

## Estimation of Single Crystal Integrated X-ray Intensity within a Designated ( $\Delta\omega$ , $\Delta 2\theta$ ) Domain

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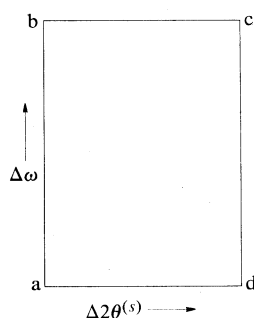
### Abstract

It is shown that measurement of the integrated intensity of a Bragg X-ray reflection within a precisely defined area of the ( $\Delta\omega$ ,  $\Delta 2\theta$ ) distribution (Mathieson 1982a) is possible using a standard scintillation detector. The method involves an aperture system in front of the detector, consisting of two halves which are independently controlled so that both the width and position of the aperture are variable and can follow the  $\Delta 2\theta$  boundaries of the sections of any specified convex domain in ( $\Delta\omega$ ,  $\Delta 2\theta$ ) space, as the specimen crystal steps in  $\Delta\omega$ . By taking account of the dispersion of the wavelength, crystal mosaicity and source components, the method can (a) exclude those extraneous contributions which, particularly at low  $\theta$  angles, constitute a major error source with conventional fixed-aperture procedures and (b) obviate the so-called truncation error at high  $\theta$  angles. This boundary-following method therefore provides, by a simple instrumental operation, a much closer estimate of the true integrated intensity of a Bragg reflection from a small single crystal than is feasible with the use of a fixed aperture. Once the main parameters of the experiment are determined, the procedure requires no greater expenditure of time than the traditional fixed-aperture method.

### 1. Introduction

The classical procedure (Bragg 1914) for the measurement of the integrated intensity of a Bragg X-ray reflection, via a reflection profile, has remained essentially unchanged in its fundamentals. It uses a wide aperture in front of the detector, the width of the aperture remaining unchanged during the measurement operation. The integration is therefore carried out over the rectangular area depicted in Fig. 1 in terms of the local angular coordinates ( $\Delta\omega$ ,  $\Delta 2\theta^{(s)}$ ) (see also Fig. 6 in Mathieson 1982a). The angular displacement of the specimen crystal is  $\Delta\omega$ , and  $\Delta 2\theta^{(s)}$  represents the equivalent angular displacement *in the local frame of the detector* when a scan procedure  $s$  is being used. [A scan involves an angular displacement of the *diffractometer arm carrying the detector* ( $2\theta$  axis) correlated with the angular displacement of the specimen crystal ( $\omega$  axis). The scan ratio  $s$  indicates the type of scan,  $s = 0$  corresponding to the  $\omega$  scan,  $s = 1$  to the  $\omega/\theta$  scan and  $s = 2$  to the  $\omega/2\theta$  scan.] The region, shown in Fig. 1, of the local angular coordinates sampled ( $\Delta\omega$ ,  $\Delta 2\theta$ ) is invariant with respect to scan procedure (see Mathieson 1983a).

In a recent work (Mathieson 1982a) which investigated Bragg reflections in terms of the two-dimensional ( $\Delta\omega$ ,  $\Delta 2\theta$ ) distributions, it was pointed out that the classical prescription, summarized above, includes contributions which, in a strict sense, are extraneous to the measurement and vary with  $\theta$  so that the classical integration



**Fig. 1.** Area  $abcd$  in  $(\Delta\omega, \Delta 2\theta^{(s)})$  space over which integration is carried out in the case of the classical fixed-aperture procedure. The angular displacement of the specimen crystal is  $\Delta\omega$ , while  $\Delta 2\theta^{(s)}$  is the equivalent angular variable across the aperture  $ad (=bc)$  for the scan procedure  $s$ .

procedure has an inbuilt variable systematic error. An alternative improved prescription was proposed which only took account of the contributions within designated limits and hence excluded the extraneous contributions. The prescription was proposed specifically in relation to the  $\omega/2\theta$  scan and it was stated that an expeditious means of effecting it was by use of a linear position-sensitive detector. An alternative means was suggested, by which the prescription could be put into practice using the standard scintillation detector and a narrow aperture, this being referred to as the  $\omega/2\theta$  'slice' scan procedure. While the slice scan necessarily involves an additional outlay of time, it does allow exploration of the  $(\Delta\omega, \Delta 2\theta)$  distribution and so permits a closer inspection of the influence of the main parameters of the experiment, namely the crystal mosaic distribution  $\mu$ , the source distribution  $\sigma$  and the wavelength distribution  $\lambda$ . An application of this procedure (Mathieson 1983*b*) has been given to demonstrate that peak and background can be differentiated in a more objective way using two-dimensional  $(\Delta\omega, \Delta 2\theta)$  data than is feasible with a traditional one-dimensional reflection profile.

Clearly, there are advantages in terms of precision and, one presumes, accuracy in deriving measurements in the form of a two-dimensional distribution in  $(\Delta\omega, \Delta 2\theta)$  space, with its increased potential with respect to resolution and information content. There are, however, many crystallographers who do not seek to explore every Bragg reflection in such detail, but, in order to attain physically significant structure factor magnitudes, require simply to determine values of integrated intensity corresponding to that within the  $(\Delta\omega, \Delta 2\theta)$  area designated by the improved prescription. While this can be achieved using point-by-point measurement as indicated by Mathieson (1982*a*), or more expeditiously with a position-sensitive detector, the question arises as to whether it is at all feasible to bypass this process and arrive more directly at an estimation of the integral within the specified area.

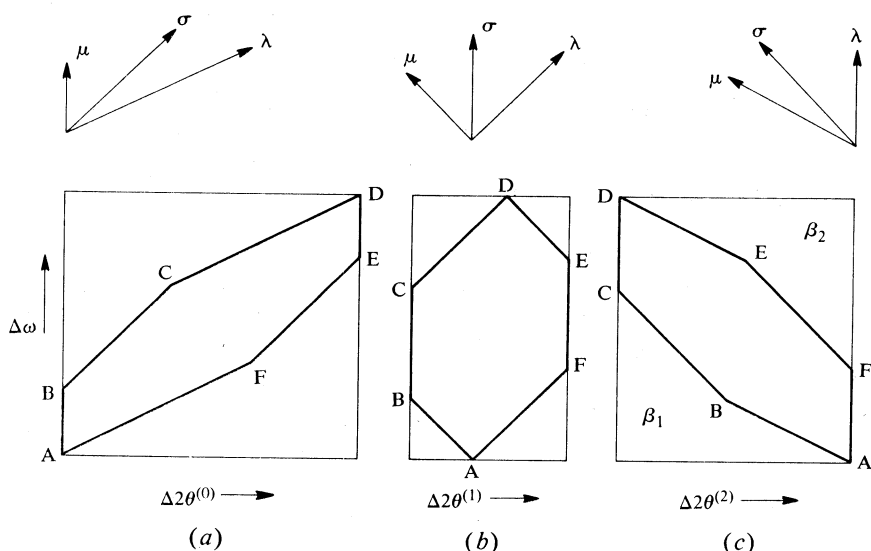
## 2. Outline of Method

A simple solution is provided by the addition of a relatively trivial mechanical facility to any diffractometer under computer control. Its feasibility is linked to the particular property of the standard NaI(Tl) scintillation detector of having a uniform response over an extended area of its active surface.

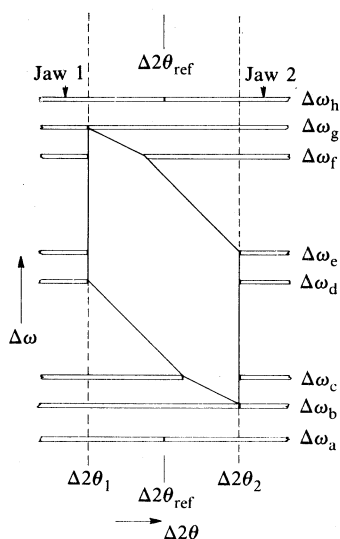
To outline the idea, let us first detail the truncated areas within which the intensity is to be measured, the outer limits of which are set in terms of the parameters  $\mu, \sigma, \lambda$ . These areas are the six-sided figures ABCDEF depicted in Figs 2*a-c* for the main scan procedures  $\omega$ ,  $\omega/\theta$  and  $\omega/2\theta$  respectively.

The method of integrating the intensity within the area ABCDEF involves placing

in front of the detector an aperture system consisting of two parts, each capable of being moved by a stepping motor. Under control from the computer, the positions of the two aperture halves are adjusted as the specimen crystal rotation  $\Delta\omega$  is stepped so that the size of the aperture and its relative position can be varied as required. The sequence of opening and closing and the range of movement are dependent on the particular scan procedure nominated and on the parameters  $\mu, \sigma, \lambda$ .



**Fig. 2.** Outer limits of the six-sided domain ABCDEF in  $(\Delta\omega, \Delta 2\theta^{(s)})$  space corresponding to designated ranges of the experiment parameters  $\mu, \sigma, \lambda$ . The domain is indicated for the different scan procedures (a)  $\omega$  ( $s = 0$ ), (b)  $\omega/\theta$  ( $s = 1$ ) and (c)  $\omega/2\theta$  ( $s = 2$ ). The loci of the  $\mu, \sigma, \lambda$  parameters are shown in each diagram.



**Fig. 3.** Positions of the two halves of the aperture system, jaw 1 and jaw 2, are shown at each stage in the progression of the specimen crystal movement  $\Delta\omega$  from stage a to h. Outer limits of the aperture jaws for this case are  $\Delta 2\theta_1$  and  $\Delta 2\theta_2$ . The value at the centre position is  $\Delta 2\theta_{ref}$ , and is equivalent to the  $2\theta$  dial reading of the detector arm of the diffractometer.

Consider the sequence for the case of the  $\omega/2\theta$  scan as indicated in Fig. 3, cf. Fig. 2c. Let us start at position  $\Delta\omega_a$  just before the measurement is initiated. Both jaws are at  $\Delta 2\theta_{\text{ref}}$ , i.e. the aperture is closed in its central position. When  $\Delta\omega_b$  is reached, both jaws move to  $\Delta 2\theta_2$ , the aperture remaining closed. As  $\Delta\omega$  is stepped, jaw 2 remains stationary and jaw 1 moves to the left at an angular rate equivalent to twice that of  $\Delta\omega$ , until  $\Delta\omega_c$  is reached when it slows to the same rate as  $\Delta\omega$ . This continues until it reaches  $\Delta\omega_d$  when jaw 1 stops at  $\Delta 2\theta_1$  and thereafter remains stationary. When  $\Delta\omega_e$  is reached, jaw 2 starts moving left at an angular rate the same as  $\Delta\omega$  until  $\Delta\omega_f$  is reached when it speeds up to twice the rate of  $\Delta\omega$ . When  $\Delta\omega_g$  is reached, the aperture is now closed and the measurement is completed. At  $\Delta\omega_h$ , both jaws are returned to  $\Delta 2\theta_{\text{ref}}$ .

Although demonstrated for the case of a six-sided figure, the method is completely flexible and any convex domain can be outlined to a good approximation. For example, by appropriate programming, one could outline an ellipsoidal shape, relevant to neutron diffraction single crystal studies.

To establish estimates of the background due to general scatter or thermal diffuse scatter for correction of the measured integrated intensity within the area ABCDEF, integration over selected areas outside the truncated area can be carried out, the decision as to the appropriate region depending on the conditions and parameters of the experiment. Thus the region to the right of AF or to the left of CD in Fig. 2c would have a minimal  $\lambda$  contribution. For proper scaling of the correction, allowance would have to be made for the relative area of the background estimate to the area of ABCDEF and its shape in relation to the resolution (instrument) function.

### 3. Discussion

Preliminary exploration of a selection of Bragg reflections using a narrow aperture (Mathieson 1982a) can establish the parameters for the distributions associated with the main factors  $\mu, \sigma, \lambda$ . This then allows estimation of the angular ranges equivalent to the appropriate limits  $\mu_1-\mu_2, \sigma_1-\sigma_2, \lambda_1-\lambda_2$  chosen by the experimenter for all the Bragg reflections in the range of reciprocal space to be explored. This defines the area ABCDEF for each reflection within which the intensity is to be integrated. Under these circumstances, the question of the so-called truncation error at high  $\theta$  angles or the need for its correction does not arise, thus removing a source of uncertainty which has proved difficult to assess using the conventional fixed-aperture method. Also, it should be noted that, since the  $\mu$  and  $\sigma$  factors generally show zero or small dispersion with  $\theta$ , whereas the  $\lambda$  factor has considerable dispersion, the *proportional* contribution of the extraneous components to the conventional wide-aperture procedure, namely  $\beta_1, \beta_2$  in Fig. 2c (and equivalent areas in Figs 2a and 2b), is greatest at low  $\theta$  angles, the region which is most significant with respect to extinction problems and contains the most significant information on bonding effects.

With aperture control of the type discussed, one can use any of the scan procedures. However, in the case of the  $\omega$  and  $\omega/\theta$  scans, the required aperture range will increase considerably with increases in  $\theta$  (see Fig. 4 of Mathieson 1982a). By contrast, for the  $\omega/2\theta$  scan, the aperture range will be relatively constant. Some variation may be necessary to allow for anisotropy of the  $\mu$  distribution but this will mostly be relatively small. (For the  $\omega/2\theta$  scan, the increase in the area due to the  $\lambda$  dispersion is taken up wholly by  $\Delta\omega$ .)

With measurements made using this controlled-aperture procedure, one can derive, as in the case of the fixed aperture, a one-dimensional profile from the intensity sums at each  $\Delta\omega$  step on the way to the full integration. This does not have the resolution capabilities of the two-dimensional distribution but it would allow the application of routine checks to detect significant deviations from profile shapes established by experience with this method. It should be noted that, in addition to losing the resolution capabilities, one also foregoes the information content of the two-dimensional distribution which could be of value in the study of the variation of extinction within the reflection.

The boundary-following method will provide a closer estimate of the 'true' value of the integrated intensity than is feasible for methods using a fixed aperture. Combined with on-line correction for dead-time (Mathieson 1982*b*), the approximation will be further improved.

The method clearly has considerable potential for exploration of general regions of reciprocal space as well as at reciprocal lattice points. For such studies, the  $(\Delta\omega, \Delta 2\theta)$  shape chosen would have to accord with the resolution (instrument) function.

To put the controlled-aperture procedure into practice, the drive to the aperture jaws, i.e. the stepping motors and any associated gearing, will have to be selected with some care. The drive will have to mate with the distance  $d$  of the aperture system from the specimen crystal so that the unit steps of the jaws are exactly the same as the unit steps of  $\Delta\omega$ , say  $0.01^\circ$  or  $0.005^\circ$ . The exact equality of the units can be assured by a final minor adjustment of  $d$ . [An alternative procedure is to use a symmetrically opening aperture (Mathieson 1980) combined with an appropriate displacement of the detector arm. Operationally, the separation of the displacements of the aperture jaws from that of the detector arm is preferred.]

*Note:* The discussion of the  $(\Delta\omega, \Delta 2\theta)$  distribution by Mathieson (1982*a*) refers to (a) a small crystal specimen and (b) does not involve a monochromator. The distributions for other cases remain still to be studied.

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