Table 1. *Correlation factors, R, between data sets corrected as described in text*

Data sets		(i)	(ii)	(iii)
A	*B*	Data uncorrected	Data Lp corrected	Data equation (16) corrected
Cu	Co	0·12	0·19	0·10
Cu	Cr	0·55	0·67	0·23
Co	Cr	0·45	0·60	0·16

since the magnitude of the correction required increases sharply for reflections at higher angles, the improved agreement achieved in the present case is particularly striking in that all of the data used were at relatively low angle.

It is interesting to note that in all cases the agreement falls off markedly when only Lp corrections are applied, even in comparison with the results for uncorrected data. Unfortunately, it is precisely this correction which is most often applied to fiber data.

It is important to recognize that the functional form of the arc correction factor corresponds to a general reduction in intensity with increasing angle and layer line height analogous to, but significantly different from, the effect of a temperature factor. Neglect of the correction in a structure analysis not only results in abnormally high temperature factors and standard deviations, but also affects the final structure. This is particularly true in the analysis of macromolecular structures displaying packing disorders.

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Determination of Reduced Cells

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An analysis is given of the relation between the reduced cells defined by Niggli and the cells obtained by applying Buerger's algorithm. It is shown that in many instances a cell based on the shortest three non-coplanar translations must be transformed to obtain the reduced cell. The required transformations for all cases have been derived and are presented in this paper.

Introduction

In an important work on lattice geometry Niggli (1928) has pointed out that any crystal lattice can be represented by a positive ternary quadratic form. He has defined as *reduced cell* the cell that satisfies the conditions derived from the reduction theory of quadratic forms (Seeber, 1831; Dirichlet, 1850; Eisenstein, 1851). Such a cell provides a unique description of the lattice and is defined independently of lattice symmetry. In addition it must be primitive because one of the properties is that it is built on the shortest three non-coplanar lattice translations. Niggli has derived geometrically the reduced forms for all the Bravais lattices but he has not given any general method for converting an arbitrary primitive cell into the reduced cell.

The procedure given by Buerger (1957, 1960) and extended by Davis (1961) transforms any primitive cell into one based on the shortest three non-coplanar translations – the Buerger cell. This cell, although closely related to Niggli's reduced cell, is not unique in many cases. Some of the ambiguities associated with the Buerger cell have been discussed by Allmann (1968), especially in relation to the standard setting used by Donnay, Donnay, Cox, Kennard & King (1963) in the determinative listing of triclinic substances.

The algorithm proposed by Delaunay (1933) converts any primitive cell into a standard form involving

four vectors that make obtuse angles with one another. The end point of the Delaunay transformation – the Delaunay cell – is not necessarily based on the shortest three non-coplanar translations and is not unique in all cases (Delaunay, 1933; Patterson & Love, 1957).

Thus, at the present time, the only available unambiguous description of a lattice is the one based on the reduced cell defined by Niggli. In some cases this cell can be derived simply by applying Buerger's algorithm. Whenever the endpoint of this procedure is not Niggli's cell, the Buerger reduction must be completed by means of appropriate transformations. These transformations have been derived and are presented in this paper.

General

We will represent a primitive cell of lattice parameters $a,b,c,\alpha,\beta,\gamma$, by the matrix

$$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ S_{23} & S_{13} & S_{12} \end{pmatrix} = \begin{pmatrix} \mathbf{a}.\mathbf{a} & \mathbf{b}.\mathbf{b} & \mathbf{c}.\mathbf{c} \\ \mathbf{b}.\mathbf{c} & \mathbf{a}.\mathbf{c} & \mathbf{a}.\mathbf{b} \end{pmatrix} . \quad (1)$$

In addition we will require that the cell be right-handed and that it be given in its normal character representation, in which the three interaxial angles are either all acute or all obtuse (Azároff & Buerger, 1958). This insures that the S_{ij} $(i\neq j)$ are all positive (Type I cell) or all negative (Type II cell). If one or more of the S_{ij} is zero, the cell will be considered to be of Type II.

The cell represented by matrix (1) is reduced if, and only if, the following conditions are satisfied (Niggli, 1928):

(*A*) Positive reduced form, Type I cell, all angles $<90°$. Main conditions:

$$S_{11}\leq S_{22}\leq S_{33};\quad S_{23}\leq \tfrac{1}{2}S_{22};\quad S_{13}\leq \tfrac{1}{2}S_{11};\quad S_{12}\leq \tfrac{1}{2}S_{11}. \quad (2)$$

Special conditions:

$$\left.\begin{array}{lll} (a) & \text{If } S_{11}=S_{22} & \text{then} \quad S_{23}\leq S_{13}. \\ (b) & \text{If } S_{22}=S_{33} & \quad\quad S_{13}\leq S_{12}. \\ (c) & \text{If } S_{23}=\tfrac{1}{2}S_{22} & \quad\quad S_{12}\leq 2S_{13}. \\ (d) & \text{If } S_{13}=\tfrac{1}{2}S_{11} & \quad\quad S_{12}\leq 2S_{23}. \\ (e) & \text{If } S_{12}=\tfrac{1}{2}S_{11} & \quad\quad S_{13}\leq 2S_{23}. \end{array}\right\} \quad (3)$$

(*B*) Negative reduced form, Type II cell, all angles $\geq 90°$. Main conditions:

$$\begin{gathered} S_{11}\leq S_{22}\leq S_{33};\ |S_{23}|\leq \tfrac{1}{2}S_{22}; \\ |S_{13}|\leq \tfrac{1}{2}S_{11};\ |S_{12}|\leq \tfrac{1}{2}S_{11}. \\ (|S_{23}|+|S_{13}|+|S_{12}|)\leq \tfrac{1}{2}(S_{11}+S_{22}). \end{gathered} \quad (4)$$

Special conditions:

$$\left.\begin{array}{lll} (a) & \text{If } S_{11}=S_{22} & \text{then} \quad |S_{23}|\leq |S_{13}|. \\ (b) & \text{If } S_{22}=S_{33} & \quad\quad |S_{13}|\leq |S_{12}|. \\ (c) & \text{If } |S_{23}|=\tfrac{1}{2}S_{22} & \quad\quad S_{12}=0. \\ (d) & \text{If } |S_{13}|=\tfrac{1}{2}S_{11} & \quad\quad S_{12}=0. \\ (e) & \text{If } |S_{12}|=\tfrac{1}{2}S_{11} & \quad\quad S_{13}=0. \\ (f) & \text{If } (|S_{23}|+|S_{13}|+|S_{12}|)=\tfrac{1}{2}(S_{11}+S_{22}) & \\ & \quad\quad \text{then} \quad S_{11}\leq 2|S_{13}|+|S_{12}|. \end{array}\right\} \quad (5)$$

As shown by Buerger (1957, 1960), the main conditions define a cell based on the shortest three non-coplanar translations. Conditions (3*a*) and (3*b*) or (5*a*) and (5*b*) make it possible to label the cell edges uniquely when two of them are equal. The other special conditions define the unique reduced cell in a lattice where there is more than one symmetrically independent cell based on the shortest three translations.

The equalities between the scalars shown in the left columns of conditions (3) and (5) may occur accidentally or systematically depending on the particular geometrical properties of a lattice. As an example of an ambiguity that occurs systematically, let us consider a face-centered cubic lattice defined by the usual cubic cell edge a_0. If we describe this lattice by means of a primitive cell derived from the cubic cell by transformation $0\frac{1}{2}\frac{1}{2}/\frac{1}{2}0\frac{1}{2}/\frac{1}{2}\frac{1}{2}0$, we get

$$\begin{pmatrix} S_{11} & S_{11} & S_{11} \\ \tfrac{1}{2}S_{11} & \tfrac{1}{2}S_{11} & \tfrac{1}{2}S_{11} \end{pmatrix},$$

with $S_{11}=a_0^2/2$. If we now use another primitive cell obtained by the transformation $\frac{1}{2}\frac{1}{2}0/\bar{\frac{1}{2}}\frac{1}{2}0/0\bar{\frac{1}{2}}\frac{1}{2}$, we have

$$\begin{pmatrix} S_{11} & S_{11} & S_{11} \\ -\tfrac{1}{2}S_{11} & -\tfrac{1}{2}S_{11} & 0 \end{pmatrix},$$

again with $S_{11}=a_0^2/2$. Both primitive cells satisfy the main conditions. Note however, that the second cell violates condition (5*b*) and must be rejected, while the first cell, which obeys all conditions (3), is the reduced cell. An example of ambiguity due to accident is given in the next section.

Determination of the reduced cell

Let **S** be the matrix of a primitive cell (in its normal representation), which satisfies the main conditions appropriate for the cell type, but fails to satisfy one of the special conditions. Then the reduction must be completed by means of a transformation

$$\mathbf{S}\rightarrow\mathbf{S}' \quad (6)$$

where **S**′ is the matrix representing the reduced cell. As an example of how this transformation can be determined, let us consider a Type I cell of matrix

$$\mathbf{S}=\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ \tfrac{1}{2}S_{22} & S_{13} & S_{12} \end{pmatrix}, \quad (7)$$

such that the S_{ij} satisfy conditions (2). In addition let us assume that there are no other special relations between the matrix elements. As $S_{23}=\frac{1}{2}S_{22}$ then we can change the c axis with

$$\mathbf{c}_1=\mathbf{c}-\mathbf{b},$$

in which $|\mathbf{c}_1|=|\mathbf{c}|$ and the new cell is represented by the matrix

$$\mathbf{S}'=\begin{pmatrix} S'_{11} & S'_{22} & S'_{33} \\ S'_{23} & S'_{13} & S'_{12} \end{pmatrix}\equiv\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ -\tfrac{1}{2}S_{22} & S_{13}-S_{12} & S_{12} \end{pmatrix}. \quad (8)$$

If the first cell is based on the shortest three non-coplanar translations, so is the second. We have to show that of the two cells (7) and (8) only one satisfies

condition (3*c*), *i.e.* is the reduced cell. Two cases have to be taken into consideration:

(*a*) $S_{12}<S_{13}$. *A fortiori* we have $S_{12}<2S_{13}$ and cell (7) is reduced; cell (8), which is of Type II, is not reduced because by definition, $S_{12}\neq 0$.

(*b*) $S_{12}>S_{13}$. In this case both cells are of Type I. It is possible for two cells of Type I to be based on the shortest three translations (Fig. 1). As the initial cell is triacute, the projection of *a* must be located somewhere in the shaded area. If, in addition, *a* projects in the cross-hatched area then we have $\mathbf{a}\wedge\mathbf{c}_1>90°$ and this cell, in normal representation, is of Type I. Thus the two cells are of the same type. Let us now suppose $S_{12}<2S_{13}$. Cell (7) is reduced and cell (8) is not because we have:

$$S_{12}-2S_{13}=-\varepsilon<0$$
$$2S'_{13}=2(S_{12}-S_{13})=S_{12}-\varepsilon$$

and, in view of $S_{12}'=S_{12}$,

$$S'_{12}>2S'_{13}\,.$$

If $S_{12}>2S_{13}$, then cell (7) is not reduced and cell (8) is reduced because

$$S_{12}-2S_{13}=\varepsilon>0$$

and

$$2S'_{13}=2(S_{12}-S_{13})=S_{12}+\varepsilon\,,$$

so that we have $S_{12}=S'_{12}<2S'_{13}$.

Finally, for $S_{12}=2S_{13}$, the two cells are indistinguishable and they are represented by the matrix

$$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ \frac{1}{2}S_{22} & \frac{1}{2}S_{12} & S_{12} \end{pmatrix}\,. \qquad (9)$$

In this particular lattice the two cells are related by the symmetry introduced by the condition $S_{12}=2S_{13}$. Matrix (9) represents an end-centered monoclinic lattice, while matrices (7) and (8) represent a triclinic lattice.

The matrix of the transformation from (7) to (8) is $\bar{1}00/0\bar{1}0/0\bar{1}1$. By following a similar procedure all cases corresponding to Niggli's special conditions for cells of Type I and II have been derived, and the results are presented in Table I. The matrices are given in their normal representation and the transformation from cell S to cell S′ is shown in the fourth column.

Any given cell S in Table 1 is based on the shortest three non-coplanar translations and it is unreduced if the scalars are related as indicated in column 3. In this case the transformation will give a cell S′ that satisfies the special condition violated by S. In certain lattices more than one transformation has to be applied before the reduced cell is obtained. Matrix S′, therefore, must be tested against the special conditions appropriate for the cell type and, if necessary, transformed again. The order in which the transformations are applied is irrelevant.

Discussion

In addition to their theoretical interest, reduced cells have two important applications in crystallography (see, for example, Azároff & Buerger, 1958): (*a*) they make it possible to determine the Bravais lattice from an arbitrary primitive cell of the lattice, and (*b*) they provide a possible method for the classification of crystalline substances.

(*a*) *Determination of the Bravais lattice*

The reduced cells for all the Bravais lattices have been derived by Niggli and tables of Niggli's matrices, together with the transformation matrices from the reduced to the conventional cell have been given by Buerger (1957) and Azároff & Buerger (1958).

If any primitive reciprocal cell can be derived from the X-ray diffraction patterns, then the corresponding direct cell, which is also primitive, can be reduced according to the procedure given in the previous sections. The Bravais lattice* can then be determined from a table of Niggli's forms. This application of reduced cells may save much of the preliminary work normally needed in crystal-structure analysis. The use of reduced cells becomes particularly useful when crystals are grown and studied under special conditions, such as high pressure, high or low temperature, in which it is difficult or impossible to determine the lattice symmetry by conventional means.

(*b*) *Classification of crystalline substances*

The present determinative listing of crystalline substances is made on the basis of cell dimensions within each crystal system. The choice of a conventional cell

* We would like to emphasize that the lattice symmetry determined by means of reduced cells is purely metric and it may be the same as or higher than the true symmetry of the lattice of the crystal structure.

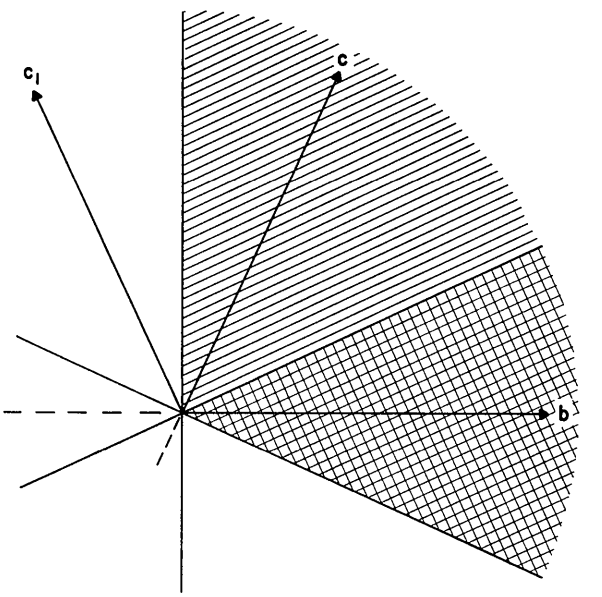

Fig. 1. Transformation of axes in a cell of Type I in which $S_{23}=\frac{1}{2}S_{22}$. The two cells formed by **a**, **b**, and **c** and by **a**, **b**, and $\mathbf{c}_1$ are both based on the shortest three translations and are of the same type if **a** projects in the cross-hatched area and of different type if **a** projects in the hatched area.

Table 1. *Transformations for determining the reduced cell from an unreduced cell based on the shortest three translations of the lattice*

Type of cell S*	Matrix of cell S	Relations between scalars	Transformation matrix S to S′	Matrix of cell S′	Type of cell S′
I or II	$\begin{pmatrix} S_{11} & S_{11} & S_{33} \\ S_{23} & S_{13} & S_{12} \end{pmatrix}$	$\mathbf{a}\cdot\mathbf{c} < \mathbf{b}\cdot\mathbf{c}$	$0\bar{1}0/\bar{1}00/00\bar{1}$	$\begin{pmatrix} S_{11} & S_{11} & S_{33} \\ S_{13} & S_{23} & S_{12} \end{pmatrix}$	I or II
I or II	$\begin{pmatrix} S_{11} & S_{22} & S_{22} \\ S_{23} & S_{13} & S_{12} \end{pmatrix}$	$\mathbf{a}\cdot\mathbf{b} < \mathbf{a}\cdot\mathbf{c}$	$\bar{1}00/00\bar{1}/0\bar{1}0$	$\begin{pmatrix} S_{11} & S_{22} & S_{22} \\ S_{23} & S_{12} & S_{13} \end{pmatrix}$	I or II
I	$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ \frac{1}{2}S_{22} & S_{13} & S_{12} \end{pmatrix}$	$2\mathbf{a}\cdot\mathbf{c} < \mathbf{a}\cdot\mathbf{b}$	$\bar{1}00/0\bar{1}0/0\bar{1}1$	$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ \frac{1}{2}S_{22} & S_{12}-S_{13} & S_{12} \end{pmatrix}$	I
I	$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ S_{23} & \frac{1}{2}S_{11} & S_{12} \end{pmatrix}$	$2\mathbf{b}\cdot\mathbf{c} < \mathbf{a}\cdot\mathbf{b}$	$\bar{1}00/0\bar{1}0/\bar{1}01$	$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ S_{12}-S_{13} & \frac{1}{2}S_{11} & S_{12} \end{pmatrix}$	I
I	$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ S_{23} & S_{13} & \frac{1}{2}S_{11} \end{pmatrix}$	$2\mathbf{b}\cdot\mathbf{c} < \mathbf{a}\cdot\mathbf{c}$	$\bar{1}00/\bar{1}10/00\bar{1}$	$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ S_{13}-S_{23} & S_{13} & \frac{1}{2}S_{11} \end{pmatrix}$	I
II	$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ -\frac{1}{2}S_{22} & S_{13} & S_{12} \end{pmatrix}$	$\mathbf{a}\cdot\mathbf{b} \neq 0$	$100/0\bar{1}0/0\bar{1}\bar{1}$	$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ \frac{1}{2}S_{22} & \lvert S_{13}\rvert+\lvert S_{12}\rvert & \lvert S_{12}\rvert \end{pmatrix}$	I
II	$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ S_{23} & -\frac{1}{2}S_{11} & S_{12} \end{pmatrix}$	$\mathbf{a}\cdot\mathbf{b} \neq 0$	$\bar{1}00/010/\bar{1}0\bar{1}$	$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ \lvert S_{23}\rvert+\lvert S_{12}\rvert & \frac{1}{2}S_{11} & \lvert S_{12}\rvert \end{pmatrix}$	I
II	$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ S_{23} & S_{13} & -\frac{1}{2}S_{11} \end{pmatrix}$	$\mathbf{a}\cdot\mathbf{c} \neq 0$	$\bar{1}00/\bar{1}\bar{1}0/001$	$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ \lvert S_{23}\rvert+\lvert S_{13}\rvert & \lvert S_{13}\rvert & \frac{1}{2}S_{11} \end{pmatrix}$	I
II	$\begin{pmatrix} S_{11} & S_{22} & S_{33} \\ X & S_{13} & S_{12} \end{pmatrix}$	$2\lvert\mathbf{a}\cdot\mathbf{c}\rvert+\lvert\mathbf{a}\cdot\mathbf{b}\rvert<\mathbf{a}\cdot\mathbf{a}$	$\bar{1}00/0\bar{1}0/111$	$\begin{pmatrix} Y & Z & S_{33} \\ & & S_{12} \end{pmatrix}$	II

where $X=\frac{1}{2}(S_{11}+S_{22}-2\lvert S_{13}\rvert-2\lvert S_{12}\rvert)$ $\quad Y=\lvert S_{12}\rvert+\lvert S_{23}\rvert-S_{22}$ $\quad Z=\lvert S_{12}\rvert+\lvert S_{13}\rvert-S_{11}$

* All cells given in normal representation.

dictated by lattice symmetry is possible in all crystal systems except triclinic and monoclinic. Triclinic substances have been listed in terms of a cell obtained either with the Delaunay reduction (Donnay, Nowacki & Donnay, 1954) or with the Buerger reduction (Donnay *et al.*, 1963). In both cases it is possible to have ambiguous results. For example, in 50 triclinic reductions performed with Buerger's algorithm, we found five ambiguous cases. For this reason we recommend the use of Niggli's reduced cell which is uniquely defined in all cases.

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