Diffracted Beam Crystal Centering and Its Application to High-Pressure Crystallography

BY HUBERT E. KING JR*

Department of Earth and Space Sciences, State University of New York, Stony Brook, New York 11794, USA

AND LARRY W. FINGER

Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20008, USA

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Abstract

Deviations in the position of a crystal from the center of a goniostat and diffractometer alignment errors can be calculated from the observed angles for diffracted radiation. The present study includes a derivation of equations for the general setting \( \omega \neq 0 \) and a scheme for transformation of these equations into other diffractometer coordinate systems. This method is illustrated by determination of centering errors for FeS in a diamond-anvil cell. In addition, unit-cell parameters for this crystal at high pressure are precisely determined with angular data collected by this technique.

Introduction

When a single-crystal diffraction experiment is performed with a four-circle diffractometer, systematic deviations in the position of the diffracted radiation occur unless the crystal is located at the mechanical center of the goniostat. If the crystal is enclosed in an apparatus that limits optical accessibility, it is necessary to use an alternative to conventional optical centering. This situation often arises when the environment of the crystal is being controlled under conditions other than ambient, e.g., high-pressure, diamond-anvil cell. Hamilton (1974) has outlined a procedure for crystal centering that uses the observed angles for centered reflections to determine various errors, including the offset of the crystal. Two of Hamilton's equations, however, apply only for reflections in the bisecting plane. Hamilton's definitions are re-stated below, transformed into the Busing & Levy (1967) coordinates, will be used.

Discussion

Before equations describing systematic variations in observed diffraction angles may be defined, several definitions and assumptions must be stated. The diffractometer conventions and coordinate systems defined by Busing & Levy (1967) are used.

\( \Delta x - \Delta y \) correction

The corrections for centering errors in the equatorial plane are derived by starting with a centered crystal that is at the angle settings required to observe a reflection. If the crystal is displaced along \( x \) and \( y \), adjustments to the instrument settings are required to return to diffracting conditions. Only the \( \omega \) and \( \theta \) settings must be considered because the \( x \) and \( y \) displacements are parallel to the equatorial plane.

The \( \omega \) and \( \theta \) adjustments can be derived by examining the diffraction geometry of a four-circle diffractometer (Fig. 1) viewed normal to the equatorial plane. The X-ray source is at point \( O \), and the goniostat center at point \( O \). The detector moves in an arc that contains points \( O' \) through \( O' \). The 'ideal' angles are a \( 2\theta \) setting of \( 2\theta \), and an \( \omega \) setting of \( \omega \). The \( \omega \) setting shown in this figure is not the 'ideal' setting.

First consider an offset in the \( x \) position. The crystal is displaced from point \( O \) to \( D \) (a negative \( x \) displacement). Because the X-ray beam is divergent, the crystal must be rotated by \( S \), to maintain diffraction conditions; the detector is rotated from \( O' \) to \( D' \). The \( 2\theta \) setting at point \( D \) differs from the 'ideal' \( 2\theta \) by the angle \( D'O'C \). The value of this angle is found by noting that

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* Address from 1 September 1979: IBM T. J. Watson Research Center, PO Box 218, York Town Heights, New York 10598, USA.

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where $R_c$ is the crystal-to-detector distance. The length $O_cD_c$ is approximately equal to $OA + AA'$ (Fig. 1) and is given by

$$O_cD_c \approx OD \cos (\theta + \Delta \omega) + R_c \sin S'_x.$$  

(2)

The $\Delta \omega$ term is typically less than 0.5° and can be ignored. Equation (1) becomes

$$\sin D_c\hat{O}O_c = \Delta x \cos \theta/R_c + \sin S'_x.$$  

(3)

where $OD$ has been replaced by the magnitude of the $x$ displacement. The sign of $\Delta x$ is arbitrary; it was chosen as positive to conform with Hamilton's definitions. The omega correction can be determined from

$$\sin S'_x = OD \cos (\theta - \Delta \omega)/O_cD.$$  

(4)

From the arguments used above, this equation is rewritten as

$$\sin S'_x = \Delta x \cos \theta/R_c,$$  

(5)

where $R_c$ is the 'effective' distance from the crystal to the X-ray source. For small angular displacements, $\sin x \approx x$ (in rad). Thus, (5) is rewritten as

$$S'_x = \Delta x \cos \theta/R_c.$$  

(6)

Similarly, the $2\theta$ correction (3) is rewritten as

$$D_c\hat{O}O_c = C'_x + S'_x,$$  

(7)

where $C'_x$ is defined as

$$C'_x = \Delta x \cos \theta/R_c.$$  

(8)

Under a transformation of axes, $S'_x$ and $C'_x$ are equivalent to the terms $S_y$ and $C_y$ of Hamilton.

From arguments similar to those for $\Delta x$, it can be shown that the corrections for $\Delta y$ are given by

$$S'_y = \Delta y \sin \theta/R_s,$$  

(9)

and

$$D_c\hat{O}O_c = C'_y - S'_y,$$  

(10)

where

$$C'_y = \Delta y \sin \theta/R_c.$$  

(11)

When the crystal is displaced along both $x$ and $y$ (point $O'$ in Fig. 1), the $\omega$ setting is

$$D = \omega_t + \omega_o + \theta - S'_x + S'_y,$$  

(12)

and the $2\theta$ setting is

$$T = 2\theta_t + 2\theta_o - C'_x - C'_y - S'_x + S'_y.$$  

(13)

$T$ and $D - \theta$ are the measured values of $2\theta$ and $\omega$. The terms with a subscript of zero are the display values of the corresponding axis when the angle is set to a true value of zero.

$\Delta z$ correction

If a centered crystal at the 'ideal' settings is displaced along $z$ (Fig. 2, point $O'$), the $\gamma$ setting must be changed to maintain diffracting conditions. In such a position, the normal to the diffracting plane is in the plane defined by points $O_s, O'$ and $O_c$. The $\gamma$ adjustment is proportional to the angle defined by

$$\sin \tau = OO'/OE.$$  

(14)

The length of $OO'$ is equal to $\Delta z$, and $OE$ is given by (Fig. 3)

$$OE = O'F - EF,$$  

(15)

where points $F$ and $D$ are defined by the intersections of line $O'F$ with lines $O_sO_s'$ and $O_cO_c'$, respectively. The length of $O'F$ is $R_s \sin \theta$. Using the similar triangles $EFO_s$ and $EDO_c$ and simplifying, one obtains the length of $EF$:

$$EF = \sin \theta (R_s - R_c)(1 + R_c/R_s).$$  

(16)

Equation (14) is rewritten as

$$\sin \tau = \frac{\Delta z}{2 \sin \theta (R_s + R_c)}.$$  

(17)

If the diffractometer is in the bisecting position, the $\gamma$ rotation axis is normal to the plane containing the angle $\tau$, and $\Delta \gamma = \tau$; however, in the general setting, the $\gamma$ rotation axis makes an angle of $\omega$ with the plane containing the angle $\tau$. Therefore,

$$\sin \Delta \gamma = \sin \tau \cos \omega,$$  

(18)

and the correction term is approximated by

$$\Delta \gamma \approx \frac{\Delta z \cos \omega}{2 \sin \theta (R_s + R_c)}.$$  

(19)

If the instrument is not in the bisecting condition, a rotation about the $\gamma$ axis will necessitate a rotation about $\omega$ to re-establish the diffracting condition. This
rotation, however, has a second-order dependence on \( r \) and is ignored in this treatment.

\( \Delta h \) correction

If the counter aperture is offset vertically from the equatorial plane, centering the diffracted beam in the counter requires an adjustment of the 'ideal' \( \chi \) setting similar to that derived in the preceding section. The angle of interest (see Fig. 4) is given by

\[
\sin \tau = EE'/OE .
\]  

The length of \( OE \) is known from the preceding derivations. The counter offset, \( \Delta h (O,O') \) in Fig. 4, can be related to \( EE' \) by

\[
\Delta h/(O,E + O,E) = EE'/OE ,
\]

which can be further simplified with the similar triangles \( O,EF \) and \( O,ED \) in Fig. 3:

\[
EE' = \Delta h/(1 + R_c/R_s) .
\]

By analogy with the results from the \( \Delta z \) crystal offset, the correction for a counter-height aperture error in the general setting is

\[
\Delta \chi_c = -\Delta h \cos \omega/(2R_s \sin \theta) .
\]

The negative sign is necessary to preserve the parity of the \( \chi \) rotation as defined by Busing & Levy (1967). The reader should note that an error in the vertical position of the source is essentially equivalent to an error in the counter height.

Error determination

When the previously derived error terms are all non-

\[
T = 2\theta_0 + 2\theta_0 + C_x + C_y + S_x + S_y ,
\]

\[
D = \omega_0 + \omega_0 + \theta + S_x + S_y ,
\]

\[
A = \chi_0 + \chi_0 + \Delta \chi_x + \Delta \chi_y ,
\]

and \( \varphi, T, D - \theta_0, C_x \) and \( A \) are the observed angle settings for \( 2\theta_0, \omega_0 \) and \( \chi_0 \) respectively. Obviously, data from additional orientations of that same reflection will be required to solve for the 12 unknowns involved in (25). An infinite number of possible orientations exist; however, for the set of eight reflections chosen by Hamilton the resolution of the displacement errors is maximized. Some initial orientation is chosen as a reference setting, and three additional orientations are chosen whose \( \theta \)-system axes lie along either the positive or the negative direction of the corresponding axis in the reference setting. Then, these four settings are observed at positive and negative \( 2\theta_0 \). In order to solve the resulting equations, the contribution of each component to \( T, D \) and \( A \) at the seven additional settings must be written in terms of those at the reference (first) setting. The relationships among the 'true' angles are given by Hamilton as Table 3.3.1 and reproduced here as part of Table 1. The zero errors of the angles remain constant. The displacement error terms have fixed magnitudes but variable signs from setting to setting. The following discussion shows how to determine these signs with a superset of Hamilton's rules (expanded to include coordinate system transformations). The \( A_0 \) (Hamilton, 1974, p. 277) to \( \theta \)-system transformation is given as an example.

The sign of each contribution to \( T, D \) and \( A \) is a function of both the sign of the error term itself and the sign of its multiplier in the equation. First, consider the error term. The sense of the crystal displacement relative to the first setting and the definition of the error term determines its sign. The relative displacement is obtained by choosing a positive \( (\Delta x, \Delta y, \Delta z) \) crystal displacement for the first setting and determining how this vector will be reoriented \( (\pm \Delta x, \pm \Delta y, \pm \Delta z) \) for the seven additional settings. The eight sets of coordinates appropriate for the \( A_0 \) system are given in Hamilton's Table 3.5A. This table can be rewritten (Table 1) for the \( \theta \)-coordinate system by a right-handed interchange of the \( x \) and \( y \) axes. (Because \( \Delta x \) and \( \Delta y \) are chosen as positive for the first setting, the sign change is unimportant in constructing this table.) The values in Table 1 can be used only with the error terms defined within the \( \theta \) system. Those for the \( A_0 \) system (Hamilton's equations 2–4) are rewritten in the \( \theta \) system by substituting the appropriately transformed axes:

\[
C_x = \Delta x \cos \theta/R_s = C_y ,
\]

\[
C_y = \Delta y \sin \theta/R_s = -C_x ,
\]

\[
S_x = \Delta x \cos \theta/R_s = S_y ,
\]

\[
S_y = \Delta y \sin \theta/R_s = -S_x ,
\]

(26)
Table 1. Reflection indices, diffractometer angles and displacements for settings used in crystal centering

<table>
<thead>
<tr>
<th>Setting no.</th>
<th>Indices</th>
<th>Angles</th>
<th>Displacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>hh\ell</td>
<td>(2\theta) (\omega) (\chi) (\pi + \varphi)</td>
<td>(\Delta x) (\Delta y) (\Delta z)</td>
</tr>
<tr>
<td>2</td>
<td>hh\ell</td>
<td>(2\theta) (-\omega) (-\chi) (\varphi)</td>
<td>(-\Delta x) (-\Delta y) (-\Delta z)</td>
</tr>
<tr>
<td>3</td>
<td>hh\ell</td>
<td>(-2\theta) (\omega) (\pi + \chi) (\varphi)</td>
<td>(\Delta x) (\Delta y) (\Delta z)</td>
</tr>
<tr>
<td>4</td>
<td>hh\ell</td>
<td>(-2\theta) (-\omega) (-\pi + \chi) (\varphi)</td>
<td>(-\Delta x) (-\Delta y) (-\Delta z)</td>
</tr>
<tr>
<td>5</td>
<td>hh\ell</td>
<td>(-2\theta) (\omega) (\pi + \varphi)</td>
<td>(\Delta x) (\Delta y) (\Delta z)</td>
</tr>
<tr>
<td>6</td>
<td>hh\ell</td>
<td>(-2\theta) (-\omega) (-\pi + \varphi)</td>
<td>(-\Delta x) (-\Delta y) (-\Delta z)</td>
</tr>
<tr>
<td>7</td>
<td>hh\ell</td>
<td>(-2\theta) (\omega) (-\chi) (\varphi)</td>
<td>(-\Delta x) (-\Delta y) (-\Delta z)</td>
</tr>
<tr>
<td>8</td>
<td>hh\ell</td>
<td>(-2\theta) (-\omega) (\chi)</td>
<td>(-\Delta x) (-\Delta y) (-\Delta z)</td>
</tr>
</tbody>
</table>

Table 2. Contributions to observed angles for settings used in crystal centering

<table>
<thead>
<tr>
<th>Setting no.</th>
<th>(T)</th>
<th>(D)</th>
<th>(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(2\theta + 2\theta + C_x - C_y + S_x + S_y)</td>
<td>(\omega + \omega + \theta + S_x + S_y)</td>
<td>(\chi + \varphi + A_{\chi\varphi} - A_{\chi\varphi})</td>
</tr>
<tr>
<td>2</td>
<td>(-2\theta + 2\theta + C_x + C_y - S_x - S_y)</td>
<td>(-\omega + \omega - \theta - S_x - S_y)</td>
<td>(-\chi + \varphi + A_{\chi\varphi} + A_{\chi\varphi})</td>
</tr>
<tr>
<td>3</td>
<td>(-2\theta + 2\theta + C_x + C_y + S_x + S_y)</td>
<td>(\omega + \omega + \theta + S_x + S_y)</td>
<td>(\chi + \varphi + A_{\chi\varphi} - A_{\chi\varphi})</td>
</tr>
<tr>
<td>4</td>
<td>(-2\theta + 2\theta + C_x + C_y + S_x + S_y)</td>
<td>(-\omega + \omega - \theta - S_x - S_y)</td>
<td>(-\chi + \varphi + A_{\chi\varphi} + A_{\chi\varphi})</td>
</tr>
<tr>
<td>5</td>
<td>(2\theta + 2\theta + C_x + C_y + S_x + S_y)</td>
<td>(\omega + \omega + \theta + S_x + S_y)</td>
<td>(\chi + \varphi + A_{\chi\varphi} - A_{\chi\varphi})</td>
</tr>
<tr>
<td>6</td>
<td>(-2\theta + 2\theta + C_x - C_y + S_x + S_y)</td>
<td>(\omega + \omega + \theta + S_x + S_y)</td>
<td>(\chi + \varphi + A_{\chi\varphi} - A_{\chi\varphi})</td>
</tr>
<tr>
<td>7</td>
<td>(-2\theta + 2\theta + C_x + C_y + S_x + S_y)</td>
<td>(-\omega + \omega - \theta - S_x - S_y)</td>
<td>(-\chi + \varphi + A_{\chi\varphi} + A_{\chi\varphi})</td>
</tr>
<tr>
<td>8</td>
<td>(-2\theta + 2\theta + C_x + C_y + S_x + S_y)</td>
<td>(\omega + \omega + \theta + S_x + S_y)</td>
<td>(\chi + \varphi + A_{\chi\varphi} - A_{\chi\varphi})</td>
</tr>
</tbody>
</table>

where the unprimed quantities show the equivalence with Hamilton's terms. Because \(z(A_\theta) = z(O)\), \(A_{\chi\varphi}\) and \(A_{\chi\varphi}\) are unchanged.

The sign of the multipliers in the equations for \(T\), \(D\) and \(A\) can be determined by using Hamilton's equations (2), (3), (5) and (6), appropriately modified for the redefinition of the error terms in (26). The \(\chi\) rotation of the Busing & Levy (1967) diffractometer is negative relative to Hamilton's definitions; therefore, from his equations (2) and (3), \(A_{\chi\chi}\) and \(A_{\chi\chi}\) (modified for the general setting) are

\[
A_{\chi\chi} = \pm \Delta h \cos \omega/(2R_c \sin |\theta|),
\]

where the upper signs are taken at positive two theta.

The equations for \(2\theta\) and \(\omega\) (Hamilton's equations 5 and 6) for negative \(\omega\) parity and modified by (26) are

\[
\Delta \omega = S_x + S_y
\]

and

\[
\Delta 2\theta = C_x + C_y + S_x + S_y.
\]

As before, the upper signs are used at positive \(\theta\). In (27) and (28) the absolute value of \(\theta\) is used. The variable signs in these equations could also be controlled by the sign of \(\theta\). To maintain continuity with Hamilton's equations, however, his technique is used here.

From Table 1 and (27) and (28), equations for \(T\), \(D\) and \(A\) at all eight settings can be determined and are listed in Table 2. From the appropriate linear combination of terms from this table, the values for the unknowns in (25) are found to be as follows:

\[
2\theta_0 = \frac{1}{8} \sum_{i=1}^{8} T_i,
\]

\[
C_x + S_y = \frac{1}{8} \sum_{i=1}^{8} (T_i - T_2 - T_3 - T_4 + T_5 + T_6 - T_7 - T_8),
\]

\[
C_y + S_x = \frac{1}{8} \sum_{i=1}^{8} (-T_2 + T_3 + T_4 + T_5 - T_6 - T_7 + T_8),
\]

\[
\omega_0 = \frac{1}{8} \sum_{i=1}^{8} D_i,
\]

\[
S_x = \frac{1}{8} \sum_{i=1}^{8} (D_1 - D_2 - D_3 + D_4 - D_5 + D_6 + D_7 + D_8),
\]

\[
S_y = \frac{1}{8} \sum_{i=1}^{8} (D_1 - D_2 - D_3 + D_4 - D_5 + D_6 + D_7 - D_8),
\]

\[
\chi_0 = \frac{1}{8} \sum_{i=1}^{8} A_i,
\]

\[
A_{\chi\chi} = \frac{1}{8} \sum_{i=1}^{8} (-A_1 + A_2 + A_3 - A_4 + A_5 + A_6 - A_7 + A_8 + 4\pi),
\]

\[
A_{\chi\chi} = \frac{1}{8} \sum_{i=1}^{8} (-A_1 - A_2 + A_3 + A_4 + A_5 - A_6 + A_7 + A_8).
\]

The crystal displacements \(A_x', A_y'\) and \(A_z'\) obtained from (29) are in the \(\theta\)-coordinate system. Because the position of the crystal can ordinarily be adjusted only in the \(\phi\)-coordinate system, a transformation, defined by the inverse of the matrix \((R)\) given in Busing & Levy's (1967) equation (47), must be applied.

**Experimental**

The displacements in (26) and (27) are defined relative to \(R_x\) and \(R_c\); therefore, these lengths must be determined for a diffractometer. \(R_c\) can be measured directly or obtained from the specifications. The term \(R_x\) is a measure of the divergence of the primary beam and must be determined experimentally. An optically...
Table 3. Sample calculation for crystal centering

<table>
<thead>
<tr>
<th>Setting no.</th>
<th>T</th>
<th>D</th>
<th>A</th>
<th>φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40-084</td>
<td>4-849</td>
<td>13-55</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>40-017</td>
<td>4-808</td>
<td>-13-50</td>
<td>180</td>
</tr>
<tr>
<td>3</td>
<td>-4-009</td>
<td>-4832</td>
<td>-166-49</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>-40-029</td>
<td>-4829</td>
<td>-166-48</td>
<td>180</td>
</tr>
<tr>
<td>5</td>
<td>40-095</td>
<td>35-266</td>
<td>166-50</td>
<td>180</td>
</tr>
<tr>
<td>6</td>
<td>40-078</td>
<td>35-239</td>
<td>-166-44</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>-4-126</td>
<td>-35-237</td>
<td>-13-53</td>
<td>180</td>
</tr>
<tr>
<td>8</td>
<td>-48089</td>
<td>-35-200</td>
<td>13-56</td>
<td>0</td>
</tr>
</tbody>
</table>

From (29):

(a) \(2\theta_0 = 40-081\)°
(b) \(2\theta_0 = -0-013\)°
(c) \(C_z + S_z = 0-012\)°
(d) \(C_z - S_z = 0-001\)°
(e) \(\omega_0 = -15.203\)°
(f) \(\omega_0 = 0-008\)°

centered crystal is displaced along \(x\), and \(C_z\) and \(S_z\) are determined from (29). From (26) it can be shown that \(R_s = R_d(C_z/S_z)\). Because both \(C_z\) and \(S_z\) are small, the error in this calculation is large; therefore, several determinations are recommended. \(R_s\) should be redetermined whenever there is a change in operating conditions that affects the beam divergence, i.e. changes in X-ray tube, collimators and take-off angle.

In the laboratories of the authors, the diffractometer automation systems include routines to collect automatically the eight sets of \(T, D\) and \(A\) data and to solve (29) for the unknowns. A typical set of data and the resulting calculated values for a crystal mounted in a Merrill & Bassett (1974) diamond-anvil cell are shown in Table 3. The diffractometer used to collect these data has \(R_s = 236-5, R_d = 386-4\) mm. Therefore, the counter-height error is \(-0-032\) mm and the crystal displacement \((\Delta x', \Delta y', \Delta z')\) is \(-0-006, -0-015, -0-011\) mm, respectively. The centering routines have a resolution of \(0-0025\)° on \(2\theta\) and \(\omega\) and \(0-01\)° on \(\chi\); thus the sample is centered within the resolution of the instrument \((\simeq \pm 0-030\) mm). An additional constraint on resolution is that several of the equations derived above are valid only for small errors in crystal position and diffractometer errors. The user should always correct the errors in an iterative fashion.

In addition to determining the errors in the centering of crystals for which direct viewing is partially or completely restricted, the technique described above has been used to determine the misalignment of diffractometers. As noted above, the correction terms of (29) are useful in adjustment of the vertical height of the X-ray tube and in finding the true zeros of the instrument's angles. The tube height calculations are particularly valuable because they may be used with reflections at any value of \(\chi\). Manual alignment procedures usually require \(\chi = 90°\). It is clear that additional information about diffractometer and goniostat misalignment could be obtained from procedures similar to those developed here. For example, if the \(\omega\) axis is not perpendicular to the incident beam, changes in \(\omega\) will affect the apparent counter height. However, a complete development of these procedures is outside the scope and purpose of this paper.

The technique is also useful for determination of unit-cell parameters with increased precision. For example, if the method of Tichý (1970) is used to refine the unit-cell data for FeS at \(33-3 \times 10^8\) Pa, values of \(a = 5-862 (5), b = 5-867 (6), c = 11-58 (1)\) Å, \(\alpha = 90-0 (1), \beta = 90-10 (9)\) and \(\gamma = 120-05 (6)\)° are obtained from the centered angles for eleven reflections. On the other hand, if the eleven sets of 'true' angles obtained by the process described above are used in the refinement, the unit-cell parameters are \(a = 5-861 (3), b = 5-861 (2), c = 11-577 (7)\) Å, \(\alpha = 90-00 (5), \beta = 90-05 (4)\) and \(\gamma = 120-01 (3)\)°. The reduction in the uncertainty results from the correction for systematic errors and the reduction of random errors through averaging increased numbers of observations.

The diffracted beam centering technique is most useful for experiments utilizing high-pressure or high-temperature devices. Because the precision of the observations is increased, small variations in the unit cell with temperature and pressure may be resolved. In addition, motion of the sample during the experiment may be detected.

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