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Asymmetric Bragg Reflexion and Extinction-Free Measurement

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With an extended-face crystal specimen whose surface has been polished optically flat, the normalized intensity [Mathieson, *Acta Cryst.* (1975), A**31**, 769–774] has been measured for both positive and negative asymmetry to the practical limits permitted by the experimental setup. By contrast with the results with an abraded surface (Mathieson, *loc. cit.*), the normalized intensity for the optically flat surface increases from the value at the symmetric position, symmetrically with increase in magnitude of the asymmetry. The increase is interpreted as due to a decrease in extinction arising from the reduction of contributions from single and multiple scattering as the surface progressively plays a greater role in the diffraction process. As a consequence, the normalized intensity is free of extinction at the positive and negative limits of asymmetry and can, therefore, at these limits, be equated exactly with the intensity derived from simple kinematical theory, *viz.*

$$\varrho_0'(0)=\frac{1}{2\mu_0(\lambda)}\,\frac{1}{\sin 2\theta}\left(\frac{Ne^2}{mc^2}|F|\right)^2\lambda^3\left(\frac{1+\cos^2 2\theta}{2}\right).$$

Under these circumstances, the various terms in the formula are exactly defined and the values of structure factors derived will therefore be absolute. A test has been made with the 200 reflexion of LiF and Cu $K\bar{\alpha}$ radiation, in which the ratio of the extrapolated value (present estimate for ideally-imperfect crystal) is compared to the symmetric value for a nominally perfect crystal with the corresponding theoretical ratio by the use of the formulae of Hirsch & Ramachandran [*Acta Cryst.* (1950), **3**, 187–194]. Comments are offered on the traditional attitude to the symmetric reflexion technique and on the significance of the present experiment for the general basis of deriving extinction-free data.

Introduction

In the last 60 years or so, the subject of asymmetric Bragg reflexion in relation to intensity has received only fragmentary attention, usually associated with monochromator design. This neglect has meant that the opportunity of recognizing an experimentally simple procedure to obtain extinction-free data has been delayed until now.

The first observations on asymmetric reflexion were made by Bragg (1914) in the first quantitative measurements with a diffractometer (ionization spectrometer). He noted that the intensity diffracted from an extended-face crystal depended on the slope, α, of the crystal surface to the crystal plane being measured, as viewed by the incident beam, the angle of diffraction being 2θ. When the angle of incidence was $\theta-\alpha$ (negative asymmetry), Fig. 1(*a*), the integrated intensity was larger than when it was $\theta+\alpha$ (positive asymmetry), Fig. 1(*c*). The difference was ascribed to the different absorptive paths through the specimen. He advised that the two measurements, one for $-\alpha$ and the other for $+\alpha$ (the latter obtained by turning the specimen around), should be averaged and that this mean value should be taken to correspond to the value for the symmetric reflexion, *i.e.* with $\alpha=0°$ (Fig. 1*b*).

This early comment on the relevance of asymmetric-reflexion measurement appeared to establish a viewpoint concerning symmetric Bragg reflexion being the appropriate and proper reference. This viewpoint, lent additional weight by Darwin's (1914) development of the theory of X-ray reflexion,* has dominated studies of reflexion from extended-face crystals and, as a consequence, systematic exploration of the region of

* Note the comment by Darwin (1914, p. 315) concerning the symmetric case: 'This gets rid, both for theory and experiment, of a great deal of rather complicated geometry, which is useful in investigating the structure of crystals, but *has nothing to do with the nature of reflexion*' (my italics).

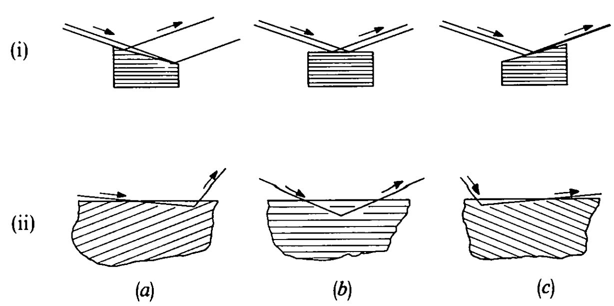

Fig. 1. Reflexion from an extended-face crystal: (*a*) asymmetric with $-\alpha$ (negative asymmetry), (*b*) symmetric with $\alpha=0°$, (*c*) asymmetric with $+\alpha$ (positive asymmetry). Series (i) illustrates the change in the breadth of the diffracted beam relative to that of the incident beam. Series (ii) illustrates the difference in beam path, the total path for incident-plus-diffracted beam being the same in each. This series draws attention to the change in depth-penetration, z, for equal total path with change in asymmetry. In the limits, $\beta=\pm1$, $z=0$.

asymmetry in respect of intensity has been discouraged. This may be contrasted with the use of asymmetric reflexion for determination of X-ray refractive indices, *e.g.* Davis & Terrill (1922) and later work (see James, 1948).

In fact, it came to be accepted generally that the effect of asymmetry on intensity was essentially geometrical and therefore that such measurements could be corrected to the reference symmetric value by an appropriate factor, $(1-\cot\theta\tan\alpha)$, (James, 1948, p. 279). This viewpoint has continued to retain its status in standard works, *e.g. International Tables for X-ray Crystallography* (1959) p. 291; Weiss (1966) equation 123. It is understandable, therefore, that with the weight of opinion there appeared to be little reason for active study of the region of asymmetry.

Concern with asymmetric reflexion was activated however from a somewhat unexpected quarter. Stephen & Barnes (1935) outlined a new technique for obtaining sharp X-ray powder patterns involving asymmetric reflexion from a flat powder specimen and, in passing, proposed an interesting method of obtaining a narrow beam of plane-polarized X-rays which involved asymmetric reflexion from a single crystal. It was on the basis of this suggestion that Fankuchen (1937) devised a 'condensing' monochromator. Some time later, interest in this type of monochromator led to a systematic experimental investigation of the positive asymmetry region (Fig. 1*c*) by a group at Cambridge University, England (Evans, Hirsch & Kellar, 1948). Their work was the first to show that the geometrical factor did not represent the whole story. They drew attention to the existence of the 'surface layer' produced by light abrasion and its effect on the diffracted *specific intensity* (Gay & Hirsch, 1951; Gay, Hirsch & Kellar, 1952; see definition on p. 613). Much later the development of a 'defocusing' monochromator (Mathieson, 1975*a*) led to an extension of the work into the negative asymmetry region (Fig. 1*a*) and to an examination of *integrated intensity* over both regions by Mathieson (1975*b*) who pointed out, *inter alia*, the relevance of these studies to the standard intensity formula.

Basically, the work referred to above was of an experimental nature. Apart from the treatment by Darwin (1922, equation 7.2), only one theoretical investigation of reflexion has given serious consideration to the aspect of asymmetry. This was the study by Hirsch & Ramachandran (1950) of the reflecting power of perfect absorbing crystals in relation to various factors. There it was suggested that 'accurate determinations of structure factors may be made by use of asymmetric reflexions for which the integrated reflexion becomes more nearly independent of the texture of the crystals'. Only one practical test of this possibility was made (Gay, 1952). No further exploration of this method of determining structure factors has taken place until the present investigation on asymmetric reflexion with an extended-face crystal surface polished optically flat. This new study has shown that the technique can achieve extinction-free intensity data by extrapolation to the limits of asymmetry at which the process of diffraction matches the requirements of the simple kinematical theory. A brief report has been presented elsewhere (Mathieson, 1976).

Observations

The experimental procedure was largely as detailed in Mathieson (1975*b*); hereinafter M75. The only difference was that the crystal boule of LiF, cut at 19·3° to the 200 plane ($\theta=22{\cdot}5°$ for Cu $K\alpha$), was ground and then polished to an optically flat finish with a maximum deviation of *ca* one fringe over the working area.

Measurements of the integrated intensity of 200 by $\omega/2\theta$ scan were carried out at 10° intervals in φ over the full range of φ. Measurements at φ and $180°-\varphi$ correspond to the angle $+\alpha$ and those at $180°+\varphi$ and $360°-\varphi$ to the angle $-\alpha$ (see Fig. 3 in M75).

Combination of the four values at φ, $180°-\varphi$, $180°+\varphi$ and $360°-\varphi$ yields the mean of values at $+\alpha$ and $-\alpha$, the variation of this mean with $|\alpha|$ being shown in Fig. 2 (*cf.* Fig. 4 of M75). A general comment may be offered here that the results presented in both these figures show serious deviation from the constancy implied in the suggestion of Bragg (1914) and shown by the dashed line in Fig. 2. The results observed for the optically flat surface have an opposite trend to that for the abraded surface.

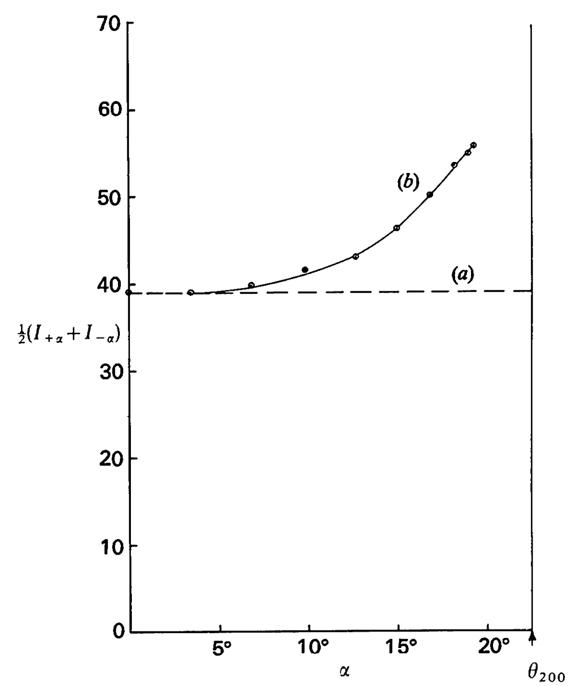

Fig. 2. Variation of the average value of $(I_{+\alpha}+I_{-\alpha})$ with $|\alpha|$. (*a*) expected variation according to Bragg (1914), (*b*) experimental results.

The variation of the experimental intensities with α over the major part of the range, with limits at $-\theta$ and $+\theta$, is depicted in Fig. 3 as curve (*b*). The geometrical function, $1-\cot\theta\tan\alpha$ (see equation 1 in M75) or $1-\beta$ if we define $\beta=\cot\theta\tan\alpha$, would correspond to an intensity trend shown as curve (*a*). The two curves, (*a*) and (*b*), are arbitrarily scaled to coincide at $\alpha=0°$, *i.e.* $\beta=0$ (*cf.* Fig. 5 of M75).

Following M75, introduction of the factor, $(1-\beta)^{-1}$, normalizes the measurements to effectively equal scattering volume at the symmetric position, $\beta=0$. The results are shown as curve (*b*) in Fig. 4. The theoretical curve, based on equation (2) of M75 is shown as curve (*a*). Again, the curves (*a*) and (*b*) are arbitrarily scaled to coincide at $\beta=0$ (*cf.* Fig. 6 of M75).

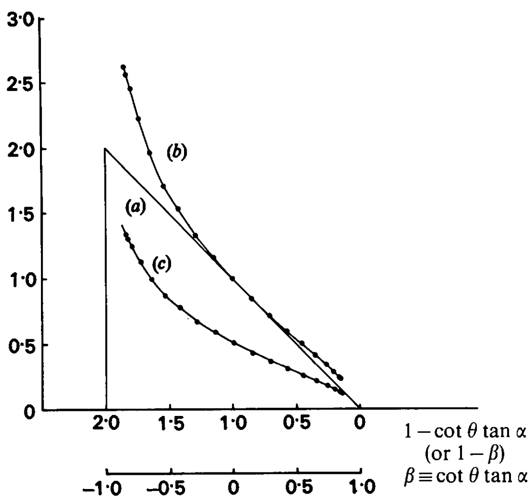

Fig. 3. Plot of measured intensity against β (also $1-\beta$, see M75, Fig. 5): (*a*) theoretical, based on the geometrical factor alone, (*b*) experimental data, arbitrarily scaled to approximate coincidence at $\beta=0$. When the absolute scale has been established, curve (*b*) is adjusted to curve (*c*).

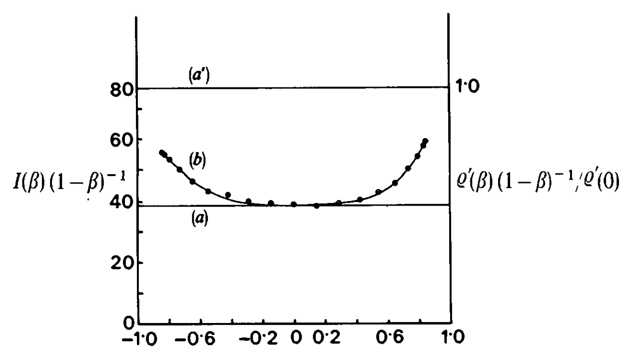

Fig. 4. The normalized intensity plotted against β. This curve, (*b*), and that for the theoretical curve, (*a*), for the 'ideally imperfect' crystal are arbitrarily brought to coincidence at $\beta=0$. When the absolute scale has been established, curve (*a*) is adjusted to curve (*a'*).

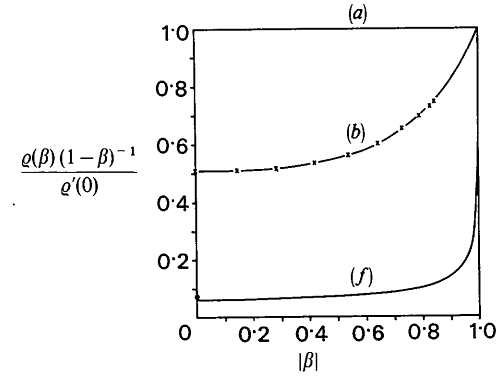

Fig. 5. Plot of the average of values of normalized intensity at positive and negative values of β (curve *b*), extrapolated to $|\beta|=1$. Curve (*a*) is the line for the 'ideally-imperfect' crystal which determines the scale of unity on the right. Curve (*f*) is the theoretical curve for 200 of LiF with Cu $K\bar{\alpha}$ radiation and $\mu_0=32{\cdot}2$ cm^{-1} calculated from H & R (see Fig. 6).

Comparison of Figs. 3 and 4 shows very clearly that correction for the geometrical component reveals the functional form of the remaining factor(s) whose physical basis remains to be identified. The symmetry of the factor(s) in terms of the variable β is obvious, curve (*b*) in Fig. 4 being essentially symmetric about $\beta=0$. The explanation for the deviation from exact symmetry seems most likely to be as follows.* Orientation of the crystal to ensure that the normal to the crystal plane under study is exactly parallel to the φ axis is not a straightforward procedure. Orientation parallel to $\varphi=0°/180°$ (see Fig. 2 of M75) can be reasonably well established by equalizing the intensities. However, parallel to $\varphi=90°/270°$, the intensities are markedly different (Fig. 3), so that the question of the proper adjustment is not clear and adjustment is, at present, attempted by close inspection of the peak scan and peak 2θ position. Any error in this setting will show up as an asymmetry of the normalized curve since the values would appear at $(+\beta+\Delta\beta)$ and $(-\beta+\Delta\beta)$ rather than at $+\beta$, *i.e.* the curve would be simply displaced along a symmetric locus.

This being so, the averaging of the normalized intensities at nominal $+\beta$ and $-\beta$ is the obvious step to correct for the error $\Delta\beta$. The resultant average for the present data is shown in Fig. 5, curve (*b*).

As a consequence of the deviation from exact symmetry in Fig. 4, the averages in Fig. 5 at higher $|\beta|$ differ slightly from the corresponding averages in Fig. 2, since the normalized values in positive and negative regions are of similar magnitude whereas, for the unnormalized, there is considerable disparity in magnitude. With exact symmetry in Fig. 4, the results in Figs. 5 and 2 would be identical.

* Another factor which may have a role to play is the different wavelength dispersion in the positive and negative asymmetry regions, while the possibility that there is a real but minor difference between the form of approach to the limits $\beta=+1$ and -1 should not be overlooked. Further investigations with an improved experimental setup will be required.

This then is about as far as one can proceed with the data as measured and following the data treatment developed in M75. It is now necessary to look more closely at the process of asymmetric diffraction and identify the physical factor associated with the new effect whose trend is shown in Fig. 4.

Interpretation

The new effect, as displayed in Fig. 4(*b*) has several characteristics which, taken together, signal an observation of considerable interest and significance.

The main characteristics are: (i) the normalized integrated intensity increases with increase in asymmetry, $|\beta|$; (ii) the normalized integrated intensity is essentially symmetric about $\beta=0$; (iii) the magnitude of the normalized intensity locates the situation nearer to the kinematical limit than to the dynamical limit.

The most striking of these characteristics is, of course, the increase in intensity. Since the basic geometrical factor has been already taken into account in deriving the normalized intensity, the most probable reason for an increase in intensity is a trend with asymmetry which affords a closer approach to the upper limit of diffracted intensity set by the kinematical formula; or, put in another way, by a decrease in the effect of extinction. Basically, extinction is a concomitant of diffraction whether the latter is coherent (primary extinction) or incoherent (secondary extinction) (Darwin, 1922). So why should asymmetric reflexion be relevant to this decrease in the effect of extinction? The second characteristic noted above provides a clue. The fact that the behaviour is largely symmetric about $\beta=0$, the symmetric reflexion position (Fig. 1*b*), recalls the earlier similar observation in M75, in relation to the 'surface layer', that this symmetry about $\beta=0$ is associated with the symmetry of the total path of the incident-plus-diffracted beams. The comparable situations for an equal total path for the regions of negative and positive asymmetry and for the symmetric position, to focus attention on the role of the surface, are illustrated in Fig. 1(ii).

Let us therefore consider the role of the beam path in relation to asymmetric Bragg reflexion. For the case of negative asymmetry, Fig. 1(*a*) (ii), the incident beam enters the surface at a progressively more shallow angle as $\beta \to -1$. When diffraction occurs, the beam exits after a progressively shorter traverse of the crystal. As a result, the opportunity for, and hence probability of successive scattering events progressively decreases with the approach to $\beta=-1$. Not only that, but the higher the order of scattering, the more rapidly does the probability decrease. Thus, in the diffracted-beam direction, the probabilities rank as $1>3>5>\ldots>(2n+1)$-scattering, so that near the limit, single-scattering events contribute most to the intensity to be measured by the detector. However, as $\beta \to -1$, the *specific intensity* [the intensity per unit area cross-section of the diffracted beam (Evans, Hirsch & Kellar, 1948)] tends to zero. Now the total intensity is made up of specific intensity contributions from a progressively larger surface area with a proportionate increase of the diffracted-beam cross-section. The total, *i.e.* integrated, intensity at the limit does not go to infinity but to a definite value which is twice the theoretical kinematical value (James, 1948; Hirsch & Ramachandran, 1950). The normalized integrated intensity is then equal to the theoretical kinematical value in this limit.

For the case of positive asymmetry, Fig. 1(*c*) (ii), the incident beam enters the surface at a progressively steeper angle as $\beta \to +1$. The diffracted beam in its travel to the surface has, for this configuration, ample opportunities for successive scattering. However, as the asymmetry increases, the probabilities of the higher-order multiply-scattered photons *reaching the detector* changes so that again the higher-order components decrease more rapidly than the lower-order components. Towards the limit, only single scattering gives a significant contribution to the intensity reaching the detector. In the limit, even single-scattering events are eliminated and the total integrated intensity is zero – although the specific intensity rises to twice the theoretical kinematical value (Hirsch & Ramachandran, 1950) and the normalized intensity to the theoretical kinematical value. In essence, the change of asymmetry, starting from the symmetric position, $\beta=0$, may be thought of as acting as a progressive filter to remove $(2n+2)$-scattering events from the transmitted beam and to modify the relative contributions of $(2n+1)$-scattering events in the diffracted beam, the higher-order components being reduced more rapidly. Alternatively, we may say that the interaction between the incident and diffracted beams is progressively decoupled. In the negative asymmetry limit, the specific intensity goes to zero while in the positive asymmetry limit, the integrated intensity goes to zero. In both limits, the normalized intensity goes to the theoretical kinematical value.

So the process of asymmetric reflexion, as it tends to the limits of $\beta=\pm 1$, brings the physical condition of the diffraction process nearer to (and, in the limit, equal to) the basic assumption underlying the formula associated with the simple kinematical theory. That assumption is that as the X-ray beam progresses through the crystal it only loses energy due to simple absorption. In this, the simplest form of the kinematical theory, the process of diffraction does not abstract energy from the incident beam. As a result, some, *e.g.* Kato (1974), have been critical of the relevance of the theory. However, such critics have failed to note that the theory is perfectly valid provided one satisfies the basic requirement that the total or specific diffracted energy is zero. Measurements which accord with this assumption are, by definition, free of extinction.

Hence, what is required to achieve extinction-free data with the use of the technique of asymmetric reflexion is to *extrapolate measurements to the limiting values* $\beta=-1$ *and* $\beta=+1$.

The rather detailed outline of the physical picture of diffraction over the full range of asymmetry is given here because this aspect of the subject has received little attention in the past in respect of intensity.

The only experiment, similar in type to the present one, which displayed this characteristic of increase in intensity with asymmetry was one carried out some 25 years ago. Gay (1952) used the technique of the Cambridge group, *i.e.* measurement of specific-intensity change in the positive asymmetry region, to assess the capability of this method for the establishment of accurate structure factors. Two reflexions of quartz, $10\bar{1}1$ and $20\bar{2}2$, were selected. The specimens used were two natural crystals, carefully chosen and tested by interferometric and X-ray methods to ensure that they were relatively free of highly disordered material on their surfaces. There is however no indication to show that tests for the overall flatness were of concern. It was assumed, referring to the crystal interior, that 'the texture of these crystals is probably intermediate between the theoretically perfect and mosaic states'. No treatment was given to the surface of these crystals prior to the measurements. The results were compared with the theory of Hirsch & Ramachandran (1950) (hereinafter H & R) for perfect absorbing crystals.

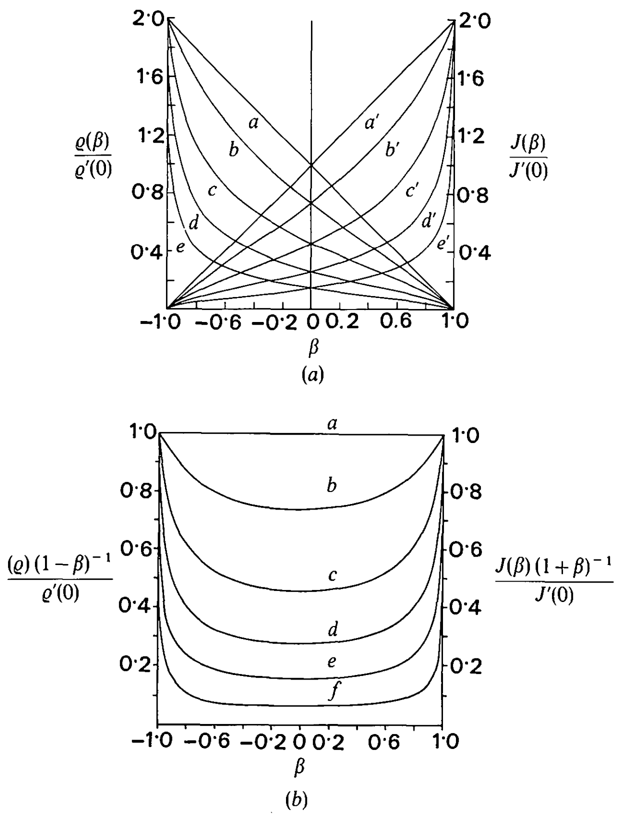

Fig. 6. (*a*) Reproduction of the curves in Fig. 2 of H & R. Line (*a*) is for the theoretical ideally imperfect crystal (with zero secondary extinction). Lines (*b*) (*c*), (*d*) and (*e*) are for a perfect crystal with $|g(0)|$ values as designated in Fig. 2 of H & R. (*b*) Conversion of these curves to a normalized basis, for both integrated intensity, ϱ, and specific intensity, J. With the addition of the curve (*f*), calculated from H & R for 200 of LiF with Cu $K\bar{\alpha}$ radiation and $\mu_0=32{\cdot}2$ cm^{-1}.

For our present purposes it is necessary to give an outline of the treatment of H & R. They carried out a theoretical investigation of the integrated Bragg reflexion of perfect absorbing crystals as a function of the degree of asymmetry, the structure factor and the absorption coefficient. These results were related to the corresponding theoretical integrated reflexion for a mosaic crystal, the expression for which was derived from James (1948). We should note at this stage that the latter formula relates to an ideally mosaic, absorbing crystal and ignores not only the existence of multiple diffraction but even the diminution of the transmitted beam due to previous single-scattering events. H & R presented the variation of intensity with asymmetry in a very compact form, expressing the relation of the perfect-crystal intensity, $\varrho(\beta)$, at asymmetry β, to the corresponding ideally mosaic-crystal intensity at the symmetric position, $\beta=0$, $\varrho'(0)$, as a ratio, $\varrho(\beta)/\varrho'(0)$. Curves were given for a series of values of $|g(0)|$, specified in their paper; $|g(0)|$, *inter alia*, is inversely dependent on $|F|$. For ease in reference and because they are required for our discussion, their curves (Fig. 2 in H & R) are reproduced here as Fig. 6(*a*). The original curves were presented, not only for the integrated intensity, ϱ, but also for the specific intensity, J. The mutual symmetry of $\varrho(\beta)/\varrho'(0)$ and $J(\beta)/J'(0)$ about $\beta=0$ should be noted. When the ordinate is modified to present the normalized integrated intensity, Fig. 6(*b*), the skewing influence of the geometrical factor in Fig. 6(*a*) is removed and the internal symmetry of this function about $\beta=0$ is made evident.*

The corresponding normalized specific intensity curves, $J(\beta)/J'(0).\ (1+\beta)^{-1}$, are, of course, coincident with those for the normalized integrated intensity.

My first reaction to the experimental results in Figs. 2–5 was to assume that they were directly related to the theoretical results of H & R and that the measurement of asymmetric reflexion with an optically flat finished surface could provide some information concerning the primary extinction condition of the specimen. Further consideration of the third characteristic noted above, namely the level of diffracted intensity, and of etching experiments to be described later, led to a realization that the extinction in my case was more of the 'secondary' or incoherent type. It was concluded therefore that the effect of asymmetry on intensity was not limited to the case of the perfect crystal, *i.e.* coherent interaction,

* (*a*) The actual preparation of Fig. 6(*b*) was from a magnified version of Fig. 2 of H & R.

(*b*) It can be shown that the relation

$$\frac{\varrho(\beta)}{\varrho'(0)}\cdot\frac{1}{1-\beta}=\frac{|g(0)|}{\sqrt{(1-\beta^2)}\,.\exp\left\{-\left[|g(0)|\frac{1}{\sqrt{(1-\beta^2)}}+\ln\frac{32}{3\pi}\right]\right\}+|g(0)|}$$

holds. This is seen to be an even function of β (*i.e.* symmetric).

as treated by H & R, but that a similar functional dependence occurs in the case of the mosaic crystal, *i.e.* incoherent interaction. So, for real crystals, there would be a family of curves, dependent on the level of secondary extinction and on the magnitude of the structure factor. Since the interaction is spatially incoherent in the case of secondary extinction, the curves for comparable structure-factor values would be more shallow than those for the case of primary extinction (Fig. 6*b*).* We may provisionally accept that the family of curves of normalized intensity $\varrho_s'(\beta)/\varrho_0'(0)$ against β will also be symmetric about $\beta=0$ and converge to unity at $\beta=-1$ and $\beta=+1$. Possible forms of theoretical curves for secondary extinction are under consideration.

So, for secondary as well as primary extinction and therefore for intermediate cases where the level of coherence/incoherence is not clear-cut and which may be described as involving a 'mixture' of primary and secondary extinction, extrapolation of normalized values to $\beta=-1$ and $+1$ will yield numerical values which are free of extinction. At this limit, the relevance of the distinction between primary and secondary extinction vanishes.

Being free of extinction, these intensity values can be equated to those given by the simple kinematical formula for Bragg reflexion from extended-face crystals, namely

$$\varrho_0'(0)=\frac{Q}{2\mu_0(\lambda)}$$

$$=\frac{1}{2\mu_0(\lambda)}\,\frac{1}{\sin 2\theta}\left(\frac{Ne^2}{mc^2}|F|\right)^2\lambda^3\left(\frac{1+\cos^2 2\theta}{2}\right). \quad (1)$$

The formula is well-defined in respect of those factors – the absorption coefficient, the power to which the wavelength and the bracket containing $|F|$ are raised and the polarization factor – which are modified under extinction. Furthermore, with extended-face crystals, the question of placing intensity measurement on an absolute basis is experimentally straightforward, so that combination of these two circumstances means that the method is capable in principle of establishing values of structure factors which are absolute.

Numerical aspects

In the *Observations* section the scale relation of the experimental data, curves (*b*) in Figs. 3–5, to the corresponding theoretical curves (*a*), was not known. They were therefore arbitrarily made to coincide at the symmetric position, $\beta=0$. It is evident from the *Interpretation* above that use of that point of coincidence is quite erroneous since it obscures scale relations, the proper locations for coincidence being at $\beta=+1$ and $\beta=-1$. Although not attainable experimentally, extrapolation to these limits (or to the limit, $|\beta|=1$, in Fig. 5) can define these points and hence establish the unity scale for $\varrho_0'(\beta)/[\varrho_0'(0)(1-\beta)]$. For reasons which are not clear, Gay retained curve coincidence at $\beta=0$, see Figs. 1 & 2 in Gay (1952). Since there is, at present, no theoretical basis for the shapes of curves of normalized intensity which relate either to secondary extinction or to an admixture of secondary/primary extinction, an empirical curve was found [Fig. 5, curve (*b*)] which fitted the averaged data up to the observational limit, $\beta=0{\cdot}845$, and then extrapolation to $\beta=1{\cdot}0$ was carried out. The function found to fit was $A+B(1-\cosh k\beta)$ where A is the count at $\beta=0$ and B and k are determined by a fit to the ten points in Fig. 5, curve (*b*). The unity scale thus established is shown as curve (*a*) in Fig. 5.

With this operation, the means of applying the correct scale to the original data is available. Thus, in Fig. 3, curve (*b*) properly scaled is transformed into curve (*c*). In Fig. 4, the scale for unity is given by line (*a*′).

To assess whether the kinematical limit has been effectively established, a simple, relatively direct test is to compare the experimental and theoretical values of the ratio of the integrated intensity of the 'perfect' crystal to that of the 'ideally-imperfect' crystal, $\varrho(0)/\varrho_0'(0)$.

The theoretical value for the 200 reflexion of LiF, for Cu $K\bar{\alpha}$ radiation with $\mu=32{\cdot}2$ cm^{-1}, can be determined by application of the appropriate formulae in H & R, yielding a value of 0·0637. The full variation with asymmetry for this reflexion is shown in Fig. 6(*b*), curve (*f*).

For the experimental value of the ratio, the integrated intensity from a freshly-cleaved surface of a LiF boule in the symmetric position was determined under the same experimental conditions which yielded the data in Fig. 5, curve (*b*). The resultant ratio was 0·070.

An alternative procedure was to progressively etch the polished surface until the measured integrated intensity stabilized at its minimum value corresponding to the crystal matrix (Mathieson, 1976). Details on these experiments and their relevance to the nature of the abraded layer will be reported elsewhere.

The fact that the experimental and theoretical ratios are of comparable magnitude, relative to unity, substantiates the extrapolated value as being near to the kinematical limit value. The main uncertainty in deriving the present experimental result is probably the implicit assumption that the cleaved surface is representative of an ideally 'perfect' LiF crystal. If this assumption is not exactly true, then the ratio would be slightly above that of the theoretical ratio, as is indeed the situation observed.

Within the limits of the experimental data and the theoretical calculations, it would appear that the essential experimental capability of the technique has been validated. Its capabilities in respect of accuracy and precision remain to be explored.

* The symbol used for integrated intensity for an imperfect crystal is ϱ' (as in H & R); for the theoretical ideally imperfect crystal with zero extinction $\varrho_0'(\beta)$ is used while $\varrho_s'(\beta)$ corresponds to a real imperfect crystal with a measure of extinction.

Discussion

The most striking observation that one can make about this investigation, is that, despite its experimental simplicity, it has not been performed previously. The neat technique of varying asymmetric reflexion with a single specimen – used by the Cambridge group and by the present author – was introduced by Hatley (1924) for study of X-ray refractive index. It is therefore clear that, in a technical sense, the present experiment could have been carried out in the 1920s. In mitigation of the delayed recognition of its potential, it may be noted that the full significance of the role of the crystal surface in respect of diffraction only became evident with the conjunction of three factors: (i) observations over the full practical extent of both positive and negative asymmetry; (ii) normalization of the intensity data and (iii) use of an optically flat surface.

In the work of the Cambridge group, under (i) only the positive asymmetry region was explored while under (iii) only the matter of serious localized rugosities (Gay, 1952), and not that of the overall flatness of the surface, was a significant question.

My previous work (M75) introduced and combined the first two factors, and one of the conclusions from that study was a recognition (*a*) of the value of a series of measurements done with controlled adjustment of a relevant physical variable and (*b*) that, for that experiment, the variable, β, is related to the beam path. Exploration of the effect of variable path in respect of the transmission (Laue) technique, arising from recognition of this factor in the Bragg technique, has now received preliminary attention (Lawrence & Mathieson, 1977). In the case of M75, the path was assumed to be through the abraded 'surface layer'. Now, the model of the 'surface layer', used by the Cambridge group and by myself, is simplistic and physically unrealistic [see also comments by Gay, Hirsch & Kellar (1952) and Hirsch (1950)]. So, following certain simple observations on the surface, to be presented separately, it was decided that a clarification of this aspect could be achieved by repetition of the experiment with a specimen with an optically-flat surface. This then was the reason for the introduction of the third factor. In the event, while the investigation did throw some light on the question raised, it proved to be of far greater significance for the problem of extinction. Indeed the matter of the surface was the key which opened up the way to experimental solutions to the problem of extinction.

Of course, with hindsight, it now seems glaringly obvious that it is under the extremes of asymmetry that the effect of the nature of the crystal surface is not only most obvious but also most significant, both for absorptive effects which cause a downward turn of normalized intensity (Fig. 6 in M75) and for decoupling of multiple diffraction, leading to reduction of extinction, which causes an upward turn of normalized intensity with increase in asymmetry (Fig. 4). We recognize that towards the limits of asymmetry, we are more and more concerned with what happens at and near the surface, and, of course, at the limit, we are only concerned with the surface. The question indeed narrows down to the process of diffraction at the surface.

Again, with hindsight, we may turn to Darwin's (1914, p. 686) comments on the surface which, in the light of the above, contained more wisdom concerning extinction than either he or the others of that period found means to put into appropriate experimental form. Speaking of a crystal surface, he said 'There is on the average the same probable number of reflexions (*i.e.* total intensity – my addition) when the crystal (surface – my addition) is broken into many plates as when it is broken into few, or finally as when it is perfect. We conclude that there is no average improvement or deterioration of reflexion when the *surface of the crystal* (my italics) is broken up.

'When we come to consider the inside of the crystal the matter is quite different'.

At this point, Darwin then plunged into the discussion of how to deal with the diffraction process in the interior, thereby failing to explore the full significance of his own commentary.

This comment in fact identifies the source of the extinction problem and recognizes that it is associated with multiple-diffraction processes and that these have maximum probability in the interior. Viewed in this light, it is clear that one way to bypass extinction is to avoid allowing this opportunity to occur, and to ensure that the diffracted intensity which is actually measured only arises at the surface. This condition is satisfied at the limits of asymmetry, as we have shown. It is also clear, from Darwin's words, why the perfect crystal and the mosaic crystal are, under such circumstances, equivalent and indistinguishable.

It may be useful to comment on this situation starting from the zero-extinction limit-of-asymmetry position. As one moves from this position and the beam begins to go below the surface, coupling of the incident and *n*-diffraction beams begins to increase. Also, the magnitudes of the coupling coefficients γ_n (Lawrence & Mathieson, 1977) are likely to change gradually. This makes the development of a theoretical approach rather more complex than is allowed for in Darwin's (1922) treatment with constant γ_n coefficients.

The requirement that the surface be as flat as possible is self-evident. The nearer to the asymmetry limit, the more severe does this requirement become. Very close to the limit, due recognition of the influence of refractive index would be necessary. However, even with relatively narrow beams and a crystal of 15–20 mm diameter, the tilt angle may only be able to approach within 1–3° from the limit, whereas the influence of refractive index would require a much smaller deviation angle to become significant (James, 1948).

This paper is mainly concerned to draw attention to the potential of this technique. Further exploration will be carried out with a new device using highlymonochromatic plane-polarized X-rays (Calvert, Killean & Mathieson, 1974). By measurements with Si, a quantitative test of the technique can be made against the accurate absolute structure factor values of Aldred & Hart (1973) derived from application of a dynamical technique.

Summary

(1) This investigation makes one point very clearly concerning a basic technique in crystallography, namely Bragg reflexion from extended-face crystals. It shows that the symmetric configuration, Fig. 1(*b*), which has been traditionally accepted as the most appropriate, is, in fact, the least suitable for the derivation of physically-significant structure factors. The symmetric configuration, in reality, incorporates the maximum systematic error due to extinction (see Fig. 5).

(2) By contrast, the configurations with asymmetry, which have generally been abjured – with the sole exception of Gay (1952), involve less extinction. By extrapolation to the limits of asymmetry, values of intensity free of extinction can be derived.

(3) This investigation shows one way (Method I) by which it is possible to establish an experimental situation which, *via* extrapolation, can achieve matching of the physical conditions corresponding to the basic assumptions underlying the formula associated with the kinematical limit. This represents a different experimental viewpoint and approach concerning extinction, its elimination and therefore the attainment of extinction-free, *i.e.* absolute, values of structure factors. From recognition of this viewpoint, other methods (which may be used separately or in combination with asymmetric reflexion) have suggested themselves.

Thus, Method II (Mathieson, 1977) involves use of plane-polarized X-rays of variable wavelength reflecting in the π mode to allow extrapolation to $2\theta = 90°$. Other methods will be discussed subsequently.

(4) Because the methods proposed aim in the limit to achieve a zero-extinction physical situation, the question of whether the extinction is primary or secondary is irrelevant. Basically, the problem of extinction can be bypassed by use of a null method.

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