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The Conventional Bravais Unit Cell from Diffractometer Data*

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With the use of modern single-crystal diffractometers for structure determination, the preliminary photographic study of the diffraction pattern is much abbreviated or even eliminated entirely. The dangers inherent in this omission can be reduced by systematic checking of the automatic features of diffractometer operation, and this requires a full understanding of the methods. This paper (a) describes how possible unit cell axes are found from 15—25 accurately centered reflections, in more detail than is easily available elsewhere; (b) provides a step-by-step procedure for deriving the reduced cell; and (c) indicates how International Tables for X-Ray Crystallography can be used to deduce the conventional Bravais cell from the reduced cell.

INTRODUCTION

The increasing sophistication of automatic single-crystal diffractometers has made it possible, and perhaps even common, to carry out a complete structure determination without a preliminary photographic study of the diffraction pattern. Crystallographers are well aware of the dangers of omitting the study of Weissenberg and precession photographs of a suitably oriented crystal: sets of weak reflections may go unnoticed, symmetry elements may not be discovered, diffractometer time can be wasted on twinned or distorted crystals, and so on. Nevertheless, the speed and other advantages of using a crystal in a random orientation on the diffractometer encourage the bypassing of the photographic study. The purpose of this note is to indicate how to reduce the associated dangers by a systematic procedure for determining the appropriate conventional unit cell from diffractometer data.

Some of the procedures described parallel those included in the P3 computer program[1] provided with the current models of the Nicolet diffractometer, but they can readily be programmed for other systems.

The process of finding appropriate axes by diffractometer begins with a set of a dozen or more carefully centered reflections. These may have been found by systematic search through reciprocal space, or by a search guided by a preliminary random-orientation oscillation or other photograph. From the coordinates of the corresponding points in reciprocal space the Nicolet program generates a list of candidates for cell axes. The appropriate axes can then be selected either by the crystallographer or automatically by the com-

* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

puter program. In either case errors are possible, so it is important to understand the logic of the methods, and to use the one to check the other. The following sections describe how the candidate axes are generated, the reduced cell is selected, and the conventional Bravais lattice is found.

Lattice Vectors from Representative Reflections

From a set of representative reflections (lattice vectors in reciprocal space) it is possible to deduce all the shorter vectors in the direct lattice, which include the possible unit cell axes. The algorithm for this procedure was devised by Sparks[1] under the name »autoindexing« procedure, and is described more fully by Sparks[2].

Let X represent the column matrix composed of the three components of a reciprocal lattice point on arbitrarily defined Cartesian axes. These axes are fixed to the crystal, but if all instrument angles are set at zero, the axes coincide with corresponding Cartesian axes fixed to the instrument. The components are readily deduced from the angle settings at which a reflection is observed, and vice versa. Let H represent similarly the column matrix composed of the indices, h, k, l, that is, the components of the same reciprocal latice point on appropriate reciprocal axes. These column matrices are related by the orientation matrix A according to the equation

$$X = AH \tag{1}$$

Thus, knowledge of the orientation matrix permits us to determine the Cartesian coordinates of any reflection from its indices, and therefrom the angle settings at which it can be observed on the diffractometer. It is easy to see that the elements of the orientation matrix are just the Cartesian components of the reciprocal lattice axes.

$$A = \begin{bmatrix} a_x^* & b_x^* & c_x^* \\ a_y^* & b_y^* & c_y^* \\ a_z^* & b_z^* & c_z^* \end{bmatrix} \tag{2}$$

by looking at the reciprocal lattice points 100, 010, 001.

The orientation matrix can be inverted since the three reciprocal axes are not coplanar, and hence A is a nonsingular matrix. Then from eq. (1) the relation

$$A^{-1} X = H \tag{3}$$

follows, which permits the indices to be found from the coordinates of a reflection.

Now extend the definition of X so that it is composed of the coordinates of three reflections, arranged column by column. The definition of H is similarly extended to contain the indices of the same three reflections. Then eqs. (1) and (3) still hold. The matrix X is now a 3×3 square matrix, and is nonsingular if the reciprocal lattice vectors of the three reflections are not coplanar; consequently, it can be inverted. In this case the equation

follows from eq. (3). This result permits calculation of the inverse of the orientation matrix from the Cartesian coordinates and indices of three (noncoplanar) reflections.

The elements of the inverse orientation matrix are readily identified as the Cartesian coordinates of the (direct) axes.

$$A^{-1} = \begin{bmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{bmatrix} \tag{5}$$

since $A^{-1} A = E$. Consequently, eq. (4) generates direct axes from Cartesian coordinates and indices of three reflections. Some one axis, say a, is given by the first row:

$$[a_x\, a_y\, a_z] = [h_1\, h_2\, h_3]\, X^{-1} \tag{6}$$

where h_1, h_2, and h_3 are the first Miller indices for the three reflections. Since the indices are initially unknown, the autoindexing procedure allows h_1, h_2, and h_3 to take on a range of small integer values in a systematic way. Equation (6) thus generates many vectors in direct space, some of which may be primitive axes.

If the three reciprocal lattice vectors that form X are regarded as defining a reciprocal unit cell, that is, if they are taken as 100, 010, and 001, then H is the identity matrix, $X^{-1} = A^{-1}$ from eq. (4), and so from eq. (5) it is apparent that the rows of X^{-1} represent the corresponding direct lattice unit cell. If X represents a primitive reciprocal cell, then X^{-1} represents a primitive direct cell; if X represents a multiple of a primitive cell, then X^{-1} represents a submultiple of a primitive cell. Hence the three shortest noncoplanar reciprocal vectors are chosen to form X, so that the direct cell is most likely to be primitive. In any case all linear combination of the tentative direct cell axes, which are generated by eq. (6), will include all direct lattice vectors, but if the original reciprocal cell were too big, the direct cell will be too small, and additional vectors will appear that are not lattice vectors of the true lattice. The erroneous vectors produced by eq. (6) can be screened out by use of one element of eq. (3), say the 11 element:

$$[a_x\, a_y\, a_z] \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = h_1 \tag{7}$$

The possible lattice vectors $[a_x\, a_y\, a_z]$ from eq. (6) will automatically be consistent with eq. (7) when x, y, z, represents one of the originally chosen reciprocal vectors, but need not be consistent if the Cartesian coordinates represent one of the as yet unused reciprocal vectors in the original set. Each potential axis vector is then tested against all remaining reciprocal vectors, by use of eq. (7); the left-hand side multiplies out to an integer for a consistent potential axis, to a fraction for an inconsistent potential axis.

In this way a number of lattice vectors are derived, all consistent with the original observed reflections, in the sense that the reflections would have integer indices if described on any three noncoplanar lattice vectors in the resultant set. From such a set of lattice vectors the crystallographer can

proceed in two ways: examine the list for vectors that suggest a unit cell with recognizable symmetry (e. g., vectors of equal length, orthogonal vectors, etc.), or deduce the reduced cell and use its dimensions to derive the conventional Bravais cell. In either approach, only metric properties of the lattice are employed, so that the symmetry of the suggested Bravais cell must be confirmed subsequently by examination of reflection intensities.

Only the second approach is described here: derivation of the reduced cell, and from it, the conventional Bravais cell. The starting point is the selection of three of the vectors generated as described above as axes to describe a primitive unit cell. Usually these will be chosen as the three shortest vectors that are not coplanar. It is important to verify that the cell is actually primitive by checking that none of the three axes has to be doubled (or tripled). This can be done by looking for extra layer lines on rotation photographs about each of the three axes, or with diffractometer only by looking for possible low-angle reflections with half-integral (or third-integral) indices.

From this arbitrary primitive cell the reduced cell can be derived.

The Reduced Cell

The reduced cell is defined (Niggli[4]; Buerger[5,6]; Santoro and Mighell[7]; Gruber[8]) by a series of conventions in such a way that it is uniquely specified for any particular lattice. The main conventions are:

1. The cell is primitive.

2. The cell is constructed on the three shortest noncoplanar lattice vectors.

3. All interaxial angles are either acute (Type I) or else obtuse or right angles (Type II).

4. The axes are labelled so that $a \leq b \leq c$ and the senses are chosen so that the axes form a right-handed set.

In special cases, additional conventions have to be adopted to yield the unique Niggli reduced cell; see Santoro et al.[7]

An alternative to the reduced cell is the Delaunay cell. The relation of this cell to the reduced cell is described by Allmann[9] (and references therein). The Delaunay cell appears to have less usefulness for single-crystal work, and will not be discussed further.

The Buerger reduced cell can be formed from an arbitrary primitive cell that already obeys the labelling convention 4 by means of one of the procedures outlined by Buerger[5,6]. The version most natural for computer implementation is not, however, described in detail. The necessary steps are indicated in the following procedure. The reduction process begins at step 0 and continues in sequence except where branches are indicated. First a check is made (step 0) that the three initial lattice vectors satisfy conventions 1 and 4, and are not coplanar. Then all simple linear combinations of these axes are examined (steps 1—7) to see if any are smaller than one or more of the original axes. If the linear combination is written as

$$t = ua + vb + wc \tag{8}$$

then its squared length is

$$t^2 = u^2a^2 + v^2b^2 + w^2c^2 + 2uv\, a \cdot b + 2vw\, b \cdot c + 2wu\, c \cdot a \tag{9}$$

which can be compared with c^2, b^2, and a^2 (tests T1 and T2). In the suggested procedure the magnitudes of u, v, and w are limited, at each step, to 1 or 0. If t is smaller than c, b, or a, then t replaces one of the original axes, and the process repeats until no further change is made. At each step (tests T1 and T2) the sense of t must be chosen, and the remaining axes relabelled, so that convention 4 is observed. This process ensures that convention 2 is satisfied, as well as conventions 1 and 4.

0. Ensure that axes are primitive, noncoplanar, right-handed, and in the order $a \leq b \leq c$.

1. Calculate $b \cdot c$, $c \cdot a$, and $a \cdot b$.
   If $c \cdot a < 0$, calculate t^2 for $t = [101]$ and go T1.
   If $c \cdot a = 0$, go to 2.
   If $c \cdot a > 0$, calculate t^2 for $t = [\bar{1}01]$ and go to T1.

2. If $b \cdot c < 0$, calculate t^2 for $t = [011]$ and go to T1.
   If $b \cdot c = 0$, go to 3.
   If $b \cdot c > 0$, calculate t^2 for $t = [0\bar{1}\bar{1}]$ and go to T1.

3. If $a \cdot b < 0$, calculate t^2 for $t = [110]$ and go to T2.
   If $a \cdot b = 0$, go to 4.
   If $a \cdot b > 0$, calculate t^2 for $t = [\bar{1}10]$ and go to T2.

4. Calculate t^2 for $t = [111]$ and go to T1.

5. Calculate t^2 for $t = [\bar{1}11]$ and go to T1.

6. Calculate t^2 for $t = [1\bar{1}1]$ and go to T1.

7. Calculate t^2 for $t = [\bar{1}\bar{1}1]$ and go to T1.

8. If $b \cdot c < 0$, set $\lambda_a = 1$
   If $b \cdot c = 0$, set $\lambda_a = 0$
   If $b \cdot c > 0$, set $\lambda_a = -1$
   If $c \cdot a < 0$, set $\lambda_b = 1$
   If $c \cdot a = 0$, set $\lambda_b = 0$
   If $c \cdot a > 0$, set $\lambda_b = -1$
   If $a \cdot b < 0$, set $\lambda_c = 1$
   If $a \cdot b = 0$, set $\lambda_c = 0$
   If $a \cdot b > 0$, set $\lambda_c = -1$
   If $(a \cdot b)(b \cdot c)(c \cdot a) < 0$, go to 10.
   If $(a \cdot b)(b \cdot c)(c \cdot a) = 0$, go to 9.
   If $(a \cdot b)(b \cdot c)(c \cdot a) > 0$, change signs of λ_a, λ_b and λ_c and go to 10.

9. Replace zero λ-values with 1 or -1 so that there are either none or two negative λ_a, λ_b, λ_c.

10. Replace a by $\lambda_a a$, b by $\lambda_b b$, c by $\lambda_c c$.

T1. If $t^2 - c^2 \geq 0$, return to next number.
   If $t^2 - b^2 \geq 0$, replace c by t, and go to 1.
   If $t^2 - a^2 \geq 0$, replace c by b, b by $-t$, and go to 1.
   If $t^2 - a^2 < 0$, replace c by b, b by a, a by t, and go to 1.

T2. If $t^2 - b^2 \geq 0$, return to next number.

If $t^2 - a^2 \geq 0$, replace b by t, and go to 1.

If $t^2 - a^2 < 0$, replace b by a, a by $-t$, and go to 1.

It is possible to reduce the number of calculations of t^2 by introducing further tests. For example, the cell diagonals [111], $[\bar{1}11]$, $[1\bar{1}1]$, $[\bar{1}\bar{1}1]$ (steps 4—7) need be examined only for cells of Type II, which can be recognized by the product $(a \cdot b)(b \cdot c)(c \cdot a)$ being negative (or zero). Such refinements are omitted in the interest of simplicity.

Convention 3 may then be satisfied by changing the senses of pairs of axes so that $a \cdot b$, $b \cdot c$, and $c \cdot a$ all have the same sign; zero is included in the type with negative signs. This procedure is included in steps 8—10.

If one starts with the list of lattice vectors described in the previous section, it is easy to follow through the procedure to derive the Buerger reduced cell. If a computer program finds some »reduced« cell automatically, it should be checked by following the procedure. This is necessary not merely because the program may not do exactly what one expects, but also because of situations where judgement is required. If any of the scalar products $a \cdot b$, $b \cdot c$, $c \cdot a$ are very small, a decision must be made whether to consider them as zero. If some do vanish, then the signs of the others must be made negative to satisfy convention 3. If any is small but nonvanishing, then the signs of all may be positive, and a different reduced cell results.

If special relations exist among the cell dimensions, as occurs with lattices of higher symmetry, then further transformations are required to go from the Buerger reduced cell to the unique Niggli reduced cell. For example, if $a^2 = b^2$ and $|a \cdot c| < |b \cdot c|$, then the transformation 0 —1 0/—1 0 0/0 0 —1. must be applied so that $|a \cdot c'| > |b \cdot c'|$. The requisite transformations are tabulated by Santoro et al.[7] and are not included in the procedure.

Conventional Bravais Lattice from Reduced Cell

A systematic method for deriving the axes of the conventional Bravais lattice from the reduced cell, as defined in the preceding section, has been provided by Mighell and Rodgers[10]; their Table I is a revision of the table prepared by Mighell, Santoro and Donnay[11]. If ambiguities have led to more than one possible reduced cell, each must be compared to the table entries to find the alternative possible Bravais cells.

Each Bravais cell that results, except for a triclinic cell, implies a Laue symmetry higher than 1 for the reciprocal lattice. The preceding steps have ensured only that the geometry of the lattice is consistent with this symmetry. However, the actual existence of symmetry elements must still be confirmed by comparison of reflection intensities that should be equal for certain symmetry elements. This can be done either by auxilliary photographs or by diffractometer measurements of reflections that should be equivalent by symmetry.

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SAŽETAK

Konvencionalna Bravaisova jedinična ćelija iz difraktometrijskih podataka

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