The use of Buerger's algorithm in crystallographic calculations.

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Summary. Buerger (Zeits. Krist., 1957, vol. 109, p. 42) describes an algorithm for deriving data for the reduced unit cell from those obtained for an arbitrary crystal setting. It is shown that indices can be added to the algorithm so that one also derives the transformation matrix for the change of setting. Conversely, a known transformation matrix forms a set of instructions for using the algorithm to transform unit cell data, whether X-ray or morphological, from the initial to the final setting. One can thus use the algorithm to calculate the lengths of any unit cell vectors and the angles between them, and, using reciprocal cell data, to obtain any interfacial angles. Worked examples of these applications show that the proposed calculation method is shorter and simpler than those at present accepted.

IN the triclinic crystal system, the choice of axes is arbitrary and it is frequently necessary to change from one choice to another. The preferred choice is usually the axes of the reduced cell, at angles as near right as possible. The transformation matrix for the required change may or may not be known; it is usually known for the recalculation of goniometric results to a new setting, and the normal spherical trigonometrical methods of doing this are described in standard textbooks; it is usually unknown for the reduction of X-ray measurements to the reduced cell, when two procedures are possible. The standard procedure is based on Delaunay's representation of the unit cell and is fully described, e.g. by Ito (1950) and Henry and Lonsdale (1952); it yields only cells having all angles obtuse. Buerger (1957) has introduced a second method of cell-reduction that is simpler than the Delaunay procedure and has the great virtue that it yields the reduced cell with angles as near right as possible, regardless of whether all are obtuse or one is acute. With minor modifications, Buerger's method can be applied to a variety of crystallographic calculations to give simplified procedures and it is the purpose of this paper to describe these applications.

In Buerger's method the cell is represented by a^2, b^2, c^2, $bc\cos\alpha$, $ca\cos\beta$, $ab\cos\gamma$, and they are written in the triangular array below:

$$\begin{array}{ccc} & [001] & \\ & c^2 & \\ & ca\cos\beta \quad bc\cos\alpha & \\ [100]\ a^2 & ab\cos\gamma \qquad b^2\ [010] & \end{array} \quad = \quad \begin{array}{ccc} & [001] & \\ & s_{33} & \\ & s_{31} \quad s_{23} & \\ [100]\ s_{11} & s_{12} \qquad s_{22}\ [010] & \end{array}$$

The meaning of the symbols s_{11}, &c., as used by Buerger, will be clear from the above. It is convenient to add the indices at the corners of the array as shown.

Buerger obtains the reduced cell by using the following transformation or algorithm:

$$\begin{array}{ccc} & [001] & \\ & s_{33} & \\ & s_{31} \quad s_{23} & \\ [100]\ s_{11} & s_{12} \qquad s_{22}\ [010] & \end{array} \longrightarrow \begin{array}{ccc} & [001] & \\ & s_{33} & \\ & s_{31} \quad (s_{23}+ms_{31}) & \\ [100]\ s_{11} & (s_{12}+ms_{11}) \qquad (s_{22}+2ms_{12}+m^2s_{11})\ [m10] & \end{array}$$

m

This transformation can clearly be applied in six possible directions in the array, two opposite directions parallel to each of the three sides, and m can be any positive or negative integer. The new indices are those of the new axes in terms of the original choice of axes; thus the new b-axis above is the $[m10]$ vector of the old cell; so that, written in columns, the new indices form the zone-symbol transformation matrix from the new to the original setting, Z_{21}; here $Z_{21} = [1m0/010/001]$. It follows that, written in rows, the indices form the face-index transformation matrix, F_{12}, from the original to the new axes; here $F_{12} = [100/m10/001]$.

The aim of a cell-reduction is to apply the above transformation as many times and in as many directions as necessary, until the terms in the middle of the sides of the triangle are brought as near zero as possible, that is so that each is less than half either of its neighbouring corner terms. Furthermore, any two midpoint terms can be changed in sign, with corresponding sign changes in the indices at the corner between them, and this is finally applied so as to make the midpoint terms adjacent to the new c-axis negative. The new axes are, of course, selected so as to make $c^2 < a^2 < b^2$.

Experience has shown that cell-reduction can equally well be carried out in reciprocal space,[1] when the cell is represented by:

[1] *It seems possible that for a triclinic reduced cell with one angle very near 60° or 120°, or rather with a midpoint term very nearly one-half of an adjacent corner term, the reduced reciprocal cell may differ from the reduced real cell. In such cases one would wish to check the reduced reciprocal cell elements by converting to real cell elements and thence to* s_{11}, &c., *for possible further reduction in real space.*

$$\begin{array}{ccc} & (001) & \\ & c^{*2} & \\ & c^*a^*\ \cos\beta^*\quad b^*c^*\cos\alpha^* & \\ (100)\ a^{*2} & a^*b^*\cos\gamma^* & b^{*2}\ (010) \end{array} \quad = \quad \begin{array}{ccc} & (001) & \\ & s^*_{33} & \\ & s^*_{31}\quad s^*_{23} & \\ (100)\ s^*_{11} & s^*_{12} & s^*_{22}\ (010) \end{array}$$

The transformation is carried out as above, and the indices now yield F_{21} when written in columns and Z_{12}, the zone-symbol transformation matrix, when written in rows. The new axes are selected to make $c^{*2}>a^{*2}>b^{*2}$, and the midpoint terms adjacent to the new c^*-axis are made positive.

Example 1. A crystal of cobaltomenite, adjusted to an arbitrary axis, yielded zero and first layer Weissenberg photographs from which one could find:

$$\begin{array}{ccc} & (001) & \\ & c^{*2} & \\ & c^*a^*\cos\beta^*\quad b^*c^*\cos\alpha^* & \\ (100)\ a^{*2} & a^*b^*\cos\gamma^* & b^{*2}\ (010) \end{array} \quad = \quad \begin{array}{ccc} & (001) & \\ & 0{\cdot}0323 & \\ & -0{\cdot}0316\quad -0{\cdot}0001_5 & \\ (100)\ 0{\cdot}0884_5 & -0{\cdot}0511 & 0{\cdot}0857_5\ (010) \end{array}$$

One then has, tackling first the most glaring midpoint anomaly (italicized):

$$\begin{array}{ccc} & (001) & \\ & 0{\cdot}0323 & \\ & \textit{-0·0316}\quad -0{\cdot}0001_5 & \\ (100)\ 0{\cdot}0884_5 & -0{\cdot}0511 & 0{\cdot}0857_5\ (010) \end{array} \longrightarrow \quad \begin{array}{ccc} & (001) & \\ 1\swarrow & 0{\cdot}0323 & \\ & 0{\cdot}0007\quad -0{\cdot}0001_5 & \\ (101)\ 0{\cdot}0575_5 & -0{\cdot}0512_5 & 0{\cdot}0857_5\ (010) \end{array}$$

and by repeating the procedure along the base of the triangle:

$$\begin{array}{ccc} & (001) & \\ & 0{\cdot}0323 & \\ & 0{\cdot}0007\quad -0{\cdot}0001_5 & \\ (101)\ 0{\cdot}0575_5 & \textit{-0·0512}_5 & 0{\cdot}0857_5\ (010) \end{array} \longrightarrow \quad \begin{array}{ccc} & (001) & \\ & 0{\cdot}0323 & \\ & 0{\cdot}0007\quad 0{\cdot}0005_5 & \\ (101)\ 0{\cdot}0575_5 & 0{\cdot}0063\ \xrightarrow[1]{} & 0{\cdot}0408\ (111) \end{array}$$

yielding a reduced reciprocal cell with its angles already appropriately all acute (midpoint terms all positive). The reciprocal cell elements can readily be derived from the above: $a^* = 0{\cdot}202$ Å.$^{-1}$, $b^* = 0{\cdot}180$ Å.$^{-1}$, $c^* = 0{\cdot}240$ Å.$^{-1}$, $\alpha^* = 89{\cdot}1°$, $\beta^* = 82{\cdot}5°$, $\gamma^* = 89{\cdot}1°$, and from the indices $Z_{12} = [111/001/101]$, i.e. the initial choice of c-axis, the rotation axis of the Weissenberg photographs, is the [111] vector of the reduced cell. It is clear, even from the final triangular array, that since the two midpoint terms adjacent to the new b-axis are nearly zero within the probable measurement error, the reduced cell is dimensionally nearly primitive monoclinic about b. From the information yielded by Z_{12} it was easy to reset the crystal to the b-axis and confirm the monoclinic symmetry.

It may be noted that symmetry in the reduced cell introduces special relations between various of the s_{11}, &c., or certain terms take special values. A list of the standard forms for s_{11}, &c., is given by Buerger (1957), who also lists the appropriate transformation matrices F_{12} for transforming the reduced to the conventional cell (the two may differ, e.g. when the latter is centred).

Unlike cell-reduction, for some crystallographic calculations the face-index matrix is already known or easily determined, and it is required to recalculate cell elements to a new setting. The normal methods are often laborious. The recalculation can be done as if it were a cell-reduction, by the method outlined above, but using now the face-index matrix as a set of instructions for carrying it out (or the zone-symbol matrix when one is dealing with the reciprocal cell). For this purpose one may note two other transformations of the triangular array.

Firstly, if one is only interested in cell angles or axial ratios, the six numbers may *all* be multiplied by a given factor without altering the cell or the corner indices. Thus the array may be divided by b^2 to give a representation of the cell in terms of the morphological elements:

$$\begin{array}{ccccc} & & [001] & & \\ & & (c/b)^2 & & \\ & & (c/b)(a/b)\cos\beta & (c/b)\cos\alpha & \\ [100] & (a/b)^2 & (a/b)\cos\gamma & & 1\ [010] \end{array}$$

Secondly, *one* axis may be multiplied by an appropriate integer, m,[1] with a corresponding change in the corner indices and adjacent midpoint terms:

$$\begin{array}{ccccc} & & [001] & & \\ & & s_{33} & & \\ & & s_{31} \quad s_{23} & & \\ [100] & s_{11} \quad s_{12} \quad s_{22} & [010] & \longrightarrow & \end{array} \qquad \begin{array}{ccccc} & & [001] & & \\ & & s_{33} & & \\ & & s_{31} \quad ms_{23} & & \\ [100] & s_{11}\ ms_{12} & m^2 s_{22} & [0m0]\times m & \end{array}$$

Example 2. In reviewing the crystallographic data for anapäite, it became clear that Popoff (1902) had miscalculated his cell elements from his original measurements. These were recalculated in the usual way to yield:

$$a:b:c = 1{\cdot}4233:1:1{\cdot}1213,$$
$$\alpha = 97^\circ\,12\tfrac{1}{2}',\ \beta = 95^\circ\,16\tfrac{1}{2}',\ \gamma = 70^\circ\,10\tfrac{1}{2}'.$$

Palache (1933) gave further measurements and cell elements in a new setting, together with the face-index transformation matrix Popoff→

[1] In some cases, when transforming reciprocal cell data using a zone-symbol transformation matrix, m may be a simple positive or negative fraction, both in this transformation and in that first described.

Palache $F_{12} = [101/020/\bar{1}01]$. From the data above, calculation proceeded:

$$\begin{array}{ccccc} & & [001] & & \\ & & 1\cdot2571 & & \\ & -0\cdot1467 & & -0\cdot1407 & \\ [100]\ 2\cdot0257 & & 0\cdot4832 & & 1\cdot0000\ [010] \end{array} \longrightarrow \ \bar{1}\nearrow \ \begin{array}{ccccc} & & [\bar{1}01] & & \\ & & 3\cdot5762 & & \\ & -2\cdot1724 & & -0\cdot6239 & \\ [100]\ 2\cdot0257 & & 0\cdot4832 & & 1\cdot0000\ [010] \end{array}$$

$$\longrightarrow \begin{array}{ccccc} & & [\bar{1}01] & & \\ & & 3\cdot5762 & & \\ & -4\cdot3448 & & -1\cdot2478 & \\ [200]\ 8\cdot1028 & & 1\cdot9328 & & 4\cdot0000\ [020] \\ \times 2 & & & & \times 2 \end{array} \longrightarrow \ 1\swarrow \ \begin{array}{ccccc} & & [\bar{1}01] & & \\ & & 3\cdot5762 & & \\ & -0\cdot7686 & & -1\cdot2478 & \\ [101]\ 2\cdot9894 & & 0\cdot6850 & & 4\cdot0000\ [020] \end{array}$$

$$\overset{\times 1/4}{\longrightarrow} \begin{array}{ccccc} & & [\bar{1}01] & & \\ & & 0\cdot8941 & & \\ & -0\cdot1922 & & -0\cdot3145 & \\ [101]\ 0\cdot7474 & & 0\cdot1713 & & 1\cdot0000\ [020] \end{array}$$

from which the axial ratios and interaxial angles are readily extracted to give $a{:}b{:}c = \sqrt{0\cdot7474}{:}1{:}\sqrt{0\cdot8941} = 0\cdot8645{:}1{:}0\cdot9456$, $\alpha = \cos^{-1}(-0\cdot3145/\sqrt{0\cdot8941 \times 1}) = 109^\circ\ 15\tfrac{1}{2}'$, $\beta = 103^\circ\ 36'$, $\gamma = 78^\circ\ 34\tfrac{1}{2}'$. These results are now in good agreement with Palache's, and were actually confirmed by the much more laborious calculation using spherical trigonometry.

One can clearly use the same method, applying the transformation matrices listed by Buerger, to convert reduced to conventional cells after cell reduction. Moreover, the method can also obviously be applied to determine the lengths of cell vectors or the angles between them, e.g. the inter-edge angles of crystal faces, using data for the real cell, or else to determine interfacial angles using data for the reciprocal cell.

Example 3. Small prisms of synthetic cobaltomenite were available, with striated faces too small for goniometry. X-ray and optical examination showed that the prism faces were $(hk0)$ and the terminal face $(h0\bar{l})$. From measurement of inter-edge angles on the various faces under the microscope, the diagonal $[l0h]$ of the terminal face was inclined at $61\tfrac{3}{4}^\circ \pm 2^\circ$ to the prism axis $[00l]$. The X-ray measurements yielded elements $a{:}b{:}c = 0\cdot8592{:}1{:}0\cdot7352$, $\beta = 98^\circ\ 58\tfrac{1}{2}'$, from back reflection oscillation photographs. One may calculate various angles $[l0h]{:}[001]$ using one side only of the triangular array:

$$\begin{array}{l} [100]\ s_{11}\quad s_{31}\quad s_{33}\ [001] = [100]\ 0\cdot7382 \quad -0\cdot0985 \quad 0\cdot5405\ [001] \\ \qquad\qquad\qquad\qquad\quad \rightarrow [101]\ 1\cdot0817 \quad 0\cdot4420 \quad 0\cdot5405\ [001] \\ \qquad\qquad\qquad\qquad\qquad\qquad \overset{\longleftarrow\!\!-\!\!-\!\!-\!\!-\!\!-}{\ \ 1} \end{array}$$

whence $[101]{:}[001] = \cos^{-1}(0\cdot4420/\sqrt{(1\cdot0817 \times 0\cdot5405)}) = 54^\circ\ 40'$. $[101]$ is thus about 7° off the terminal face diagonal, a discrepancy confirmed

almost exactly by an oscillation photograph taken with the X-ray beam perpendicular to the terminal face. The above calculation can readily be extended to other indices, to match by trial and error the observed angle. Thus, omitting abortive trials, the calculation might proceed:

[101]	1·0817	0·4420	0·5405	[001] →	[505]	27·0425	2·2100	0·5405	[001]
						×5			
				→	[504]	23·1630	1·6695	0·5405	[001]
						←	−1		

whence [504]:[001] = 61° 51′, in best agreement with the observed angle. The terminal face, therefore, has diagonals [010] and [504] and is thus $(40\bar{5})$.

The application of this calculating method to other cases will be obvious from the above. Clearly the full triangular array is required when dealing with [*hkl*] vectors or (*hkl*) faces.

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