On the definition and practical use of crystal-based azimuthal angles

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On the Definition and Practical Use of Crystal-Based Azimuthal Angles

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Abstract

A diffractometer-independent definition of the azimuthal angle ψ of a Bragg reflection is proposed. After completion of intensity measurement, instrument-dependent and partly redundant quantities such as orientation matrix and setting angles may be replaced by ψ values without loss of information. Data-treatment software, such as absorption- and anisotropic-extinction-correction programs, become instrument independent and completely general. Formulae are given to compute ψ for equatorial and non-equatorial diffraction geometries.

Introduction

The geometry of a Bragg reflection in X-ray or neutron diffraction is not completely characterized by the lattice constants of the crystal and the Miller indices *hkl* of the reflecting plane. The calculation of absorption and TDS corrections and the refinement of anisotropic extinction corrections require information on the azimuthal angle ψ of rotation of the crystal about the reciprocal-space vector $\mathbf{r}^*_{hkl}$. For each reflection *hkl*, this angle must be defined with respect to an orientation $\psi = 0$ of the crystal. To our knowledge all commercial manufacturers of four-circle diffractometers define the zero position at the bisecting position $\omega = \theta$ of the instrument. This definition has several disadvantages. As soon as the crystal is taken off the diffractometer and the orientation matrix is lost, values of ψ with respect to the bisecting position become meaningless. The calculation of transmission factors provides an illustration. The shape of the crystal is described by the indices h, k, l and distances d of its faces with respect to a lattice-based coordinate system. These data are then transformed into a diffractometer-fixed coordinate system using the orientation matrix. This matrix cannot be recomputed from ψ angles, or even from the setting angles 2θ, ω, χ and φ if automatic realignments of the crystal have occurred during data collection which are not recorded on the reflection data file. In addition, both the setting angles and the orientation matrix depend on the manufacturer's choice of the senses of rotation of the circles and on the diffractometer-fixed coordinate system. Absorption-correction programs using this kind of machine-dependent information are thus susceptible to errors and need to be adapted to, and tested for, the locally used instrument; major modifications may be required for data obtained with two-circle instruments (Weissenberg geometry) and area detectors.

All these difficulties disappear if the zero position of ψ is defined with respect to the crystal lattice. The geometry of a Bragg reflection is then completely specified by four values, namely h, k, l and ψ. No additional information about the instrument used for the measurements need be retained in a crystallographic data file (Brown, 1983, 1985, 1988), or taken into account during data treatment and structure refinement. In particular, absorption-correction programs become generally applicable and easy to use. The advantage of an instrument-independent definition of ψ was clearly emphasized by Busing & Levy (1967), but as far as we know their advice has not been heeded by manufacturers and software developers. In this paper, we demonstrate a simple and easily implemented method of defining the zero position of ψ.

Definition of the zero position of ψ

In the following, we distinguish between *physical vectors* such as direct- and reciprocal-lattice vectors $\mathbf{r}_{uvw}$ and $\mathbf{r}^*_{hkl}$, and *algebraic vectors* representing physical vectors in a given coordinate system. Algebraic vectors are assumed to be column vectors; row vectors are identified by the symbol T for transposed. In the lattice base, a direct-space vector $\mathbf{r}_{uvw} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$ is represented by the algebraic vector $\mathbf{u}^T = (u, v, w)$; a reciprocal-space vector $\mathbf{r}^*_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ is represented by $\mathbf{h}^T = (h, k, l)$. In a unitary base, we use the same symbol for a physical vector and the corresponding algebraic vector.

Fig. 1 shows the geometry of a Bragg reflection from the plane (*hkl*). All vectors shown are unit vectors: $\mathbf{p}$ and $\mathbf{d}$ represent the primary and diffracted beams, respectively; $\mathbf{f}$ is the normal to the reflecting

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plane; **g** is perpendicular to the plane containing (**p**, **d**, **f**); **e** lies in the intersection of these two planes; **e**, **f** and **g** define a right-handed coordinate system, *i.e.* $\mathbf{e}\times\mathbf{f}.\mathbf{g}=+1$. The vector **q** lies in the plane (*hkl*) and is the reference direction defining the zero position of ψ: for $\psi=0$, **q** coincides with **g**. The ψ rotation about **f** is defined to be positive if the crystal has been turned from this position *counterclockwise* when viewing the plane along $-\mathbf{f}$, in agreement with standard mathematical usage. Thus, $\mathbf{g}\times\mathbf{q}.\mathbf{f}=+\sin\psi$. **e**, **f**, **g** are related to **d** and **p** by

$$\begin{aligned}\mathbf{e}&=-(\mathbf{d}+\mathbf{p})/(2\cos\theta);\\ \mathbf{f}&=\mathbf{r}^*_{hkl}/\|\mathbf{r}^*_{hkl}\|=\lambda\mathbf{r}^*_{hkl}/(2\sin\theta)\\ &=(\mathbf{d}-\mathbf{p})/(2\sin\theta);\\ \mathbf{g}&=(\mathbf{d}\times\mathbf{p})/\sin 2\theta.\end{aligned}\tag{1}$$

ψ is calculated from **e**, **g** and **q** by using the scalar products $\cos\psi=\mathbf{q}.\mathbf{g}$, $\sin\psi=\mathbf{q}.\mathbf{e}$. If all vectors are defined in a unitary coordinate system, this may be put in a concise form by defining a vector $\boldsymbol{\psi}$,

$$\boldsymbol{\psi}^T=(\sin\psi,0,\cos\psi)=\mathbf{q}.(\mathbf{e},\mathbf{f},\mathbf{g}),\tag{2}$$

where (**e**, **f**, **g**) is represented by a 3×3 matrix. The reference vector **q** is represented by the direct-space vector $\mathbf{r}_{uvw}$ normalized to unit length, $\mathbf{q}=\mathbf{r}_{uvw}/\|\mathbf{r}_{uvw}\|$, and defined to be orthogonal to **f** so that $\mathbf{f}.\mathbf{q}=\mathbf{h}^T\mathbf{u}=0$. We propose the convention

$$\begin{aligned}\mathbf{u}^T&=(k-l,l-h,h-k), &&\text{except for } h=k=l;\\ &=(h,\bar{h},0), &&\text{for } h=k=l.\end{aligned}\tag{3}$$

In the calculation of absorption corrections or the refinement of anisotropic extinction, one requires the components of **d** and **p** for the reflection **h** at azimuth ψ. These may be obtained from **f**, **q** and ψ by the equations

$$\begin{aligned}\mathbf{g}&=\mathbf{q}\cos\psi-(\mathbf{f}\times\mathbf{q})\sin\psi;\\ \mathbf{e}&=\mathbf{q}\sin\psi+(\mathbf{f}\times\mathbf{q})\cos\psi;\\ \mathbf{d}&=-\mathbf{e}\cos\theta+\mathbf{f}\sin\theta;\\ \mathbf{p}&=-\mathbf{e}\cos\theta-\mathbf{f}\sin\theta.\end{aligned}\tag{4}$$

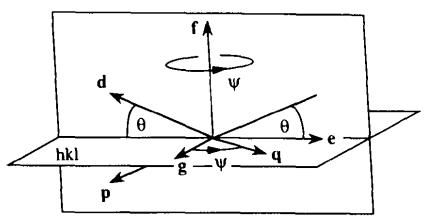

Fig. 1. Definition of the azimuthal angle ψ.

Equatorial geometry

(1) *Calculation of* ψ

Consider a four-circle equatorial-plane diffractometer with circles 2θ, ω, χ and φ. There will be an instrument-defined right-handed laboratory-fixed unitary coordinate system denoted by **x**, **y**, **z**. The orientation matrix **UB** (Busing & Levy, 1967) transforms the coordinates h, k, l of a reciprocal-space vector represented by the vector **h** into coordinates in the laboratory-fixed coordinate system:

$$\mathbf{f}=\mathbf{UBh}/\|\mathbf{UBh}\|.\tag{5}$$

Likewise the $\psi=0$ reference vector **u** defined by (3) transforms to **q** in the laboratory-fixed coordinate system by the relationship

$$\mathbf{q}^T=\mathbf{u}^T(\mathbf{UB})^{-1}/\|\mathbf{u}^T(\mathbf{UB})^{-1}\|.\tag{6}$$

The rotations engendered by the movement of the circles will be represented by matrices whose forms depend on the choice of the laboratory-fixed system of axes, and on the instrument-defined senses of rotations. For the 2θ, χ and φ circles, these matrices are denoted by $2\boldsymbol{\Theta}$, **X** and $\boldsymbol{\Phi}$, respectively. Owing to the geometry of diffraction, it is helpful to make a conventional separation for the movement of ω. We define ω as the angle between the normal to the χ circle and the incident-beam direction, the sense of rotation being the same as 2θ; the bisecting position is thus at $\omega=\theta$. The deviation of ω from the bisecting position is symbolized by $\Delta\omega=\omega-\theta$. The rotation matrices corresponding to ω and $\Delta\omega$ are $\boldsymbol{\Omega}$ and $\boldsymbol{\Delta}$, respectively. The orientation of the crystal at zero setting angles is represented in Fig. 2 by the vectors **e**, **f**, **g** and **q** of a lattice plane (*hkl*) which is to be rotated into reflecting position at an azimuthal angle ψ. The orientation of the crystal at setting angles ω, $\Delta\omega$, χ and φ different from zero is obtained by multiplying **e**, **f**, **g** and **q** with the rotation matrices $\boldsymbol{\Omega}$, $\boldsymbol{\Delta}$, **X** and $\boldsymbol{\Phi}$. The position of the detector at the angle 2θ is obtained with the matrix $2\boldsymbol{\Theta}$. All these matrices represent *active* rotations.

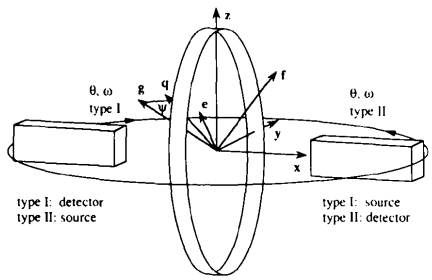

Fig. 2. Four-circle diffractometer at zero setting angles; definition of type-I and type-II diffractometers, and of the laboratory-fixed coordinate system.

The reflecting position of the crystal as shown in Fig. 1 may be attained in two steps: (i) φ, χ and $\Delta\omega$ rotations turn **e**, **f**, **g** into an orientation with **e** pointing towards the primary beam and **f** in the equatorial plane pointing towards the position the detector would occupy at $2\theta = +\pi/2$; (ii) an additional ω rotation of the crystal by θ to satisfy Bragg's law, with the reflected beam being measured after rotation of the detector by 2θ. After the φ, χ, $\Delta\omega$ rotations, the components of **e**, **f**, **g** with respect to the laboratory-fixed system of axes **x**, **y**, **z** are identical for all planes (*hkl*) and angles ψ. They depend only on the definition of **x**, **y**, **z**, and may be represented by the matrix **W**. The components with respect to **x**, **y**, **z** of **e**, **f**, **g** prior to rotation are easily computed from the setting angles for the reflection:

$$\mathbf{\Delta X \Phi (e, f, g) = W}, \quad \mathbf{(e, f, g) = \Phi^T X^T \Delta^T W}. \quad (7)$$

To obtain ψ for this setting, we use (2) with algebraic vectors:

$$\boldsymbol{\psi}^T = \mathbf{q}^T(\mathbf{e, f, g}) = \mathbf{q}^T \mathbf{\Phi}^T \mathbf{X}^T \mathbf{\Delta}^T \mathbf{W}, \quad (8)$$

and inserting (6) for $\mathbf{q}^T$, we obtain

$$\boldsymbol{\psi}^T = \mathbf{u}^T(\mathbf{UB})^{-1} \mathbf{\Phi}^T \mathbf{X}^T \mathbf{\Delta}^T \mathbf{W} / \|\mathbf{u}^T(\mathbf{UB})^{-1}\|. \quad (9)$$

(2) *Unit-cell transformations*

It may arise that data collected in one unit cell need transforming into another. This section establishes the transformation properties of ψ. Fig. 3 shows the relevant vectors in the reflecting plane; subscripts n and o refer to the new and old cells respectively. All physical vectors are represented in the lattice base. Clearly, $\psi_n = \psi_o + \Delta\psi$, where $\Delta\psi$ is the angle to turn the old reference vector $\mathbf{q}_o$ into the new one $\mathbf{q}_n$. $\Delta\psi$ is given by the vector and scalar products $\sin\Delta\psi = \|\mathbf{q}_o \times \mathbf{q}_n\|$, $\cos\Delta\psi = \mathbf{q}_o \cdot \mathbf{q}_n$. Let the cell transformation be specified as a change in Miller indices, $\mathbf{h}_n = \mathbf{T}\mathbf{h}_o$. The direct-space reference vectors $\mathbf{q}_n$ and $\mathbf{q}_o$ are obtained by normalization from the coordinate vectors $\mathbf{u}_n$ and $\mathbf{u}_o$, defined by (3) in terms of $\mathbf{h}_n$ and $\mathbf{h}_o$ in the new and old lattice bases respectively. In the new lattice base $\mathbf{u}_o$ becomes $\mathbf{o}_n = (\mathbf{T}^T)^{-1}\mathbf{u}_o$. The components of the algebraic vector product $\mathbf{v}_n = \mathbf{o}_n \times \mathbf{u}_n$ are the reciprocal-space coordinates of a vector proportional to $\mathbf{q}_o \times \mathbf{q}_n$. Defining $\mathbf{G}_n$ and $\mathbf{G}_n^*$ to be the metrics of direct and reciprocal space of the new cell,

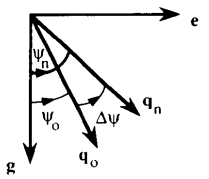

Fig. 3. Vectors needed for unit-cell transformations.

one therefore obtains

$$\begin{aligned} \Delta\boldsymbol{\psi}^T &= (\sin\Delta\psi, 0, \cos\Delta\psi) \\ &= s(\mathbf{v}_n^T \mathbf{G}_n^* \mathbf{v}_n, 0, \mathbf{o}_n^T \mathbf{G}_n \mathbf{u}_n) \quad (10) \\ s^{-2} &= (\mathbf{o}_n^T \mathbf{G}_n \mathbf{o}_n)(\mathbf{u}_n^T \mathbf{G}_n \mathbf{u}_n). \end{aligned}$$

In a Fortran program using the function ATAN2, it is unnecessary to evaluate the normalization factor s.

(3) *Dealing with manufacturer's design*

The information content of output files from diffractometers currently available is diverse. Some examples are listed below.

Case (*a*). For each reflection, the setting angles 2θ, ω, χ and φ are output, and the orientation matix **UB** is output each time it is changed. The ψ of each reflection is easily calculated from (9). Fig. 2 shows two of the most common definitions of the laboratory-fixed system of axes and sense of rotation of the 2θ and ω circles. We call a diffractometer type I if 2θ and ω turn *clockwise*, and type II if 2θ and ω turn *anticlockwise* when viewed along $-\mathbf{z}$. **z** is along the $2\theta/\omega$ axis normal to the equatorial plane, **x** is antiparallel (type I) or parallel (type II) to the primary beam, and **y** lies in the equatorial plane and points towards the detector when 2θ is set to $+\pi/2$. The matrix **W** of (9) is

$$\mathbf{W} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \text{ for type I,}$$
$$\mathbf{W} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \text{ for type II.} \quad (11)$$

Case (*b*). 2θ, ω, χ and φ are output, but only the **UB** matrix at the *end* of data collection is available. The calculation of ψ through (3), (6) and (9) depends on knowing **UB**: if **UB** has changed during data collection due to automatic realignment, the calculation of ψ for all reflections prior to the last reorientation will be inaccurate.

Case (*c*). For each reflection, only the azimuthal angle with respect to the bisecting position as zero is available. An obvious strategy for the calculation of ψ is to use **UB** to calculate the ψ angle of the bisecting position and then apply $\psi = \psi_{\text{bisecting}} + \psi_{\text{manufacturer}}$. There are two potential sources of error in such a procedure. Firstly, one has to be sure of the sense of rotation of ψ adopted by the manufacturer. Secondly, there are two bisecting positions, $\Delta\omega = 0$, at χ_0, φ_0 and at $\pi - \chi_0$, $\pi + \varphi_0$ whose ψ angles differ by π. One of these has been chosen by the manufacturer for the definition of $\psi = 0$. On most instruments, measurements are usually carried out limiting the movement of the φ box to below the equatorial plane of the χ

circle and this criterion is used to define $\psi_{\text{bisecting}} = 0$. If the reflections of a crystal mounted permanently on a support were measured on both a type I and a type II instrument in this standard bisecting position, the respective ψ angles would differ by π. Since the reflecting position is attained by aligning **g** with +**z** on type I, and with −**z** on type II instruments, **g**(bisecting) at zero setting angles lies in the plane (**f**, **z**), pointing towards the upper hemisphere for type I, and towards the lower hemisphere for type II; the vector **e**(bisecting) lies in the equatorial plane. The components of these vectors can therefore be computed directly from the components f_1, f_2, f_3 of **f**:

$$\begin{aligned}\mathbf{e}^T(\text{bisecting}) &= \pm[f_2(1-f_3^2)^{-1/2}, -f_1(1-f_3^2)^{-1/2}, 0];\\ \mathbf{g}^T(\text{bisecting}) &= \pm[-f_1f_3(1-f_3^2)^{-1/2},\\ &\qquad -f_2f_3(1-f_3^2)^{-1/2}, (1-f_3^2)^{1/2}];\\ &\quad + \text{ for type I, } - \text{ for type II.}\end{aligned} \tag{12}$$

A safe procedure is to reproduce the manufacturer's algorithm for the calculation of setting angles at azimuth ψ with respect to the bisecting position from h, k, l and **UB**, and then to calculate ψ from (9).

Case (d). One commercial system allows $|\mathbf{UB}|$ to be negative and thus the lattice base to be left-handed without warning or indication. To correct this situation, all h, k, l should be changed into $\bar{h}$, $\bar{k}$, $\bar{l}$. With our choice of **u** given in (3), $\mathbf{u}_n = -\mathbf{u}_o = \mathbf{o}_n$, $\mathbf{v}_n = \mathbf{0}$ and $\Delta\psi = 0$ from (10). ψ is thus invariant under this transformation.

Non-equatorial geometry

Fig. 4 shows a non-equatorial reflection on a type I instrument as may be encountered in Weissenberg geometry or on an area detector. The direction of the diffracted beam **d** is defined by the equatorial angle $2\theta'$ and the elevation angle ν. Spherical trigonometry gives for the Bragg angle

$$\cos 2\theta = \cos 2\theta' \cos \nu. \tag{13}$$

The components of **d** and **p** in Fig. 4 are

$$\begin{aligned}\mathbf{d}^T &= [\mp\cos \nu \cos 2\theta', \cos \nu \sin 2\theta', \sin \nu],\\ \mathbf{p}^T &= [\mp 1, 0, 0],\end{aligned} \tag{14}$$

the upper sign corresponding to type-I and the lower sign to type-II instruments. We denote by **e**′, **f**′, **g**′ the positions of the vectors **e**, **f**, **g** of Fig. 2 after rotations by φ, χ and ω (*not* $\Delta\omega$): $(\mathbf{e}', \mathbf{f}', \mathbf{g}') = \mathbf{\Omega X \Phi}(\mathbf{e}, \mathbf{f}, \mathbf{g})$. Application of (1) gives

$$\begin{aligned}\mathbf{e}'^T &= [\pm(1+\cos \nu \cos 2\theta'),\\ &\qquad -\cos \nu \sin 2\theta', -\sin \nu]/2\cos\theta;\\ \mathbf{f}'^T &= [\pm(1-\cos \nu \cos 2\theta'),\\ &\qquad \cos \nu \sin 2\theta', \sin \nu]/2\sin\theta;\\ \mathbf{g}'^T &= [0, \mp\sin \nu, \pm\cos \nu \sin 2\theta']/\sin 2\theta.\end{aligned} \tag{15}$$

At zero setting angles, we get for both types of diffractometer

$$\begin{aligned}(\mathbf{e}, \mathbf{f}, \mathbf{g}) &= \mathbf{\Phi}^T\mathbf{X}^T\mathbf{\Omega}^T(\mathbf{e}', \mathbf{f}', \mathbf{g}')\\ &= \mathbf{\Phi}^T\mathbf{X}^T\mathbf{\Delta}^T\mathbf{\Theta}^T(\mathbf{e}', \mathbf{f}', \mathbf{g}')\end{aligned} \tag{16}$$

where $\mathbf{\Theta}$ represents an ω rotation by θ. $\mathbf{\Theta}^T(\mathbf{e}', \mathbf{f}', \mathbf{g}')$ corresponds to the matrix **W** of (7) and reduces to (11) for $\nu = 0$. The reference vector **q** is obtained from (3) and (6) with the orientation matrix **UB**, as for the equatorial geometry. For the Weissenberg geometry, **UB** may be calculated from the indices and setting angles ω of two zero-layer reflections.

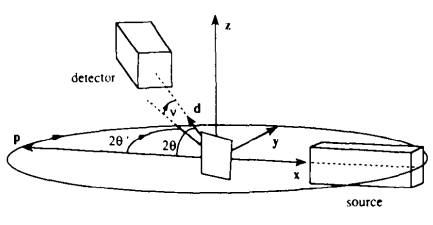

Fig. 4. Geometry of a non-equatorial reflection for a type-I instrument.

Concluding remarks

We have shown that the ψ angle of a Bragg reflection hkl defined with respect to the crystal lattice can be obtained from the orientation matrix **UB** and the setting angles 2θ, ω, χ and φ. For a reflection measured at the bisecting position, it may also be obtained from the **UB** matrix alone using (12). The expressions used to calculate ψ depend on the instrument used for the experiment: the rotation matrices $2\mathbf{\Theta}$, $\mathbf{\Omega}$, $\mathbf{\Delta}$, **X** and $\mathbf{\Phi}$ depend on the senses of rotation of the axes, and **UB** depends on the laboratory-fixed coordinate system chosen by the manufacturer. It would therefore be most efficient to calculate ψ at data-collection time, since all the necessary information is then readily available and the additional computing expense is minimal. Reflection-data output files could be shortened since setting angles are redundant information; they may easily be recomputed from h, k, l and ψ if **UB** is known and have no significance if **UB** is lost. In addition, reflection-data files of some commercial diffractometers currently available are incomplete and lead to inaccurate or ambiguous calculations of ψ.

It is our firm opinion that all diffractometer software should be designed, or if possible redesigned, to use only a crystal-based azimuth as described here. As existing commercial diffractometer software does not carry out this calculation, an optimal strategy is to compute ψ in an instrument-specific program immediately after completion of the diffraction experiment while the necessary orientation information is still available to the experimenter. In order to minimize error and loss of information, this program should have direct access to the computer controlling

the diffractometer and should output the data in a standardized instrument-independent format. Programs (Flack & Blanc, 1989) using the Standard Crystallographic File Structure (Brown, 1983, 1985, 1988) have been written to implement this technique for the three types of commercial four-circle diffractometers available to us.

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