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Towards General Diffractometry. I. Normal-Beam Equatorial Geometry

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Abstract

Eulerian and κ goniometers, as well as real diffractometers with unavoidable misalignments of their shafts, are described as special cases of a general four-circle normal-beam equatorial diffractometer. The performance of these instruments can be improved by defining rotations about their real axes. Methods for transformation of the setting angles between the geometries based on different goniometer axes and procedures for positioning reflections are described. Analytical solutions for the transformations between Eulerian and the general version of the normal-beam equatorial diffractometer are presented.

1. Introduction

For several decades, diffractometers have been the fundamental tools in crystallographic research. Most common and commercially available are four-circle diffractometers, in which the detector moves in the horizontal (equatorial) plane and the incident beam is normal to the $\boldsymbol{\theta}$ axis and to crystal oscillation axis $\boldsymbol{\omega}$; the so-called normal-beam equatorial geometry (Arndt & Willis, 1966). The geometry of these diffractometers is the main subject of this paper. It will be shown that designs of such four-circle diffractometers, Eulerian and κ, can be described within the single concept of a general equatorial diffractometer (GED). Additionally, the axes of the GED are defined individually, which applies to real diffractometers with possible misalignment of their shafts. This particularly concerns the $\boldsymbol{\varphi}$ and $\boldsymbol{\theta}$ axes: owing to the mechanical limitations, the short $\boldsymbol{\varphi}$ shaft can often be tilted by several hundredths of a degree to the $\boldsymbol{\theta}$ shaft. In the general formalism, the inclination between $\boldsymbol{\varphi}$ and $\boldsymbol{\theta}$ is one of the goniometer parameters, it is included explicitly in the formulae for setting-angle calculations and therefore causes no errors in results, even if it reaches several degrees. However, the general formalism introduces some complications into the analytical formulae of the goniometer setting angles. In this report, general conditions for rotations of diffractometer axes are discussed. Convenient apparatus-dependent calculation procedures for setting angles and two general methods of the transformation of setting angles between geometries based on different axes are described. The transformations provide a means of easy crystal positioning of the axes on a real instrument and of analyzing these data while referring *e.g.* to the idealized Eulerian cradle. Analytical solutions for such transformations between the Eulerian and GED geometries are presented.

In this work, we have adapted the nomenclature for representations of vectors and rotations after Busing & Levy (1967), but in our notation vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ of the laboratory system correspond to vectors $\mathbf{e}_2$ and $-\mathbf{e}_1$, respectively, of the laboratory system in the quoted work. We also changed the sign of the $\boldsymbol{\chi}$ axis: in our notation, all positive angles correspond to left-handed rotations about the corresponding axes of the laboratory system, whereas, in Busing & Levy (1967), the $\boldsymbol{\chi}$ axis is right-handed. Table 1 lists the symbols used in the text.

2. Normal-beam equatorial geometries

2.1. *The Eulerian geometry*

The design of the first commercially manufactured four-circle diffractometers was based on Euler's concept of orientation procedure in three-dimensional space, hence the so-called Eulerian geometry. Its most important feature is orthogonality of the diffractometer axes $\boldsymbol{\chi}$ and $\boldsymbol{\omega}$. The schematic representation of such a goniometer is shown in Fig. 1.

The $\boldsymbol{\varphi}$ axis is collinear with $\boldsymbol{\omega}$ when $\chi = 0^\circ$, but it can be rotated about the $\boldsymbol{\chi}$ axis to assume any angle between 0 and 360°. The Eulerian geometry has been comprehensively described in the literature (*e.g.* Busing & Levy, 1967; Hamilton, 1974).

Owing to the orthogonality of the axes, calculations of the setting angles are simple and the operation of the Eulerian cradle often corresponds to requirements for positioning the crystal. Thus, the 'natural' modes of Eulerian goniometer operation are commonly in use. In the bisecting mode of data collection, the Eulerian $\boldsymbol{\omega}$ axis is not used for the crystal positioning and it is fixed to zero. Consequently, the $\boldsymbol{\chi}$ circle is perpendicular to the crystal scattering plane and bisects the angle formed by the incident and diffracted beams. The sequence of the $\boldsymbol{\varphi}$ and $\boldsymbol{\chi}$ rotations positioning the crystal in the bisecting mode is shown in Fig. 2. In the parallel mode, $\omega = 90^\circ$ and the $\boldsymbol{\chi}$ circle is parallel to the crystal scat-

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Table 1. *Nomenclature*

GED	General equatorial diffractometer, in which angle α between axes $\boldsymbol{\theta}$ and $\boldsymbol{\xi}$ can assume any values and axes $\boldsymbol{\theta}$, $\boldsymbol{\omega}_\xi$ and $\boldsymbol{\varphi}_\xi$ are not constrained to coincide when the goniometer is zero positioned. In this paper, only axes $\boldsymbol{\theta}$ and $\boldsymbol{\varphi}_\xi$ are allowed to diverge by angle β
$\mathrm{Ang}(x, y)$	Trigonometric function $\mathrm{atan}(x, y)$, introduced by Busing & Levy (1967)
$\mathbf{h}$	Reciprocal-vector representation in the reference system of Cartesian axes rigidly attached to the $\boldsymbol{\varphi}$ axis
$\mathbf{h}_\theta$	Reciprocal-vector representation in the reference system of Cartesian axes rigidly attached to the $\boldsymbol{\theta}$ axis
$\mathbf{e}_k$	kth versor, *i.e.* the unit vector, of the laboratory reference system
$\mathcal{G}_i$	Goniometer geometry denoted i ($i = \chi$ for an Eulerian goniometer, $i = \kappa$ for a κ goniometer and $i = \xi$ for a GED goniometer)
$\mathbf{g}_{i,k}$	kth axis of a goniometer designed in $\mathcal{G}_i$ geometry
$\mathcal{S}_{i,k}$	Type of positioning mode named k in $\mathcal{G}_i$ geometry
$a_{i,k}$	Rotation angle about axis k in geometry $\mathcal{G}_i$
$a^m_{i,k}$	Rotation angle about axis k in $\mathcal{S}_{i,m}$ positioning mode
$a^\psi_{i,k}$	Rotation angle about axis $\mathbf{g}_{i,k}$, used to construct a ψ rotation in $\mathcal{G}_i$ geometry
$\mathbf{R}_i$	Rotation matrix for a $\mathcal{G}_i$-geometry goniometer
$\mathbf{R}(\mathbf{g}, a)$	Matrix representation of rotation through angle a about vector $\mathbf{g}$
$\mathbf{R}_{i,k}(\mathbf{h})$	Matrix representation of the rotation setting vector $\mathbf{h}$ in a diffraction position using $\mathcal{S}_{i,k}$ positioning mode in $\mathcal{G}_i$ geometry
$D_{i,k}$	Domain of operator $\mathbf{R}_i$ for a given $\mathcal{S}_{i,k}$ positioning mode
$\Re^3$	Euclidean three-dimensional space
$\mathcal{I}(\mathcal{S}_{i,k} \rightarrow \mathcal{S}_{j,k})$	Intergeometrical transformation of setting angles where $\mathcal{S}_{i,k}$ is the 'source' positioning mode and $\mathcal{S}_{j,k}$ is the 'destination' one
$\mathbf{a}$; a	Arbitrary axis; angle or rotation about this axis
$\boldsymbol{\psi}$; ψ	Axis of rotation coincident with the scattering vector; respective rotation angle
$\boldsymbol{\varphi}, \boldsymbol{\chi}, \boldsymbol{\omega}$; φ, χ, ω	Eulerian goniometer axes; respective rotation angles; where ω is the deviation of the scattering vector from the $\boldsymbol{\chi}$-circle plane (Busing & Levy, 1967). In many instruments, ω is differently defined, as the angle between the $\boldsymbol{\chi}$ axis and $\mathbf{e}_1$.
$\boldsymbol{\varphi}_\kappa, \boldsymbol{\kappa}, \boldsymbol{\omega}_\kappa$; $\varphi_\kappa, \kappa, \omega_\kappa$	κ goniometer axes; respective rotation angles
$\boldsymbol{\varphi}_\xi, \boldsymbol{\xi}, \boldsymbol{\omega}_\xi$; $\varphi_\xi, \xi, \omega_\xi$	GED goniometer axes; respective rotation angles
α	Angle between axes $\boldsymbol{\kappa}$ and $\boldsymbol{\theta}$ in a κ geometry or, more generally, between axes $\boldsymbol{\xi}$ and $\boldsymbol{\theta}$ in a GED goniometer
β	Angle between axes $\boldsymbol{\varphi}_\xi$ and $\boldsymbol{\theta}$ in a GED geometry

tering plane. The most efficient mode for measuring reflections for a crystal enclosed in a diamond-anvil high-pressure cell (Merrill & Bassett, 1974) requires that the Eulerian φ angle is fixed to zero (Finger & King, 1978). The procedure of positioning Eulerian diffractometer angles for this $\varphi = 0°$ mode, when the φ angle is redundant, is shown in Fig. 3. Other geometries of goniometers do not allow these modes of positioning the crystals to be so clearly defined as in the Eulerian geometry.

2.2. *The κ geometry*

The κ goniometer, designed by Poot (1972) of Enraf–Nonius, has now become as common as the Eulerian goniometer. The typical construction of a κ goniometer is shown in Fig. 4. The non-orthogonal α angle between the $\boldsymbol{\kappa}$ and $\boldsymbol{\theta}$ axes considerably changes the analytical description of rotations. Usually, an angle α of 50° is chosen, although other values of α are also used, *e.g.* $\alpha = 55°$ in diffractometer CRYSTAN-GM 6.0 manufactured by MAC Science Co., Ltd. The $\omega = 0°$ and $\varphi = 0°$ positioning modes described above for the Eulerian geometry cannot be straightforwardly obtained for a κ goniometer. However, the formulae for transformations between the Eulerian and κ geometries are relatively simple and therefore often crystal positioning rotations are calculated in the Eulerian geometry, *e.g.* in the bisecting mode, and then transformations to the equivalent κ rotations are calculated. The specific features of the κ geometry can be illustrated by a procedure positioning vector $\mathbf{h}$ into the diffracting position by using a simple sequence of κ-goniometer rotations presented in Fig. 5, analogous to those shown above for an Eulerian cradle. This κ setting is different from any of the settings described for the Eulerian diffractometer and is more prone to convergence of the $\boldsymbol{\varphi}$ shaft with the incident beam on either side of the crystal (leading either to collisions with the collimator or to increased background due to the primary beam scattered from the goniometer head). A variety of other sequences of rotations, *e.g.* involving only two of the three goniometer axes, can be used for this goniometer, however the latter are not sufficient for positioning all reflections.

2.3. *The GED geometry*

Kucharczyk *et al.* (1986) modified the κ diffractometer by allowing the $\boldsymbol{\varphi}_\kappa$ axis not to coincide with the $\boldsymbol{\theta}$ axis (see Fig. 6). An additional instrumental parameter, angle β, describes the tilt between the $\boldsymbol{\varphi}_\kappa$ and $\boldsymbol{\theta}$ axes. It can be seen from Fig. 6 that a single angle β suffices for measuring the misalignment of the $\boldsymbol{\varphi}_\kappa$ and $\boldsymbol{\theta}$ axes, when axis $\boldsymbol{\varphi}_\kappa$ and the β angle are contained in the $\mathbf{e}_1\mathbf{e}_3$ plane. If the $\boldsymbol{\varphi}_\kappa$ axis is off the $\mathbf{e}_1\mathbf{e}_3$ plane, it can be moved to this plane by a rotation of $\boldsymbol{\kappa}$; then the zero position of the $\boldsymbol{\kappa}$ axis should be redefined.

The $\beta \neq 0$ modification imposes fewer mechanical restrictions on the instrument and enhances the general character of the mathematical description of rotations and setting angles for such a goniometer. This is achieved at the expense of increased complexity of calculations in this geometry. This can be illustrated by the procedure bringing a given vector $\mathbf{h}$ to its diffraction position by applying a sequence of rotations about the goniometer axes. One such procedure is shown in Fig. 7.

The diffractometer with misaligned $\boldsymbol{\varphi}_\kappa$ and $\boldsymbol{\theta}$ axes may be further generalized by allowing the α angle to assume any value between 45 and 90°. A diffractometer so designed can be described by the α and β angles and will be referred to as a general equatorial diffractometer (GED). It comprises the Eulerian and κ geometries as special cases when $\alpha = 90°$, $\beta = 0°$ and $\alpha = 50°$, $\beta = 0°$, respectively. For the purpose of the general discussion to follow, the axes of this diffractometer will be denoted $\boldsymbol{\varphi}_\xi$, $\boldsymbol{\xi}$, $\boldsymbol{\omega}_\xi$ and $\boldsymbol{\theta}$.

3. General equatorial diffractometer

3.1. *The GED goniometer geometry*

The principal task of a goniometer is to reorient a sample crystal to its scattering positions. In other words, a given reciprocal-space vector must be rotated to the diffraction direction $\mathbf{h}_\theta = (0, |\mathbf{h}|, 0)$. Such a setting can be obtained as a combination of rotations about three cradle axes. A set of axes can be defined by their unit vectors:

$$\mathcal{G}_i = \{\mathbf{g}_{i,1}, \mathbf{g}_{i,2}, \mathbf{g}_{i,3}\}. \quad (1)$$

These three vectors describe a diffractometer geometry. A setting rotation operator can be expressed in terms of the $\mathcal{G}_i$ geometry in the following form:

$$\mathbf{R}_i = \mathbf{R}(\mathbf{g}_{i,1}, a^k_{i,1})\mathbf{R}(\mathbf{g}_{i,2}, a^k_{i,2})\mathbf{R}(\mathbf{g}_{i,3}, a^k_{i,3}), \quad (2)$$

where $\{a^k_{i,m}\}$ are values of the setting angles.

The infinite number of possible choices of the diffractometer angles sets for a given vector $\mathbf{h}$ corresponds to the possibility of rotation about the scattering vector, the so-called ψ rotation. The infinity of the positioning modes can be described as

$$\mathcal{S}_{i,k} = \begin{cases} a^k_{i,1}(\mathbf{h}) \\ a^k_{i,2}(\mathbf{h}), \\ a^k_{i,3}(\mathbf{h}) \end{cases} \quad (3)$$

where index k labels different settings. The setting angles in different positioning modes differ only by a ψ rotation one from another.

The choice of the goniometer axes set $\mathcal{G}_i$ is not arbitrary because it affects the accessibility to the reciprocal space as well as the ability to perform ψ rotations. In the definition of the goniometer rotations operator, the inaccessible reciprocal-space regions should be treated separately because of the matrix indeterminacies. Therefore, for a given goniometer geometry $\mathcal{G}_i$, we can define a goniometer rotation operator in such a way that it becomes a zero matrix for inaccessible regions. The reciprocal space can then be divided as follows:

$$\begin{gathered} \Re^3 = D_{i,k} \cup L_{i,k} \\ L_{i,k} = \left\{L^G_i \cup L^S_{i,k} \cup L^C\right\} \\ \forall_{\mathbf{h}\in L_{i,k}} \mathbf{R}_{i,k}(\mathbf{h}) = 0, \end{gathered} \quad (4)$$

where:

$D_{i,k}$ is the accessible reciprocal-space region for which the goniometer rotation operator is defined according to the positioning mode, thus

$$D_{i,k} = \Re^3 \setminus L_{i,k};$$

L^G_i is the reciprocal-space region inaccessible for a given goniometer geometry. Geometries for which $L^G_i \neq \{\emptyset\}$ are of no practical interest. For example, a GED goniometer with $\beta = 0°$ and $\alpha < 45°$, or $\alpha = 50°$

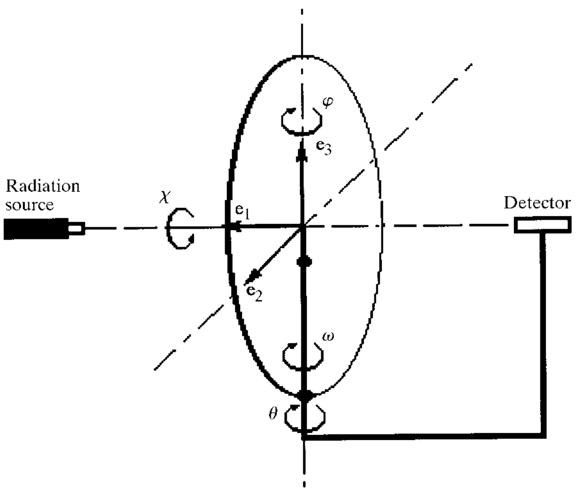

Fig. 1. Schematic drawing of the Eulerian four-circle diffractometer. All the goniometer axes $\boldsymbol{\varphi}$, $\boldsymbol{\chi}$ and $\boldsymbol{\omega}$ are shown in their zero positions: axes $\boldsymbol{\varphi}$ and $\boldsymbol{\omega}$ are parallel and $\boldsymbol{\chi}$ is perpendicular to $\boldsymbol{\omega}$ and $\boldsymbol{\theta}$.

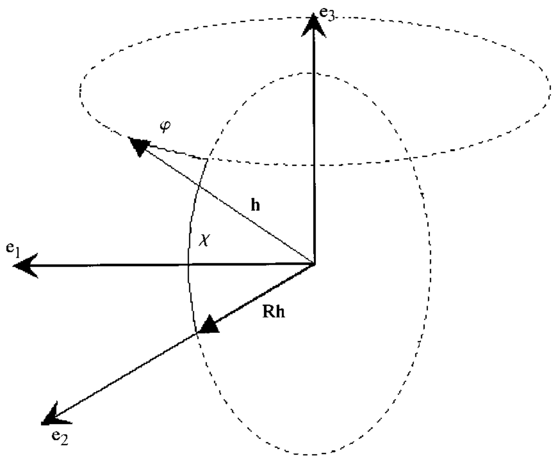

Fig. 2. Procedure of positioning reciprocal vector $\mathbf{h}$ into the diffracting position in the bisecting mode using an Eulerian cradle. First, the $\mathbf{h}$ vector is rotated about the $\boldsymbol{\varphi}$ axis to the $\mathbf{e}_2\mathbf{e}_3$ plane, and then it is rotated about the $\boldsymbol{\chi}$ axis and placed along vector $\mathbf{e}_2$. The $\boldsymbol{\omega}$ axis is redundant in this procedure.

and $\beta > 10°$ both have $L_i^G \neq \{\emptyset\}$, *i.e.* the reciprocal vectors close to the $\mathbf{e}_3$ axis could not be brought into a scattering position;

$L_{i,k}^S$ is the reciprocal-space region inaccessible for a given positioning mode. If $L_i^G = \{\emptyset\}$, then each vector $\mathbf{h} \in L_{i,k}^S$ may be accessed in a different positioning mode. Usually, $L_{i,k}^S \neq \{\emptyset\}$ for the settings transformed from another geometry;

L^C is the reciprocal-space region inaccessible due to experimental restrictions, *e.g.* such as imposed by the high-pressure chamber of a Merrill–Bassett diamond-anvil cell (Merrill & Bassett, 1974).

3.2. *Transformations between goniometer geometries*

Intergeometrical transformations between two goniometers $\mathcal{G}_i$ and $\mathcal{G}_j$ may be indispensable in experimental practice. One may wish to reproduce crystal orientation on two different diffractometers, as in the method in which the ψ-angle definition is independent of the crystal mounting or diffractometer type (Schwarzenbach & Flack, 1992*a*,*b*) or when an experiment is planned in advance assuming a convenient diffractometer geometry and then another type of diffractometer is used for measurements, also with misaligned axes. In other words, a diffractometer geometry $\mathcal{G}_j$ is to be used for an experiment, whereas the experiment requires the positioning mode $\mathcal{S}_{i,k}$ designed in another $\mathcal{G}_i$ geometry. Owing to its simplicity, the Eulerian diffractometer is often chosen as a reference for the non-Eulerian geometries (see §2.2 above). For example, one may wish to collect data in the bisecting mode using the GED goniometer. Below, in §§3.2.1 and 3.2.2, we present two methods for the intergeometrical transformations of setting angles. The explicit formulae derived for these transformations between the ideal Eulerian and GED goniometers for two Eulerian positioning modes are given in §4.

It should be noted that the problem of intergeometrical transformations in the form presented above always has two solutions corresponding to two equivalent rotations about a virtual axis $\mathbf{a}$ by angle a and angle $a' = a - 2\pi$. This means that for a given rotation $\mathbf{R}(\mathbf{a}, a)$ also the opposite rotation $\mathbf{R}(\mathbf{a}, a')$ will result in the same final position, although the path traced by vector $\mathbf{h}$ during the rotation is different. This implies that the intergeometrical transformations always have two equivalent solutions.

3.2.1. *The direct approach*. The straightforward approach to the transformation problem of finding cradle rotations in a $\mathcal{G}_j$ geometry from the known rotations in geometry $\mathcal{G}_i$ can be defined by the following equation:

$$\forall_{\mathbf{h}\in D_{i,k}\cap D_{j,k}} \forall_{\mathbf{h}'\in\Re^3} \mathbf{R}_{i,k}(\mathbf{h})\mathbf{h}' = \mathbf{R}_{j,k}(\mathbf{h})\mathbf{h}'. \qquad (5)$$

This condition requires that if some vector $\mathbf{h}$ is positioned by a rotation $\mathbf{R}_{i,k}$ in a $\mathcal{G}_i$ geometry and also an equivalent $\mathbf{R}_{j,k}$ rotation in geometry $\mathcal{G}_j$ is considered, then all the other vectors should assume identical orientations in the laboratory system after either of these rotations.

The right side of equation (5) depends on the reference geometry, thus, if one wants to solve it for a given geometry, the following substitution can be made:

$$[\mathbf{R}_{j,k}]_{mn} = [\mathbf{M}]_{mn}, \qquad (6)$$

where $\mathbf{M}$ is an unspecified matrix used to make the solution of equation (5) independent of the reference geometry. While solution of the goniometer equation, *i.e.* (6), for the κ goniometers with $\beta = 0°$ is relatively

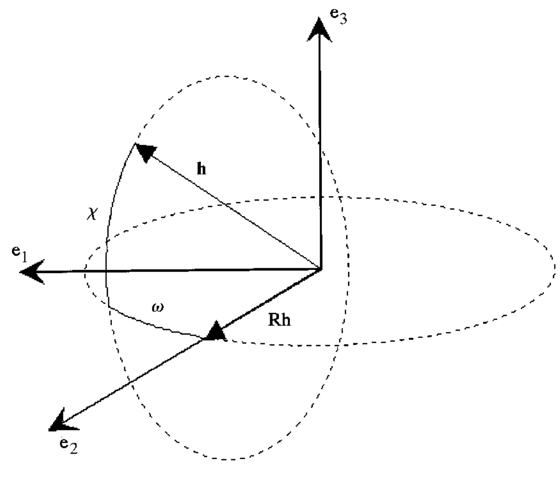

Fig. 3. Mode $\varphi = 0°$ of the $\mathbf{h}$-vector positioning: first it is rotated about χ to the $\mathbf{e}_1\mathbf{e}_2$ plane, and then it is rotated about ω to superimpose with $\mathbf{e}_2$. The φ axis is redundant.

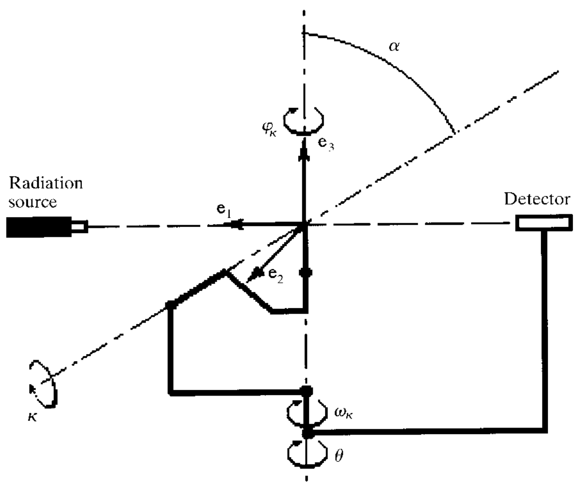

Fig. 4. Schematic drawing of a κ goniometer. The goniometer axes are denoted φ_κ, κ and ω_κ; α is the angle between axes κ and θ.

simple, changes in β considerably contribute to this complication. An iterative approximated procedure of solving the last equation for the general goniometer, with no restrictions set on the orientation of axes (in the GED, axes $\boldsymbol{\theta}$ and $\boldsymbol{\omega}_\xi$ are restricted to coincide for $\xi = 0°$), was described by Thomas (1990). In §4, we present the analytical solution of (6) for the GED goniometer. This solution in general can be written as

$$\mathcal{I}(\mathcal{S}_{i,k} \to \mathcal{S}_{j,k}) = \begin{cases} a_{j,1} = a_{j,1}(\{a_{i,m}\}) \\ a_{j,2} = a_{j,2}(\{a_{i,m}\}) \\ a_{j,3} = a_{j,3}(\{a_{i,m}\}) \end{cases}. \quad (7)$$

The $\mathcal{G}_j$ geometry setting angles calculated from the angles derived in the $\mathcal{G}_i$ geometry retain the crystal orientation with respect to the laboratory system. In this method, no positioning mode specific for the $\mathcal{G}_j$ geometry is needed.

3.2.2. *The ψ-rotation approach*. If goniometer $\mathcal{G}_j$ has its unique positioning mode called $S_{j,l}$ (*e.g.* see §§2.2 and 2.3), which is different from the required positioning mode $S_{i,k}$ of the reference diffractometer, another method of transformation can be applied. Because different positioning modes differ only by a ψ rotation, we can write the following equation:

$$\forall_{\mathbf{h}\in D_{i,k}\cap D_{j,k}} \forall_{\mathbf{h}'\in\Re_3} \mathbf{R}_{i,k}(\mathbf{h})\mathbf{h}' = \mathbf{R}(\boldsymbol{\psi}, \psi)\mathbf{R}_{j,l}(\mathbf{h})\mathbf{h}'. \quad (8)$$

As in (5), the required rotation $\mathbf{R}_{i,k}$ of the reference geometry reorients the whole reciprocal space in the same way as the product of an unknown ψ rotation $\mathbf{R}(\boldsymbol{\psi}, \psi)$ and the known rotation $\mathbf{R}_{j,l}$ defined in the $\mathcal{G}_j$ geometry.

Solution of (8), ψ, provides the difference between the original and required settings. In some special reference positioning modes, presented in §4, ψ depends only on the $\mathcal{G}_j$ setting angles, but in general it depends on the setting angles of both $\mathcal{G}_j$ and $\mathcal{G}_i$.

The ψ rotation, expressed by means of the $\mathcal{G}_j$ cradle rotations, has the following form:

$$\mathbf{R}_j(\boldsymbol{\psi}, \psi) = \mathbf{R}(\mathbf{g}_{j,1}, a^{\psi}_{j,1})\mathbf{R}(\mathbf{g}_{j,2}, a^{\psi}_{j,2})\mathbf{R}(\mathbf{g}_{j,3}, a^{\psi}_{j,3}). \quad (9)$$

It can be solved by the method presented by Busing & Levy (1967). Three shaft rotations $\{a^{\psi}_{j,m}\}$ of goniometer $\mathcal{G}_j$ combine into the ψ rotation. Therefore, the inter-geometrical transformation can be written as

$$\mathcal{I}(S_{j,l} \to \mathcal{S}_{j,k}) = \begin{cases} a_{j,1} = a^{l}_{j,1} + a^{\psi}_{j,1} \\ a_{j,2} = a^{l}_{j,2} + a^{\psi}_{j,2} \\ a_{j,3} = a^{l}_{j,3} + a^{\psi}_{j,3} \end{cases}. \quad (10)$$

Such an approach is suitable when modifications of a given positioning mode are required, *e.g.* for avoiding errors in reflection-intensity measurements due to simultaneous diffraction by diamond anvils in high-pressure experiments (Loveday *et al.*, 1990). The crystal positioned in the $\varphi = 0°$ mode can be simply rotated by small ψ values.

4. Transformations between the Eulerian and GED geometries

We denote the GED goniometer axes as $\mathbf{g}_{\xi,1} = \boldsymbol{\omega}_\xi$, $\mathbf{g}_{\xi,2} = \boldsymbol{\xi}$, $\mathbf{g}_{\xi,3} = \boldsymbol{\varphi}_\xi$ and the Eulerian goniometer axes as $\mathbf{g}_{\chi,1} = \boldsymbol{\omega}$, $\mathbf{g}_{\chi,2} = \boldsymbol{\chi}$, $\mathbf{g}_{\chi,3} = \boldsymbol{\varphi}$. Then the axial operators for the GED could be defined in the following way:

$$\begin{aligned} \mathbf{R}_\xi(\boldsymbol{\omega}_\xi, \omega_\xi) &= \mathbf{R}(\mathbf{e}_3, \omega_\xi) \\ \mathbf{R}_\xi(\boldsymbol{\xi}, \xi) &= \mathbf{R}(\mathbf{e}_2, -\alpha)\mathbf{R}(\mathbf{e}_3, \xi)\mathbf{R}(\mathbf{e}_2, \alpha) \\ \mathbf{R}_\xi(\boldsymbol{\varphi}_\xi, \varphi_\xi) &= \mathbf{R}(\mathbf{e}_2, -\beta)\mathbf{R}(\mathbf{e}_3, \varphi_\xi)\mathbf{R}(\mathbf{e}_2, \beta). \end{aligned} \quad (11)$$

The elements of the Eulerian-goniometer rotation matrix $\mathbf{R}_\chi$ follow from Busing & Levy (1967), where the changes described in §1 and Table 1 are:

$$\begin{aligned} [\mathbf{R}_\chi]_{11} &= \cos(\varphi)\cos(\omega) - \sin(\varphi)\sin(\omega)\cos(\chi) \\ [\mathbf{R}_\chi]_{12} &= \cos(\omega)\sin(\varphi) + \cos(\chi)\cos(\varphi)\sin(\omega) \\ [\mathbf{R}_\chi]_{13} &= \sin(\omega)\sin(\chi) \\ [\mathbf{R}_\chi]_{21} &= -\sin(\varphi)\cos(\omega)\cos(\chi) - \cos(\varphi)\sin(\omega) \\ [\mathbf{R}_\chi]_{22} &= \cos(\varphi)\cos(\omega)\cos(\chi) - \sin(\varphi)\sin(\omega) \\ [\mathbf{R}_\chi]_{23} &= \cos(\omega)\sin(\chi) \\ [\mathbf{R}_\chi]_{31} &= \sin(\varphi)\sin(\chi) \\ [\mathbf{R}_\chi]_{32} &= -\cos(\varphi)\sin(\chi) \\ [\mathbf{R}_\chi]_{33} &= \cos(\chi). \end{aligned} \quad (12)$$

4.1. *The direct approach*

Below, the solution of (6) for the case of GED geometry is presented. The explicit form of the GED goniometer equation takes the form

$$\mathbf{R}_\xi = \mathbf{R}_\xi(\boldsymbol{\omega}_\xi, \omega_\xi)\mathbf{R}_\xi(\boldsymbol{\xi}, \xi)\mathbf{R}_\xi(\boldsymbol{\varphi}_\xi, \varphi_\xi) = \mathbf{M}. \quad (13)$$

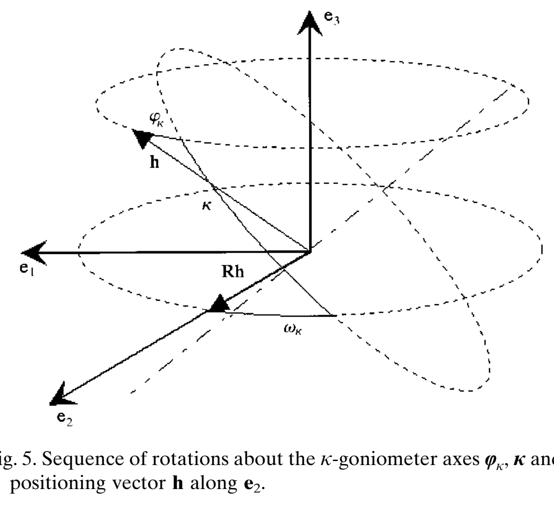

Fig. 5. Sequence of rotations about the κ-goniometer axes $\boldsymbol{\varphi}_\kappa$, $\boldsymbol{\kappa}$ and $\boldsymbol{\omega}_\kappa$ positioning vector $\mathbf{h}$ along $\mathbf{e}_2$.

The solution of this equation consists in finding the formulae combining $\boldsymbol{\omega}_\xi$, $\boldsymbol{\xi}$ and $\boldsymbol{\varphi}_\xi$ with the **M**-matrix elements.

While $\cos(\xi)$ is easy to determine, it is more complicated to obtain $\sin(\xi)$ needed for defining the sign of ξ. To simplify the calculations, the following procedure is employed to determine ξ:

(*a*) determine the $|\xi|$ value from $\cos(\xi)$;

(*b*) use $\xi = +|\xi|$ to determine the φ_ξ value;

(*c*) check if the sign choice was correct by comparing some independent ω_ξ element of $\mathbf{R}_\xi$ with the corresponding element of the **M** matrix (in this step, the **M** element should be replaced by the appropriate element of the Eulerian rotation matrix $\mathbf{R}_\chi$);

(*d*) if this test result is positive, then $\xi = +|\xi|$, if not, the sign of ξ sould be changed to $\xi = -|\xi|$.

The relevant formulae are listed below:

$$\xi = +|\xi| = \mathrm{Ang}(\sin(\xi), \cos(\xi)), \tag{14}$$

where

$$\cos(\xi) = \frac{\mathbf{M}_{31}\sin(\beta) - \mathbf{M}_{33}\cos(\beta) + \cos(\alpha)\cos(\beta-\alpha)}{\sin(\alpha)\sin(\beta-\alpha)}$$
$$\sin(\xi) = \sin(|\xi|).$$

The φ_ξ value for $\xi = +|\xi|$ is

$$\varphi_\xi = \mathrm{Ang}(\sin(\varphi_\xi), \cos(\varphi_\xi)), \tag{15}$$

where

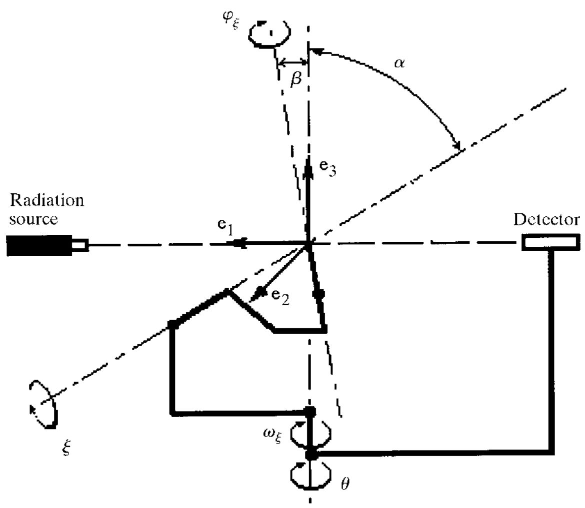

Fig. 6. Schematic drawing of the GED goniometer. The goniometer axes are denoted $\boldsymbol{\varphi}_\xi$, $\boldsymbol{\xi}$ and $\boldsymbol{\omega}_\xi$, α is the angle between axes $\boldsymbol{\xi}$ and $\boldsymbol{\omega}_\xi$, analogously to a κ goniometer, and β describes the misalignment between $\boldsymbol{\varphi}_\xi$ and $\boldsymbol{\theta}$.

$$\sin(\varphi_\xi) = \frac{-\cos(\beta)A\mathbf{M}_{32} + B[\mathbf{M}_{31} + \sin(\beta)D]}{\cos(\beta)(A^2+B^2)}$$
$$\cos(\varphi_\xi) = \frac{[\mathbf{M}_{31} + \sin(\beta)D](-A) - \mathbf{M}_{32}\cos(\beta)B}{\cos(\beta)(A^2+B^2)}$$
$$A = \cos(\alpha)\sin(\alpha-\beta) - \cos(\xi)\sin(\alpha)\cos(\alpha-\beta)$$
$$B = -\sin(\xi)\sin(\alpha)$$
$$D = \cos(\alpha)\cos(\alpha-\beta) + \cos(\xi)\sin(\alpha)\sin(\alpha-\beta).$$

A condition testing the sign of ξ can be written as

$$|-B\cos(\varphi_\xi) - A\sin(\varphi_\xi) + \mathbf{M}_{32}| = 0. \tag{16}$$

Then the formula for determining ω_ξ takes the form

$$\omega_\xi = \mathrm{Ang}(\sin(\omega_\xi), \cos(\omega_\xi)), \tag{17}$$

where

$$\sin(\omega_\xi) = -[(E\mathbf{M}_{23} + F\mathbf{M}_{13})\cos(\beta) - (E\mathbf{M}_{21} + F\mathbf{M}_{11})\sin(\beta)](E^2+F^2)^{-1}$$
$$\cos(\omega_\xi) = [(E\mathbf{M}_{13} - F\mathbf{M}_{23})\cos(\beta) - (E\mathbf{M}_{11} - F\mathbf{M}_{21})\sin(\beta)](E^2+F^2)^{-1}$$
$$E = \cos(\xi)\cos(\alpha)\sin(\alpha-\beta) - \sin(\alpha)\cos(\alpha-\beta)$$
$$F = \sin(\xi)\sin(\alpha-\beta).$$

Equations (14)–(17) provide the recipe for obtaining the setting angles in any positioning mode. The important feature of this solution is that it is independent of both the reference geometry and the reference positioning mode. To obtain transformation $\mathcal{I}(\mathcal{S}_{\chi,k} \to \mathcal{S}_{\xi,k})$ between the Eulerian reference and GED geometries, the following substitution should be made:

$$\mathbf{M} = \mathbf{R}_\chi. \tag{18}$$

For transformations from other geometries, **M** should be replaced by appropriate goniometer rotation matrices.

4.2. *The ψ-rotation approach*

This section presents the solutions of (8) for the GED geometry and the positioning mode described in Fig. 7. The positioning mode is indicated by the index 'n'. The Eulerian bisecting mode and mode $\varphi = 0°$ are chosen for reference.

(i) $\mathrm{GED}(n) \to \mathrm{GED}(\varphi = 0°)\mathcal{I}(S_{\xi,n} \to \mathcal{S}_{\xi,\varphi=0°})$

$$\psi = -\mathrm{Ang}(p_2, p_1), \tag{19}$$

where

$$
\begin{aligned}
p_1 &= p_{11} + p_{12} + p_{13} \\
p_2 &= p_{21} + p_{22} + p_{23} \\
p_{11} &= \cos(\alpha - \beta)[\cos(\varphi_\xi)\cos(\beta)p_{112} + p_{111}] \\
p_{111} &= \cos(\omega_\xi)\sin(\beta)\sin(\alpha) \\
p_{112} &= \cos(\omega_\xi)\cos(\xi)\cos(\alpha) - \sin(\omega_\xi)\sin(\xi) \\
p_{12} &= -\sin(\alpha - \beta)[\cos(\omega_\xi)p_{122} - p_{121}] \\
p_{121} &= \sin(\omega_\xi)\sin(\xi)\sin(\beta) \\
p_{122} &= \cos(\xi)\sin(\beta)\cos(\alpha) - \cos(\varphi_\xi)\cos(\beta)\sin(\alpha) \\
p_{13} &= -\sin(\varphi_\xi)\cos(\beta)p_{131} \\
p_{131} &= \cos(\omega_\xi)\sin(\xi)\cos(\alpha) + \sin(\omega_\xi)\cos(\xi) \\
p_{21} &= \cos(\alpha - \beta)[p_{211} - \sin(\beta)\cos(\alpha)] \\
p_{211} &= \cos(\varphi_\xi)\cos(\xi)\cos(\beta)\sin(\alpha) \\
p_{22} &= -\sin(\alpha - \beta)(p_{221} + p_{222}) \\
p_{221} &= \cos(\varphi_\xi)\cos(\beta)\cos(\alpha) \\
p_{222} &= \cos(\xi)\sin(\beta)\sin(\alpha) \\
p_{23} &= -\sin(\varphi_\xi)\sin(\xi)\cos(\beta)\sin(\alpha)
\end{aligned}
$$

(ii) $\mathrm{GED}(n) \to \mathrm{GED}(\omega = 0^\circ)\mathcal{I}(S_{\xi,n} \to \mathcal{S}_{\xi,\omega=0^\circ})$

$$\psi = \mathrm{Ang}(f_1, f_2), \tag{20}$$

where

$$
\begin{aligned}
f_1 &= f_{11} + f_{12} + f_{13} - f_{14} - f_{15} \\
f_2 &= f_{21} + f_{22} + f_{23} \\
f_{11} &= f_{111}[\cos(\varphi_\xi) - 1] \\
f_{111} &= \cos(\omega_\xi)\cos(\xi)\sin(\beta)\cos(\beta)\cos^2(\alpha) \\
f_{12} &= \cos(\alpha)(f_{123}f_{124} + f_{122} + f_{121}) \\
f_{121} &= -\sin(\varphi_\xi)\cos(\omega_\xi)\sin(\xi)\sin(\beta) \\
f_{122} &= \sin(\omega_\xi)\sin(\xi)\sin(\beta)\cos(\beta)[1 - \cos(\varphi_\xi)] \\
f_{123} &= \cos^2(\beta) + \cos(\varphi_\xi)\sin^2(\beta) \\
f_{124} &= \cos(\omega_\xi)\sin(\alpha)[\cos(\xi) - 1] \\
f_{13} &= \cos(\omega_\xi)\sin(\beta)\cos(\beta)\sin^2(\alpha)[\cos(\varphi_\xi) - 1] \\
f_{14} &= f_{141}[\cos^2(\beta) + \cos(\varphi_\xi)\sin^2(\beta)] \\
f_{141} &= \sin(\omega_\xi)\sin(\xi)\sin(\alpha) \\
f_{15} &= \sin(\varphi_\xi)\sin(\omega_\xi)\cos(\xi)\sin(\beta) \\
f_{21} &= \cos^2(\alpha)[\cos^2(\beta) + \cos(\varphi_\xi)\sin^2(\beta)] \\
f_{22} &= f_{221}[\cos(\varphi_\xi) - 1][\cos(\xi) - 1] \\
f_{221} &= \sin(\beta)\cos(\beta)\sin(\alpha)\cos(\alpha) \\
f_{23} &= \sin(\alpha)[f_{231} - \sin(\varphi_\xi)\sin(\xi)\sin(\beta)] \\
f_{231} &= \cos(\xi)\sin(\alpha)[\cos^2(\beta) + \cos(\varphi_\xi)\sin^2(\beta)].
\end{aligned} \tag{21}
$$

The formulae presented above allow two Eulerian positioning modes to be obtained on a GED diffractometer by simply adding to the original GED angles the further rotations of the goniometer axes, positioning the crystal at the required ψ's, according to equation (10).

5. Conclusions

A general description of a four-circle diffractometer goniometer, comprising the Eulerian and κ goniometers as special cases, and allowing the $\boldsymbol{\varphi}$ and $\boldsymbol{\theta}$ axes not to be parallel, has been presented. Precise explicit formulae for setting diffractometer angles and transforming them between diffractometer geometries have been derived and successfully applied on four-circle and six-circle KUMA GED diffractometers. Their application improves the accuracy of the goniometer operations and of the measured diffraction data. Inevitable small misalignments of $\boldsymbol{\varphi}$ and $\boldsymbol{\theta}$ axes in real diffractometers equipped with programs assuming ideal geometries do not cause serious errors in routine measurements owing to the large divergence of the graphite-monochromated X-ray beams (Katrusiak & Ryan, 1988) and to the applied scanning techniques. However, for larger $\boldsymbol{\varphi}/\boldsymbol{\theta}$ misalignments, or when low divergence beams are applied, *e.g.* at synchrotrons or from low mosaicity monochromators, precise formulae accounting for the misalignments are indispensable. Another straightforward application of the formulae are precise transformations between different goniometer geometries. To facilitate their use, two transformation procedures have been described, based on: (i) direct transformations and (ii) ψ-angle rotations. The first one is an efficient way of running diffractometer programs, the second is an easy method for applying the transformations by rotating angle ψ.

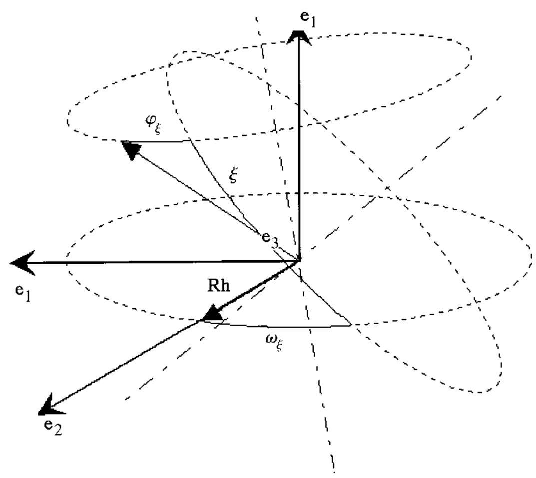

Fig. 7. A positioning mode of the GED goniometer. Vector **h** is first rotated around the $\boldsymbol{\varphi}_\xi$ axis to reach the $\mathbf{e}_1\mathbf{e}_3$ plane, then rotated around the $\boldsymbol{\xi}$ axis to reach the $\mathbf{e}_1\mathbf{e}_2$ plane, and finally is brought by a rotation about axis $\boldsymbol{\omega}_\xi$ to the $\mathbf{e}_2$ direction.

Finally, it can be remarked that a further step in the general description of four-circle diffractometer rotations would be explicit introduction of the ω/θ misalignments and the possible deviations of the primary beam. Owing to the mechanical construction of the diffractometers, the ω/θ misalignments are usually negligibly small compared to the β-angle magnitudes, while a possible inclination of the primary beam from the detector plane can be eliminated or accounted for in calculations (Declercq *et al.*, 1986). On the other hand, it can be anticipated that the introduction of all the possible instrumental misalignments will considerably increase the complexity of the formulae, much more than introduction of angle β only in the formulae presented in this paper. Certain of these general features are being naturally introduced into the formalism of a six-circle diffractometer. The general formulation of the equation can also be applied for designing new goniometers with new α and β angles and for predicting their mechanical conditions or their limitations of access to reciprocal space.

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References

Arndt, U. W. & Willis, B. T. M. (1966). *Single Crystal Diffractometry*, p. 37. Cambridge University Press.

Busing, W. R. & Levy, H. A. (1967). *Acta Cryst.* **22**, 457–464.

Declercq, J. P., Tinant, B. & Van Meerssche, M. (1986). *J. Appl. Cryst.* **19**, 222–223.

Finger, L. W. & King, H. (1978). *Am. Mineral.* **63**, 337–342.

Hamilton, W. C. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 273–284. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Katrusiak, A. & Ryan, T. W. (1988). *Acta Cryst.* A**44**, 623–627.

Kucharczyk, D., Malinowski, M., Paciorek, W. & Uszyński, I. (1986). *KM-4 Diffractometer Users Manual.* KUMA Diffraction, Wrocław, Poland.

Loveday, J. S., MacMahon, M. I. & Nelmes, R. J. (1990). *J. Appl. Cryst.* **23**, 392–396.

Merrill, L. & Bassett, W. A. (1974). *Rev. Sci. Instrum.* **45**, 290–294.

Poot, S. (1972). United States Patent No. 3,636,347.

Schwarzenbach, D. & Flack, H. D. (1992*a*). *J. Appl. Cryst.* **25**, 69–72.

Schwarzenbach, D. & Flack, H. D. (1992*b*). *J. Appl. Cryst.* **25**, 455–459.

Thomas, D. J. (1990). *Acta Cryst.* A**46**, 321–343.