Intensity Measurements of Twinned or Grown-together Crystals on Single-Crystal Diffractometers

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The overlapping of reflexions during the intensity measurement of a polycrystal (grown-together single crystals) can be checked by formulae given in this paper. These formulae are based on scan mode, scan width and detector aperture.

(1) Introduction

A polycrystal consists of twinned or arbitrarily grown-together single crystals. If the reciprocal lattices of these different single crystals do not fully coincide, it is in principle possible to investigate their crystal structures by means of the non-coinciding Bragg reflexions, but often it is difficult to decide between overlapping and non-overlapping reflexions. In this paper we give detailed formulae to identify the overlapping of reflexions during data collection for the widely used \( \theta/2\theta \) and \( \omega \) scan modes in bisecting position. The formulae have been tested during structure investigations of twinned crystals.

(2) Mathematical background

We assume a crystal is composed of two single crystals with not fully coinciding reciprocal lattices. The reflexion intensities of these crystals are to be measured on a four-circle diffractometer.

The rectangular coordinate system of the diffractometer and the rotation directions of the circles are given in Fig. 1. A reciprocal lattice point \( P^* \) is described in the reciprocal lattice by \( H=\begin{pmatrix} h \\ k \end{pmatrix} \) and in the coordinate system of the diffractometer by \( X=\begin{pmatrix} x \\ y \end{pmatrix} \). According to Busing & Levy (1967) the orientations of the single crystals 1 and 2 on the diffractometer are given by \((UB)_1\) and \((UB)_2\). In addition (Benes & Tichy, 1975),

\[
X_1 = (UB)_1 H_1, \\
H_2 = (UB)_2^{-1} X_1.
\]

\( H_2 \) are the coordinates of \( P'_1 \) in the reciprocal lattice of crystal 2. Normally, \( H_2 \) has no integer values. By rounding off, \( H_2 \) is transformed to \( H' \) which are the coordinates of \( P'_2 \). \( H + \mathbf{I} \) with \( \mathbf{I} = \begin{pmatrix} i_1 \\ i_2 \\ i_3 \end{pmatrix} \) are the coordinates of the points \( P'_2 \) in the neighbourhood of \( P'_1 \). These points may influence the intensity measurement of \( P'_1 \). In order to check this, we need the \((\theta, \chi, \varphi)\) values for \( P'_1 \) and the \( P'_2 \) points. They can be calculated by the following equations, which are derived from Figs. 1 and 2:

\[
d^* = (x^2 + y^2 + z^2)^{1/2} \\
\theta = \arctan \left[ d^* (4 - d^*^2)^{-1/2} \right] \\
\chi = -\arctan \left[ z (x^2 + y^2)^{-1/2} \right] \\
\varphi = \arctan (xy^{-1})
\]

For the bisecting position, \( \omega \) equals \( \theta \).

(3) Criteria for overlapping

In the following we assume a rectangular counter aperture. The horizontal and vertical aperture and the scan width are designated as \( U_h, U_v \) and \( \text{SWD} \) respectively. Their values are given in radians. In Fig. 3(a)-(c) those parts of the reciprocal space are drawn which pass through the Ewald sphere and diffract into the counter during an intensity measurement.
3.1. \( \omega \) scan

If \( P'_1 \) lies on the Ewald sphere, all points of the reciprocal space lying on \( BP'_1D \) diffract simultaneously into the counter with the opening \( U_h \) (Fig. 3a). During a scan with the width \( SWD \), the point \( A \) moves along the line \( A'A'' \) and correspondingly \( B \) along \( B'B'' \), \( P_1 \) along \( C'C'' \) and \( D \) along \( D'D'' \). It follows that the area \( B'B''D''D' \) is measured during an \( \omega \) scan. The 20 values of this area are given by the circle section \( BD = U_h \), which can be formulated as

\[
\Delta 2\theta = |2\theta(P'_1) - 2\theta(P'_2)| \leq U_h/2.
\] (1)

Furthermore, for the circle sections around \( O \), \( B'B'' \) equals \( C'C'' \) equals \( D'D'' \) equals \( SWD \). This can be expressed as a \( \Delta \phi \) condition for the \( P'_2 \) points. For \( \chi = 0 \),

\[
\Delta \phi = |\phi(P'_1) - \phi(P'_2)| \leq SWD/2.
\]

For \( \chi \neq 0 \) this equation changes into

\[
\Delta \phi \leq \arcsin \left( \frac{\sin SWD/2}{\cos \chi} \right),
\] (2)

This follows from Fig. 3(a) by replacing \( OP'_1 \) by \( OP'_1 \cos \chi \).

A similar condition for \( \Delta \chi \) can be taken from Fig. 3(c), which is derived from Fig. 3(a) and (b):

\[
\sin \Delta \chi = \frac{U_v/2}{2 \sin \theta}.
\]

For small \( \Delta \chi \) values

\[
\Delta \chi = |\chi(P'_1) - \chi(P'_2)| \leq U_v(4 \sin \theta)^{-1}.
\] (3)

3.2. \( \theta/2\theta \) scan

The area diffracting into the counter during a \( \theta/2\theta \) scan is given by \( B'B''D''D' \) of Fig. 3(b). The position of \( U_h \) is now given by \( BD \) for \( A \), \( B'D' \) for \( A' \) and \( B''D'' \) for \( A'' \). The range of 20 values can be read from the Ewald sphere belonging to \( A \), if circles are drawn (with their centre at \( O \)) through \( B' \) and \( D'' \). They cut the Ewald sphere at \( B''' \) and \( D''' \). It follows that

\[
B'''D''' = B''C''' + C''P'_1 + P'_1C'' + C''D'''
= U_h/2 + SWD + SWD + U_h/2.
\]

Therefore,

\[
\Delta 2\theta \leq U_h/2 + SWD.
\] (4)

The limits of the \( \phi \) values can be taken from the angle relations \( BAD = U_h \) and \( BOD = BAD/2 = U_h/2 \) (cf. Fig. 3b). For \( \chi = 0 \)

\[
\Delta \phi \leq U_h/4.
\]

Fig. 2. Ewald construction of the diffraction condition.

Fig. 3. Parts of the reciprocal space which are used for the intensity measurements. (a), (b) Parts given by the scan width SWD and the horizontal aperture \( U_h \) for the \( \omega \) and the \( \theta/2\theta \) scan respectively. The dotted lines represent the projections of the boundaries of \( \Delta \phi_{\max} \) for all \( \chi \) values. (c) The part of reciprocal space given by the vertical aperture \( U_v \). In the figures the Ewald sphere moves and the reciprocal space keeps at rest.
For $\chi \neq 0$ this is modified to

$$
\Delta \phi \leq \arcsin \left( \frac{\sin \frac{\Delta \chi}{4}}{\cos \chi} \right).
$$

The $\Delta \chi$ condition is the same for both the $\omega$ and the $\theta/2\theta$ scan.

### 3.3. Counters with circular aperture

A safe approximation for this aperture type with an opening angle $U_c$ is $U_c = U_c = U_c$ in (1)-(5).

The exact condition for overlapping can be evaluated by calculating $U_c'$ from (3):

$$
U_c' = 4 \Delta \chi \sin \theta.
$$

Overlapping can occur for

$$
U_c' \leq U_c.
$$

In this case we can calculate $U_h$ by

$$
U_h = \left[ U_c^2 - (U_c')^2 \right]^{1/2}.
$$

This value must be substituted into (1), (2), (4), and (5).

### 3.4. Beam divergence, mosaic spread and wavelength spread

Beam divergence, mosaic spread and wavelength spread cause a broadening of the reflexion profile. The peak width for each crystal can be estimated by

$$
PW = A + B \tan \theta.
$$

PW must be added to (1) to (6).

### 3.5. Overlap conditions

A reciprocal-lattice point $P_2'$ influences the intensity measurement of $P_1'$ only if its $\Delta \theta$, $\Delta \phi$, and $\Delta \chi$ values are smaller than the values given in (1)-(5) increased by $PW$ of (7).

A comparison of Fig. 3(a) and (b) shows that the parts of reciprocal space used for intensity measurements are not identical. Therefore, twins should be measured in $\omega$ and $\theta/2\theta$ scan modes in order to get the full resolving power of a four-circle diffractometer for the standard procedures of intensity measurements (bisecting position).

### (4) Analysis of the intensity measurements

With these criteria one should classify the measured intensities into four groups. (I) Reflexions whose intensities are not falsified by others. (II) Reflexions which overlap only by considering their peak width (PW). They should only be ignored during structure determination if their background measurements are unbalanced. (III) Reflexions which coincide almost completely. They should be omitted from the data set. (IV) Reflexions which coincide completely (only for twinned crystals) because of the twinning condition; (perhaps one direction or a plane of the reciprocal lattice). The intensities of these reflexions should be analysed by means of the volume ratio of the two individual crystals.

#### (5) An example

The program was tested with Tl$_2$PbI$_4$. This substance has an orthorhombic crystal structure with $a = 8.95$, $b = 9.67$, $c = 18.18$ Å. The crystals are almost always twinned. The twinning plane is (110). If both the crystal and its twin are described in a right-handed system, then the angle between the $a$ and $a'$ axes and between the $b$ and $b'$ axes is $94.45^\circ$. The $hkl$ reflexions from the crystal and the $hhl$ reflexions of the twin identically overlap each other; however, their respective $hhl$ and $hkl$ reflexions are separated because of the angle between the $a$ and $a'$ axes and $b$ and $b'$ axes.

For the structure determination, the $hkl$ and $hhl$ reflexions (there are $1460$ per octant) of one individual crystal were measured with both the $\omega$ scan and $0/20$ scan techniques used. The following parameters were used for these measurements: $SWD = 0.8^\circ$, $U_h = 1^\circ$, $U_c = 1^\circ$. The maximum peak width observed was $PW = 0.65^\circ$. The results given by the overlap program were that $32\%$ of the $hkl$ reflexions and $19\%$ of the $hhl$ reflexions showed overlap effects when measured either in the $\omega$ or in the $0/20$ scan mode. Some of the reflexions overlapped in one octant were not overlapped in the other. Only $12\%$ of the symmetry-related reflexions from both octants together were affected by overlap.

The structure was determined with a data set composed of all the unoverlapped reflexions. The equivalent reflexions that were unoverlapped in both octants were averaged together. The reflexions from each octant were unoverlapped in that octant, but overlapped in the other. Only $12\%$ of the symmetry-related reflexions from both octants together were affected by overlap.

In order to use as large a data set as possible for the final refinement the following procedure was used. The overlapped reflexions with $F_o < F_r$ were removed from the set of overlapped reflexions and added to the set of averaged reflexions. These reflexions were in fact not affected by overlap after all. The $001$ intensities were corrected according to the volumes of the two parts. After this was done the final data set used contained $91\%$ of the possible reflexions. From a refinement of this data set an $R$ value of $R_{aniso} = 0.04$ was obtained. The overlapping caused the remaining $9\%$ of the reflexions to have incorrect intensities. A calculation with these intensities alone yielded $R_{aniso} = 0.21$.

### References


† A computer program (Fortran) which checks the reflexions for overlapping is available from the authors.