and the vector **s** will be called χ_s' and is equal to $|90°+\chi_s|$ or $|90°-\chi_s|$. One can then write the following equations directly by an inspection of Fig. 5.

$$\psi_p^i=\psi_p^0+\pi/2\pm\Delta\psi_p \text{ (modulo } \pi) \quad (A13)$$

$$\cos(\varphi_s-\varphi_p)=\frac{\cos\pi/2-\cos\chi_p'\cos\chi_s'}{\sin\chi_p'\sin\chi_s'} \quad (A14)$$

$$\cos\psi_p^0=\frac{\cos\chi_s'-\cos\chi_p'\cos\pi/2}{\sin\chi_p'\sin\pi/2} \quad (A15)$$

$$\cos(\pi/2-\theta_s)=\sin(\pi/2-\theta_p)\cos\Delta\psi_p\,. \quad (A16)$$

In (*A*13), the double sign is for $i=1$ or 2. (*A*14) and (*A*15) are obtained by application of (*A*1) on vectors φ axis, **p** and **s** and on vectors **p**, φ axis and **s** respectively. With the introduction of a new variable $\varepsilon_p=\pi/2-\Delta\psi_p$, these equations can be rewritten as

$$\psi_p^i=\psi_p^0\pm\varepsilon_p \text{ (modulo } \pi) \quad (A17)$$

$$\cos(\varphi_s-\varphi_p)=\pm\frac{\sin\chi_p\sin\chi_s}{\cos\chi_p\cos\chi_s} \quad (A18)$$

$$\cos\psi_p^0=\pm\frac{\sin\chi_s}{\cos\chi_p}=\pm\frac{\cos\chi_s}{\sin\chi_p}\cos(\varphi_s-\varphi_p) \quad (A19)$$

$$\sin\varepsilon_p=\frac{\sin\theta_s}{\cos\theta_p}\,. \quad (A20)$$

It can be shown by considering all possible sign conventions and diffractometer settings that the ambiguity in sign in (*A*19) should be removed by requiring that $\varphi_s-\varphi_p$ and ψ_p^0 belong to the same or different quadrants depending respectively on whether the senses of the φ and ψ rotations are the same or different.

This set of equations can be written for each of the four vectors **k**, $\bar{\mathbf{k}}$, **l** and **l**′. These give all the ψ angles necessary for all eight vectors of intersection, from which proper sets of four vectors must be selected according to Fig. 2. These considerations give (19) to (24) and the rules for selecting proper signs and branches of the cosine function as stated with these equations in the main text.

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A Semi-empirical Absorption-Correction Technique for Symmetric Crystals in Single-Crystal X-ray Crystallography. II

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This is the second part of a two-part series. The first part described the technique in the case when the symmetry axis is coincident with the instrument φ axis. This paper describes the procedure to follow when the orientation of the symmetry axis is arbitrary.

Introduction

In the previous paper (Lee & Ruble, 1977), a procedure for the semi-empirical absorption correction has been presented for the case where a crystallographic twofold axis is coincident with the instrument φ axis. However, there are cases where aligning a symmetry axis along the φ axis presents serious practical problems. This will be the case if the crystal is so ill-formed that the crystallographic symmetry axis is impossible to identify under microscopic examination. In the case of protein crystals, which have to be mounted in capillary tubes, the difficulty also arises if the shape of the crystal is very anisotropic and also such that the symmetry axis runs along the short dimension of the crystal. The crystal, in this case, will tend to orient itself such that its long dimension is parallel to the capillary axis, making it difficult to align the short dimension along the φ-axis. In such cases, one may be forced to collect data with the symmetry axis considerably off the φ axis.

Even for well shaped crystals, it is rather tedious to align the symmetry axis accurately along the φ-axis and one wants to know the amount of inaccuracy that can be tolerated. This information can be obtained only by considering the general case.

For these reasons, we consider in this paper the general case when the symmetry axis is not coincident with the φ axis. The geometries involved in this case can be quite complex and the various angle calculations can best be done with a more formal, analytical approach. We begin our discussion by developing this analytical technique.

Coordinate transformations

1. *Two kinds of coordinate systems*

It is convenient to define and use the following two types of coordinate systems.

(*A*) *The space-fixed coordinate system S*. The positive x axis runs from the crystal toward the X-ray source, the positive y axis runs from the crystal toward the detector when $2\theta = +90°$, and the z axis is defined so as to complete a right-handed orthogonal coordinate system. This is similar but not identical to Hamilton's (1974) coordinate system D. On the Syntex $P\bar{1}$ system, the z axis defined in this way runs vertically down.

(*B*) *The crystal-fixed coordinate system* **h**. These are fixed to the crystal. One defines one system for each reflection **h** as follows. Turn the diffractometer until the crystal is in the diffracting position for the reflection **h** in the bisecting mode. In general there are eight different diffractometer settings at which this happens (Hamilton, 1974). We shall arbitrarily choose one of these by stipulating that at this position 2θ is in the range of 0 to 180°, ω [we use Hamilton's (1974) 'alternate' definition for this angle] from 0 to 90°, and χ from -90 to $+90°$. We shall call this position BPL (bisecting mode, positive 2θ, and lower hemisphere). At this position, $\psi=0$ and $\omega=\theta$. Now make an ω rotation until $\omega=0$. The crystal-fixed coordinate system **h** is defined to coincide with the space-fixed coordinate system S when the crystal is in this orientation. Note that the vector **h** points toward the positive y direction in this coordinate system.

2. *Relation between two coordinate systems*

Turn the diffractometer until $\omega=0$, $\chi=90°$, and $\varphi=0$. The matrix that relates the coordinates of any one vector in the S and **h** coordinate systems when the crystal is in this orientation is given by (Fig. 1)

$$\begin{pmatrix} x^{\mathbf{h}} \\ y^{\mathbf{h}} \\ z^{\mathbf{h}} \end{pmatrix} = \mathbf{M}^{\mathbf{h}S} \begin{pmatrix} x^S \\ y^S \\ z^S \end{pmatrix}, \quad \begin{pmatrix} x^S \\ y^S \\ z^S \end{pmatrix} = \mathbf{M}^{S\mathbf{h}} \begin{pmatrix} x^{\mathbf{h}} \\ y^{\mathbf{h}} \\ z^{\mathbf{h}} \end{pmatrix} \qquad (1)$$

$$\mathbf{M}^{\mathbf{h}S} = \begin{pmatrix} \cos\varphi_{\mathbf{h}} & 0 & -\sin\varphi_{\mathbf{h}} \\ \cos\chi_{\mathbf{h}}\sin\varphi_{\mathbf{h}} & \sin\chi_{\mathbf{h}} & \cos\chi_{\mathbf{h}}\cos\varphi_{\mathbf{h}} \\ \sin\chi_{\mathbf{h}}\sin\varphi_{\mathbf{h}} & -\cos\chi_{\mathbf{h}} & \sin\chi_{\mathbf{h}}\cos\varphi_{\mathbf{h}} \end{pmatrix} \qquad (2)$$

$$\mathbf{M}^{S\mathbf{h}} = (\mathbf{M}^{\mathbf{h}S})^{-1} = (\mathbf{M}^{\mathbf{h}S})^T \qquad (3)$$

where $x^{\mathbf{h}}$, $y^{\mathbf{h}}$, $z^{\mathbf{h}}$ and x^S, y^S, z^S are the coordinates of the arbitrary vector in the coordinate systems **h** and S, respectively, and $\chi_{\mathbf{h}}$ and $\varphi_{\mathbf{h}}$ are the χ and φ angles when the reflection **h** is in the diffracting position BPL. Superscript T in (3) indicates transpose. It should be noted that, in arriving at the explicit expression (2), we used certain conventions concerning the sense of φ and χ rotations. These are the same as

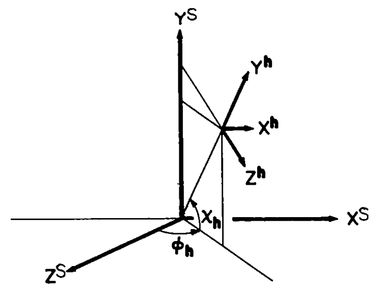

Fig. 1. Relation between the space-fixed and the crystal-fixed coordinate systems S and **h** at $\omega=0°$, $\chi=90°$, and $\varphi=0°$. The χ circle is in the y^Sz^S plane, the φ axis is along the y^S axis which points toward the detector when $2\theta = +90°$, and the χ axis is along the x^S axis which points toward the X-ray source. The diffraction vector **h** points toward the positive y^h axis. The two coordinate systems can be made to coincide by turning the crystal around the φ axis by an angle $\varphi_{\mathbf{h}}$ followed by a rotation around the χ axis by an angle $\chi_{\mathbf{h}} - 90°$. After these rotations, a single ω rotation will bring the reflection **h** in the diffracting position BPL (see text).

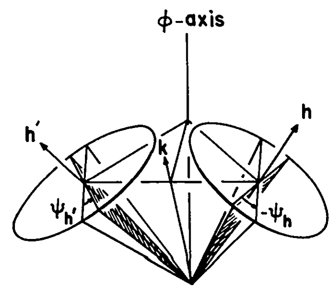

Fig. 2. Relation between the symmetric and the bisecting mode of data collection. The vector **k** is along a twofold symmetry axis of the crystal and the vectors **h** and **h**′ are related by the twofold symmetry. In the bisecting mode, $\psi_{\mathbf{h}}=0$ and the diffraction plane of **h** (shaded) is perpendicular to the plane that contains the φ axis and the vector **h**. This plane must be rotated about **h** by an angle $\psi_{\mathbf{h}}$ in order to make it perpendicular to the plane of **h** and **k**. Similarly, the diffraction plane of **h**′, initially in the bisecting mode at $\psi_{\mathbf{h}'}=0$ (shaded), can be brought to be perpendicular to the plane of **h**′ and **k** by rotating it by a (different) angle $\psi_{\mathbf{h}'}$ about **h**′. After these ψ rotations, the incident and reflected beam directions of **h**′ are related to those of **h** by the twofold symmetry about **k**.

those defined by Hamilton (1974). For diffractometer systems that use different conventions, the sign of the affected angle(s) must be changed before use.

Let **k** and **h** be any two reflections. The relation between the two crystal-fixed coordinate systems **k** and **h** can be described as follows. Let $x^{\mathbf{k}}$, $y^{\mathbf{k}}$, $z^{\mathbf{k}}$ and $x^{\mathbf{h}}$, $y^{\mathbf{h}}$, $z^{\mathbf{h}}$ be the coordinates of one single arbitrary vector in these two coordinate systems. Then

$$\begin{pmatrix} x^{\mathbf{k}} \\ y^{\mathbf{k}} \\ z^{\mathbf{k}} \end{pmatrix} = \mathbf{M}^{\mathbf{kh}} \begin{pmatrix} x^{\mathbf{h}} \\ y^{\mathbf{h}} \\ z^{\mathbf{h}} \end{pmatrix} \quad (4)$$

where $\mathbf{M}^{\mathbf{kh}} = \mathbf{M}^{\mathbf{k}S}\,\mathbf{M}^{S\mathbf{h}}$ or

$$\mathbf{M}^{\mathbf{kh}} = \begin{pmatrix} \cos\Delta\varphi_{\mathbf{hk}} & \cos\chi_{\mathbf{h}}\sin\Delta\varphi_{\mathbf{hk}} & \sin\chi_{\mathbf{h}}\sin\Delta\varphi_{\mathbf{hk}} \\ -\cos\chi_{\mathbf{k}}\sin\Delta\varphi_{\mathbf{hk}} & \cos\chi_{\mathbf{k}}\cos\chi_{\mathbf{h}}\cos\Delta\varphi_{\mathbf{hk}}+\sin\chi_{\mathbf{k}}\sin\chi_{\mathbf{h}} & \cos\chi_{\mathbf{k}}\sin\chi_{\mathbf{h}}\cos\Delta\varphi_{\mathbf{hk}}-\sin\chi_{\mathbf{k}}\cos\chi_{\mathbf{h}} \\ -\sin\chi_{\mathbf{k}}\sin\Delta\varphi_{\mathbf{hk}} & \sin\chi_{\mathbf{k}}\cos\chi_{\mathbf{h}}\cos\Delta\varphi_{\mathbf{hk}}-\cos\chi_{\mathbf{k}}\sin\chi_{\mathbf{h}} & \sin\chi_{\mathbf{k}}\sin\chi_{\mathbf{h}}\cos\Delta\varphi_{\mathbf{hk}}+\cos\chi_{\mathbf{k}}\cos\chi_{\mathbf{h}} \end{pmatrix} \quad (5)$$

where $\Delta\varphi_{\mathbf{hk}} = \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}}$. Obviously

$$\mathbf{M}^{\mathbf{hk}} = (\mathbf{M}^{\mathbf{kh}})^{-1} = (\mathbf{M}^{\mathbf{kh}})^{T}. \quad (6)$$

It is worth noting here the special significance of the element $M_{22}^{\mathbf{kh}}$. It is clear from the definition of the matrix, (4), that this element is equal to the cosine of the angle between the two vectors **h** and **k**. Equation (5), therefore, gives this angle, $\varrho_{\mathbf{hk}}$, in terms of the diffractometer setting angles (at BPL) for the two reflections:

$$M_{22}^{\mathbf{kh}} = \cos\varrho_{\mathbf{hk}} = \cos\chi_{\mathbf{h}}\cos\chi_{\mathbf{k}}\cos\Delta\varphi_{\mathbf{hk}} + \sin\chi_{\mathbf{h}}\sin\chi_{\mathbf{k}}. \quad (7)$$

We will be particularly interested in the case where **k** is along the crystallographic **b*** axis, which we suppose to be the direction of the twofold rotation symmetry axis, and where **h** is on the same k level as **k**. In this case we have $\mathbf{h} = hkl$ and $\mathbf{k} = 0k0$ and

$$M_{22}^{\mathbf{kh}} = \cos\varrho_{\mathbf{h}} = \frac{|k|b^*}{|\mathbf{h}|} = \frac{|k|\lambda b^*}{2\sin\theta_{\mathbf{h}}} \quad (8)$$

where λ is the wavelength of the radiation, $\theta_{\mathbf{h}}$ is the Bragg diffraction angle of **h**, and the subscript **k** on the angle ϱ has been suppressed.

Symmetric mode of data collection

The absorption-correction scheme detailed in the previous paper was based on the observation that the incident and reflected beam directions of a given reflection **h** and its symmetry equivalent **h**′ exactly coincided with those of the reflection $\mathbf{k} = 0k0$ on the same k level at a properly chosen pair of ψ angles. This was true because the crystal was mounted such that its symmetry axis **b** was parallel to the φ axis and the intensities of **h** and **h**′ were measured in the bisecting mode. If the crystal is mounted such that its symmetry axis is *not* parallel to the φ axis, this condition can be obtained only when the data are collected at non-zero ψ angles. We will use the term symmetric when the data are collected such that the diffraction plane of a reflection **h** (the plane that contains **h** and the incident and reflected beams) is perpendicular to the plane that contains **h** and the *symmetry axis* (Fig. 2). In this mode of data collection, the incident and reflected beam directions of **h** and **h**′ are related by the twofold symmetry. In contrast, in the bisecting mode of data collection the diffraction plane of **h** is perpendicular to the plane that contains **h** and the *φ axis* of the instrument. This latter plane is not always coincident with the plane that contains **h** and the symmetry axis unless the symmetry axis coincides with the φ axis.

In order to demonstrate the usefulness of the symmetric mode of data collection, it must be shown that the incident and reflected beams of reflections **h** and **h**′ lie on the surface of the diffraction cone of **k** at the same k level. This can be shown as follows. First, one calculates the coordinates of the unit vectors along the incident beam (actually antiparallel to the incident beam) and the reflected beam directions of a reflection **h** at some ψ angle $\psi_{\mathbf{h}}$ in the coordinate system **h**. Obviously (Fig. 3)

$$\begin{pmatrix} x_i^{\mathbf{h}} \\ y_i^{\mathbf{h}} \\ z_i^{\mathbf{h}} \end{pmatrix} = \begin{pmatrix} \pm\cos\theta_{\mathbf{h}}\cos\psi_{\mathbf{h}} \\ \sin\theta_{\mathbf{h}} \\ \pm\cos\theta_{\mathbf{h}}\sin\psi_{\mathbf{h}} \end{pmatrix} \quad (9)$$

where the subscript i indicates that the coordinates are for the ray directions. The double sign is for the incident (upper sign) and the reflected (lower sign) beam directions. [This equation (and Fig. 3) assumes that a positive ψ rotation advances a right-handed screw along the positive **h** direction. If a diffractometer system uses a different convention, the sign of ψ must be changed before use.] The angle ϱ_i between a ray direction i and the vector **k** can then be obtained by computing the y component of these vectors in the coordinate system **k** with (4);

$$y_i^{\mathbf{k}} = \cos\varrho_i = M_{22}\sin\theta_{\mathbf{h}} \pm\cos\theta_{\mathbf{h}}(M_{21}\cos\psi_{\mathbf{h}} + M_{23}\sin\psi_{\mathbf{h}}). \quad (10)$$

In this equation, the superscript **kh** of the matrix $\mathbf{M}^{\mathbf{kh}}$ has been suppressed.

Now we recognize from Fig. 2 that the ϱ angles of the incident and reflected beam directions of a reflection **h** are the same when and only when **h** diffracts in the symmetric mode. Inspection of (10) then allows one to write

$$M_{21}\cos\psi_{\mathbf{h}} + M_{23}\sin\psi_{\mathbf{h}} = 0, \quad (11)$$

or

$$\tan\psi_{\mathbf{h}} = -M_{21}/M_{23}, \quad (12)$$

as the condition for the symmetric mode of data collection. (This equation gives two solutions for $\psi_{\mathbf{h}}$, 180° apart from one another. Both are valid solutions.)

Equation (10) itself becomes

$$\cos \varrho_i = M_{22} \sin \theta_{\mathbf{h}} \quad (13)$$

which, when combined with (8), becomes

$$\cos \varrho_i = |k|\lambda b^*/2 \,. \quad (14)$$

This equation shows that both the incident and reflected beam directions of all reflections $\mathbf{h}=hkl$ lie on the surface of one cone, the diffraction cone of $\mathbf{k}=0k0$. The combination of this fact and the fact that the incident and reflected beam directions of $\mathbf{h}$ and $\mathbf{h}'$ conform to the twofold symmetry about $\mathbf{k}$ ensures that it is always possible to find two ψ angles about the reflection $\mathbf{k}$ at which the ray directions exactly coincide with those of $\mathbf{h}$ and $\mathbf{h}'$ diffracting in the symmetric mode. Equation (14) is of course identical to (A11) of Lee & Ruble (1977), as it should since the bisecting mode and the symmetric mode of data collection are identical when the symmetry axis is parallel to the φ axis.

Absorption-correction procedure

Based on the observation made in the above section, it is now a simple matter to modify the absorption-correction scheme of the previous paper so that it is applicable to the case of general crystal mounting. We again start with the assumption that the transmission factor of a reflection can be approximated by

$$T = R(i)R(r)S(\theta, \mu R) \quad (15)$$

where the symbols used are the same as in Lee & Ruble (1977). This equation is then written for reflections $\mathbf{h}=hkl$ and $\mathbf{h}'=\bar{h}k\bar{l}$ measured in the symmetric mode and also for the reflection $\mathbf{k}=0k0$ measured at two appropriate ψ angles, $\psi^1_{\mathbf{k}}$ and $\psi^2_{\mathbf{k}}$, at which the incident and reflected beam directions coincide with those of $\mathbf{h}$ and $\mathbf{h}'$. The four equations thus obtained can then be combined to give

$$I^0_{\mathbf{h}} = \left[\frac{I_{\mathbf{h}} I_{\mathbf{h}'}}{I_{\mathbf{k}}(\psi^1_{\mathbf{k}}) I(\psi^2_{\mathbf{k}})}\right]^{1/2} \frac{S(\mathbf{k})}{S(\mathbf{h})} I^0_{\mathbf{k}} \,. \quad (16)$$

The angles $\psi^1_{\mathbf{k}}$ and $\psi^2_{\mathbf{k}}$ are given by (see Appendix)

$$\psi^i_{\mathbf{k}} = \psi^0_{\mathbf{k}} \pm \varepsilon \ (\text{modulo } \pi) \quad (17)$$

$$\tan \psi^0_{\mathbf{k}} = -M_{12}/M_{32} \quad (18)$$

$$\tan \varepsilon = \tan \theta_{\mathbf{h}} \sin \varrho_{\mathbf{h}} \,. \quad (19)$$

In these equations, i is 1 or 2, $\psi^0_{\mathbf{k}}$ is the $\psi_{\mathbf{k}}$ angle when the vector $\mathbf{h}$ is in the plane bisecting the incident and reflected beams of $\mathbf{k}$, M_{12} and M_{32} are the elements of the matrix $\mathbf{M}^{\mathbf{kh}}$ given in (5), ε is the angle $\theta_{\mathbf{h}}$ projected on the plane perpendicular to $\mathbf{k}$, and $\varrho_{\mathbf{h}}$ is the angle between the vectors $\mathbf{h}$ and $\mathbf{k}$ given in (8). These equations reduce to (7) and (8) of Lee & Ruble (1977) when the $\mathbf{b}^*$ axis is parallel to the φ axis.

The absorption-correction procedure is basically the same as that detailed in Lee & Ruble (1977) except that (16) is used instead of (6) of that paper. This entails, of course, that the bulk of the data are collected in the symmetric mode at ψ angles calculated by (12) and that the ψ scan intensity data of $\mathbf{k}$ are tabulated as a function of ψ instead of φ. Otherwise the procedure is exactly the same as in Lee & Ruble (1977).

It is perhaps appropriate to note here, however, some of the undesirable features of the symmetric mode of data collection when the symmetry axis makes a large angle with respect to the φ axis. These can be seen by inspection of the matrix elements involved in (12). For instance, when $\chi_{\mathbf{h}}=0$, (12) becomes $\tan \psi_{\mathbf{h}} = -\tan \Delta \sin \Delta\varphi_{\mathbf{hk}}$ where $\Delta = 90° - \chi_{\mathbf{k}}$ is the deviation of the symmetry axis from the φ axis. If $\Delta\varphi_{\mathbf{hk}}$ is near 90°, $\psi_{\mathbf{h}} = -\Delta$. However, at $\chi=0$, no ψ-scan is in fact possible. Therefore, unless $\Delta=0$, there will usually be some reflection for which the symmetric mode of data collection is impossible. For crystals such as those of the biological macromolecules that have to be enclosed in a capillary tube, additional problems exist. For those reflections that have to be collected at large

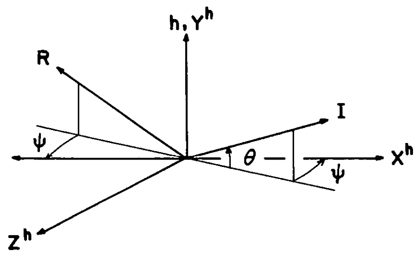

Fig. 3. Orientation of the incident (I) and reflected (R) beam directions of a reflection $\mathbf{h}$ in the coordinate system $\mathbf{h}$.

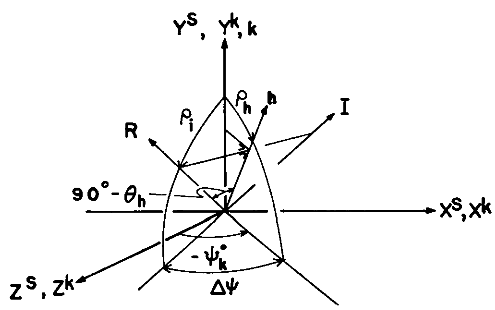

Fig. 4. Orientation of the incident (I) and reflected (R) beam directions of a reflection $\mathbf{h}$ in the symmetric mode in the coordinate system S when the diffractometer is turned until the reflection $\mathbf{k}$ is in the diffracting position BPL and then turned further by an ω rotation until $\omega=0$. In this orientation, the crystal-fixed coordinate system $\mathbf{k}$ coincides with S and the χ circle lies in the $y^{\mathbf{k}}z^{\mathbf{k}}$ plane. $\psi^0_{\mathbf{k}}$ is the angle by which the $\mathbf{hk}$ plane must be rotated around $\mathbf{k}$ to make it coincident with the y^Sz^S plane and $\Delta\psi$ is the angle between the $\mathbf{hk}$ plane and the plane that contains $\mathbf{k}$ and a ray direction $\mathbf{R}$ or $\mathbf{I}$.

ψ-values, the angle between the X-ray beam and the capillary tube may become quite small. These reflections will then suffer a heavy absorption from the capillary. It is therefore desirable that the symmetry axis be aligned as closely along the φ axis as possible.

Bisecting-mode approximation

Commonly available diffractometer softwares utilize the bisecting mode of data collection. It then becomes important that the symmetry axis be aligned accurately along the φ axis. This alignment is tedious but not particularly difficult, once the crystal is mounted with its symmetry axis roughly along the φ axis. The degree of accuracy required may be estimated as follows.

If the symmetry axis is not coincident with the φ axis, data should be collected at non-zero ψ values given by (12). The bisecting mode of data collection then amounts to assuming that the intensities vary little over this ψ range. Inspection of the matrix elements involved shows that the maximum ψ value occurs at $\Delta\varphi_{\mathbf{hk}}=90°$, in which case (12) becomes

$$\tan \psi_{\mathbf{h}} = \tan \Delta / \cos \chi_{\mathbf{h}} \tag{20}$$

or for small Δ

$$\psi_{\mathbf{h}} = \Delta / \cos \chi_{\mathbf{h}} \tag{21}$$

where $\Delta = 90° - \chi_{\mathbf{k}}$ is the deviation of the symmetry axis from the φ axis. These equations show that the worst case occurs when $\Delta\varphi_{\mathbf{hk}}=90°$ and $\chi_{\mathbf{h}}=90°$. In fact, when $\chi_{\mathbf{h}}=90°$ (12) gives $\psi_{\mathbf{k}}=\Delta\varphi_{\mathbf{hk}}$. Since $\Delta\varphi_{\mathbf{hk}}$ can take any value, this result shows that if a reflection other than the reference reflection occurs at $\chi=90°$, the approximation will fail. For a reflection at $\Delta\varphi_{\mathbf{hk}}=90°$ and $\chi_{\mathbf{h}}=85°$, (21) gives $\psi_{\mathbf{h}}=11{\cdot}5\ \Delta$. Assuming that the transmission factor does not vary seriously over a range of about 10° in ψ, this result indicates that a Δ value of better than about 1° must be achieved if the bisecting data collection mode is used. There may be a few reflections within 5° of the φ axis and at $\Delta\varphi_{\mathbf{hk}}=90°$ for which even this accuracy is inadequate, but the number of such reflections will be small.

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APPENDIX

Equations (17) to (19) may be derived in the following manner. Consider Fig. 4 which shows the diffraction vector of a reflection $\mathbf{h}=hkl$ and its incident and reflected beam directions in the symmetric mode. The coordinate system shown is the space-fixed system S and the crystal orientation is such that the crystal-fixed system $\mathbf{k}=0k0$ coincides with S. The angle between $\mathbf{h}$ and y^S in this crystal orientation is $\varrho_{\mathbf{h}}$ as given by (8) and the angle between a beam direction and y^S is ϱ_i as given by (14). Since the incident and reflected beam directions of $\mathbf{k}$ make the same angle ϱ_i with the vector $\mathbf{k}$ and hence with y^S axis, I or R becomes coincident with a ray direction of $\mathbf{k}$ when the crystal is rotated around $\mathbf{k}$ until it lies in the x^Sy^S plane. The amount of this rotation is $\psi^1_{\mathbf{k}}$ or $\psi^2_{\mathbf{k}}$ of (16). Inspection of Fig. 4 gives

$$\psi^i_{\mathbf{k}} = \psi^0_{\mathbf{k}} \pm \Delta\psi + \pi/2 \ (\text{modulo } \pi) \tag{A1}$$

in which the double sign is for $i=1$ or 2. By introducing a new variable

$$\varepsilon \equiv \pi/2 - \Delta\psi \tag{A2}$$

($A1$) becomes (17).

The angle $\psi^0_{\mathbf{k}}$ is the $\psi_{\mathbf{k}}$ angle when $\mathbf{h}$ is in the y^Sz^S plane. It is also the angle that the projection of $\mathbf{h}$ on the $x^{\mathbf{k}}z^{\mathbf{k}}$ plane makes with $z^{\mathbf{k}}$ axis. Therefore

$$\tan \psi^0_{\mathbf{k}} = -x^{\mathbf{k}}_{\mathbf{h}}/z^{\mathbf{k}}_{\mathbf{h}} \tag{A3}$$

where $x^{\mathbf{k}}_{\mathbf{h}}$ and $z^{\mathbf{k}}_{\mathbf{h}}$ are the x and z coordinates of the unit vector along $\mathbf{h}$ in the coordinate system $\mathbf{k}$. But, since $\mathbf{h}$ is along the $y^{\mathbf{h}}$ axis, (4) gives

$$\begin{pmatrix} x^{\mathbf{k}}_{\mathbf{h}} \\ y^{\mathbf{k}}_{\mathbf{h}} \\ z^{\mathbf{k}}_{\mathbf{h}} \end{pmatrix} = \begin{pmatrix} M_{12} \\ M_{22} \\ M_{32} \end{pmatrix}. \tag{A4}$$

Combining ($A3$) and ($A4$), one obtains (18).

The angle $\Delta\psi$ is the projection of the angle $90° - \theta_{\mathbf{h}}$ on the $x^{\mathbf{k}}z^{\mathbf{k}}$ plane. With equation ($A1$) of Lee & Ruble (1977) used on vectors $\mathbf{k}$, $\mathbf{R}$, and $\mathbf{h}$, one obtains

$$\cos \Delta\psi = \frac{\cos(\pi/2 - \theta_{\mathbf{h}}) - \cos \varrho_i \cos \varrho_{\mathbf{h}}}{\sin \varrho_i \sin \varrho_{\mathbf{h}}}. \tag{A5}$$

A lengthy but straightforward manipulation of this equation with the aid of equations (8), (14), and ($A2$) yields (19).

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