Crystal Orientation and X-ray Pattern Prediction Routines for Area-Detector Diffractometer Systems in Macromolecular Crystallography

BY A. MESSERSCHMIDT and J. W. PFLUGRATH

Max-Planck-Institut für Biochemie, D-8033 Martinsried bei München, Federal Republic of Germany

(Received 6 June 1986; accepted 31 March 1987)

Abstract

Routines for crystal orientation and the prediction of expected reflections which are part of the data collection software package MADNES for area-detector diffractometer systems in macromolecular crystallography are described. This package is designed to be area-detector-system independent. In addition to refining crystal cell lengths and angles, crystal orientation, crystal-to-detector distance, position of the primary beam on the detector, and rotation of the detector around the primary beam, the orientation routine also refines the effective mosaic spread of the crystal, the beam inclination angle $\mu$, and the detector tilt angle $\tau$. A prealignment procedure is described for rapid rough orientation of the crystal. The routines are written in Fortran 77 in a modular way so that they may be used independently of MADNES and each other.

Introduction

For the collection of X-ray diffraction data with a two-dimensional position-sensitive detector (PSD), the crystal cell parameters, the crystal orientation and the detector position must be accurately determined in order to predict exactly the locations of reflections on the detector. This is true whether the detector is a piece of film, a multiwire proportional counter (MWPC) or a phosphor screen coupled to a television camera. Film and electronic PSD techniques differ mainly in the sensitivity and speed of obtaining digitized information from a plane of reciprocal space. With the MWPC or the television camera this information is immediately available at the end of the X-ray exposure, while with film there is some delay because of development and optical scanning. This immediacy of data collection allows one readily to investigate reciprocal space with finer sampling intervals which, although physically possible with film, is unfeasible in practice.

Several program packages for film-data evaluation already exist, as extensively described in Arndt & Wonacott (1977). Systems for area-detector diffractometers also exist, but they are dedicated to special hardware configurations, such as the programs of Howard, Nielsen & Xuong (1985) for the multiwire area-detector diffractometer at the University of California, San Diego, the software system of Blum, Metcalf, Harrison & Wiley (1985) for the Xentronics multiwire area-detector diffractometer at Harvard University, and the software of Thomas, van der Putten & Kiers (1986) for the Enraf–Nonius FAST television area-detector diffractometer. In contrast, we have developed crystal and detector orientation routines, together with a reflection prediction routine, as part of the area-detector-independent program system MADNES (Pflugrath & Messerschmidt, 1985) which has been implemented for an Enraf–Nonius FAST television diffractometer. The routines are written in Fortran 77 in a modular way so that they may be used independently of MADNES and each other. For example, we use the same routines to refine crystal cell parameters and crystal orientation with digitized films from rotation cameras.

I. Arrangement of X-ray source, four-circle goniostat and area detector

In the algorithms we describe, the X-ray source, four-circle goniostat and area detector must be arranged as illustrated in Fig. 1. The goniostat must provide
rotation about the $\omega$, $\varphi$, $\chi$ and $\tau$ axes (Eulerian geometry). Conversion to $\kappa$ geometry is mathematically straightforward. The area detector is mounted on the $\tau$ arm and can be moved forwards and backwards to achieve different crystal-to-detector distances. The detector can be swung to either side of the primary beam to collect higher-resolution data. The $\omega$ and $\tau$ axes must be coincident but not necessarily perpendicular to the primary beam.

Three important coordinate systems are marked in Fig. 1. The first is the diffractometer coordinate system designated $X_D$, $Y_D$, $Z_D$. The second, a millimetre coordinate system associated with the plane of the detector, has its origin near the position of the primary beam on the untitled detector with $X_f$ parallel to $X_D$ and $Y_f$ parallel to $Y_D$. The third system is the actual pixel coordinate system of the detector shown as $YMS$, $ZMS$ in Fig. 1. We have used the Enraf–Nonius designation for the pixel coordinate system, but in our detector-independent system this is unimportant. In order to maintain detector independence all algorithms use the millimetre coordinate system $X_f$, $Y_f$. Subroutines $PXTOMM$ and $MMTOPX$ are used to convert from pixels to mm and from mm to pixels, respectively. Therefore, a variety of detectors with different pixel sizes and spatial distortion characteristics can be accommodated by changing only these two subroutines.

Other arrangements of the rotation axes would affect the diffraction-geometry formulae in the orientation and prediction routines, but it should be relatively easy to adapt these routines to the desired situation.

II. Useful rotations about the $Y$ and $Z$ axes of the diffractometer coordinate system

Rotations about the $Y$ and $Z$ axes of the diffractometer coordinate system are normally not supplied by the hardware (rotation about $X_D$ is identical with a rotation about the $\omega$ axis). For the prealignment procedure as well as for the flexibility of examining all regions of reciprocal space, however, it is useful to be able to rotate about these fictitious axes.

The subroutines $ROTY$ and $ROTZ$ calculate the corresponding new goniostat angles. We now give a brief description of how this is done mathematically for the rotation around $Y_D$. The vector triple $(X_D, Y_D, Z_D)$ denotes the diffractometer coordinate system

$$A_D = \begin{pmatrix} X_D \\ Y_D \\ Z_D \end{pmatrix}$$

and $(X_G, Y_G, Z_G)$ the goniometer-head coordinate system

$$A_G = \begin{pmatrix} X_G \\ Y_G \\ Z_G \end{pmatrix}$$

Both vector triples will be treated as $3 \times 1$ matrices. Fig. 2 shows the positions of $A_D$ and $A_G$ which are coincident at $\varphi$, $\chi$, $\omega = 0$ and the position of $A_G$ after rotations marked by dashed arcs about $\varphi$, $\chi$ and $\omega$.

The position of $A_D$ with respect to $A_G$ after the rotations is determined by the matrix equation

$$A_D = \Omega \chi \Phi A_G$$

with

$$\Phi = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \cos \Phi & -\sin \Phi \\ 0 & \sin \Phi & \cos \Phi \end{pmatrix},$$

$$\chi = \begin{pmatrix} \cos \chi & -\sin \chi & 0 \\ \sin \chi & \cos \chi & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\Omega = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \Omega & -\sin \Omega \\ 0 & \sin \Omega & \cos \Omega \end{pmatrix}.$$
In a similar way, rotations about the axes of the diffractometer system for other types of goniostats or even goniometer heads may be derived. Since the prealignment routines call the subroutines ROTY and ROTZ, only these routines would have to be changed for these other systems.

III. Prealignment

Our method of refining the exact camera parameters, orientation matrix and cell parameters requires a knowledge of the corresponding parameters within certain error limits. The error limits for the camera parameters are about 1% of their absolute values and about ±1.5° for the mis-setting angles necessary to form the orientation matrix. Normally, the camera parameters can be read out from the diffractometer system with sufficient accuracy and the approximate cell parameters are available from preinvestigation on a film camera. The mis-setting angles, which correspond to rotations about the X_D, Y_D and Z_D axes respectively, are determined by the routine ALIGN which also allows a rough determination of the cell parameters.

The prealignment routine is now described in some detail, first with some comments on the theoretical background. Any reciprocal-lattice plane which cuts the Ewald sphere does so in a circle. Connection of the perimeter of this circle to the centre of the Ewald sphere results in a cone for the diffracted beams. Parallel reciprocal-lattice planes generate a set of concentric cones. The axis of these cones corresponds to the direct-lattice vector perpendicular to these lattice planes. The detector plane has to be perpendicular to the primary beam for the prealignment procedure, so that the cones intersect the detector plane in ellipses as depicted in Fig. 3. The ellipses of the zeroth and first cones are shown.

After a search for a possible cone, the prealignment routine has to determine the intersection point S of the cone axis with the detector plane from an X-ray small-angle-rotation image (typical values from 0.1 to 0.5°).

For a quick, less accurate, prealignment one can select the centre of this ellipse which is, to a first approximation, a circle. In our case, the centre is selected by moving a cursor displayed on a television monitor. A more accurate method is to select with the cursor at least five reflections on the ellipse whose centres are then accurately determined. The module ALIELL then calculates the coordinates of the centre E and the lengths of the half axes of this ellipse by a least-squares fit. In either case, ALIGN calculates the \( \bar{\mu}_x \) and \( \bar{\mu}_y \) values and also performs the goniostat rotations. For the sake of clarity, some well-known formulae are written down.

The spatial mis-setting angle \( \bar{\mu} \) is given by

\[
\bar{\mu} = \arctan \left( \frac{BS}{DX} \right) \tag{5}
\]

The component \( \bar{\mu}_x = \arctan \left( \frac{Y_S}{DX} \right) \) is the mis-setting angle about the X_D axis and \( \bar{\mu}_y = \arctan \left( \frac{X_S}{DX} \right) \) about the Y_D axis.

The following relations hold:

\[
EC' = EC = A = \text{length of long half axis}
\]

\[
BC = A - EB
\]

\[
BC' = A + EB;
\]

\[
v_n - \bar{\mu} = \arctan \left( \frac{BC}{DX} \right)
\]

\[
v_n + \bar{\mu} = \arctan \left( \frac{BC'}{DX} \right) \tag{7}
\]

from which \( v_n \) and \( \bar{\mu} \) can be obtained.

The reciprocal-lattice spacing \( d^* \) is then

\[
d^* = \frac{\cos \bar{\mu} - \cos v_n}{\lambda n} \tag{8}
\]

where \( \lambda \) is the X-ray wavelength and \( n \) is the order of the diffraction cone. The direct-length constant \( l \) parallel to the cone axis is \( l = 1/d^* \).

For \( n = 0 \), \( d^* \) is not determined. This case is treated separately in the program. Once \( \bar{\mu} \) is known, \( BS = (\tan \bar{\mu})DX \) is calculated, and from this a scale factor \( SCAL = BS/EB \). We then obtain

\[
X_S = X_E \times SCAL
\]

\[
Y_S = Y_E \times SCAL \tag{9}
\]

\( X_E \) and \( Y_E \) are the coordinates of the centre of the ellipse and are calculated by the routine ALIELL. \( X_S \) and \( Y_S \) are needed to determine \( \bar{\mu}_x \) and \( \bar{\mu}_y \). The correction for \( \bar{\mu}_x \) is simply an addition to the current

Fig. 3. Diffraction geometry for the ALIGN procedure.
A. MESSERSCHMIDT AND J. W. PFLUGRATH

The procedure is repeated for another direct-cell axis. For crystal systems with cell angles unequal to 90° it is necessary to rotate the second direct-cell axis only into the $Y_0Z_0$ plane. There is an option for activating only the rotation about the $Y_0$ axis. The accuracy of the prealignment procedure is about 1°.

IV. Determination of the exact camera parameters, orientation matrix and cell parameters

Determination of the exact camera parameters, orientation matrix and cell constants is accomplished by the program IDXFST, which is based on IDXREF (Nyborg, Wonacott, Thierry & Champness, 1975), but with major changes. It requires as input the detector pixel coordinates $Y_M$, $Z_M$ and the central $\theta$ values for a few dozen fully recorded reflections with a suitable $\phi$ separation (90° is the optimal value). To get these we use the FIND subroutine. It exposes for each of two zones an overview rotation image and a series of small-angle-rotation images (e.g. 0° 1°). The detector pixel coordinates are converted immediately to mm by the routine PXTOMM and all mathematical operations are performed with mm units. By changing only the PXTOMM routine, the program can be adapted to other types of detectors. For example, we have a version which transforms digitized film coordinates from a data tablet into mm. We use this version to orient and process rotation films.

Our general rotation axis for the rotation-method geometry used in data collection is the $\omega$ axis. The incident beam is allowed to have an inclination angle $\mu$ with respect to the equatorial plane of the Ewald sphere. Fig. 4 shows the apparent diffraction geometry used through all corresponding routines. The detector is tilted around the $\tau$ axis which is coincident with the $z$ axis in this figure. The orthonormal reciprocal $x$, $y$, $z$ coordinate system and the mm coordinate system $X_F$, $Y_F$ on the detector are internal IDXFST coordinate systems and are easily transformed to the diffractometer coordinate system and $X_\omega$, $Y_\omega$ coordinate system on the detector, respectively. The incident X-ray beam lies in the $xz$ plane. There is no loss of generality because an incident beam with a $y$ component can be reduced to the case indicated with a corrected tilt angle $\tau$ for the detector and $\phi$ around the $\omega$ axis. If the reciprocal-lattice (r.l.) point intersects the Ewald sphere in a point $P$, the diffracted beam hits the detector in point $P'$ (see also Fig. 4).

Let us define some useful camera parameters to be refined in the subroutine INDEXI (see Figs. 4 and 5), which correspond to several intermediate coordinate systems on the detector: the inclination angle $\mu$, the perpendicular distance from crystal to detector $DX$, the detector tilt angle $\tau$, the detector twist angle OMEGA, and the corrections to the centre of the primary beam, $CCX$ and $CCY$.

Subroutine INOUTI uses the results of FIND, namely the position on the detector and the rotation angle for a group of reflections. It also divides the reflections into two groups of desired resolution limits. One can carry out the refinement with inner or outer reflections, that is, reflections below a given resolution or reflections above another resolution. At the beginning of refinement it is better to use inner reflections because of the smaller sensitivity to deviations from the correct orientation. For accurate refinement of the cell parameters it is better to use higher-indexed reflections. $XCEN$, $YCEN$ denote the currently assumed position of the centre of the primary beam on the untilted detector. The correction to this ‘known’ position is represented by $CCX$ and $CCY$. We obtain new coordinates for a reflection in the $XP$, $YP$ coordinate system as

$$XP = XF - (XCEN + CCX)$$
$$YP = YF - (YCEN + CCY).$$

Fig. 4. Diffraction geometry as applied in the INDEXI routine. $x$, $y$, $z$: IDXFST internal coordinate system; CPB: centre of primary beam on detector; $\mu$: inclination angle of primary beam; $\tau$: tilt angle of detector; $DX$: normal distance of crystal from detector; $P$: reciprocal-lattice (r.l.) point on Ewald sphere; $P'$: position of diffraction spot on detector generated by r.l. point $P$; $X$, $Y$: coordinates of $P'$ in the $XPR'$, $YPR'$ coordinate system; $D = DX/\cos \tau$.

Fig. 5. Internal coordinate systems on the detector for the IDXFST routines. $OS = DX \tan \tau$, $SO' = DX(\tan \mu)/\cos \tau$, centre of primary beam on tilted detector in $O'$. 
A possible twist of the detector around the detector normal is corrected by a rotation OMEGA and leads to the new coordinates

\[
X_{PR} = X_P \cos(\text{OMEGA}) + Y_P \sin(\text{OMEGA})
\]

\[
Y_{PR} = -X_P \sin(\text{OMEGA}) + Y_P \cos(\text{OMEGA}).
\]

Finally, a tilt of the detector about the axis \(\tau\) and an inclination of the incident beam about \(\mu\) yields the coordinates in the \(X_{PR}', Y_{PR}'\) system with the centre of the primary beam at point \(O'\) on the tilted detector.

\[
X_{PR}' = X_{PR} + DX \tan \tau
\]

\[
Y_{PR}' = Y_{PR} - DX \left(\tan \mu\right)/\cos \tau.
\]

In order to determine the indices of the reflections, INDEXI needs starting values for the camera parameters and for the orientation matrix (e.g. from prealignment). It transforms the \(X_F, Y_F\) coordinates of the reflection into \(X_{PR}', Y_{PR}'\) coordinates. From these coordinates and the central \(\phi\) value the orthogonal normal reciprocal \((x, y, z)\) coordinates will be calculated. Fig. 6 explains the two general diffraction angles \(\gamma\) and \(\nu\).

We obtain, for the coordinates of the reflection in the \(X_{PR}', Y_{PR}'\) coordinate system,

\[
X = (DX \sin \gamma)/\cos (\gamma - \tau) \cos \tau
\]

\[
Y = -DX \left(\tan \mu\right)/\cos \tau + (DX \tan \nu)/\cos (\gamma - \tau).
\]

A short calculation gives

\[
\tan \gamma = (X \cos^2 \tau)/(DX - X \sin \tau \cos \tau)
\]

\[
\tan \nu = (Y/DX + (\tan \mu)/\cos \tau) \cos (\gamma - \tau).
\]

Now we can compute the reciprocal polar coordinates \(\zeta, \xi, \phi\). From Figs. 7 and 8 the following formulae are derived:

\[
\zeta = \sin \nu - \sin \mu
\]

\[
\xi = (\cos^2 \mu + \cos^2 \nu - 2 \cos \mu \cos \nu \cos \gamma)^{1/2}
\]

(cosine rule, Fig. 8)

The reciprocal coordinates of the reflection on the Ewald sphere in the \(x, y, z\) coordinate system are

\[
X_R = \xi \cos \phi
\]

\[
Y_R = \xi \sin \phi
\]

\[
Z_R = \zeta.
\]

For the indexing we need the unrotated reciprocal coordinates of the reflection:

\[
X_0 = (\cos \phi_e)X_R + (\sin \phi_e)Y_R
\]

\[
Y_0 = -(\sin \phi_e)X_R + (\cos \phi_e)Y_R
\]

\[
Z_0 = Z_R.
\]

\(\phi_e\) is the central \(\phi\) value of the reflection.

The position of a reciprocal-lattice point in the internal \(x, y, z\) coordinate system is given by

\[
\begin{pmatrix}
X_0 \\
Y_0 \\
Z_0
\end{pmatrix}
= C
\begin{pmatrix}
h \\
k \\
l
\end{pmatrix}
\]

\(C\) is the unit matrix.

\[
\text{rotation axis}
\]

Fig. 7. Perspective view of the Ewald sphere for the calculation of the reciprocal polar coordinates \(\zeta, \xi, \phi\) of the spot \(P\) on the Ewald sphere.

\[
\text{Rotation axis}
\]

Fig. 8. View along the \(z\) axis of the Ewald sphere shown in Fig. 7.

\[
\text{Equatorial plane}
\]

Incident beam

Ewald sphere

Equatorial plane

Zero layer

nth layer

Incident beam

Diffused beam

Ewald sphere

Incident beam

Diffused beam

90°

D

1

l

L'

P

X

\(CL = DX/\cos \tau, CL' = DX/\cos (\gamma - \tau)\), application of sine rule in triangle \(CLL'\) yields coordinate \(X\) [equation (13)].

Fig. 6. Definition of diffraction angles \(\gamma\) and \(\nu\). \(CL = DX/\cos \tau, CL' = DX/\cos (\gamma - \tau)\), application of sine rule in triangle \(CLL'\) yields coordinate \(X\) [equation (13)].
with

\[
C = \Phi_I \times \Phi_{II} \times \Phi_X \times A,
\]

\[
A = \begin{pmatrix}
    a^* & b^* & c^*\\
    a^* & b^* & c^*\\
    a^* & b^* & c^*
\end{pmatrix}
\]

= matrix of the components of the reciprocal-cell vectors with respect to the diffractometer coordinate system,

\[
\Phi_X = \begin{pmatrix}
    1 & 0 & 0 \\
    0 & \cos \varphi_x & -\sin \varphi_x \\
    0 & \sin \varphi_x & \cos \varphi_x
\end{pmatrix}
\]

and \(\Phi_{II}\) and \(\Phi_I\) are the corresponding rotation matrices about the y and z axes.

The program now calculates fractional indices from the following expression:

\[
\begin{pmatrix}
    H \\
    K \\
    L
\end{pmatrix} = C^{-1} \begin{pmatrix}
    X_0 \\
    Y_0 \\
    Z_0
\end{pmatrix}.
\]

These fractional indices \(H, K, L\) are rounded to integral indices \(h, k, l\), with allowance for systematic extinctions based on the space group.

The integral indices \(h, k, l\) are now taken to calculate the theoretical positions of the reflections on the detector \(X_E, Y_E\) in the original \(X_F, Y_F\) coordinate system. First we use (18), then the inverse of (17). Subroutine CYANU gives the angles \(\gamma\) and \(\nu\) from the reciprocal coordinates of the spot on the Ewald sphere \(X_R, Y_R, Z_R\), and (13) gives the \(X, Y\) coordinates in the \(X_{PR'}, Y_{PR'}\) coordinate system. Use of the inverse formulae (10)–(12) leads to the desired \(X_E, Y_E\) coordinates.

The function which is minimized by nonlinear least squares is the sum

\[
S = \sum_{i=1}^{N} \frac{[(X_F_i - X_{Ei})^2 + (Y_F_i - Y_{Ei})^2]}{D_i},
\]

with \(D_i^{-1} = (X_{Ei}^2 + Y_{Ei}^2)^{-1/2}\) as weight, and \(N\) = number of reflections. During refinement of the detector position, any of the parameters may be held fixed, either alone or in combination with others.

Up to six unit-cell parameters (depending on the independent crystal parameters of the crystal symmetry system) and the three mis-setting angles are refined in the routine REFORT. To avoid the crystal-specific MATS routine of IDXREF (Nyborg et al., 1975) for the orientation matrix derivatives, we introduced a new routine, MATFST, which is controlled by the AXES command of our newly designed user interface for IDXFST and now supports all space groups for all crystal orientations. REFORT refines the sum

\[
S_1 = \sum_{i} [(R_{oi} - R_{ci})/d^*]^2,
\]

where \(R_{oi} = 1\) = distance of the observed r.l. point on the Ewald sphere from the centre of the Ewald sphere,

\[
R_{ci} = \left[ 1 + 2(\cos \mu)X_R + 2(\sin \mu)Y_R + X_R^2 + Y_R^2 + Z_R^2 \right]^{1/2} = \text{distance of calculated r.l. point near the Ewald sphere to the centre of the Ewald sphere},
\]

and \(d^* = (X_{R}^2 + Y_{R}^2 + Z_{R}^2)^{1/2}\) (scale in relative r.l. units).

The inclination angle \(\mu\) is not refined in REFORT, in order to avoid strong correlation with \(\Phi_{II}\). Only the independent parameters of the corresponding crystal system are refined. As in the refinement of the camera parameters, one may fix any of the independent parameters.

REFORT also carries out a linear least-squares refinement of the effective mosaic spread \(\Delta\) based on observed reflection \(\phi\) ranges from FIND and calculated \(\phi\) ranges from equation (33) of the next section.

INDEXI prints out the refined camera parameters and REFORT the refined cell parameters and mis-setting angles (these are in the IDXFST internal coordinate system as well as in the diffractometer coordinate system). Table 1 shows the results of IDXFST runs for ascorbate oxidase \((a = 106.3, b = 104.9, c = 113.2 \text{ Å})\) and creatinase \((a = 60.9, b = 110.8, c = 62.5 \text{ Å}, \beta = 101.9°)\) with data measured on an Enraf–Nonius FAST diffractometer. The convergence radius of REFORT is about \(\pm 1.5°\) for the mis-setting angles and \(\pm 1\%\) in cell parameters, but depends on the size of the cell constants and with the camera parameters especially on the size of DX. For the camera parameters \(\mu, \tau\) and \(\text{OMEGA}\) it is about \(\pm 0.2°\) for typical DX values between 50 and 100 mm on the FAST system. For these values, the radius of
Table 1. Results of 1DXFST runs for ascorbate oxidase (a) and creatinase (b) with data measured on an Enraf-Nonius FAST diffractometer (e.s.d.'s in parentheses)

<table>
<thead>
<tr>
<th>Camera parameters</th>
<th>CCX (mm)</th>
<th>CCY (mm)</th>
<th>OMEGA (°)</th>
<th>DX (mm)</th>
<th>μ (°)</th>
<th>τ (°)</th>
<th>RMS RESID (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>-0.062(7)</td>
<td>-0.177(7)</td>
<td>-1.391(23)</td>
<td>61.104(24)</td>
<td>0.05(1)</td>
<td>-0.04(1)</td>
<td>0.132</td>
</tr>
<tr>
<td>(b)</td>
<td>-0.114(21)</td>
<td>-0.264(20)</td>
<td>-1.380(49)</td>
<td>55.957(42)</td>
<td>0.02(1)</td>
<td>0.01(2)</td>
<td>0.300</td>
</tr>
</tbody>
</table>

Mis-setting angles (°)

<table>
<thead>
<tr>
<th>PHIX</th>
<th>PHIY</th>
<th>PHIZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0.161(41)</td>
<td>-0.409(88)</td>
</tr>
<tr>
<td>(b)</td>
<td>0.065(7)</td>
<td>-0.425(6)</td>
</tr>
</tbody>
</table>

Cell parameters (Å and °)

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>c</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>RMS RESID (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>106.348(196)</td>
<td>104.929(81)</td>
<td>113.156(39)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>(b)</td>
<td>60.915(50)</td>
<td>110.760(38)</td>
<td>62.475(51)</td>
<td>90.00</td>
<td>101.94(1)</td>
<td>90.00</td>
</tr>
</tbody>
</table>

Number of reflections used in refinement

<table>
<thead>
<tr>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
</tr>
<tr>
<td>(b)</td>
</tr>
</tbody>
</table>

Convergence of DX is about ±0.3 mm and for CCX and CCY about ±0.1 to ±0.2 mm.

V. Prediction of reflections in the MADNES system

Our prediction algorithm is based on that of the FILME program (Schwager, 1975) but with essential changes for the introduction of the μ geometry. Other prediction algorithms used in film evaluation packages are discussed by Taupin (1985) and for area-detector diffractometer systems by Howard et al. (1985) and Thomas et al. (1986).

The procedure needs many of the values that were refined: the six camera parameters, the unit-cell parameters, the three mis-setting angles, X-ray wavelength, spectral dispersion and effective mosaic spread. Other input values serve to limit the reflections that will be predicted: the starting and ending rotation values, the resolution, the space group for systematic extinctions and the size of the detector. As output, the procedure produces a list of predicted reflections with their h,k,l values, detector coordinates YMS, ZMS, the central μ value μc, a μ range value for this reflection and the Lorentz-polarization factor. The reflections are sorted with increasing μ start values, that is, where they begin to traverse through the Ewald sphere.

At the beginning, the program calculates the matrix C of equation (16) and forms the matrix

\[ \Phi C \]

Define μ, the half-width of the predicted region, as

\[ \mu = (\Phi_{\text{end}} - \Phi_{\text{start}})/2. \]

Then the midpoint of the predicted μ region is just

\[ \Phi_{\text{m}} = \Phi_{\text{start}} + \mu. \]

In order to loop through h,k,l indices in an optimum way the indices I_i (i = 1, ..., 3) are determined that show what reciprocal-lattice (r.l.) axis is nearest to the X_D axis (I_1), to the Y_D axis (I_2), and to the Z_D axis (I_3). I_i can have values from 1 to 3 for a*, b*, c*, respectively. Next, the direction cosines RL,RM,RN of the I_3 axis are calculated:

\[ \begin{align*}
RL &= \frac{\Phi(1,I_3)}{A_{I_3}} \\
RM &= \frac{\Phi(2,I_3)}{A_{I_3}} \\
RN &= \frac{\Phi(3,I_3)}{A_{I_3}}
\end{align*} \]

where

\[ A_{I_3} = \left( \frac{1}{AP(I_3)^2 + AP(I_3)^2 + AP(I_3)^2} \right)^{1/2} \]

is the length of the I_3 axis.

The program passes through three nested loops for HKL(I_i). HKL(I_1) varies slowest, HKL(I_2) medium, and HKL(I_3) fastest. Lower and upper limits for HKL(I_1) and HKL(I_2) are predetermined by the given resolution-limiting sphere. Starting and ending values for HKL(I_3) are individually determined for each r.l. row. Fig. 9 shows the actual situation where HKL(I_1) = l, HKL(I_2) = h, and HKL(I_3) = k. The outer loops always define one r.l. row, [HKL(I_1),HKL(I_2),HKL(I_3)] [with HKL(I_1) and HKL(I_2) fixed for a special row], with its reference point P(l,y,z) used in the line equation (26) with indices HKL(I_1),HKL(I_2),0 [it belongs to the r.l.
plane \((\text{HKL}(I_1),\text{HKL}(I_2),0)\) which the two outer loops go through]. In Fig. 9 the r.l. row \([2k\overline{l}]\) and the point \((201)\) are indicated. The intersection points for the row considered with the two limiting Ewald spheres for \(+\alpha\) and \(-\alpha\) and with the resolution sphere are computed. The centres of the limiting spheres for \(+\alpha\) and \(-\alpha\) can be seen in Fig. 10. Their coordinates in the diffractometer coordinate system are derived by a simple rotation of the centre of the Ewald sphere \((-\sin \mu, 0, \cos \mu\) around the \(X_0\) axis about \(+\alpha\) and \(-\alpha\), respectively.

Fig. 11 explains the situation in the \(Y_0,Z_0\) plane of Figs. 9 and 10 with all three limiting spheres. The equations for the limiting spheres are, in relative r.l. units,

first restricting sphere:
\[
(x + \sin \mu)^2 + [y - (\sin \alpha) \cos \mu]^2 + [z - (\cos \alpha) \cos \mu]^2 = 1, \tag{25a}
\]
second restricting sphere:
\[
(x + \sin \mu)^2 + [y + (\sin \alpha) \cos \mu]^2 + [z - (\cos \alpha) \cos \mu]^2 = 1, \tag{25b}
\]
resolution-limiting sphere:
\[
x^2 + y^2 + z^2 = \left(1/d_{\min}\right)^2. \tag{25c}
\]
The equation for a line in an orthonormal coordinate system through a point \(P_1(x_1,y_1,z_1)\) parallel to the direction vector \(R(\text{RL},\text{RM},\text{RN})\) is, in parameter form,
\[
x = x_1 + (\text{RL})t, \quad y = y_1 + (\text{RM})t, \quad z = z_1 + (\text{RN})t. \tag{26}
\]

This can be substituted into the three sphere equations and gives quadratic equations which are easily solved. Their solutions correspond to the intersections of the line with the sphere in question. The reciprocal coordinates \(x_1,y_1,z_1\) of the spot \((\text{HKL}(I_1),\text{HKL}(I_2),0)\) are derived from
\[
x_1 = \text{AP}(1,I_1)\text{HKL}(I_1) + \text{AP}(1,I_2)\text{HKL}(I_2)
\]
\[
y_1 = \text{AP}(2,I_1)\text{HKL}(I_1) + \text{AP}(2,I_2)\text{HKL}(I_2)
\]
\[
z_1 = \text{AP}(3,I_1)\text{HKL}(I_1) + \text{AP}(3,I_2)\text{HKL}(I_2). \tag{27}
\]

Each quadratic equation can have two, one or no solutions. It is tested if the r.l. row intersects or touches the resolution sphere. If not, the next r.l. row is examined. Now the \(z\) values of the intersection points of this line with the three spheres are calculated and the two lowest of these values are taken as \(z_{\text{min}}\) and \(z_{\text{max}}\), one neglects the minimal value of the resolution-sphere solution. In the case of larger prediction batch widths \(2\alpha\), as indicated in Fig. 11, it is possible that the r.l. line has two active parts in the shaded area. This is also taken into account by extra tests. Fig. 12 illustrates the evaluation of the starting and ending values for \(\text{HKL}(I_3)\). We obtain
\[
\text{HKL}(I_3)_{\text{min}} = \text{INT}\{[z_{\text{min}} - (\text{HKL}(I_1),\text{HKL}(I_2),0)z] \times \text{AP}(3,I_3)^{-1}\}
\]
\[
\text{HKL}(I_3)_{\text{max}} = \text{INT}\{[z_{\text{max}} - (\text{HKL}(I_1),\text{HKL}(I_2),0)z] \times \text{AP}(3,I_3)^{-1}\}. \tag{28}
\]
Now we have all loop limits and can obtain the desired index triples \((h,k,l)\) and thence calculate the reciprocal coordinates \(x,y,z\) with \(\varphi = \Phi_m\) belonging to each triple by an equation like (18) with \(\text{AP}\) instead of \(\mathbf{C}\). The spot must now be rotated about the \(X_D\) axis onto the Ewald sphere in the reflection position. The equation for the Ewald sphere is

\[- 2z \cos \mu + 2x \sin \mu + d^* z = 0.\]

(29)

As for a rotation around the \(X_D\) axis, \(x_{\text{new}} = x\), we obtain

\[z_{\text{new}} = d^*/(2 \cos \mu) + x \tan \mu,\]

\[y_{\text{new}} = (d^* x - x^2 - z_{\text{new}}^2)^{1/2}.\]

(30)

The value \(\Delta \varphi\) which must be added to \(\Phi_m\) to get the predicted central \(\varphi\) value \(\varphi_c\) is derived from the two equations for the \(X_D\) rotation,

\[y_{\text{new}} = y \cos \Delta \varphi - z \sin \Delta \varphi\]

\[z_{\text{new}} = y \sin \Delta \varphi + z \cos \Delta \varphi,\]

as

\[\sin \Delta \varphi = (z_{\text{new}} y - y_{\text{new}} z)/(y^2 + z^2)\]

(31)

and

\[\varphi_c = \Phi_m + \Delta \varphi.\]

What remains is the calculation of the detector coordinates. For this, (13) is used. We find the diffraction angles \(\nu\) and \(\gamma\) from

\[\sin \nu = (\sin \mu + x_{\text{new}})\]

\[\cos \gamma = \frac{(2 \cos 2 \mu - 2x_{\text{new}} \sin \mu - x_{\text{new}}^2 - y_{\text{new}}^2 - z_{\text{new}}^2)}{2 \cos \mu (\cos^2 \mu - 2x_{\text{new}} \sin \mu - x_{\text{new}}^2)^{1/2}}.\]

(32)

To arrive at the final detector coordinates in the mm coordinate system \(X_f, Y_f\), we use the inverse equations in the order (12), (11), (10) and convert these \(X_F, Y_F\) coordinates to \(X_f, Y_f\) coordinates. These mm coordinates are then converted to the pixel coordinates YMS and ZMS by the routine MMTOPX. Thus, only the routine MMTOPX would need to be changed for another kind of detector.

The reflection range \(\varphi_R\) is determined from equation (VII.17) of Greenhough & Helliwell (1982) modified for inclined geometry.

\[\varphi_R \sim 2 \varepsilon L\]

(33)

with Lorentz factor

\[L = 2[4 \xi^2 - d^* 4 - 4 d^* 2 (\zeta \sin \mu + \sin^2 \mu)]^{-1/2}\]

(also taken in the Lorentz–polarization factor), and

\[\varepsilon = \frac{1}{2} [\Delta d^* \cos \varTheta + (\delta \lambda / \lambda) d^* \sin \varTheta]\]

with

\[\xi = y_{\text{new}}^2 + z_{\text{new}}^2\]

\[\zeta = x_{\text{new}}\]

\[\Delta = \text{effective mosaic spread}\]

\[\varTheta = \text{Bragg angle}\]

\[\delta \lambda / \lambda = \text{spectral dispersion}.\]

This means that we follow the treatment of mosaicity and beam divergence of Greenhough & Helliwell (1982). The prediction algorithm was tested for \(\mu = 0\) and the results were compared with those from the old algorithm. No differences appeared. With \(\mu \neq 0\) several lists of reflections were predicted and input to the refinement procedure started with deviating start values for the camera parameters, mis-setting angles and cell parameters. IDXFST refined exactly to the original values of the prediction calculation. This was a good test for IDXFST as well as for the new prediction algorithm. Our standard Fortran 77 version is able to predict 400 reflections per second of CPU time on a Digital Equipment Corp. MicroVAX II and has successfully operated during numerous routine measurements on the Enraf–Nonius FAST diffractometer installed in our laboratory over the last several months.

**Concluding remarks**

These orientation and prediction subroutines deal with nearly general diffraction geometry concerning the position of the crystal rotation axis and incidence of the primary beam as well as the location of the detector and can be used either on different PSD–diffractometer systems or in connection with film techniques. The only thing one has to do is to replace the direct and inverse conversion routines from the detector mm coordinate system to the pixel or scanner coordinate system by the appropriate subroutines. If the position of the detector were different from the arrangement described here, one would have to rewrite only the mapping of the reciprocal coordinates of the reflections on the Ewald sphere to the detector coordinates and vice versa. Despite the fact that the crystal rotation axis is fixed in
the mathematical formalism one can accomplish rotations around any desired crystal directions by using the software-supplied rotations around the \( Y_D \) and \( Z_D \) axes. For a general position of the detector one could think of six necessary parameters (three translations and three rotations). Our algorithm contains five parameters [three translations (CCX, CCY, DX) and two rotations (\( \tau \), OMEGA)]. The third rotation around the \( Y_f \) axis of the detector could be quickly introduced if necessary. In our application with measurements on the FAST diffractometer there was no compulsion to do this, as the results of the measurements show.

For the future it would be desirable to use eigenvalue filtering for the parameters in the least-squares refinement as is done in the parameter refinement program of the ROCKS system of Reeke (1984). Eigenvalue filtering detects strong correlations of parameters and can be used to decouple them. IDXFST refines sums \( S \) and \( S_1 \) separately and decouples DX from the cell parameters by this method. The two strong correlations between CCX and \( \tau \) and CCY and \( \mu \) are taken into account by the following procedure. Determine CCX and CCY at \( \mu = 0 \) and \( \tau = 0 \) (\( \mu \) and \( \tau \) are fixed, once the system has been calibrated). If \( \mu \) and \( \tau \) then need to be refined, take the values for CCX and CCY, keep them fixed and refine \( \mu \) and \( \tau \). This yields consistent results.

The MADNES system, of which the described routines are part, requires, for example, on a MicroVAX II a memory size of 3 Mbyte, predicts about 400 reflections per second of CPU time and takes about 30 s CPU time for the refinement of the already mentioned parameters.

We are grateful to Professor R. Huber for his great interest and valuable remarks during this work. AM is indebted to the Bundesministerium für Bildung und Wissenschaft of the Federal Republic of Germany for financial support. Mrs K. Epp is thanked for drawing the figures.

References


