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A Method for Location of the Peaks in Step-Scan-Measured Bragg Reflexions

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A method for location of the peak in a step-scan-measured Bragg reflexion profile is described. It leads to a ratio between the standard deviation of the intensity and the intensity, $\sigma(I)/I$, which is near minimum. The method is based on the observation that if $\sigma(I)/I$ is calculated for all possible peak widths for a given profile then $\sigma(I)/I$ is minimum near the true value of the peak width, and minimal $\sigma(I)/I$ can thus be used as a criterion for correct location of the peak. The intensity determined this way is however in general slightly underestimated, and the bias as well as possible corrections are discussed. In addition a simple function resembling $\sigma(I)/I$, which has proved to be useful for practical applications, is given.

Introduction

When the profile of a Bragg reflexion is known at a sufficient number of points, it is possible to determine the intensity of the reflexion. This is done by integrating (summing the individual profile intensity measurements) over the part of the profile assumed to contain elastically diffracted radiation, and subtracting from this integral the background intensity, which is assessed from the remaining part of the profile. In the following we assume for simplicity that the profile does not contain appreciable contributions from white radiation streaks or from thermal diffuse scattering.

The amount of data required to put this method into use for intensity measurements in single-crystal structure determination is quite extensive, and a usual way of overcoming this difficulty is to perform the integration at the time of measurement through use of the so-called background–peak–background (BPB) method.

Knowledge of the profile of the Bragg reflexion nevertheless gives obvious advantages over the BPB method. In cases where an intensity is in question the BPB measurement gives little alternative but remeasurement, while the profile data for a reflexion may be reexamined for individual features. Besides, as the peaks may vary in position and width for different reflexions, the BPB method must use a peak scan width wider than the optimal width. The intensity obtained from a profile measurement, which includes determination of this optimal width, will therefore have smaller standard deviation than the BPB intensity, if the same time is spent on the two measurements, or conversely, the time one has to spend on a reflexion to obtain a certain standard deviation is smaller for a profile than for a BPB measurement.

Location of the background

Let the points of the profile be

$$I(i) \quad i=1\ldots n$$

measured for the same length of time at n equidistant angular settings

$$\theta(i) \quad i=1\ldots n$$

of the crystal when rotated through the Bragg reflecting position. The integrated intensity of the reflexion is then given by

$$I=\sum^{p}[I(i)-B(i)] \tag{1}$$

where the summation is over the p points in the centre of the profile which contains Bragg scattering, and $B(i)$, the background, is a function derived from the remaining b points, the background. The variance based on counting statistics is approximately

$$\begin{aligned}\operatorname{var}(I) &\simeq \operatorname{var}\left[\sum^{p} I(i)\right]+\operatorname{var}\left[\sum^{p} B(i)\right]\\ &\simeq \sum^{p} I(i)+\sum^{p}\operatorname{var}[B(i)],\end{aligned} \tag{2}$$

assuming Poisson distribution for the $I(i)$.

The main difficulty in calculating I consists then in locating the p points over which to integrate. Bartl & Schuckmann (1966) have shown that the background can be located by projecting the profile points on to the intensity axis. The background level is then given by the point on the intensity axis where the density of points is highest. Slaughter (1969) has described a method in which variations of the double difference $\{\Delta^2=[I(i+1)-I(i)]-[I(i)-I(i-1)]\}$ and the curvature are used to determine the peak position. A different approach to the problem is given by Diamond (1969). A profile based on previous measurements is fitted to the actual profile by the method of least squares, thereby avoiding the problem of determining the peak position. This method is especially useful for low-intensity reflexions. A somewhat similar approach has been suggested by Norrestam (1972), who obtained the intensity by first subtracting from each $I(i)$ the minimal count found, and then fitting the resulting profile to a Gaussian by means of least-squares methods.

The ratio $\sigma(I)/I$ for different data processing and data collecting methods can be taken as a measure of the quality of the method, *i.e.*, the smaller the ratio the better the method. Accordingly, the best limits for the peak in a given profile are then those corresponding to a minimum in $\sigma(I)/I$, when this quantity is calculated for the limits of the peak taking all possible values, and we actually find that the limits obtained this way coincide quite well with the true positions. The following argument was our starting point:

Let I and $\sigma(I)$ be determined by (1) and (2), and let $B(i)$ be known (for example a constant value). If the range of summation (p) is wider than the true peak then in (2) $\sum^{p} I(i)$ will be bigger than for the true peak, and, as the background is based on fewer points, $\mathrm{var}\,[\sum^{p} B(i)]$ will be bigger too, leading in all to a bigger var (I) and a ratio $\sigma(I)/I$ which is larger than that for the true peak width, assuming I to be unaltered.

If the summation range decreases, both I and $\sigma(I)$ will decrease and for a very small range I will go to zero making $\sigma(I)/I$ very big. So a minimum will exist for some intermediate range of summation, possibly near the true value. This minimum will be found for $\mathrm{d}I/I$ identical to $\mathrm{d}\sigma(I)/\sigma(I)$, where d indicates the change in the quantities as the summation range decreases. To obtain an estimate for the location of this minimum we make a few simple assumptions.

First we will assume that the background can be written as

$$\sum^{p} B(i) = \frac{p}{b} \sum^{b} I(i) = pB$$

and

$$\mathrm{var}\left[\sum^{p} B(i)\right] = \left(\frac{p}{b}\right)^2 \sum^{b} I(i) = \frac{p}{b} \sum^{p} B(i),$$

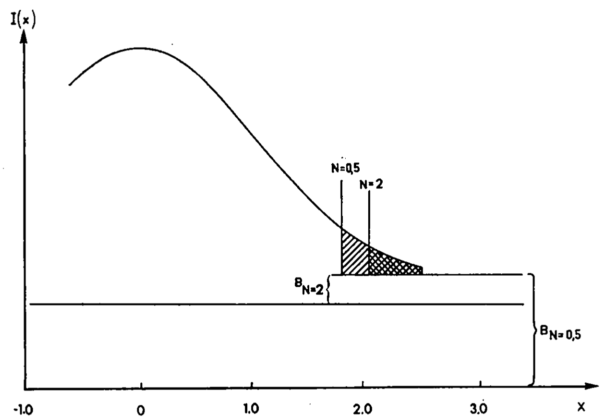


Fig. 1. Profile consisting of unit normal-distribution-shaped Bragg scattering and a constant background. The background is varied to obtain two 'intensity–background' ratios, N, and for the two cases the computed location of the point dividing peak and background is given together with the bias in intensity indicated by shaded areas.

where B is the mean background value, and secondly we will assume that we are studying a range where p is not too different from b, so that derivatives of the form $\mathrm{d}(p/b)$ will be small. We then get, if we decrease the summation over the peak by one point, j:

$$\frac{\mathrm{d}I}{I} = \frac{\mathrm{d}\sum^{p} I(i) - \mathrm{d}\left[\frac{p}{b} \sum^{b} I(i)\right]}{I} = \frac{-\frac{n}{b}[I(j)-B]}{\sum^{p} I(i) - \sum^{p} B(i)}$$

where $n=p+b$, and similarly we get

$$\frac{\mathrm{d}\sigma(I)}{\sigma(I)} = \frac{\mathrm{d}\ \mathrm{var}\ (I)}{2\ \mathrm{var}\ (I)} = \frac{\mathrm{d}\sum^{p} I(i) + \mathrm{d}\left[\left(\frac{p}{b}\right)^2 \sum^{b} I(i)\right]}{2\ \mathrm{var}\ (I)} = \frac{-\left(1-\left(\frac{p}{b}\right)^2\right) I(j) - 2\frac{pn}{b^2} B}{2\left[\sum^{p} I(i) + \frac{p}{b} \sum^{p} B(i)\right]}\,.$$

We will now assume that j is to be found in the tail of the Bragg scattering so that B, the mean background, is only slightly different from the true value, and we can then introduce an 'intensity–background' ratio

$$N = \sum^{p} [I(i) - B(i)] / \sum^{p} B(i)\,.$$

Further we will express the maximum Bragg scattering in terms of the integrated intensity and we then get:

$$I(m) - B = f' \sum^{p} [I(i) - B(i)] = f'N \sum^{p} B(i) = f'pNB = fNB\,.$$

In most cases we find that within a set of profiles obtained under fixed experimental conditions the shape of the Bragg scattering is the same for all profiles, and in this case f takes the same value for all profiles in the set. We then get for the condition

$$\frac{\mathrm{d}I}{I} = \frac{\mathrm{d}\sigma(I)}{\sigma(I)}:\quad \frac{\frac{n}{b}[I(j)-B]}{N} = \frac{\left[1-\left(\frac{p}{b}\right)^2\right][I(j)-B] + \left(\frac{n}{b}\right)^2 \frac{1}{fN}[I(m)-B]}{2\left(N+\frac{n}{b}\right)}$$

or

$$\frac{I(j)-B}{I(m)-B} = \frac{1}{f(N+2)}\,. \tag{3}$$

Now, to get a numerical estimate of $I(j)$ and thereby of j we assume the shape of the Bragg scattering to be a unit normal distribution

$$I(X) - B(X) = \phi(X) = \frac{I}{\sqrt{2\pi}} \exp\left(-\frac{X^2}{2}\right)\,.$$

We will restrict the scattering to $|X| < 2\cdot5$, whereby the cut-off value is 4% of the peak value, a shift which would be barely observable in a real profile, and we will replace summation by integration and j by X_j. We then get the intensity

$$I \simeq \int_{-2\cdot5}^{2\cdot5} \phi(X)\mathrm{d}X = N\int_{-2\cdot5}^{2\cdot5} B(X)\mathrm{d}X = 5NB$$

and

$$I(X_m) - B = \frac{I}{\sqrt{2\pi}} = \frac{5NB}{\sqrt{2\pi}},$$

i.e.

$$f = \frac{5}{\sqrt{2\pi}}.$$

Introducing this into equation (3) we get

$$\frac{I(X_j)-B}{I(X_m)-B} = \frac{\sqrt{2\pi}}{(N+2)5}.$$

So, if a minimum is obtained for example by varying the right-hand limit of the peak then the bias in the peak location to the right is

$$\Delta b = 2\cdot5 - X_j$$

and the bias in the intensity is

$$\Delta I = \int_{X_j}^{2\cdot5} \phi(X)\mathrm{d}X.$$

Table 1 gives a series of values for Δb and ΔI as a function of N. In addition, the values for a triangular peak shape are given, in which case $f=2$ so that $[I(X_j)-B]/[I(X_m)-B]$ is $0\cdot5/(N+2)$, nearly identical to the Gaussian case, and ΔI is $0\cdot5[0\cdot5/(N+2)]^2$. The observed Bragg peaks generally have neither a Gaussian nor a triangular shape, but often something in between, as the profile is a convolution of Gaussian functions (*e.g.*, the mosaic distributions of crystal and monochromator) and triangular functions (*e.g.*, collimators). The bias in intensity is therefore probably in the worst case between 2 and 4%. As the tails of the peak are the part of the profile determined with the lowest precision it would not make sense to adjust the observed intensity by a calculated amount. It would rather be natural to increase the peak width sufficiently before the calculation of the intensity.

Table 1. *The relative height of the last point in the peak, $[I(X_j)-B]/[I(X_m)-B]$, as determined from minimal $\sigma I/I$, the bias in the background location, Δb, in percent of total peak width, and the bias in the intensity, ΔI, in percent of total intensity, as a function of N, the 'intensity–background' ratio for Bragg scattering shaped as a unit normal distribution*

In addition is given the bias in the intensity, ΔI_t, for a triangular shape of the Bragg scattering.

N	$\frac{I(X_j)-B}{I(X_m)-B}$	Δb (%)	ΔI (%)	ΔI_t (%)
0·25	0·22	15	3·5	2·5
0·50	0·20	14	3·0	2·0
1	0·16	12	2·3	1·4
2	0·13	9	1·5	0·8
4	0·08	5	0·7	0·3
10	0·04	0	0	0·1

Fig. 1 gives a visualization of some of the numbers given in Table 1. Two examples are given. In both cases the Bragg scattering is taken to be the same (in arbitrary units) and a change in N is obtained by shifting the background level. Although ΔI drops quite appreciably in going from $N=0\cdot5$ to $N=2$ Δb falls much less, indicating that the easiest way to correct for the bias would be by adding 10 to 15% to all the determined full widths, as discussed above.

Nothing is however gained by improving the counting statistics. The bias is only a function of the 'intensity–background' ratio, which is not changed by longer counting time. The bias cannot be changed by increasing f either, as f is the product of the ratio f' between the maximum count and the total count and the number of points p in the peak. If the number of points is increased or decreased by a certain factor resulting from a change in step length, f' is decreased or increased by the same factor leaving the product f unchanged.

Description of $\sigma\mathcal{J}/\mathcal{J}(p)$

A determination of the best limits for the elastic peak can then be carried out by calculation of $\sigma(I)/I$ for a sufficient number of peak widths. For each case a straight line should be fitted to the points assigned as

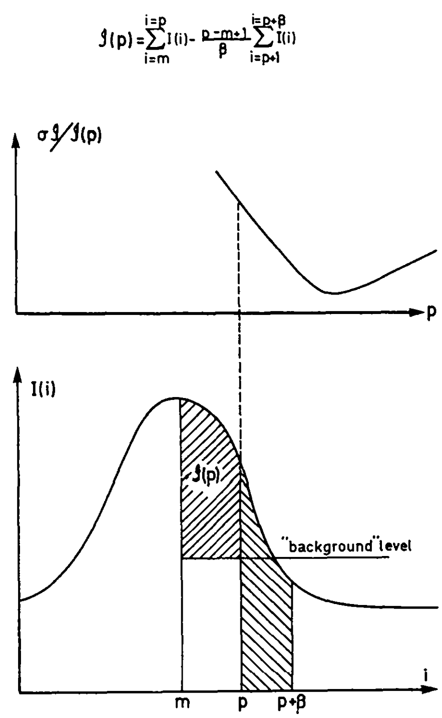


Fig. 2. Schematic representation of a reflexion profile and the corresponding $\sigma\mathcal{J}/\mathcal{J}(p)$ function. Only the right-hand side is used for this function. A similar function is then calculated for the left-hand side.

background giving $B(i)$ and var $[B(i)]$, $\sigma(I)/I$ could then be obtained, the peak location corresponding to the minimum found, and a correction introduced. This approach would however result in lengthy calculations and we have therefore constructed a simple function, $\sigma\mathscr{I}/\mathscr{I}(p)$, for determination of the limits. This function includes only data from half the profile at one time, as the profile is not necessarily symmetric. Secondly, the background $B(i)$ is approximated by a mean value, and finally not all data points in the half-profile are included for a given p, as the background is assumed to consist of a fixed, small number of points, β. This facilitates the determination of inhomogenities in peak and background.

A reflexion profile with n points is outlined in Fig. 2. It is assumed that, for each peak, the number of points at each end of the profile which represents true background measurements equals or exceeds β. The profile is divided into two parts at m, where $I(m)$ is the point of maximum counts. The values $I(i)$, $m \le i \le p$ represent the peak, and the background is determined by the next β points, so that in calculating $\sigma\mathscr{I}/\mathscr{I}(p)$ for the right-hand part of the profile we are only concerned with the points i, where $m \le i \le p+\beta$. The function $\sigma\mathscr{I}/\mathscr{I}(p)$ for the right-hand part of the profile is defined as

$$\sigma\mathscr{I}/\mathscr{I}(p)=\sigma\mathscr{I}(p)/\mathscr{I}(p) \tag{4}$$

$$\sigma\mathscr{I}(p)=\sum_{i=m}^{i=p} I(i)+\left(\frac{p-m+1}{\beta}\right)^2 \sum_{i=p+1}^{i=p+\beta} I(i)$$

$$\mathscr{I}(p)=\sum_{i=m}^{i=p} I(i)-\frac{p-m+1}{\beta} \sum_{i=p+1}^{i=p+\beta} I(i)\,.$$

$\sigma\mathscr{I}/\mathscr{I}(p)$ is calculated for all p with $m<p\le n-\beta$, and the value of p giving minimum is the limit of the peak to the right. A limit for the left-hand side of the peak is found in a similar manner.

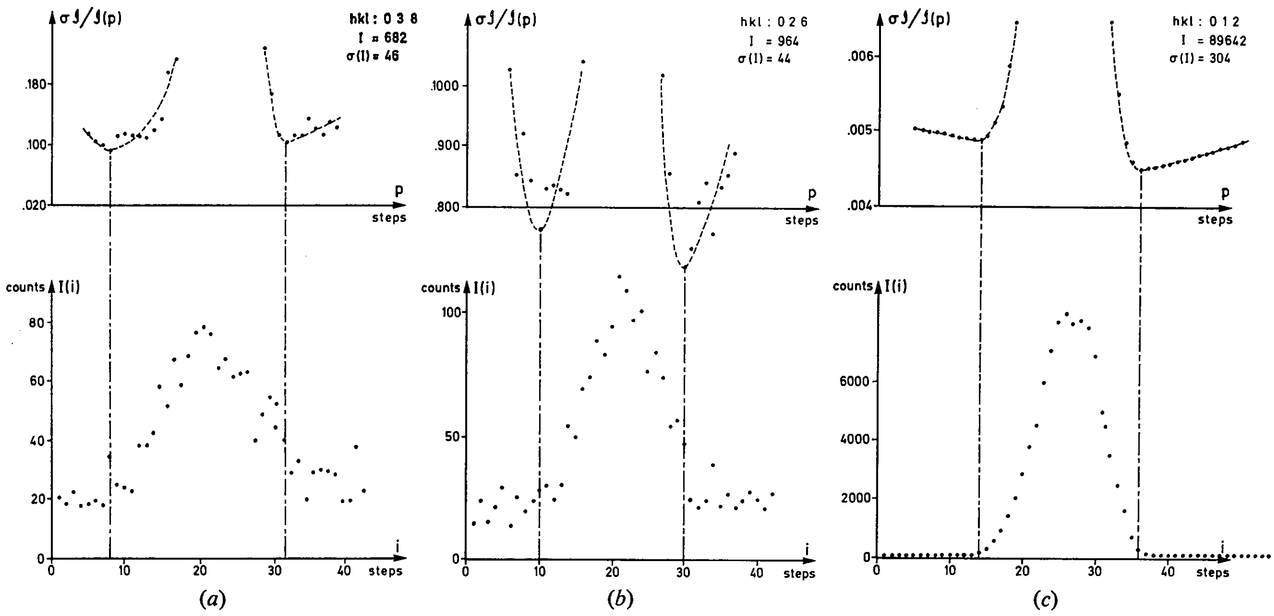
Unusual behaviour of $\sigma\mathscr{I}/\mathscr{I}(p)$ is generally an indication that the reflexion profile does not have a shape which is acceptable. This can arise for many reasons and in nearly all sets of reflexion data one will detect a few profiles with very peculiar shapes, often the result of malfunctioning equipment. Two general cases are the occurrence of negative $\sigma\mathscr{I}/\mathscr{I}(p)$ and the non-occurrence of a real minimum in the function.

The first case can arise from either spurious peaks in the background, for example tails from neighbouring reflexions, in which case the mean background value may become bigger than the mean peak value, whereby $\mathscr{I}(p)$ will become negative, or, what is the normal situation, the peak is so small, that a certain number of the $\mathscr{I}(p)$ values are negative. In this case the best approach is to store the profile until sufficient general information concerning the normal peak width is built up from other reflexions, then position the peak according to this information, make comparisons among the peak and background values, and if anything unusual is observed, then the data reduction must at least be partly manual.

The second case corresponds to the situation when the minimum, say, for the right-hand side of the profile is found for $p=n-\beta$. This indicates that insufficient background points have been measured, and that a partly manual treatment – at least a visual inspection – is necessary.

Application

The method has been used for a period of some years in data reduction of neutron diffraction data obtained at the DR3 reactor at Risø, Denmark (Lehmann &



(a) (b) (c)

Fig. 3. Three reflexion profiles, $I(i)$, and the corresponding $\sigma\mathscr{I}/\mathscr{I}(p)$ functions. The minimum corresponds to the last point in the peak.

Larsen, 1971) and at the Brookhaven High Flux Beam Reactor, U.S.A., (Lehmann, Koetzle & Hamilton, 1972). It has been found that a β which is slightly less than half the true background gives good result, and as the number of peak and background points are nearly identical then the thumb rule has been that $\beta = 0{\cdot}1n$. For each set of data the behaviour of the $\sigma\mathscr{I}/\mathscr{I}(p)$ function has been followed, and a certain number of points have been added to each side of the peak to avoid any bias in the observed intensity. The number of points added has always been fixed for a whole set of data, generally between $\beta/2$ and β for each side.

The computing time for determination of the peak width is, because of the simple structure of $\sigma\mathscr{I}/\mathscr{I}(p)$, quite small, and in fact only a few additional calculations have to be carried out, in which the mean value and the slope of the two backgrounds are compared. Several data-reduction programs have been used, and in the last version the calculations are carried out in two stages. In the first stage the peak widths for the good peaks are determined as a table function in $\sin\theta/\lambda$. These so-called good peaks are peaks for which true minima in $\sigma\mathscr{I}/\mathscr{I}(p)$ are found on both sides of the peak, where $\sigma(I)/I$ is less than 0·25, and where no negative $\sigma\mathscr{I}/\mathscr{I}(p)$ are found. The table function is then used to locate the peak for reflexions for which $\sigma(I)/I$ is greater than 0·25 or for which negative $\sigma\mathscr{I}/\mathscr{I}(p)$ values are found. When a true minimum is not found then very little can be done, and for those reflexions a warning message is given. Finally for all reflexions the backgrounds are compared as mentioned above.

In general we find that up to 10% of the reflexions will have a warning message attached, and the program is so written that a printed profile can be obtained for these reflexions. It is however only in very few cases that manual evaluation is necessary.

In Fig. 3(*a*), (*b*) and (*c*) are given three examples from the structure analysis of L-glutamic acid (Lehmann, Koetzle & Hamilton, 1972) corresponding to N nearly infinity, $N \simeq 2$ and $N \simeq 1$. The number of background points, β, is in all cases 4, and the minima corresponds to the last points in the peak. From the given examples it is not clear that I is biased, and it is only when all the data are gathered that we find clear indications that there is an effect. This is shown in Fig. 4, where the full width $\Delta\theta$ is given as a function of $\sin\theta/\lambda$. The data in this case are also divided up as a function of $I/\sigma(I)$, and it can be clearly seen that the

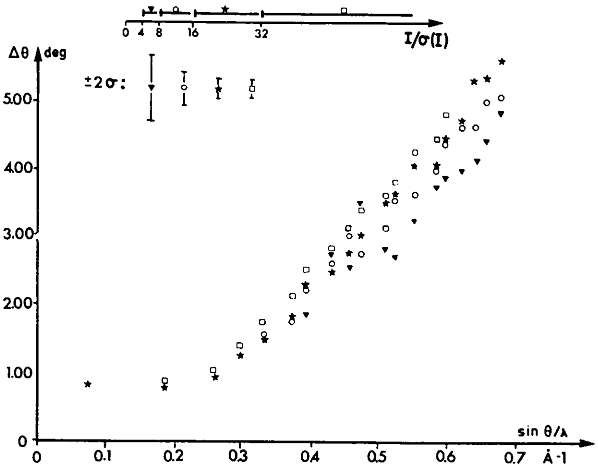


Fig. 4. The full width of the elastic peak, $\Delta\theta$, as a function of $\sin\theta/\lambda$. The reflexions are divided into groups according to $I/\sigma(I)$, and for each group an estimated $\sigma(\Delta\theta)$ is given. It can be clearly seen that weak reflexions have underestimated $\Delta\theta$. The variation of the full width with $\sin\theta/\lambda$ is as expected, giving a minimum near $\sin\theta_M/\lambda$, the focusing position. In the present experiment a Ge(111) reflexion was used giving $\sin\theta_M/\lambda = 0{\cdot}15$ Å^{-1}.

weak reflexions do tend to get their full width underestimated. This curve could actually be used to give an experimental estimate of the bias, but until now it has been found satisfactory to work with a fixed additive.

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