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Angle Calculations for 3- and 4- Circle X-ray and Neutron Diffractometers*

BY WILLIAM R. BUSING AND HENRI A. LEVY

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, *U.S.A.*

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Methods are derived for calculations useful in the operation of 3- and 4-circle X-ray or neutron single-crystal diffractometers. These include: (1) establishing the sample orientation from the cell parameters and the observed angles for two reflections, or from the observed angles for three reflections only, (2) calculating the angles for observing a given reflection either in a special setting or at a specified azimuthal angle, (3) obtaining the vectors needed for calculating absorption corrections, and (4) using observations of several reflections to refine cell and orientation parameters by the method of least squares.

It appears that 3- and 4-circle X-ray or neutron diffractometers will be used increasingly in the next few years. For this reason it seems desirable to present in a compact way some mathematical procedures that can be used with these instruments to establish sample orientation and to calculate setting angles. All of the techniques described here have been tested and found useful in our work with the Oak Ridge automatic 3-circle neutron diffractometer (Busing, Smith, Peterson & Levy, 1964) and the Oak Ridge computer-controlled 4-circle X-ray diffractometer (Busing, Ellison & Levy, 1965). Some of these calculations have been discussed in a less general way by others (Furnas & Harker, 1955; Arndt & Phillips, 1957; Willis, 1961; Santoro & Zocchi, 1964; Wooster, 1964; Rollett, 1965).

Calculations of this type will almost certainly be performed by means of a high-speed computer, and algorithms for many of the procedures are presented elsewhere (Busing & Levy, 1966). Matrix arithmetic is used extensively because the expressions in expanded form would often be too cumbersome to be useful.

Definition of diffractometer angles

The instrument arrangement which we will take as standard is illustrated schematically in Fig. 1(*a*), which shows the instrument axis as vertical. Perpendicular to this axis and passing through the instrument center is a horizontal plane. The primary beam lies in this horizontal plane and is directed at the sample which is located at the instrument center. The counter also lies in the horizontal plane and rotates about the instrument axis to make an angle 2θ with the primary beam direction. The instrument angles may be adjusted so that a diffracted beam is horizontal and enters the center of the counter.

Moving the counter through an angle of 2θ causes the crystal orienter and sample to turn through an angle of θ about the vertical axis. The orienter may also be rotated independently through an additional angle ω about the same axis. In this way the χ axis which lies in the horizontal plane is positioned to make an angle of $\theta+\omega$ with the primary beam direction. The reflecting-plane normal (scattering vector), which bisects the angle between the diffracted beam and the reverse primary beam, thus makes an angle of ω with the plane of the χ ring.

The φ shaft is supported from the χ ring which permits the φ axis to be set at an angle χ from the vertical instrument axis. The sample is assumed to be rigidly attached to the φ shaft so that it can be turned about this axis.

The diffractometer with all angles set to zero is shown schematically in Fig. 1(*b*). The senses of θ, 2θ, ω, and χ are defined by Fig. 1(*a*), which shows the instrument with these angles in the first quadrant. The zero position for φ is chosen arbitrarily, and the figure shows the direction of rotation which increases this angle.

Also shown in Fig. 1(*a*) is the angle ψ which measures the rotation of the sample about the normal to the reflecting plane of interest. With this type of diffractometer ψ motion is achieved not by the rotation of a single shaft but rather as the result of a combination of changes in ω, χ, and φ. The choice of zero for ψ will be discussed below.

These definitions will be assumed throughout this paper, but the results can be applied to instruments with other conventions by making the appropriate transformations. The 3-circle diffractometer can usually be regarded as a special case for which ω is constrained to be zero.

Coordinate transformations

Let $\mathbf{v}$ be the column vector describing some physical vector $\boldsymbol{v}$ in terms of the right-handed reciprocal lattice vectors $\boldsymbol{b}_i$ so that

$$\boldsymbol{v}=\sum_{i=1}^{3} v_i\boldsymbol{b}_i\,. \qquad (1)$$

It will be convenient to define several systems of right-handed cartesian axes which may also be used to describe $\boldsymbol{v}$.

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Let $\mathbf{v}_c$ be the description in terms of the *crystal cartesian* axes which are attached in some way to the reciprocal lattice. If we choose the x axis parallel to $\boldsymbol{b}_1$, the y axis in the plane of $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$, and the z axis perpendicular to that plane, then

$$\mathbf{v}_c = \mathbf{B}\,\mathbf{v} \tag{2}$$

where

$$\mathbf{B} = \begin{pmatrix} b_1 & b_2\cos\beta_3 & b_3\cos\beta_2 \\ 0 & b_2\sin\beta_3 & -b_3\sin\beta_2\cos\alpha_1 \\ 0 & 0 & 1/a_3 \end{pmatrix}. \tag{3}$$

Here the a_i's and α_i's and the b_i's and β_i's are the direct and reciprocal lattice parameters, respectively. This expression is related to transformations discussed by Patterson (1959*a*) and by Rollett (1965), and although our crystal cartesian system is different from those chosen by these authors, nothing in this paper except the above expression for matrix **B** depends upon this choice.

Let the φ-axis system be a set of cartesian axes rigidly attached to the φ shaft of the instrument. When all instrument angles are set to zero this system has the orientation shown in Fig. 1(*b*) with the x axis along the scattering vector, the y axis in the direction of the primary beam, and the z axis in the vertical instrument-axis direction.

Let **U** be the orthogonal matrix which relates this φ-axis system to the crystal cartesian system so that

$$\mathbf{v}_\varphi = \mathbf{U}\,\mathbf{v}_c\,. \tag{4}$$

U will be called the orientation matrix since it depends on the way in which the crystal has been mounted and also on the arc settings if a goniometer head is used. **U** may readily be derived for certain special orientations, and in later sections we will consider general ways of obtaining **U**.

In a similar way let us define three more cartesian systems attached to the χ, ω, and θ axes, respectively, and coincident with the φ-axis system when all instrument angles are zero. The vector $\boldsymbol{v}$ is transformed to these systems as follows:

$$\mathbf{v}_\chi = \mathbf{\Phi}\,\mathbf{v}_\varphi\,, \tag{5}$$
$$\mathbf{v}_\omega = \mathbf{X}\,\mathbf{v}_\chi\,, \tag{6}$$
$$\mathbf{v}_\theta = \mathbf{\Omega}\,\mathbf{v}_\omega\,, \tag{7}$$

where

$$\mathbf{\Phi} = \begin{pmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{8}$$

$$\mathbf{X} = \begin{pmatrix} \cos\chi & 0 & \sin\chi \\ 0 & 1 & 0 \\ -\sin\chi & 0 & \cos\chi \end{pmatrix}, \tag{9}$$

and

$$\mathbf{\Omega} = \begin{pmatrix} \cos\omega & \sin\omega & 0 \\ -\sin\omega & \cos\omega & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{10}$$

Finally let us define a *laboratory system* fixed with respect to the primary beam and a *2θ-axis system* attached to the counter shaft. Again these cartesian axes will be chosen to coincide with the φ-axis system when all the instrument angles are zero. A vector $\boldsymbol{v}$ is transformed to these systems as follows:

$$\mathbf{v}_l = \mathbf{\Theta}\,\mathbf{v}_\theta = \mathbf{N}\,\mathbf{v}_\omega \tag{11}$$
$$\mathbf{v}_{2\theta} = \mathbf{\Theta}\,\mathbf{v}_\theta = \mathbf{M}\,\mathbf{v}_\omega \tag{12}$$

where

$$\mathbf{\Theta} = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{13}$$

$$\mathbf{N} = \mathbf{\Theta}\,\mathbf{\Omega} = \begin{pmatrix} \cos\nu & \sin\nu & 0 \\ -\sin\nu & \cos\nu & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{14}$$

with $\nu = \omega + \theta$,
and

$$\mathbf{M} = \tilde{\mathbf{\Theta}}\,\mathbf{\Omega} = \begin{pmatrix} \cos\mu & \sin\mu & 0 \\ -\sin\mu & \cos\mu & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{15}$$

with $\mu = \omega - \theta$.

All angles except χ can be considered to be left-handed rotations about their respective axes.

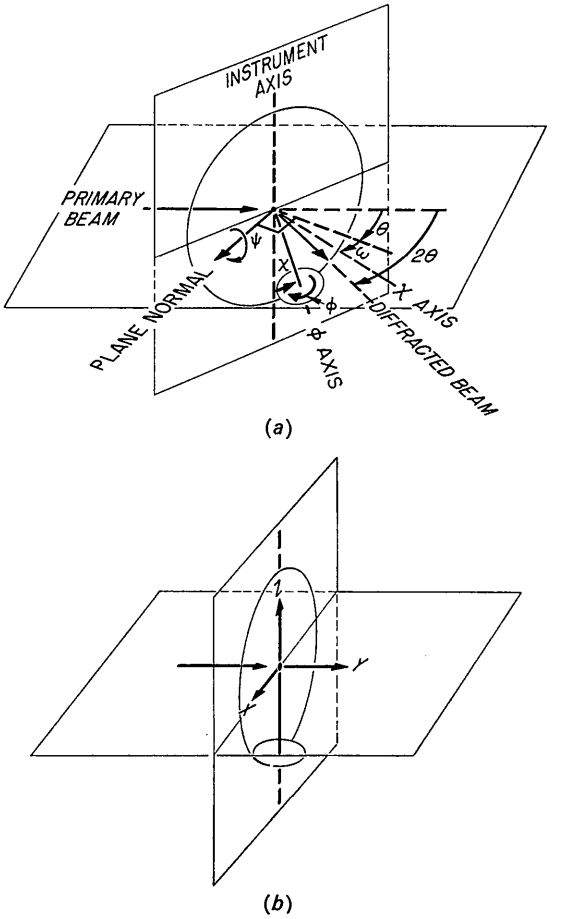

Fig. 1. Schematic representation of a 4-circle diffractometer. (*a*) The configuration when each instrument angle has a value in the first quadrant. (*b*) The instrument with all angles set to zero. The coordinate axes are those of the φ-axis, χ-axis, ω-axis, θ-axis, 2θ-axis, and laboratory systems which are all coincident under these conditions.

Basic diffractometer equations

Throughout this paper we will assume the following ideal conditions: a perfect diffractometer, a centered point sample with no mosaic spread, and a point source of monochromatic radiation. The deviations from these assumptions which are found in practice usually do not invalidate the calculations to be described. One exception is the presence of the α-doublet in the X-ray spectrum, the effect of which will be mentioned in the section on least-squares refinement.

To observe a reflection in the ideal diffractometer setting shown in Fig. 1(*a*) it is necessary for θ to satisfy the Bragg equation and for the plane normal to lie along the x axis of the θ coordinate system. If h, k, and l are the indices of the reflecting plane then the corresponding column vector in the reciprocal lattice system is

$$\mathbf{h}=\begin{pmatrix} h \\ k \\ l \end{pmatrix} . \tag{16}$$

The length q of this vector which is the reciprocal of the interplanar spacing in Å is readily found from its components in any one of our cartesian systems. For example

$$q=(h_{c1}^2+h_{c2}^2+h_{c3}^2)^{\frac{1}{2}} \tag{17}$$

where

$$\mathbf{h}_c=\mathbf{B}\,\mathbf{h}.$$

The Bragg equation is then

$$\sin\theta=\lambda q/2 . \tag{18}$$

The plane normal will have the desired direction if

$$\mathbf{h}_\theta=\mathbf{\Omega}\,\mathbf{X}\,\mathbf{\Phi}\,\mathbf{U}\,\mathbf{B}\,\mathbf{h} \tag{19}$$

has the form

$$\mathbf{h}_\theta=\begin{pmatrix} q \\ 0 \\ 0 \end{pmatrix} . \tag{20}$$

Equations (17) to (20) can be regarded as the fundamental equations for this diffractometer.

Evaluating the orientation matrix

We will now show how the orientation matrix **U** can be obtained from the observation of two reflections from non-parallel planes of known indices provided that the cell parameters are known. For reasons which will become apparent we will call these two reflections the primary and secondary orienting reflections. Let their indices be $\mathbf{h}_1$ and $\mathbf{h}_2$, respectively.

From the observation of the instrument angles ω, χ, and φ which center the diffracted beam in the counter we can obtain $\mathbf{u}_\varphi$, the description in the φ-axis system of a unit vector which has the direction of the plane normal:

$$\mathbf{u}_\varphi=\tilde{\mathbf{\Phi}}\tilde{\mathbf{X}}\tilde{\mathbf{\Omega}}\mathbf{u}_\theta=\tilde{\mathbf{\Phi}}\tilde{\mathbf{X}}\tilde{\mathbf{\Omega}}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{21}$$

or in expanded form:

$$\mathbf{u}_\varphi=\begin{pmatrix} \cos\omega\,\cos\chi\,\cos\varphi-\sin\omega\,\sin\varphi \\ \cos\omega\,\cos\chi\,\sin\varphi+\sin\omega\,\cos\varphi \\ \cos\omega\,\sin\chi \end{pmatrix} . \tag{22}$$

In this way two unit vectors $\mathbf{u}_{1\varphi}$ and $\mathbf{u}_{2\varphi}$ can be obtained from the observed angles of the primary and secondary orienting reflections, respectively.

Since the indices and cell parameters are known we can calculate the scattering vectors in the crystal cartesian system:

$$\left.\begin{aligned} \mathbf{h}_{1c}&=\mathbf{B}\,\mathbf{h}_1 \\ \mathbf{h}_{2c}&=\mathbf{B}\,\mathbf{h}_2 . \end{aligned}\right\} \tag{23}$$

Ideally the desired matrix **U** should perform the transformations

$$\left.\begin{aligned} \mathbf{h}_{1\varphi}&=\mathbf{U}\,\mathbf{h}_{1c} \\ \text{and} \\ \mathbf{h}_{2\varphi}&=\mathbf{U}\,\mathbf{h}_{2c} , \end{aligned}\right\} \tag{24}$$

so that the calculated $\mathbf{h}_{1\varphi}$ and $\mathbf{h}_{2\varphi}$ have the directions of the observed $\mathbf{u}_{1\varphi}$ and $\mathbf{u}_{2\varphi}$, respectively. However, because of experimental errors in the angle measurements or uncertainties in the cell parameters, it is not in general possible to find an orthogonal matrix **U** which satisfies both conditions. That is to say, the angle subtended by $\mathbf{h}_{1c}$ and $\mathbf{h}_{2c}$ may in general differ slightly from that subtended by $\mathbf{u}_{1\varphi}$ and $\mathbf{u}_{2\varphi}$.

In order to avoid this difficulty we will require that $\mathbf{h}_{1\varphi}$ be parallel to $\mathbf{u}_{1\varphi}$ as before, but $\mathbf{h}_{2\varphi}$ will only be constrained to lie in the plane of $\mathbf{u}_{1\varphi}$ and $\mathbf{u}_{2\varphi}$. Thus the primary reflection determines the direction of a vector in the crystal, and the secondary reflection establishes an angle of rotation about this axis.

Define a right-handed orthogonal unit-vector triple, $\mathbf{t}_{1c}$, $\mathbf{t}_{2c}$, $\mathbf{t}_{3c}$, in the crystal cartesian system so that $\mathbf{t}_{1c}$ is parallel to $\mathbf{h}_{1c}$, $\mathbf{t}_{2c}$ lies in the plane of $\mathbf{h}_{1c}$ and $\mathbf{h}_{2c}$, and $\mathbf{t}_{3c}$ is perpendicular to this plane. Define another such triple, $\mathbf{t}_{1\varphi}$, $\mathbf{t}_{2\varphi}$, $\mathbf{t}_{3\varphi}$, in the φ-axis system based in the same way on $\mathbf{u}_{1\varphi}$ and $\mathbf{u}_{2\varphi}$. Then, since these two unit-vector triples can be exactly superimposed on each other, the desired orthogonal matrix **U** will satisfy exactly the equations

$$\mathbf{t}_{n\varphi}=\mathbf{U}\,\mathbf{t}_{nc};\ n=1, 2, 3 . \tag{25}$$

These three vector equations can be written as one matrix equation

$$\mathbf{T}_\varphi=\mathbf{U}\,\mathbf{T}_c \tag{26}$$

where $\mathbf{T}_c$ is the matrix with columns $\mathbf{t}_{1c}$, $\mathbf{t}_{2c}$, and $\mathbf{t}_{3c}$ and $\mathbf{T}_\varphi$ is similarly constructed from $\mathbf{t}_{1\varphi}$, $\mathbf{t}_{2\varphi}$, and $\mathbf{t}_{3\varphi}$. Then

$$\mathbf{U}=\mathbf{T}_\varphi\mathbf{T}_c^{-1}=\mathbf{T}_\varphi\tilde{\mathbf{T}}_c \tag{27}$$

since $\mathbf{T}_c$ can be shown to be orthogonal.

A procedure for use when the lattice parameters are unknown

When the unit-cell parameters are unknown it is still possible to obtain the matrix **UB** if the setting angles can be observed for three reflections with known (or assumed) indices. Given $2\theta_i$, ω_i, χ_i, and φ_i for reflec-

tion i, we can compute the scattering vector in the φ-axis system:

$$\mathbf{h}_{i\varphi}=(2\sin\theta_i/\lambda)\mathbf{u}_{i\varphi}\,, \tag{28}$$

where $\mathbf{u}_{i\varphi}$ is obtained by equation (22). For each of the three reflections the matrix **UB** must perform the transformation

$$\mathbf{h}_{i\varphi}=\mathbf{U}\,\mathbf{B}\,\mathbf{h}_i\,, \tag{29}$$

where $\mathbf{h}_i$ is the vector of indices. Then if $\mathbf{H}_\varphi$ is a matrix made up of the three column vectors $\mathbf{h}_{i\varphi}$, and if **H** is similarly constructed from $\mathbf{h}_i$, we have

$$\mathbf{H}_\varphi=\mathbf{U}\,\mathbf{B}\,\mathbf{H} \tag{30}$$

and

$$\mathbf{U}\,\mathbf{B}=\mathbf{H}_\varphi\,\mathbf{H}^{-1}\,. \tag{31}$$

The reflections chosen must correspond to reciprocal lattice vectors which are not coplanar or the matrix **H** will be singular. The indices should be assigned so that the vectors can be described with reference to a right-handed coordinate system, and it can be shown that the determinant $|\mathbf{U}\,\mathbf{B}|$ (which has an absolute value equal to the unit cell volume) will be positive if and only if this condition is met.

When the matrix **U B** has been obtained it is possible to derive from it the corresponding cell parameters. Let us compute the matrix

$$\widetilde{\mathbf{U}\,\mathbf{B}}\,\mathbf{U}\,\mathbf{B}=\tilde{\mathbf{B}}\tilde{\mathbf{U}}\,\mathbf{U}\,\mathbf{B}=\tilde{\mathbf{B}}\,\mathbf{B}\,. \tag{32}$$

It can be shown that

$$\tilde{\mathbf{B}}\,\mathbf{B}=\mathbf{G}^{-1} \tag{33}$$

where $\mathbf{G}^{-1}$ is the reciprocal metric tensor with elements

$$(G^{-1})_{ij}=\boldsymbol{b}_i\,.\,\boldsymbol{b}_j\,. \tag{34}$$

Then **G** is the metric tensor (see, *e.g.* Patterson, 1959*b*) with elements

$$G_{ij}=\boldsymbol{a}_i\,.\,\boldsymbol{a}_j \tag{35}$$

and the direct lattice parameters are given by:

$$\left.\begin{aligned} &a_i=G_{ii}^{\frac{1}{2}} \\ \text{and}\quad &\cos\alpha_i=G_{jk}/a_ja_k;\ i\neq j\neq k\neq i\,. \end{aligned}\right\} \tag{36}$$

Angle calculations for special cases

Once the matrix **UB** has been evaluated it is possible to obtain

$$\mathbf{h}_\varphi=\mathbf{U}\,\mathbf{B}\,\mathbf{h} \tag{37}$$

for any set of indices **h**, and ways of computing instrument angles which bring this vector into the ideal reflecting position will now be discussed. With a four-circle instrument this reflecting condition can be established in an unlimited number of ways corresponding to various values of ψ, the angle of rotation of the sample about the scattering vector. It will be useful to consider two special cases in which one of the instrument angles is fixed at a convenient value.

First let us consider the *bisecting position* in which ω is constrained to be zero so that the plane of the χ ring bisects the angle defined by the reverse primary and diffracted beams. This arrangement permits access to all reflections with θ below an upper limit, and it is the only position available with most three-circle instruments.

Assume that the diffractometer initially has all angles set to zero. The vector $\mathbf{h}_\varphi$ can be brought to the scattering position by first rotating φ to bring it into the plane of the χ ring and then changing χ to bring it to the horizontal plane. The required angle changes are

$$\left.\begin{aligned} &\varphi=\operatorname{atan}(h_{\varphi 2},\,h_{\varphi 1}) \\ \text{and}\quad &\chi=a\operatorname{tan}[h_{\varphi 3},\,(h_{\varphi 1}^2+h_{\varphi 2}^2)^{\frac{1}{2}}]\,. \end{aligned}\right\} \tag{38}$$

In the above equations and throughout this paper the expression

$$\alpha=\operatorname{atan}(y,\,x) \tag{39}$$

defines an angle $\alpha=\arctan(y/x)$ in the quadrant for which the signs of $\sin\alpha$ and $\cos\alpha$ are those of y and x, respectively.

The expressions given above yield angles with $-90°\leq\chi\leq 90°$ because the square root is taken as positive. An alternative setting

$$\left.\begin{aligned} \varphi'&=180°+\varphi \\ \chi'&=180°-\chi \end{aligned}\right\} \tag{40}$$

corresponds to a rotation of 180° about the scattering vector ($\psi'=180°+\psi$).

In the bisecting position the Bragg angle which can be reached may be limited by the fact that the χ ring lies between the counter and the source. Higher Bragg angles can be reached if ω is allowed to take values which turn the χ ring past the counter so that its plane is more or less parallel to the reflecting plane. Usually the greatest range can be obtained by constraining χ to be 90°.

Consider the instrument with $\chi=90°$ and the other angles set to zero. The vector $\mathbf{h}_\varphi$ can be brought into the horizontal plane by rotating φ and it can then be brought to the scattering position by changing ω. The expressions for these angles are

$$\left.\begin{aligned} &\varphi=\operatorname{atan}(h_{\varphi 1},\,-h_{\varphi 2}) \\ \text{and}\quad &\omega=\operatorname{atan}[-(h_{\varphi 1}^2+h_{\varphi 2}^2)^{\frac{1}{2}},\,h_{\varphi 3}]\,. \end{aligned}\right\} \tag{41}$$

Compared with the bisecting position these settings correspond to a 90° rotation about the scattering vector.

Reflections with vectors nearly parallel to the φ axis are inaccessible in this arrangement because of interference between the χ ring and the counter or primary beam. The apex angles of the cones which are lost become large at low Bragg angles. Three alternative settings are available:

	1	2	3
φ'	$180°+\varphi$	φ	$180°+\varphi$
χ'	90°	$-90°$	$-90°$
ω'	$-\omega$	$180°-\omega$	$180°+\omega$
ψ'	$180°+\psi$	$180°+\psi$	ψ

but the use of these may not reduce the amount of interference significantly.

Angles for a specified azimuth

We will now consider the problem of computing the diffractometer settings for some specified value of the azimuthal angle, ψ. Let us define an instrument-angle matrix

$$\mathbf{R}=\mathbf{\Omega}\,\mathbf{X}\,\mathbf{\Phi} \tag{42}$$

which transforms a vector from the φ-axis system to the θ-axis system. For the vector to be in the scattering position we must have

$$\mathbf{R}\,\mathbf{h}_{\varphi}=\mathbf{h}_{\theta}=\begin{pmatrix}q\\0\\0\end{pmatrix}\,. \tag{43}$$

Choose some diffractometer setting which satisfies this condition and define $\psi=0$ for this configuration. We can then evaluate

$$\mathbf{R}_0=\mathbf{\Omega}_0\,\mathbf{X}_0\,\mathbf{\Phi}_0\,. \tag{44}$$

In order to rotate the sample about the reflecting-plane normal through an angle ψ measured from this zero position we generate a new matrix

$$\mathbf{R}=\mathbf{\Psi}\,\mathbf{R}_0 \tag{45}$$

where

$$\mathbf{\Psi}=\begin{pmatrix}1 & 0 & 0\\ 0 & \cos\psi & \sin\psi\\ 0 & -\sin\psi & \cos\psi\end{pmatrix}\,. \tag{46}$$

The problem then is to extract from this orthogonal matrix $\mathbf{R}$ the values of the instrument angles ω, χ, and φ to which it corresponds.

Expanding equation (42) we have:

$$\mathbf{R}=\begin{pmatrix}\cos\omega\cos\chi\cos\varphi-\sin\omega\sin\varphi & \cos\omega\cos\chi\sin\varphi+\sin\omega\cos\varphi & \cos\omega\sin\chi\\ -\sin\omega\cos\chi\cos\varphi-\cos\omega\sin\varphi & -\sin\omega\cos\chi\sin\varphi+\cos\omega\cos\varphi & -\sin\omega\sin\chi\\ -\sin\chi\cos\varphi & -\sin\chi\sin\varphi & \cos\chi\end{pmatrix} \tag{47}$$

and we see that

$$\left.\begin{aligned}\chi&=\operatorname{atan}\left[(R_{31}^2+R_{32}^2)^{\frac{1}{2}},\,R_{33}\right],\\ \varphi&=\operatorname{atan}\left(-R_{32},\,-R_{31}\right),\\ \text{and}\quad\omega&=\operatorname{atan}\left(R_{13},\,-R_{23}\right).\end{aligned}\right\} \tag{48}$$

(The more obvious expression, $\chi=\arccos R_{33}$, is not used because round-off could cause excessive errors in χ when $R_{33}\simeq\pm1$.) By taking the positive square root in the expression for χ we are choosing $\sin\chi\geq0$ so that $0\leq\chi\leq180°$. An equally valid solution for the same value of ψ is

$$\left.\begin{aligned}\chi'&=-\chi\\ \varphi'&=180°+\varphi\\ \omega'&=180°+\omega\,.\end{aligned}\right\} \tag{49}$$

In practice it is usually the range of ω which is limited by the mechanics of the instrument. The procedure should be to compute angles using equations (48), test ω, and make the transformations (49) if it is out of range. If both solutions are out of range then the specified value of ψ is not accessible for this reflection.

A singular case occurs if $R_{33}=\pm1$. Then $\cos\chi=\pm1$, $\sin\chi=0$, and the matrix becomes

$$\mathbf{R}=\begin{pmatrix}\pm\cos(\omega\pm\varphi) & \sin(\omega\pm\varphi) & 0\\ \mp\sin(\omega\pm\varphi) & \cos(\omega\pm\varphi) & 0\\ 0 & 0 & \pm1\end{pmatrix}\,. \tag{50}$$

Thus the ω and φ motions have become redundant, and this can easily be understood in terms of the instrument geometry when χ is zero or 180°. It can be shown that the continuity of an azimuthal scan can best be attained by selecting $\omega=90°$ for this singular case. The matrix then becomes

$$\mathbf{R}=\begin{pmatrix}-\sin\varphi & \cos\varphi & 0\\ \mp\cos\varphi & \mp\sin\varphi & 0\\ 0 & 0 & \pm1\end{pmatrix} \tag{51}$$

and we have

$$\left.\begin{aligned}&\varphi=\operatorname{atan}\left(-R_{11},\,R_{12}\right)\\ \text{and}\quad&\omega=90°\,.\end{aligned}\right\} \tag{52}$$

The transformations (49) are still valid for this singular case.

Now let us consider in more detail the choice of the instrument setting at which we define ψ to be zero. We could, for example, use the bisecting position as a reference, and then we would have

$$\mathbf{R}_0=\mathbf{X}_0\,\mathbf{\Phi}_0 \tag{53}$$

since $\omega_0=0$. But this choice has the disadvantage of depending on the sample mounting so that the definition of ψ would not in general be comparable for different specimens. To overcome this limitation we will describe a way of defining the reference position in terms of the crystal lattice itself.

Let $\boldsymbol{h}$ be the plane normal of the reflection to be observed and let us specify a reference vector $\boldsymbol{h}_0$ which is not parallel to $\boldsymbol{h}$. Then choose as the zero of ψ that setting for which $\boldsymbol{h}$ lies in the scattering direction and $\boldsymbol{h}_0$ lies in the horizontal plane of the instrument on the same side as the diffracted beam (*i.e.*, so that in the θ-axis system its z component is zero and its y component is positive).

The computation of $\mathbf{R}_0$ based on this definition is analogous to the determination of $\mathbf{U}$ described above. The vectors

$$\left.\begin{aligned}&\mathbf{h}_{\varphi}=\mathbf{U}\,\mathbf{B}\,\mathbf{h}\\ \text{and}\quad&\mathbf{h}_{0\varphi}=\mathbf{U}\,\mathbf{B}\,\mathbf{h}_0\end{aligned}\right\} \tag{54}$$

are first evaluated. Then the matrix $\mathbf{T}_{\varphi}$ is constructed with columns equal to $\mathbf{t}_{1\varphi}$, $\mathbf{t}_{2\varphi}$, and $\mathbf{t}_{3\varphi}$, the components of a right-handed orthogonal unit vector triple defined to have $\mathbf{t}_{1\varphi}$ parallel to $\mathbf{h}_{\varphi}$, $\mathbf{t}_{2\varphi}$ in the plane of $\mathbf{h}_{\varphi}$ and $\mathbf{h}_{0\varphi}$, and $\mathbf{t}_{3\varphi}$ perpendicular to this plane.

Now we note that our definition of zero ψ requires the orthogonal matrix $\mathbf{R}_0$ to rotate this unit vector triple into coincidence with the axes of the θ coordinate

system. The matrix which describes these axes in the θ-system is just the identity matrix so that we have

$$\mathbf{R}_0\mathbf{T}_\varphi=\mathbf{1}$$

and

$$\mathbf{R}_0=\mathbf{T}_\varphi^{-1}=\tilde{\mathbf{T}}_\varphi\,. \tag{55}$$

Vectors for calculating absorption corrections

In order to calculate absorption corrections it is generally necessary to compute for each reflection the direction cosines of the diffracted beam and of the reverse primary beam referred to some coordinate system in which the sample shape is described (see, *e.g.*, Busing & Levy, 1957). The φ-axis system may often be a suitable reference system, and the required direction cosines are just the components of the appropriate unit vectors in this system. Let $\boldsymbol{p}$ and $\boldsymbol{d}$ represent unit vectors in the primary and diffracted beam directions, respectively, so that

$$\mathbf{p}_l=\mathbf{d}_{2\theta}=\begin{pmatrix}0\\1\\0\end{pmatrix}\,. \tag{56}$$

Then the required vectors are

$$\left.\begin{aligned}-\mathbf{p}_\varphi &= -\tilde{\mathbf{\Phi}}\tilde{\mathbf{X}}\tilde{\mathbf{N}}\,\mathbf{p}_l\\ \text{and}\qquad \mathbf{d}_\varphi &=\tilde{\mathbf{\Phi}}\tilde{\mathbf{X}}\tilde{\mathbf{M}}\,\mathbf{d}_{2\theta}\,,\end{aligned}\right\} \tag{57}$$

and expanding we obtain

$$\begin{pmatrix}\sin(\theta\pm\omega)\cos\chi\cos\varphi\pm\cos(\theta\pm\omega)\sin\varphi\\ \sin(\theta\pm\omega)\cos\chi\sin\varphi\mp\cos(\theta\pm\omega)\cos\varphi\\ \sin(\theta\pm\omega)\sin\chi\end{pmatrix} \tag{58}$$

where the upper and lower signs apply to $-\mathbf{p}_\varphi$ and $\mathbf{d}_\varphi$, respectively.

If a sample has natural faces it may be preferable to refer its description to the crystal cartesian system. In this case the desired vectors, $-\mathbf{p}_c$ and $\mathbf{d}_c$, are readily obtained by multiplying $-\mathbf{p}_\varphi$ and $\mathbf{d}_\varphi$ by $\tilde{\mathbf{U}}$.

Refinement of lattice and orientation parameters

So far we have established the matrix **UB** either from known cell parameters and observations of two reflections or from observations of three reflections alone. A better procedure would be to observe angles for several reflections and to use the method of least-squares to refine the cell parameters and orientation parameters simultaneously. Computer programs are available (see, *e.g.*, Busing & Levy, 1962) which, when given a list of trial parameters, a set of observations, and a procedure for calculating the quantity comparable with these observations, will refine specified parameters by the method of least-squares. Analytical expressions for the required derivatives are not needed since these are computed numerically.

The parameter list includes the three axial lengths and three interaxial angles of the direct unit cell. In some cases these will be subject to constraints imposed by the symmetry of the crystal system. Angles with fixed values of 90° or 120° are simply not varied in the least-squares procedure. Two or more parameters can be constrained to be equal by choosing one of them to be varied and setting the others equal to it. Since numerical derivatives are obtained by recalculating the function after adding an increment to the corresponding parameter, these derivatives will be correct if the constraint is applied immediately after each parameter is incremented.

The wavelength may also be included in the parameter list since it is not always precisely known (especially in neutron diffraction work). It is clear, however, that the wavelength is redundant with the axial lengths and the four of these parameters cannot be adjusted simultaneously.

The sample orientation is represented in the parameter list by the six angles ω_1, χ_1, φ_1, ω_2, χ_2, and φ_2 for the primary and secondary orienting reflections. Only three of these angles can be varied, however, since only three parameters are required to define orientation. The variables must include two angles of the primary reflection chosen to define the direction of this vector, and one angle of the secondary reflection chosen to measure rotation of the sample about this primary vector. For example, if ω_1, χ_1, ω_2, and χ_2 are all near zero and if φ_1 and φ_2 differ by about 90°, then χ_1, φ_1, and χ_2 or ω_1, χ_1, and χ_2 are suitable variables.

After refinement, the angles ω_1, χ_1, and φ_1 define the best estimate of the direction of $\boldsymbol{h}_1$, and the calculated angles for this reflection based on the new parameters will correspond exactly to this vector. The angles ω_2, χ_2, and φ_2 no longer define $\boldsymbol{h}_2$, however, because only one of them has been varied. Instead they represent a vector direction which will yield the best estimate of the orientation matrix **U**. Calculation of angles for $\boldsymbol{h}_2$ will correctly yield the best estimate of a setting for this reflection, but these angles will generally not be the same as the refined parameters.

A reciprocal lattice vector has three independent properties consisting of two directional parameters and a length which is related to the corresponding Bragg angle. We will consider six ways of observing these variables or combinations of them, identifying these ways as observations of *types* 1 to 6. For each type of observation we will show how the corresponding calculated value can be obtained from the known instrument settings and the assumed trial parameters.

In the course of these calculations it will be convenient to distinguish the instrument dial readings and their matrices by the subscript d (*e.g.*, φ_d and $\mathbf{\Phi}_d$) since these will not in general be equal to the ideal angles used earlier in this paper. Similarly, calculated angles and their matrices will be identified by the subscript c.

Type 1 *observations*

Several ways of measuring the Bragg angle are essentially equivalent to centering the diffracted beam in the

counter and using the counter angle, $2\theta_d$, as the observation. The corresponding calculated quantity is $2\theta_c=2\theta$ where θ is obtained from the trial parameters by means of equations (17) and (18).

Type 2 observations

If the counter angle is adjusted to center the diffracted beam horizontally in the aperture, then $2\theta_d$ may be used as an observation even though the beam may not be centered vertically.

In deriving the corresponding $2\theta_c$ it will be useful to recall the diffraction equation

$$\boldsymbol{d}=\boldsymbol{p}+2\sin\theta\,\boldsymbol{u}\,. \tag{59}$$

Here $\boldsymbol{d}$, $\boldsymbol{p}$, and $\boldsymbol{u}$ are unit vectors in the directions of the diffracted beam, the primary beam, and the scattering vector, respectively. Evaluating $\boldsymbol{d}$ in the laboratory system we obtain

$$\mathbf{d}_l=\begin{pmatrix}(\sin^2 2\theta-4\sin^2\theta\,u_{\omega 3}^2)^{\frac{1}{2}}\\ \cos 2\theta\\ 2\sin\theta\,u_{\omega 3}\end{pmatrix}. \tag{60}$$

Here d_{l2} has been derived from the fact that $\mathbf{d}_l$ makes an angle of 2θ with $\mathbf{p}_l$ which is directed along the y axis. The component d_{l3} is obtained from the diffraction equation (59) remembering that $p_{l3}=0$ and that $u_{l3}=u_{\omega 3}$. Finally d_{l1} is derived from the requirement that $\boldsymbol{d}$ be a unit vector.

The quantity to be computed is the value of the counter angle, $2\theta_c$, which makes $d_{2\theta,1}=0$. We have

$$\mathbf{d}_{2\theta}=\tilde{\boldsymbol{\Theta}}_c\,\tilde{\boldsymbol{\Theta}}_c\,\mathbf{d}_l \tag{61}$$

and

$$d_{2\theta,1}=\cos 2\theta_c d_{l1}-\sin 2\theta_c d_{l2}=0 \tag{62}$$

so that

$$2\theta_c=\operatorname{atan}(d_{l1},\,d_{l2}) \tag{63}$$

and the desired expression is

$$2\theta_c=\operatorname{atan}[(\sin^2 2\theta-4\sin^2\theta\,u_{\omega 3}^2)^{\frac{1}{2}},\cos 2\theta]\,. \tag{64}$$

The vector $\mathbf{u}_\omega$ is obtained from the trial parameters and the χ and φ dial settings:

$$\mathbf{u}_\omega=\mathbf{X}_d\boldsymbol{\Phi}_d\mathbf{U}\,\mathbf{B}\,\mathbf{h}/q\,, \tag{65}$$

and the Bragg angle θ is again obtained from equations (17) and (18). It is readily seen that the result reduces to that for type 1 if the scattering vector is horizontal so that $u_{\omega 3}=0$.

Type 3 observations

It is possible to center the diffracted beam vertically in the counter by adjusting χ_d provided that ω_d is not nearly $\pm 90°$. Let the value of χ_d for this condition be taken as an observation.

The requirement is that $d_{2\theta,3}=0$, and from equations (60) and (61) we see that this reduces to $u_{\omega 3}=0$. Now

$$\mathbf{u}_\omega=\mathbf{X}_c\mathbf{u}_\chi \tag{66}$$

and

$$u_{\omega 3}=-\sin\chi_c u_{\chi 1}+\cos\chi_c u_{\chi 3}=0 \tag{67}$$

so that the calculated angle is either

$$\chi_c=\operatorname{atan}(u_{\chi 3},\,u_{\chi 1}) \tag{68}$$

or

$$\chi_c'=\chi_c+180°\,. \tag{69}$$

Here $\mathbf{u}_x$ is obtained from the trial parameters and the φ dial setting:

$$\mathbf{u}_\chi=\boldsymbol{\Phi}_d\,\mathbf{U}\,\mathbf{B}\,\mathbf{h}/q\,. \tag{70}$$

In this case and in others to be described below we have two widely separated solutions both of which are physically reasonable. A simple computational procedure is to select the result which is closest to the observation, adding or subtracting 360° if necessary to make the quantities comparable.

Type 4 observations

Vertical centering of the diffracted beam can also be obtained by adjusting φ_d provided that ω_d is not nearly 0 or 180°. Let this φ_d be taken as an observation.

Again the requirement is that $u_{\omega 3}=0$, but χ_d is known and φ_c is to be calculated. We have

$$\mathbf{u}_\omega=\mathbf{X}_d\,\boldsymbol{\Phi}_c\,\mathbf{u}_\varphi \tag{71}$$

and

$$u_{\omega 3}=-\sin\chi_d(\cos\varphi_c u_{\varphi 1}+\sin\varphi_c u_{\varphi 2})+\cos\chi_d u_{\varphi 3}\,. \tag{72}$$

Then the equation for φ_c is

$$\sin\chi_d u_{\varphi 1}\cos\varphi_c+\sin\chi_d u_{\varphi 2}\sin\varphi_c=\cos\chi_d u_{\varphi 3} \tag{73}$$

where

$$\mathbf{u}_\varphi=\mathbf{U}\,\mathbf{B}\,\mathbf{h}/q\,.$$

Equation (73) is an expression of the form

$$e\cos\varphi_c+f\sin\varphi_c=g \tag{74}$$

which has solutions

$$\left.\begin{aligned}\varphi_c&=\eta\pm\gamma\\ \text{where}\quad \eta&=\operatorname{atan}(f,\,e)\\ \gamma&=\operatorname{atan}[(e^2+f^2-g^2)^{\frac{1}{2}},\,g]\,.\end{aligned}\right\} \tag{75}$$

Again the appropriate solution is chosen as for observations of type 3. The two solutions become complex or equal if $e^2+f^2-g^2\leq 0$, but this does not occur if the type of observation is chosen in a sensible way.

Observations of types 5 and 6

Consider the observation that the Bragg condition is satisfied so that the intensity of the reflection is maximized. It is important to note that this condition can be observed with configurations other than that of Fig. 1(*a*) if the counter aperture is large enough. The requirement is only that the scattering vector $\boldsymbol{u}$ makes an angle of $90°+\theta$ with the primary beam direction, that is

$$u_{l2}=-\sin\theta\,. \tag{76}$$

Now

$$\mathbf{u}_l=\mathbf{N}_c\mathbf{u}_\omega \tag{77}$$

and

$$u_{l2}=-\sin\nu_c u_{\omega 1}+\cos\nu_c u_{\omega 2} \tag{78}$$

so that the condition becomes

$$u_{\omega 2}\cos\nu_c-u_{\omega 1}\sin\nu_c=-\sin\theta\,. \tag{79}$$

Here $\mathbf{u}_\omega$ can be evaluated from the trial parameters and instrument settings:

$$\mathbf{u}_\omega = \mathbf{X}_d \, \mathbf{\Phi}_d \, \mathbf{U} \, \mathbf{B} \, \mathbf{h}/q \,, \tag{80}$$

and θ is calculated from equations (17) and (18). Equation (79) has the form of (74) and solutions for ν_c are given by (75).

Let a type 5 *observation* be the value of ω_d which establishes the Bragg condition when $2\theta_d$ is fixed. Then the corresponding calculated value is

$$\omega_c = \nu_c - 2\theta_d/2 \,. \tag{81}$$

Let a type 6 *observation* be the value of $2\theta_d$ which establishes the Bragg condition for a given ω_d. Then the calculated quantity is

$$2\theta_c = 2(\nu_c - \omega_d) \,. \tag{82}$$

In each case there will be two computed values corresponding to the two solutions for ν_c, and the appropriate one is selected as described above.

We have used three different schemes for making observations for least-squares refinement. With a 4-circle diffractometer it is possible to vary ω_d to establish the Bragg condition while centering the reflection vertically in the counter by adjusting χ_d or φ_d. The reflection can then be centered horizontally by changing $2\theta_d$ while using a compensating ω_d motion to hold the crystal fixed in the laboratory system. The resulting settings are used as three observations of types 2, 3 or 4, and 5, and both the cell parameters and orientation parameters are adjusted. In practice it makes little difference if the $2\theta_d$ measurement is used as a type 1 observation rather than type 2.

Measurements of the Bragg angle can be used as type 1 observations for the determination of cell parameters. Such observations contain no information about the orientation and the orientation parameters should not be varied. In X-ray work it is difficult to assign an effective value to λ unless the α-doublet is resolved. For the most accurate work, therefore, the observations should be limited to regions of high Bragg angle.

Observations of type 6 can be extracted from the output data of any 3- or 4-circle instrument which records the intensity profile for a θ–2θ scan. For several years we have routinely obtained such observations from the paper-tape output of our 3-circle neutron diffractometer and used them to improve the cell and orientation parameters for subsequent angle calculations.

In principle it is possible to include in the list of variables parameters which measure the systematic errors of the experiment. These would include angular errors such as scale zero corrections or inaccurately directed instrument shafts as well as displacement errors due to non-intersecting axes or a poorly centered sample. Although we have found the adjustment of certain error parameters to be useful, we will present no further discussion of the method at this time.

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