be greater for the same reflexion, and different values for the integrated reflexion from an absorbing crystal must be expected. A calculation taking this into account will therefore involve γ_0 and γ_H, the direction cosines of the incident and diffracted beam vectors referred to the inward normal to the surface.

The equations (4.21) of Zachariasen (1944) may be solved without the simplifying condition $\gamma_0=|\gamma_H|$. The result in the reflexion method is simply that μ in equation (16) and Figs. 6 and 7 is everywhere to be replaced by

$$\mu'=\mu\,\tfrac{1}{2}(1+\gamma_0/|\gamma_H|); \tag{23}$$

the unsymmetrical reflexion method is therefore covered by the general discussion above. In the transmission method, however, the reflecting power comes to

$$\frac{\sigma}{(\sigma^2+\mu^2/G^2)^{\frac{1}{2}}}\sinh\left[(\sigma^2+\mu^2/G^2)^{\frac{1}{2}}t_0\right]e^{-(\sigma+\mu/\Gamma)t_0}, \tag{24}$$

with

$$\sigma=\frac{QW}{\gamma_0},\quad \frac{1}{\Gamma}=\frac{1}{2}\left(\frac{1}{\gamma_0}+\frac{1}{|\gamma_H|}\right),\quad\text{and}\quad \frac{1}{G}=\frac{1}{2}\left(\frac{1}{\gamma_0}-\frac{1}{|\gamma_H|}\right),$$

which is to be compared with the integrand of (18). Unfortunately, this new expression is not assimilable to (18) by any simple device, so that Figs. 6 and 8 cease to apply in the unsymmetrical transmission method, and must be redrawn in every instance.

4. PRIMARY AND SECONDARY EXTINCTION

The integrated reflexion curves which have now been plotted for non-absorbing crystals of both perfect and ideally imperfect types permit a rather illuminating comparison to be made between the primary and secondary extinction effects. We may consider first the reflexion method of Fig. 2 (*a*). The ideally imperfect crystal curve in Fig. 9 is the same as that for $\mu=0$ in Fig. 6; the other curve is taken from Fig. 1 for the perfect crystal. The two have been brought together in the following way. The abscissa of Fig. 1, $s't_0/\gamma_0$, has been written $\frac{1}{s}Q\frac{t_0}{\gamma_0}$. Comparison of the axes of the two graphs shows that the variables are similar in form, with s replaced in the mosaic crystal by η. Both s and η measure the width of the diffraction curve from the crystal, but in the mosaic crystal the width of the angular spread of the mosaic blocks has become an independent quantity, being, unlike s, not dependent on the structure factor. The graph for the ideally imperfect crystal is on a relatively smaller scale, as the relation $\eta \gg s$ is implicit in the theory.

Fig. 9 exhibits the essential contrast between the two forms of extinction. As the thickness of the crystal plate is increased, the characteristics of secondary extinction appear in the slower departure from the thin-crystal law, the rounder knee in the curve and the steady travel to infinity of the integrated reflexion. Both forms of extinction result in an early departure from the QV law with a subsequent reduction in the slope of the curve. On the other hand, where secondary extinction alone prevails, far greater Qt_0 values are covered by the thin-crystal approximation. In practice, η is of the order of $5'$, s $5''$, of arc, so that at an abscissa in Fig. 9 where the curves still approximate to the line $y=x$ the allowable value of t_0 for the same Q is some sixty times greater for the imperfect than for the perfect crystal.

With regard to the dependence of the integrated reflexion on the structure factor, the shapes of the primary and secondary extinction curves have different meanings, because s is directly proportional to F itself while η is not. For both curves the part close to $y=x$ indicates a proportionality of integrated reflexion to F^2. With primary extinction, where the curve is virtually horizontal, extinction is practically complete and the integrated reflexion is proportional to F, whereas the same result for the ideally imperfect crystal would demand a parabolic shape for the secondary extinction curve.

As it happens, the approximation to a parabola is very close in the reflexion method over quite a large range of practical cases. The integrated reflexion curve is within 5 % of the parabola $\mathscr{R}^\theta=0\cdot96\ (\eta Q t_0/\gamma_0)^{\frac{1}{2}}$ over the range 1·9–13 of $\frac{1}{\eta}Q\frac{t_0}{\gamma_0}$. Over this range, therefore, we may conclude that on the assumption of a gaussian angular distribution of mosaic blocks, severe secondary extinction in non-absorbing ideally imperfect crystals results in the integrated reflexion from a face being proportional to F, in analogy with the same rule for severe primary extinction. The constant of proportionality, however, could only be predicted if η were measured. In the next section, an experimental confirmation of this result will be quoted.

It is shown by Zachariasen (1944, p. 134) that the integrated reflexion curve for the perfect crystal using the transmission method oscillates with diminishing amplitude about its final ordinate $\frac{1}{2}\pi$. The ideally imperfect crystal curve for transmission, however, retains the steady form as shown in Fig. 6. The approximation to a parabola is here $\mathscr{R}^\theta=0\cdot85\ (\eta Q t_0/\gamma_0)^{\frac{1}{2}}$ and is accurate to 5 % only over the smaller range 1·3–6·1 in $\frac{1}{\eta}Q\frac{t_0}{\gamma_0}$.

5. NEUTRON CRYSTALLOGRAPHY

A difficulty of neutron diffraction work at the present day is the comparative weakness of the available sources of neutrons. Consequently, particular interest attaches to those methods of procedure which permit the largest crystal specimen and hence the most powerful diffracted beam.

It must also be stressed that the case of neutron diffraction involves quite a different approximation in crystallographic theory from that of X-rays. As we have seen, absorption is large or small according to whether μ is large or small compared with $Q/\eta\sqrt{(2\pi)}$. This quantity is roughly of the order of magnitude 50 for X-rays and 5 for neutrons. With X-rays μ is of the order of 10^2 cm.$^{-1}$, but with neutrons it is usually of the order of 10^{-1} cm.$^{-1}$.

The major consequences of this fact are those pointed out in § 3, that the neutron beam can always be expected to range throughout the crystal and that the relative importances of absorption and extinction are the reverse of those familiar with X-rays. In the highly absorbing case, the incident beam is limited to a thin surface layer, and the integrated reflexion for 'thick' mosaic crystals is $Q/2\mu$, remaining proportional to F^2 just as in a small crystallite. For neutrons, however, this does not apply, and the integrated reflexion is a complicated function of Q, μ and η.

Now if $\mathscr{R}^\theta/\eta$ is a simple function of Q of the form aQ^b, then the ratios of a series of values of integrated reflexion measured in arbitrary units are sufficient to provide the ratios of the respective Q values. But if the function of Q is any more complicated than aQ^b, it will not be possible to deduce relative Q's from a set of relative $\mathscr{R}^\theta$ readings without absolute measurements of some kind. There are two regions where the relation between $\mathscr{R}^\theta$ and Q is simple. These are the regions where $\mathscr{R}^\theta$ is very nearly proportional to $Q^{\frac{1}{2}}$, and where the 'thin crystal law' $\mathscr{R}^\theta = QV$ is valid.

Large crystals

In the reflexion method for a large mosaic crystal slab the $Q^{\frac{1}{2}}$ law holds to within 5 % over about a sevenfold range in $\frac{1}{\eta} Q \frac{t_0}{\gamma_0}$ as mentioned in the previous section. Table 1 shows that practical values of t_0 can be chosen such that $\frac{1}{\eta} Q \frac{t_0}{\gamma_0}$ will lie in this range for a large variety of combinations of Q and η. For example, a crystal 1 cm. thick would give proportionality to $Q^{\frac{1}{2}}$ over a range of Q from 0·003 to 0·02 if η were 15′: if η were only 1·5′, then the same range would be covered by a crystal 1 mm. thick. The values are calculated for $\gamma_0 = 0{\cdot}4$.

This conclusion explains a result given by Fermi & Marshall (1947) in their work on the single-crystal reflexion of neutrons, which was very puzzling as stated in their account. They found that the reflectivity was more nearly proportional to the structure factor than its square, i.e. to $Q^{\frac{1}{2}}$ rather than to Q. This could at first sight be taken as indicating primary extinction and perfect crystals, which would be surprising. However, as we now see, the readings are quite compatible with the idea that their crystals were mosaic.

In fact, Fermi & Marshall measured an instantaneous peak intensity, and in the absence of experimental details it is difficult to decide whether this would truly represent the maximum ordinate of the diffraction curve, or whether it would more nearly correspond to an integrated reflexion. In any case, the dependence of the maximum ordinate on $\frac{1}{\eta} Q \frac{t_0}{\gamma_0}$ is very similar to that of the integrated reflexion in the range of values concerned and has an appreciable, though slightly smaller, parabolic region. If the series of intensity readings given in their Table 1 is plotted against Q/γ_0, the resulting curves are found to include various sections of our secondary extinction curves for small μ; namely, the regions of the thin-crystal law and the parabolic law, and the region of very severe extinction where $\mathscr{R}^\theta$ increases only slightly with increase of Q.

The purpose of Fermi & Marshall's experiment was to compare with expectation sets of F values for a given substance, in order to determine whether certain nuclei were scattering in phase or antiphase. In nuclear physical experiments of this kind, in which crystals are deliberately chosen having predictable structure factors, it would be feasible to make quite accurate comparisons of structure factors on the simple assumption that they were proportional to the integrated reflexions. A crystal slab would be specially cut for each reading so that the anticipated integrated reflexion would be in the middle of the parabolic region of the curve, that is, to satisfy $t_0/\gamma_0 = 4\eta/Q$. The range of $\frac{1}{\eta} Q \frac{t_0}{\gamma_0}$ covered by the parabolic law then permits a considerable tolerance on the estimate of η without loss of accuracy in the measurement of F.

Using the transmission method, the corresponding region of an approximate $Q^{\frac{1}{2}}$ law is more restricted and is centred at a lower value of $\frac{1}{\eta} Q \frac{t_0}{\gamma_0}$.

Small crystals

In structure-analysis work, a very large number of structure factors have to be measured for each substance investigated, and the usual goniometric technique is indispensable. For a neutron diffraction study, the region of the $Q^{\frac{1}{2}}$ law might be expected to permit the use of thicker crystals without the need of absolute measurements, and hence be desirable on grounds of intensity. Unfortunately, it appears that this method loses its advantages, when applied to crystal-analysis technique.

In the first place, it must be remembered that the detailed solutions given in this paper are calculated only for plane parallel plates. Crystals cannot always be artificially made in this form, and the same solutions cannot be extended to crystals of different shape without further justification. Back-reflexion and forward-reflexion spots will correspond respectively to the reflexion and transmission methods of Fig. 2, inasmuch as all the ray paths pass through the crystal in the latter case but not in the former; but in the conventional small 'round' crystal the case of diffraction at intermediate angles is not an approximation to either method. It is highly improbable that any technique relying on severe secondary extinction could be usefully developed for crystals of any but the simplest shapes, since the measured reflexions will require to be taken at all angles to the crystal.

Moreover, even where a crystal plate can be used, the intention of the experiment is to measure a great range of structure factors, using only one crystal. The extent of the parabolic law, however, is only sufficient to determine relative Q values to 5 % over a 7 : 1 range of magnitudes even if η is known precisely. In order to avoid this limitation an absolute calibration curve of the type shown in Fig. 6 (*a*) would need to be plotted.

The region of the thin crystal law is therefore the most attractive for structure analysis if complicated absolute measurements are to be avoided. Here the practical difficulty is that of detecting the diffracted beam at all. For the present we shall only comment on the size of the crystal. The maximum thickness of crystal plate to which the QV law can be applied can be seen from the figures or from the thin-crystal criterion (11). It is of the order of a small fraction of a millimetre, which might be just practicable for neutron crystallography.

6. SUMMARY

The paper arises from the desire to extend the theory of secondary extinction to non-absorbing crystals, since absorption coefficients to neutrons are usually a small fraction of a unit. Neutron diffraction demands an altogether different approximation in crystallographic theory from that used for X-ray work. In absorbing crystals, the incident beam cannot penetrate sufficiently far for extinction to become serious, and the integrated reflexion $Q/2\mu$ remains proportional to F^2, just as in the small crystallite. This does not occur with non-absorbing crystals, and in order to avoid the effects of extinction the crystals must be very thin indeed.

A study of the equations controlling the distribution of intensity inside non-absorbing crystal plates, shows that in the reflexion method of Fig. 2 (*a*) the intensity of the incident beam is reduced linearly within the crystal as shown in Fig. 3 (*a*); in the transmission method the reduction has the exponential form of Fig. 3 (*b*). The penetration into the crystal is therefore always complete, and the reflexion does not take place in a thin surface layer only, as it does with perfect or highly absorbing crystals.

Diffraction curves from non-absorbing crystals using the reflexion method are given in Fig. 4. For weak reflexions from thin crystals, the curve has the shape of the mosaic block angular distribution function, which is assumed to be gaussian with a standard deviation η, the 'mosaic spread'. With thicker crystals and stronger reflexions the diffraction curve tends to unit amplitude over the greater part of the range of angle in which appreciable reflexion occurs, so that the integrated reflexion, which is the area under this curve, is of the order of η and ceases to depend strongly on Q. The departure from the QV law, paralleling the onset of secondary extinction, is shown in curves for crystals of different mosaic spread in Fig. 5.

A 'thin crystal', using either the reflexion or the transmission method, is found to be one having $t_0/\gamma_0 < \eta/4Q$, γ_0 being the cosine of the angle of incidence to the slab. This thickness is only of the order of 0·1 mm. in the case of neutron diffraction. A crystal is said to be 'thick' if $t_0/\gamma_0 > 50\eta/Q$. These criteria apply to 'non-absorbing' crystals, which are defined as those with $\mu < Q/50\eta$ which is of the order of 0·3 cm.$^{-1}$ 'Absorbing' crystals, whose integrated reflexion comes within 5% of $Q/2\mu$, have $\mu > 4Q/\eta$, which is about 50 cm.$^{-1}$.

The general results for the integrated reflexion for crystal plates of intermediate absorption and thickness are exhibited in detail in Fig. 6. The calculations lead to curves showing the dependence of integrated reflexion on $Q/2\mu$ (Fig. 7), and giving the optimum thickness of a crystal slab for measurements by the transmission method (Fig. 8). This latter quantity is usually taken to be $1/\mu \sec \theta_B$ when secondary extinction can be ignored.

As the integrated reflexion from 'non-absorbing' crystal plates by the reflexion method falls away from QV with increase of thickness or structure factor or decrease of mosaic spread, it passes through a 7 : 1 range of practical values in which it is closely proportional to F. The centre of the range is given by $t_0/\gamma_0 = 4\eta/Q$, which is usually of the order of millimetres. This result explains an observation of Fermi & Marshall that the apparent reflectivity of crystals to neutrons was proportional to the structure factor.

The formulae for the integrated reflexion permit an interesting analogy to be drawn between primary and secondary extinction. The curves of Fig. 9, which are explained in the text, bring the two cases together and show that η has a similar role to the quantity s in perfect-crystal theory.

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References

Bacon, G. E. & Thewlis, J. (in the Press). *Proc. Roy. Soc.* A.

Compton, A. H. & Allison, S. K. (1935). *X-rays in Theory and Experiment*. New York: Van Nostrand.

Fermi, E. & Marshall, L. (1947). *Phys. Rev.* **71**, 666.

Lonsdale, K. (1947). *Miner. Mag.* **28**, 14.

Zachariasen, W. H. (1944). *Theory of X-ray Diffraction in Crystals*. New York: Wiley.