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The Derivation of Crystal Orientation Matrix for Triclinic System on Two-circle Diffractometer

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Abstract

The limited availability of the two-circle diffractometer to collect intensity measurements down to the monoclinic system has been extended in a novel procedure to collect intensities for the triclinic system. The procedure involves the derivation of matrix elements from graphical representation of the reciprocal lattice. Offset of the origins of the upper layers from that of the zero-layer - characteristic of triclinic system - is determined and the 3 x 3 matrix elements are evaluated accordingly. Details of crystal alignment by X-rays for the triclinic system utilizing the intensities of equivalent reflections is described.
Keywords: orientation matrix ; two-circle diffractometer ; single crystal ; unit cell ; structure determination

Introduction

Although the four-circle diffratometer in which the counter rotates about the (2θ) axis in one plane and the crystal oriented to the correct angle with the incident and diffracted beams by the three axes of rotations (φ, χ and Ω) is in common use for single crystal X-ray diffractometry and structure determination, the two-circle diffractometer has also found considerable use, normally in an eqi-inclination (Weissenberg geometry) mode of operation.

The two-circle diffractometer has some advantages over the four-circle diffractometer mainly arising from its simpler construction: thus it is reliable and robust, and better suited for low temperature operation. The major drawback is the requirement that the crystal be accurately aligned so that a suitable lattice vector (usually one of the unit cell axes) is collinear with goniometer head axis (ω) [1].

The two-circle diffractometer and its modification are well suited to orthogonal crystal systems including the monoclinic in the 2nd or b setting [2]. However for the non-orthogonal crystal system – the triclinic, there is limited availability concerning the collection of intensity data [3]. We have experienced these limitations upon working on the machine when triclinic system had to treated [4-6]. Of these, the crystal orientation matrix unaccounted for the complete reciprocal lattice vectors that are necessary to satisfy diffraction condition for triclinic system i.e. the offset arising from incoincidence of crystal and reciprocal axes.

The aim of the work focuses on the derivation of the orientation matrix and the means to handle crystals with triclinic system on the two-circle diffractometer for subsequent intensity data collection.

The two-circle diffractometer

In the diffractometer, the crystal is rotated on (ω) axis, and the detector rotates on (2θ) axis by automatic setting. Inclination of the X-ray beam to the crystal (μ) is set manually.
A right-handed xyz coordinate system is defined relative to the diffractometer as shown in Figure 1.

Geometry for general orientation

General crystal orientation can be represented by 3 x 3 matrix **A** [7]

$$A = \begin{pmatrix} a^*x & b^*x & c^*x \\ a^*y & b^*y & c^*y \\ a^*z & b^*z & c^*z \end{pmatrix} \qquad (1)$$

The elements of A are the components of the three unit vectors of the reciprocal lattice with respect to a right handed coordinate system where a* lies along the x-axis of the diffractometer and a* b* plane lies in the xy plane, the z-axis is perpendicular to the xy plane.

The reciprocal lattice coordinates (xyz) of a reflection with Miller indices (hkl) are obtained by:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \mathbf{A} \begin{pmatrix} h \\ k \\ l \end{pmatrix} \qquad (2)$$

The reciprocal lattice coordinates are related to the angular settings according to Figure 2 in the following way:

$$x = (2 \sin\theta / \lambda) \sin\omega \cos\mu \qquad (3)$$
$$y = (2 \sin\theta / \lambda) \cos\omega \cos\mu \qquad (4)$$
$$z = (2 \sin\theta / \lambda) \sin\mu \qquad (5)$$

where θ is the Bragg angle
ω is the crystal rotation angle
μ is the crystal inclination angle to the X-ray beam
λ is the radiation wavelength

Reciprocal lattice construction

A specified region of the reciprocal lattice of the zero-layer (hk0) is systematically searched and the coordinates of the obtained lattice points are used to construct a two dimensional reciprocal lattice net as shown in Figure 3. A second search is performed to the 1st layer (hk1) after inclining the crystal to the X-ray beam by ($\mu_1 = \sin^{-1}(\lambda / 2c)$ where c is the mounting axis predetermined from crystal rotating method. These lattice points are drawn on the same net. The search is extended to the 2nd-layer (hk2) and its lattice points are also drawn on the same net. The direction of the offset is chosen such that a consistent shift in the origins of the upper layers to that of the zero-layer is uniquely determined.

Referring to Figure 3, the elements of **A** is then:

$$a^*_x = a^* \qquad a^*_y = 0 \qquad a^*_z = 0$$
$$b^*_x = b^* \cos\gamma^* \qquad b^*_y = b^* \sin\gamma^* \qquad b^*_z = 0$$

The elements c^*_x and c^*_y can be represented in terms of the offset vector ζ.

Referring to Figure 3, the length of ζ is:

$$[(x_n - x_{n-1})^2 + (y_n - y_{n-1})^2]^{1/2} \qquad (6)$$

And its direction with respect to x-axis **φ** is:

$$\tan^{-1} [(y_n - y_{n-1}) / (x_n - x_{n-1})] \qquad (7)$$

where n is a number defining the nth layer
x_{n-1} and y_{n-1} are the origin of the (hk0) layer.
x_n and y_n are the origin of the nth layer i.e. (hkn) n = 1, 2, …
φ is the angle the offset vector makes with the x-axis.

The elements of c* are therefore:

$c^*_x = \zeta \cos \varphi$
$c^*_y = \zeta \sin \varphi$
$c^*_z = 1 / c$ since it is the perpendicular distance between successive layers.

The final matrix **A** would be:

$$\mathbf{A} = \begin{pmatrix} a^* & b^* \cos\gamma^* & \zeta \cos\varphi \\ 0 & b^* \sin\gamma^* & \zeta \sin\varphi \\ 0 & 0 & 1/c \end{pmatrix} \qquad (8)$$

The elements of **A** are refined by least squares method for three pairs of equivalent reflections (hkl) and (-h-k-l) by the application of Eqs. 2, 3, 4 and 5; from which the unit cell parameters are obtained. An actual example is given in Table 1 for the compound [$Th(NO_3)_6$] . [($C_{10} H_8 N_2$)$_{1.5}$ NO_3] that has been utilized on the instrument [4]. The advantage of the method is that no presumption of preliminary cell is required for the determination of the unit cell parameters, therefore it is very practical.

When unit cell parameters are known for instance from X-ray photography or other diffractometric methods, the elements of **A** can also be derived in terms of the reciprocal cell axes and angles with the same consideration of a right handed system shown in Figure 4, and the application of the same rules as in Figure 3
Obviously the elements a^*_x, b^*_x and b^*_y are the same. However, from the geometry of Figure 4, one can find that:

$$c^*_x = c^* \cos\beta^* \qquad (9)$$

$$c^*_y = c^* ((\cos\alpha^* - \cos\beta^* \cos\gamma^*) / \sin\gamma^*) \qquad (10)$$

$$c^*_z = c^* ((1 - \cos^2\beta^* - ((\cos\alpha^* - \cos\beta^* \cos\gamma^*) / \sin\gamma^*)^2)^{1/2} \qquad (11)$$

If the accompanied terms with c* in c^*_x, c^*_y and c^*_z are designated by η, κ and τ respectively, the final matrix A is then:

$$A = \begin{pmatrix} a^* & b^* \cos\gamma^* & c^* \eta \\ 0 & b^* \sin\gamma^* & c^* \kappa \\ 0 & 0 & c^* \tau \end{pmatrix} \qquad (12)$$

These elements can also be refined by least squares as mentioned above to obtain the final cell parameters as shown in Table 2 for the compound $Pr(NO_3)_3 (H_2O)_4 .2H_2O$ that has been utilized on the instrument [6].

Crystal X-ray alignment

For crystal systems of high symmetry, the real and reciprocal axes are coincident and the (00l) l = 1, 2, … reflection always remain in reflecting positions at the Ewald sphere (see Figure 2 for geometrical representation) when the crystal is rotated about its mounting axis. This would facilitate correction in the misalignment of the crystal for subsequent measurements.

In low symmetry systems such as monoclinic 1st or a setting and triclinic, the (00l) lattice planes are not always in reflecting position but only when the point (00l) l = 1, 2, … pass the Ewald sphere. To find these points, part of the reciprocal space for l = 1, 2, … are explored and suitable reflections are selected. By careful monitoring of the intensities of equivalent reflections (hkl) and (-h -k -l) accurate alignment is achieved. The disadvantage in the procedure lies in the change of inclination of the crystal to the X-ray beam for each equivalent reflections monitored.

Concluding remarks

The procedure described so far has been applied successfully to calculate the unit cell parameters of the triclinic system and to collect intensity data for subsequent crystal structure determination of various compounds [4,5,6].

The prospect of using the two-circle diffractometer comes from providing excellent tuition experience for the users of this machine in understanding the underlying strategy of X-ray diffraction and crystallography.

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Table (1): General orientation cell parameter calculation

$[Th(NO_3)_6] . [(C_{10} H_8 N_2)_{1.5} NO_3]$ Rammo et.al. (1990) [4]
Triclinic
Crystal mounted about c

a* 1.1846 nm^{-1} b* 0.5165 nm^{-1} γ * 63.27 °
ζ 0.3916 nm^{-1} φ 36.62 ° 1/c 1.3109 nm^{-1}

$$A = \begin{pmatrix} 1.1846 & 0.2333 & 0.3143 \\ 0 & 0.4613 & 0.2336 \\ 0 & 0 & 1.3109 \end{pmatrix}$$

Refined unit cell parameters calculated from **A**:

a (nm)	0.9536(2)	α (°)	100.11(9)
b (nm)	2.2021(1)	β (°)	97.61(9)
c(nm)	0.7628(8)	γ (°)	114.56(3)

Table (2): Calculation of matrix A from known unit cell for subsequent refinement

Known unit cell for $Pr(NO_3)_3 (H_2O)_4 .2H_2O$ from Fuller and Jacobson (1976) [8]

a (nm)	0.9297	α (°)	72.48
b (nm)	1.2501	β (°)	68.01
c (nm)	0.6895	γ (°)	62.95

a* 1.2076 nm^{-1} b* 0.9097 nm^{-1} γ* 67.24(°)
η 0.2798 nm^{-1} κ 0.0545 nm^{-1} τ 0.9585 nm^{-1}

$$A = \begin{pmatrix} 1.2076 & 0.3519 & 0.4432 \\ 0 & 0.8389 & 0.0863 \\ 0 & 0 & 1.5183 \end{pmatrix}$$

Refined unit cell parameters obtained from **A** by Rammo (2001) [6] for $Pr(NO_3)_3 (H_2O)_4 .2H_2O$

a (nm)	0.9351(2)	α (°)	71.96(12)
b (nm)	1.2424(2)	β (°)	67.55(15)
c (nm)	0.6972(6)	γ (°)	63.70(20)

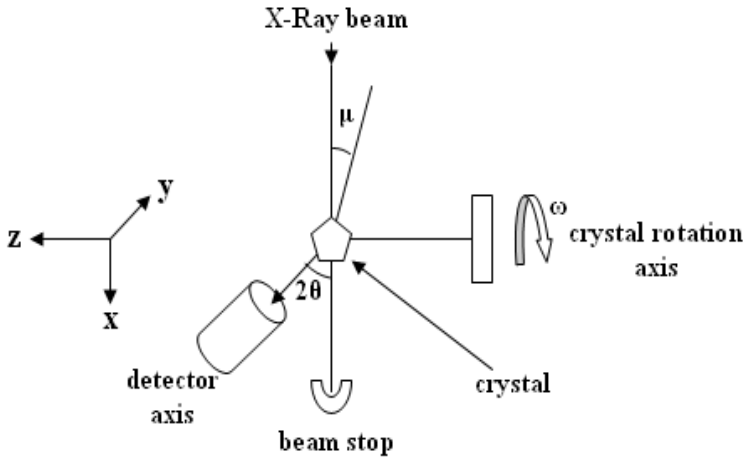

Fig. (1): Geometry of two-circle diffractometer

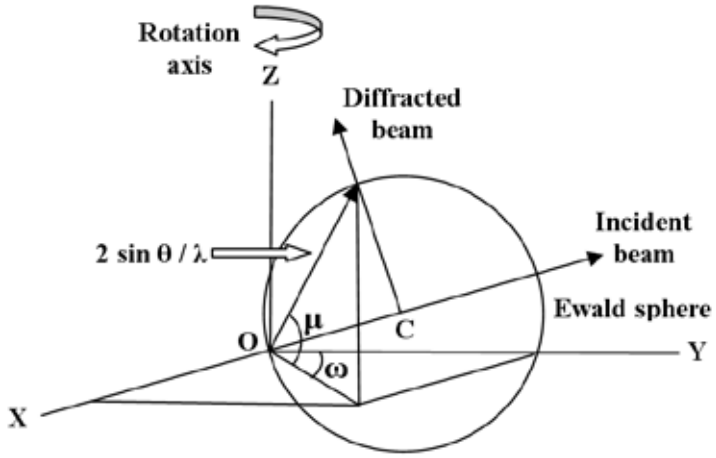

Fig. (2): Components of angular set of the reciprocal lattice vector and Ewald sphere construction

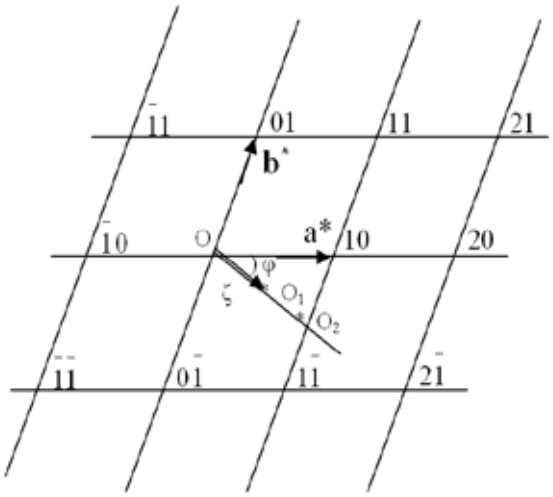

Fig. (3): Zero-layer reciprocal lattice (hk0) showing offsetting origins (O1, O2) of non-zero layers. ζ and φ are magnitude and direction of c* locus. Non-zero reciprocal layers are omitted for clarity.

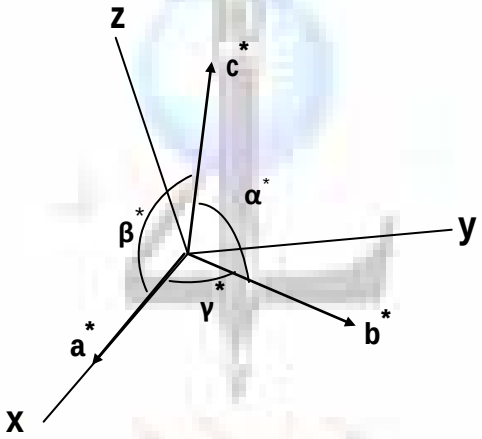

Fig. (4): Reciprocal lattice axes relative to orthogonal right-handed axes.

اشتقاق مصفوفة توجيه البلورة للنظام ثلاثي الميل لمقياس الحيودÐ Á الدائرتين

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الخلاصة

تم تمديد محدودية مقياس الحيود ذ Á الدائرتين لقياسات تجميع الشدة لغاية النظام احادي الميل بأسلوب مبتكر لتجميع الشدات للنظام الثلاثي الميل. يتضمن الاسلوب اشتقاق عناصر مصفوفة التوجيه من التمثيل البياني للشبيكة المقلوبة. اذعين(offset) نقاط اصل الطبقات العليا عنها للطبقة الصفرية والتي هي ميزة للنظام الثلاثي وتم اشتقاق وتحديد عناصر المصفوفة 3 x 3 تبعا لذلك. وصفت تفاصيل ترصيف البلورة بوساطة الأشعة السينية للنظام ثلاثي الميل بتوظيف شدات الأنعكاسات المتكافئة.

الكلمات المفتاحية : مصفوفة التوجيه ، مقياس الحيود ذو الدائرتين ، البلورة الاحادية ، خلية الوحدة ، تعيين التركيب