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The Conversion of Reduced Cells to Conventional Cells by Algebraic Means

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A simple vector algebraic method is presented which permits the symmetry of a primitive reduced cell to be recognized by systematically checking the coefficients of its quadratic form for only seven conditions and deriving from them orthogonality relations among certain lattice vectors. In this way also the matrix of the transformation of the reduced cell to the conventional cell is found. The centring properties of the conventional cell can be derived from this matrix with the aid of simple criteria. The use of rather lengthy tables of special reduced forms and of the corresponding transformation matrices which are often unreliable owing to printing errors is no longer necessary.

1. Introduction

Niggli (1928) introduced into crystallography the concept of the reduced lattice and of the reduced quadratic form and did pioneer work on the classification of lattices by their quadratic forms. Unfortunately this part of his work did not find for a long time the attention it deserves and was made more popular primarily by important papers of Buerger (1957, 1960), who presented three different reduction procedures and reproduced Niggli's tables of quadratic forms in a slightly modified shape and presented another table of matrices which transform reduced cells to conventional cells. Unfortunately these tables are not reliable owing to several printing errors. Moreover Buerger overlooked the importance of the special reduction conditions already presented by Niggli for the applicability of these tables as Santoro & Mighell (1970) pointed out.

The process of the transformation of a reduced cell, which is always primitive, to a conventional cell will be called 'normalization' in this paper. This normalization can be carried out by purely algebraic means without reference to the tables mentioned above. Because a conventional base-, body- or face-centred cell is a supercell of the reduced cell whereas its reciprocal cell is a subcell of the reduced reciprocal cell the normalization of a direct cell is slightly different from that of a reciprocal cell. These procedures will be described in § 3. The type of centring of the supercells thus obtained can be deduced by a simple analysis of the transformation matrices as described in § 2. Also unconventional orthogonal supercells (*i.e.* supercells where at least one edge is orthogonal to the two others may be obtained by the proposed normalization procedure. These unconventional supercells may be of practical value by suggesting relationships to lattices of higher symmetry.

2. Basic relations and some simple lattice types

Let the vectors $\mathbf{a}_i$ ($i=1,2,3$) be the edges of a unit cell reduced in Niggli's sense and the integers u_i the coordinates of a point $\mathbf{r}$ of the lattice defined by these vectors. By squaring a lattice vector $\mathbf{r}=\sum_{i=1}^{3} u_i\,\mathbf{a}_i$ one gets the *quadratic form* of the reduced cell

$$f(\mathbf{u})=r^2=\sum_{i,j=1}^{3} u_i\,u_j\,(\mathbf{a}_i\,\mathbf{a}_j)$$

$$=\sum_{i,j=1}^{3} s_{ij}\,u_i\,u_j \qquad (1)$$

$$\text{with}\quad s_{ij}=\mathbf{a}_i\cdot\mathbf{a}_j\,. \qquad (2)$$

This quadratic form will be represented by the so-called Niggli matrix

$$\begin{pmatrix} s_{11} & s_{22} & s_{33} \\ s_{23} & s_{13} & s_{12} \end{pmatrix}. \qquad (3)$$

Niggli's reduction conditions in terms of the coefficients s_{ij} of the quadratic form (1) were recently restated by Santoro & Mighell (1970).

The form (3) will be called reduced if and only if all these general and special conditions are satisfied. Niggli's and Buerger's tables are applicable only to such fully reduced forms.

A detailed study of Niggli's tables of reduced forms led to the conclusion that the reduced form of a lattice of higher symmetry is characterized by the fact that at least two of the following conditions are satisfied and that these conditions by the vector algebraic meanings of the s_{ij} define at least one vector $\mathbf{a}_2'$ which is orthogonal to two other vectors $\mathbf{a}_1'$ and $\mathbf{a}_3'$. These essential conditions and their vector algebraic meanings are given by the following formulae, where unequal indices represent unequal integers ≤ 3.

$$s_{ij}=0\colon\ \mathbf{a}_i\perp\mathbf{a}_j \qquad (4a)$$

$$s_{ij}-ns_{ik}=0\colon\ \mathbf{a}_i\perp(\mathbf{a}_j-n\mathbf{a}_k);\ (n \text{ integer and} \leq 2) \qquad (4b)$$

$$s_{ii}=s_{jj}\colon\ (\mathbf{a}_i-\mathbf{a}_j)\perp(\mathbf{a}_i+\mathbf{a}_j) \qquad (4c)$$

$$s_{ii}\pm ns_{ij}=0\colon\ \mathbf{a}_i\perp(\mathbf{a}_i\pm n\mathbf{a}_j);\ n=2,3 \qquad (4d)$$

$$\left.\begin{aligned} ns_{13}+s_{12}+s_{11}=0\colon\ \mathbf{a}_1\perp(\mathbf{a}_1+\mathbf{a}_2+n\mathbf{a}_3) \qquad (4e)\\ ns_{23}+s_{12}+s_{22}=0\colon\ \mathbf{a}_2\perp(\mathbf{a}_1+\mathbf{a}_2+n\mathbf{a}_3) \qquad (4f)\end{aligned}\right\} n=1,2$$

$$s_{ii}+s_{ij}+s_{jk}+s_{ik}=0\colon\ (\mathbf{a}_i+\mathbf{a}_j)\perp(\mathbf{a}_i+\mathbf{a}_k) \qquad (4g)$$

The quadratic forms of primitive cubic, tetragonal and orthorhombic cells are characterized by the fact that all three 'asymmetrical' scalars, *i.e.* the s_{ij} with $i \neq j$, are equal to zero. These cases are readily recognized and do not need any further discussion. In addition to these four lattice types (the primitive tetragonal case comprises the two types $s_{11}=s_{22}$ and $s_{22}=s_{33}$) there are 10 lattice types with $s_{ij}=s_{ik}=0$ and $s_{jk}\neq 0 (i,j,k$ permutation of $1,2,3)$. By virtue of relation $(4a)$ in these lattices the vector $\mathbf{a}_i$ is orthogonal to the vectors $\mathbf{a}_j$ and $\mathbf{a}_k$. These forms belong to primitive monoclinic cells if the scalars s_{jj}, s_{kk} and s_{jk} satisfy none of the relations $(4c)$ or $(4d)$. If only one of these conditions is satisfied the form belongs to a *C*-centred orthorhombic cell, and it belongs to a primitive hexagonal cell if both are satisfied with $n=2$, *i.e.* if

$$-2s_{jk}=s_{jj}=s_{kk}\,. \tag{5}$$

The minus sign in this relation is a consequence of the convention that all asymmetrical scalars s_{ij} are to be negative if their product is ≤ 0. The binary quadratic form defined by (5) characterizes a hexagonal lattice plane. Application of the normalization procedure to this lattice plane would yield a centred rectangular lattice plane with a ratio of $1:\sqrt{3}$ of its axes.

Before describing this procedure in detail the three rhombohedral forms which justify a special treatment are listed, because they do not belong to an orthogonal lattice, *i.e.* one where one axis is orthogonal to two others. Merely the hexagonal supercell of a rhombohedral cell is orthogonal and can be obtained by the normalization procedure. The three rhombohedral quadratic forms and their cubic special cases are:

$$\begin{pmatrix} s_{11} & s_{11} & s_{11} \\ s_{23} & s_{23} & s_{23} \end{pmatrix} \begin{matrix} \text{face-centred cubic, if } s_{23}=\tfrac{1}{2}s_{11} \\ \text{body-centred cubic, if } s_{23}=-\tfrac{1}{3}s_{11} \end{matrix} \tag{6a}$$

$$\begin{pmatrix} s_{11} & s_{11} & s_{33} \\ \tfrac{1}{2}s_{11} & \tfrac{1}{2}s_{11} & \tfrac{1}{2}s_{11} \end{pmatrix} \tag{6b}$$

$$\begin{pmatrix} s_{11} & s_{22} & s_{22} \\ \tfrac{1}{2}(\tfrac{1}{3}s_{11}-s_{22}) & -\tfrac{1}{3}s_{11} & -\tfrac{1}{3}s_{11} \end{pmatrix}. \tag{6c}$$

The form $(6a)$ exhibits directly the characteristic properties of a rhombohedral cell and does not require any transformation apart from its special cases. The transformation matrices, $\mathbf{T}=\{t_{ij}\}$, for these special cases are

$$\mathbf{T} = \begin{pmatrix} 1 & \bar{1} & 1 \\ 1 & 1 & \bar{1} \\ \bar{1} & 1 & 1 \end{pmatrix} \text{ for } s_{23}=\tfrac{1}{2}s_{11} \tag{7a}$$

and

$$\mathbf{T} = \begin{pmatrix} 1 & 0 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & 1 \end{pmatrix} \text{ for } s_{23}=-\tfrac{1}{3}s_{11}\,. \tag{7b}$$

These matrices **T** define the transformation

$$\mathbf{a}'_i = \sum_{j=1}^{3} t_{ij}\mathbf{a}_j\,, \tag{8}$$

i.e. the rows of these matrices are the new axes in terms of the original ones. The centring properties of the new cells can be deduced from these transformation matrices by the following criteria:

If the matrix **T** transforms a primitive cell to a base-centred or to a body-centred supercell its determinant $T=|\mathbf{T}|$ must be $+2$ or -2. (In the case of a negative determinant it is conventional to reverse its sign either by reversing the sign of one of its rows or by exchange of two rows.) If the subdeterminants of any row of such a matrix have no common divisor $\neq 1$ the supercell is body centred, otherwise it is base centred, provided there is no row with all coordinates being even (which can obviously be taken for granted). In the former case the sum of all three rows has only even coordinates, in the latter case there are exactly two rows the sum of which has only even coordinates.

The transformation matrix **T** defines a face-centred cell if and only if its determinant is 4 and if the sum of any two of its rows has only even coordinates. By these criteria the matrices $(7a)$ and $(7b)$ are readily recognized as belonging to face-centred and body-centred cells, respectively.

The rhombohedral unit cells of the two other lattices defined by the forms $(6b)$ and $(6c)$ are

$$= \begin{pmatrix} 0 & 0 & 1 \\ \bar{1} & 0 & 1 \\ 0 & \bar{1} & 1 \end{pmatrix} \text{ for form } (6b) \tag{9a}$$

and

$$= \begin{pmatrix} 0 & 0 & \bar{1} \\ 1 & 1 & 1 \\ 0 & \bar{1} & 0 \end{pmatrix} \text{ for form } (6c). \tag{9b}$$

These two matrices are unimodular, *i.e.* their determinants are equal to ± 1. The transformation of these cells to their hexagonal supercells can be performed by well-known formulae.

3. Description of the normalization procedure

The first step of a normalization procedure consists of checking all scalars s_{ij} and s_{ii} of a given reduced ternary quadratic form (3) for the conditions $(4a)$–$(4g)$ and writing down the pairs of orthogonal vectors derived from them. If there is no vector common to at least two such pairs of orthogonal vectors the form cannot be normalized and belongs, therefore, to a triclinic lattice. The form should also be tested if it corresponds to one of the rhombohedral forms $(6a)$–$(6c)$. If there is one vector $\mathbf{a}'_2$ normal to two other vectors $\mathbf{a}'_1$ and $\mathbf{a}'_3$ also each vector of the lattice plane defined by $\mathbf{a}'_1$ and $\mathbf{a}'_3$ is normal to $\mathbf{a}'_2$.

The two vectors

$$\mathbf{a}'_1 = \sum_{i=1}^{3} t_{1i}\,\mathbf{a}_i$$

and

$$\mathbf{a}'_3 = \sum_{i=1}^{3} t_{3i}\,\mathbf{a}_i$$

define a complete lattice plane if and only if their vector product

$$\mathbf{a}_1' \times \mathbf{a}_3' = V \cdot \sum_i h_i \mathbf{a}_i^* \qquad (10)$$

with

$$\left.\begin{aligned} &\mathbf{a}_i^* = \frac{\mathbf{a}_j \times \mathbf{a}_k}{V}\ ;\ V = (\mathbf{a}_1 \mathbf{a}_2 \mathbf{a}_3) \\ &\text{and} \\ &h_i = t_{1j} t_{3k} - t_{1k} t_{3j} \end{aligned}\right\} \quad \begin{matrix} (i,j,k \text{ cyclic} \\ \text{permutation of } 1,2,3) \end{matrix}$$

is a *primitive* vector, *i.e.* if its coordinates h_i do not have any common divisor $\neq 1$. The vectors $\mathbf{a}_i^*$ in formula (10) are obviously the reciprocal vectors of $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. The coordinates h_i are the subdeterminants of the 2×3 matrix formed by the two vectors $\mathbf{a}_1'$ and $\mathbf{a}_3'$ and also the indices of the lattice plane defined by them. If the indices h_i are divisible by $n \neq 1$ the vectors $\mathbf{a}_1'$ and $\mathbf{a}_3'$ must be replaced by two other vectors of the same lattice plane which define the complete lattice plane $(h_1 h_2 h_3) = \mathbf{h}$. If there is not any other vector orthogonal to two other ones the cell is monoclinic provided that the determinant of the transformation matrix

$$\mathbf{T} = \{t_{ij}\} = \begin{pmatrix} \mathbf{a}_1' \\ \mathbf{a}_2' \\ \mathbf{a}_3' \end{pmatrix}$$

is ± 2. If the vectors $\mathbf{a}_1'$ and $\mathbf{a}_3'$ are reduced, *i.e.* if

$$2\mathbf{a}_1' \cdot \mathbf{a}_3' \leq \mathbf{a}_1'^2 \leq \mathbf{a}_3'^2 ,$$

the monoclinic cell defined by the vectors $\mathbf{a}_i'$ can be body centred or base centred. In order to convert an unconventional body-centred monoclinic cell into a *C*-centred cell the vector $\mathbf{a}_1'$ is to be replaced by the shortest one of the vectors $\mathbf{a}_1' + \mathbf{a}_3'$ and $\mathbf{a}_1' - \mathbf{a}_3'$ and the vector $\mathbf{a}_3'$ by $\mathbf{a}_1'$. For then the sum of the first two rows has only even coordinates in conformity with the criteria of § 2.

Suppose there is another vector $\mathbf{a}_2''$ orthogonal to two vectors $\mathbf{a}_1''$ and $\mathbf{a}_3''$ and that $\mathbf{a}_2''$ belongs to the lattice plane $\mathbf{h} = (h_1 h_2 h_3)$ defined by $\mathbf{a}_1'$ and $\mathbf{a}_3'$. Then $\mathbf{a}_2''$ is orthogonal to $\mathbf{a}_2'$ and to any other vector of the lattice plane $\mathbf{h}' = (h_1' h_2' h_3')$ defined by $\mathbf{a}_1''$ and $\mathbf{a}_3''$. The intersection $\mathbf{b}$ of the two planes $\mathbf{h}$ and $\mathbf{h}'$ is then orthogonal to their normals $\mathbf{a}_2'$ and $\mathbf{a}_2''$, *i.e.* the vectors $\mathbf{a}_2''$, $\mathbf{a}_2'$, and $\mathbf{b}$ are orthogonal to each other and are the axes of an orthorhombic cell if the matrix

$$\mathbf{T} = \begin{pmatrix} \mathbf{a}_2'' \\ \mathbf{a}_2' \\ \mathbf{b} \end{pmatrix}$$

satisfies the criteria of § 2 for conventional body-, base- or face-centred cells. Otherwise the two vector triplets $\mathbf{a}_1'$, $\mathbf{a}_2'$ and $\mathbf{a}_3'$ or $\mathbf{a}_1''$, $\mathbf{a}_2''$, $\mathbf{a}_3''$ will define monoclinic cells, the smallest of which should be selected. As an illustration of this procedure the following two examples will be discussed in detail.

In the form

$$\begin{pmatrix} 4{\cdot}171 & 6{\cdot}313 & 7{\cdot}111 \\ -2{\cdot}828 & -1{\cdot}757 & -0{\cdot}657 \end{pmatrix}$$

the relations (4*e*) and (4*f*) are satisfied and consequently [112] is normal to the vectors [100] and [010]. Thus we immediately obtain the transformation

$$\mathbf{T} = \begin{pmatrix} 100 \\ 112 \\ 010 \end{pmatrix}$$

the determinant of which is -2. Because the sum of all three row vectors has only even coordinates the new cell is body centred. In order to obtain a conventional *C*-centred cell $\mathbf{a}_1'$ has to be replaced by $\mathbf{a}_1' + \mathbf{a}_3' = [110]$. In this way we finally obtain the transformation

$$\mathbf{T}' = \begin{pmatrix} 110 \\ 112 \\ 100 \end{pmatrix}$$

which transforms the original reduced form to the conventional monoclinic form

$$\begin{pmatrix} 9{\cdot}170 & 19{\cdot}274 & 4{\cdot}171 \\ 0 & 3{\cdot}514 & 0 \end{pmatrix}$$

for the *C*-centred monoclinic cell.

As a second example the lattice with the quadratic form

$$\begin{pmatrix} 3{\cdot}472 & 4{\cdot}357 & 5{\cdot}781 \\ 0{\cdot}868 & 1{\cdot}736 & 1{\cdot}736 \end{pmatrix}$$

will be normalized. From the conditions (4*a*)–(4*f*) we obtain the following orthogonality relations:

$$\left.\begin{aligned} &(a)\ [100] \perp [01\bar{1}] \\ &(b)\ [010] \perp [10\bar{2}] \\ &(c)\ [001] \perp [1\bar{2}0] \end{aligned}\right\} \text{ from } (4b)$$

$$\left.\begin{aligned} &(d)\ [100] \perp [1\bar{2}0] \\ &(e)\ [100] \perp [10\bar{2}] \end{aligned}\right\} \text{ from } (4d).$$

Relations (*d*) and (*e*) and also (*a*) imply that the vector [100] is normal to the (211) plane. Since the vector $[1\bar{2}0]$ which belongs to this plane is normal to the (010) plane by relations (*c*) and (*d*), the vector $[10\bar{2}]$ common to both planes forms together with [100] and $[1\bar{2}0]$ a set of mutually orthogonal axes. The corresponding transformation matrix

$$\mathbf{T} = \begin{pmatrix} 100 \\ 1\bar{2}0 \\ 10\bar{2} \end{pmatrix}$$

indicates a face-centred orthorhombic lattice because its determinant is equal to 4 and the sum of any two row vectors has only even coordinates. Transformation of the given reduced form by this matrix yields the conventional form

$$\begin{pmatrix} 3{\cdot}472 & 13{\cdot}956 & 19{\cdot}652 \\ 0 & 0 & 0 \end{pmatrix}.$$

The described normalization procedure can be applied to quadratic forms of direct cells as well as to those of reciprocal cells.

In the case of reciprocal quadratic forms, however, the elements t^*_{ij} of the transformation matrix **T*** thus obtained must be multiplied by g_i/D, where g_i is the greatest common divisor of the subdeterminants of the ith row and D is the determinant of the matrix **T***. By this operation is made sure that the inverse matrix of **T***, which transforms the corresponding direct cell, has only integer elements t_{ij} and that the elements of any row have no common divisor. In this way the well-known fact can easily be verified that a face-centred reciprocal cell corresponds to a body-centred direct cell and *vice versa*.

Finally it should be emphasized that it is not convenient to normalize zonal planes of the reciprocal lattice which are found during a general indexing procedure by the methods of Ito (1950) or de Wolff (1957) because then the true reduced unit cell may be missed. For if only one of the conditions (4*a*)–(4*g*) is fulfilled only one of the faces of the cell, but not the complete cell can be normalized since in this case there is no vector normal to two other vectors. The normalization procedure should, therefore, be applied only to the final reduced ternary quadratic form. A computer program accomplishing this normalization is being written and will be part of a new indexing program to be published in due course.

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A Systematic Approximate Method for the Determination of Structure Factors from a Powder Diffractogram and its Application to the Solution of the Structure of Metavariscite

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A systematic method for the approximate determination of structure factors based on measurements of the diffraction profiles of indexed powder diffractograms is described. This method, is based on considerations concerning the shape and size of the crystals, and may be applicable to the determination of some structures of low complexity. The method is tested by its application to the metavariscite structure. Results were obtained close to those calculated by single crystal techniques.

Introduction

The main difficulty in the determination of crystal structures by means of powder methods is the resolution of the diffraction peaks. These methods, however, can give useful information about atomic arrangements, in cases in which the use of single-crystal techniques is not possible. It is well known that powder methods are applicable to the solution of structures of high symmetry and low complexity where, because there is little overlapping of diffraction peaks, precise measurement of relative intensities is practicable. Diffractometer techniques present obvious advantages in the solution of this problem. These techniques permit an easier measurement of the intensities through a suitable analytical treatment of diffraction profiles.

The aim of the present work is to develop a systematic method for the calculation of the approximate F_{obs}, specially in the case of low complexity structures and heavy atoms. The method is based on the use of the height and width of each peak of a powder diffractogram, and on the consideration of the shape and size of the microcrystals.

Principle of the method

Assuming for a diffraction profile the approximation of a triangular function, the intensities, which are proportional to the areas under the peaks, can be ex-