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A Matrix Approach to Symmetry

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Abstract

In sharp contrast to other methods which focus on the consequences of symmetry (such as dot products, *d* spacings *etc.*), the matrix approach deals with symmetry in its most abstract form - represented as matrices. The basis of the matrix approach is to generate the matrices that transform the lattice into itself. The resulting group of matrices defines the holohedry of the lattice. These matrices may be used both theoretically and practically to analyze symmetry from any cell defining the lattice. The mathematics and algorithms used to analyze symmetry become extremely simple since they are based on manipulating integers and simple rational numbers using elementary linear algebra. The matrix approach provides the conceptual and practical framework required to perform experimental procedures in a logical and general manner. In practice, the symmetry matrices may be used to define the metric symmetry, the directions of the symmetry axes, the Laue symmetry, group-subgroup relationships, and conventional or standard cells. Because of its fundamental nature, the matrix approach should provide the basis for further experimental and theoretical advances in symmetry and symmetry-related topics in crystallography as well as in chemistry, physics and mathematics.

Introduction

In the collection of crystallographic diffraction data, the initial sequence of steps is directed towards defining the lattice and the crystal symmetry. In doing so, the experimentalist traditionally relies on familiar or standard orientations to guide both the collection and the evaluation of data. On the diffractometer, for example, a conventional unit cell (as defined by the magnitudes of the cell parameters) is determined and the assumed Laue symmetry is verified by taking specially oriented films or by checking the intensities of equivalent (*h*, *k*, *l*)'s listed for standard orientations. There are many valid reasons for choosing conventional cells and orientations in the latter stages of experimental work. However, by choosing specific or familiar orientations in the initial stages, assumptions are made that influence what data are collected and, consequently, mistakes are more likely to be made. The lattice and its symmetry need not be expressed with respect to a standard cell. The properties of the lattice are reflected in *any* primitive cell because translation of the primitive unit cell generates the entire lattice. The matrix approach to symmetry represents a powerful new strategy in which the emphasis is shifted from standard cells and standard orientations to matrices.

In the matrix approach to symmetry, the matrices that transform the lattice into itself are generated. This group of symmetry matrices defines the holohedry of the lattice. The metric symmetry (and any pseudosymmetry) of the lattice is determined simply by counting the number of matrices. However, the experimentalist need not rely solely on metric information. The group of matrices generated in this way may be viewed as sets of equivalent (*h*, *k*, *l*)'s represented in matrix form. Thus the Laue symmetry may be readily analyzed *without* transformation to standard or familiar orientations. Furthermore, with extremely simple mathematics, the nature and the direction of each symmetry operation of the lattice may be calculated. This information may, in turn, be used to obtain a transformation matrix to a conventional or standard cell of the lattice. A short communication on the matrix method, with emphasis on the determination of metric lattice symmetry, has been published (Himes & Mighell, 1982). A detailed account of the matrix approach to symmetry is discussed herein.

Theory

B-matrix algorithm

The basis of the matrix approach to symmetry is to generate the matrices that relate any primitive cell of the lattice to itself. Although any method that will generate the required matrices will suffice, it has been found that the *B*-matrix algorithm (Santoro, Mighell & Rodgers, 1980) is efficient and reliable. With the algorithm, the matrices *B* in the following equation are determined:

$$a_i = \sum_j B_{ij} a_j \quad (i, j = 1, 2, 3),$$

where a_i and a_j define two primitive triplets of noncoplanar translations (a triplet is called *primitive*

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when it defines a primitive cell). When using the *B*-matrix algorithm for the analysis of symmetry, one selects a primitive cell and generates a set (or sets) of symmetry matrices. Only *B* matrices with integer elements and a determinant of +1 are considered. The treatment of experimental error using the matrix method is conceptually very simple. Generated with each symmetry matrix is a 'tolerance' matrix. The tolerance matrix represents the tolerances in the unit-cell parameters required to transform the cell into itself by the specified matrix. Suppose cell 1 is defined by lattice parameters $a, b, c, \alpha, \beta, \gamma$. If, when applied to cell 1, the matrix procedure yields the matrix *B* with the tolerance matrix

$$\begin{pmatrix} \text{tol } a & \text{tol } b & \text{tol } c \\ \text{tol } \alpha & \text{tol } \beta & \text{tol } \gamma \end{pmatrix},$$

then the transformation of cell 1 by the matrix *B* will give cell 2 having lattice parameters

$$a' = a + \text{tol } a \qquad b' = b + \text{tol } b \qquad c' = c + \text{tol c}$$
$$\alpha' = \alpha + \text{tol } \alpha \qquad \beta' = \beta + \text{tol } \beta \qquad \gamma' = \gamma + \text{tol } \gamma.$$

Thus the matrix procedure enables a direct comparison of the calculated errors with the experimental errors for the refined unit cell. The computer program based on the *B*-matrix algorithm is very fast even when analyzing highly skewed unit cells. In addition, the computer time is essentially independent of the magnitudes of the tolerances specified for the unit-cell parameters.

Metric symmetry

By relating the lattice to itself, all the symmetry operations of the lattice are obtained. The metric lattice symmetry is then determined by counting the number of matrices. The greater the number of matrices found, the higher is the symmetry. Using the *B*-matrix algorithm, the numbers of matrices for the seven lattice metric symmetries are: triclinic, 1; monoclinic, 2; orthorhombic, 4; rhombohedral, 6; tetragonal, 8; hexagonal, 12; and cubic, 24.*

An important feature of the matrix approach is that one can determine the highest possible metric symmetry within any specified tolerance of the unit-cell parameters, and that all possible pseudosymmetries are immediately apparent. By initially assuming very large experimental errors, obtains a menu of all possible symmetries. Thus, to determine metric symmetry using the matrix procedure, one sets large limits for the tolerances (such as 1·0 and 6·0 for the cell edges and angles, respectively) and analyzes the set(s) of symmetry matrices and tolerance matrices obtained. In theory, it is the nature of the matrices themselves that defines the sets to be analyzed (*i.e.* those defining a symmetry group). In practice, however, the usual result is that the tolerance matrices alone clearly define the groups and all that is required to determine the metric lattice symmetry and pseudosymmetry is to count.

When the symmetry matrices are used to transform an experimentally determined unit cell, metrically similar unit cells are generated (refer to the definition of tolerance matrices). If the lattice symmetry elements correspond to crystallographic symmetry elements, then these metrically similar cells are symmetrically equivalent and the observed metric differences are due to experimental errors. The matrix approach to symmetry provides an ideal way to evaluate the experimental errors by simply averaging the set of tolerance matrices. The resulting 'error' matrix (=averaged tolerance matrix) may be compared directly to the e.s.d.'s for the refined unit cell, or it may be applied to the refined cell to calculate an idealized cell reflecting the exact metric symmetry. In either case, the extent to which the refined cell parameters deviate from the exact metric symmetry is easily established.

Laue symmetry

The symmetry operations of the lattice may be generated with the *B*-matrix algorithm by transforming the lattice into itself. The transformation of cell 1 to cell 2 can be represented by the equation:

$$\begin{pmatrix} a_2 \\ b_2 \\ c_2 \end{pmatrix} = B \begin{pmatrix} a_1 \\ b_1 \\ c_1 \end{pmatrix}$$

where (a_i, b_i, c_i), $i = 1, 2$, represents the basis vectors in direct space and

$$B = \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{pmatrix}.$$

The same matrix, *B*, can be used to transform the values of the (h, k, l)'s for the setting defined by cell 1 to the setting defined by cell 2. Thus, the *B* matrices may also be viewed as matrix representations of equivalent (h, k, l)'s. With the matrix approach to symmetry, the metric symmetry may be determined to within any specified tolerance of the unit-cell parameters, and the same group of *B* matrices may be used experimentally to determine the Laue symmetry. The metric lattice symmetry, the Laue symmetry and all possible pseudosymmetries can be readily evaluated without transformation to standard or familiar orientations. In practice, the Laue symmetry may be determined by evaluating the intensities of equivalent reflections. A more theoretical proof of the Laue symmetry, as well as an analysis of all

* To obtain a complete group of symmetry operations using the *B*-matrix algorithm, multiply the matrices by −1 to generate a set twice the size.

possible subgroups, is obtained by analyzing the B matrices themselves.

The symmetry operations of the lattice are represented by the B matrices. The values of the elements in each matrix depend upon the kind and orientation of the element with respect to the coordinate system chosen. Because the B-matrix algorithm generates matrices with a determinant of +1, the nature of the symmetry axis is found by calculating the trace of the matrix: $\mathrm{tr}(B) = b_{11} + b_{22} + b_{33}$. The trace of the matrix is invariant under similarity transformations; that is, it is independent of the basis chosen. The symmetry axis is an n-fold rotation axis where $n = 1,2,3,4,6$ for $\mathrm{tr}(B) = 3, -1, 0, 1, 2$, respectively. The direction of the axis is given by the solutions $\mathbf{q}$ of a linear algebraic equation of the form $(B - \mathbf{1})\mathbf{q} = 0$, where $\mathbf{1}$ is the identity matrix.

Transformation to a standard cell

The distribution of the symmetry elements in a lattice is well defined and may be used as a basis for choosing a conventional or standard unit cell. The same group of symmetry matrices used to determine the Laue symmetry from any primitive cell may also be used to obtain a transformation matrix to a standard or conventional cell. The matrix approach is based solely on the symmetry and, in effect, is independent of the magnitudes of the cell parameters and experimental errors. When choosing a conventional cell, any metric constraints required may be applied separately. A set of conventions used for choosing cell edges based on symmetry, plus additional metric constraints when necessary, is given in *International Tables for Crystallography* (1983), pp. 734–735.

Once the B matrices have been generated, the calculations required to obtain a transformation matrix from any primitive cell to a standard cell are easily performed by hand. The general procedure is as follows: (1) generate the matrices relating the lattice to itself; (2) experimentally determine the symmetry; (3) analyze the group of symmetry matrices: define the nature and direction of each axis; (4) choose three symmetry directions for the cell edges; (5) derive a transformation matrix. Steps 1 and 2 have been described in the previous sections. Consequently, the description of the procedure(s) to obtain a transformation matrix to a standard cell will focus on steps 3, 4 and 5. Two conceptually different approaches used to analyze the B matrices (step 3) and to derive a transformation matrix (step 5) will be discussed: (1) the lattice approach and (2) the object approach. In addition, when choosing the directions to be used as cell edges (step 4), two different approaches are described: (1) the analysis of dependency equations and (2) the analysis of determinants.

Lattice approach. This approach obtains a transformation matrix from a skewed cell to a standard cell by analyzing the symmetry of the lattice. Each B matrix is used directly to calculate the nature of the symmetry axis and the direction of the axis with respect to the lattice. Assume that the proper three directions for the cell edges have been chosen; this is easily done and will be discussed later. The task of obtaining a transformation matrix may now be viewed as a change-of-basis problem in linear algebra. That is, we have a skewed basis to be transformed to a new standard basis. The first step in solving this change-of-basis problem is to assemble an augmented matrix of lattice symmetry directions, where the directions are written as columns. The three symmetry directions chosen for the cell edges will be the first three columns in the augmented matrix and should be assembled with account taken of certain crystallographic conventions. These include the definition of a right-handed coordinate system and observation of the preferred order of the axes. As summarized below, a transformation matrix from a skewed to a standard cell is found by applying elementary row operations to the augmented matrix until a new standard basis is obtained.

skewed basis	symmetry directions (optional)	1 0 0 0 1 0 0 0 1	→

new basis	symmetry directions (new basis)	transformation matrix

The new basis can be any 3×3 matrix. However, when determining a transformation matrix to a conventional unit cell, the new basis is usually the identity matrix and the mathematical operation involved is simply taking the inverse of a 3×3 matrix by reducing an augmented matrix to row echelon form. The choice of basis influences the relationships between the remaining vectors as well as the interpretation of the last three columns to give a transformation matrix. This is especially true for centered lattices and for the rhombohedral system. Although many variations are possible owing to the many bases that can be chosen, the relationships between the vectors is well defined and, in practice, the determination of a transformation matrix is straightforward for all cases. The lattice approach may be viewed as a form of lattice or cell reduction based on the symmetry.

Object approach. The lattice approach reflects the nature of the generation of the symmetry matrices. Since the B matrices were generated by relating a cell to itself, the symmetry operations of the lattice were obtained. However, symmetry is often described in

terms of equivalent positions for objects. This is the basis used for the object approach.

As explained in the discussion of Laue symmetry, the B matrices may be viewed as matrix representations of equivalent (h, k, l)'s. Therefore, in order to shift the emphasis from lattices or (h, k, l)'s to objects or (x, y, z)'s, the nature and directions of the symmetry axes are calculated from the transposes of the inverses of the B matrices, $(B^{-1})^t$. Once again, assume that the proper three directions for the cell edges have been chosen. With this approach, the task of obtaining a transformation matrix is greatly simplified because the standard basis is the identity matrix and the standard matrix for a matrix transformation is the matrix itself [refer to ch. 5 of Anton (1984)]. This means that the transformation matrix from any skewed cell to a conventional cell is obtained directly by writing the three directions chosen for the cell edges as rows in a matrix. The transformation matrix should be assembled so that crystallographic conventions are met. The type of centering present is defined by the value for the determinant of the transformation matrix except in the orthorhombic system where additional information is sometimes required.

Select symmetry directions for cell edges. Whether the lattice or the object approach is used to determine a transformation matrix to a standard cell, a critical step is the selection of three linearly independent vectors in the proper directions to be used as directions for the cell edges. In the triclinic system, selection of the cell edges is based on metric conditions. In the monoclinic system, the only symmetry direction, a twofold axis, is labeled as **b** (the vectors **a** and **c** are chosen so that they lie in a plane perpendicular to **b** and meet additional metric constraints). The directions of the three twofold axes in the orthorhombic system are selected for the cell edges. In the rhombohedral system, the directions for any two of the three twofold axes and the direction of the threefold axis are used as directions for **a**, **b** and **c**, respectively. The resulting transformation may give either metrically rhombohedral or metrically hexagonal axes depending on the relationships between these vectors (*i.e.* the basis chosen; see *Lattice approach*). In the tetragonal system, the directions for two of five possible twofold axes are taken as the **a** and **b** axes, while the direction of a fourfold axis is selected for **c**. Similarly, in the hexagonal system, the directions for two of the seven twofold axes are selected for **a** and **b** and the direction of a sixfold axis is selected for **c**. The cell edges for the cubic system are taken along three linearly independent fourfold axes. Thus, when choosing three symmetry directions to be used as cell edges, one finds that only the tetragonal and hexagonal crystal systems appear to allow more than one possibility. The following two subsections describe simple algorithms that enable one to evaluate quickly the relationships between the symmetry elements in these systems and, consequently, provide direct ways to select the proper symmetry directions to be used as cell edges.

Analysis of dependency equations. In the tetragonal system, five of the B matrices correspond to twofold axes. Since one of these five axes is parallel to a fourfold axis, there are at most six combinations of twofold axes to be considered. Likewise, in the hexagonal system, one of the seven twofold axes is parallel to a sixfold axis, leading to at most 15 ways to choose two of the remaining six directions. The first step in this procedure is to pick any two of the possible twofold axes and arbitrarily assign these as the directions for the **a** and **b** axes. The direction used for the **c** axis is that of a fourfold axis in the tetragonal system and a sixfold axis for the hexagonal system. Next, assemble a matrix by writing the symmetry directions as columns with the first three columns representing the a, b, c directions. Using elementary row operations, reduce the matrix to row echelon form. This step gives the dependency equations for the remaining symmetry directions with respect to the basis directions chosen. Simply by inspecting the dependency relations obtained from the reduced row echelon form of the matrix, it can be determined whether a proper basis has been selected and, if not, which directions of the twofold axes should have been chosen. Each of the six combinations of the twofold axes in the tetragonal system leads to one of three recognizable types of matrices. Similarly, in the hexagonal system, each of the 15 combinations of twofold axes falls into one of four recognizable forms of matrices. When the reduced row echelon form of the matrix for the tetragonal or the hexagonal system is

$$\begin{array}{c} \text{order of axis} \\ \begin{array}{ccc|cc} 2 & 2 & 4 & 2 & 2 \end{array} \\ \left(\begin{array}{ccc|cc} 1 & 0 & 0 & 1 & 1 \\ 0 & 1 & 0 & -1 & 1 \\ 0 & 0 & 1 & 0 & 0 \end{array}\right) \end{array} \quad \text{or} \quad \begin{array}{c} \text{order of axis} \\ \begin{array}{ccc|cccc} 2 & 2 & 6 & 2 & 2 & 2 & 2 \end{array} \\ \left(\begin{array}{ccc|cccc} 1 & 0 & 0 & 1 & -1 & 1 & -2 \\ 0 & 1 & 0 & -1 & -1 & 2 & -1 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \end{array}\right) \end{array}$$

respectively, or its equivalent, the proper basis has been chosen. Perhaps the easiest way to understand the dependency equations in the reduced row echelon form of the matrix is through use of a diagram. For both the tetragonal and hexagonal systems, plot the vectors projected onto the *ab* plane and compare the respective figures with those for space groups *P4/mmm* and *P6/mmm* in *International Tables for Crystallography* (1983). With a plot of the dependency equations, one can readily visualize the vectors that have been chosen and, if necessary, which vectors should have been selected.

The analysis of dependency equations to select the directions of symmetry axes to be used as cell edges

is similar in approach to the lattice method of obtaining a transformation matrix, as both methods use elementary row operations to reduce a matrix to row echelon form. The lattice method may be viewed as a form of lattice reduction whereas the analysis of dependency equations may be viewed as a form of symmetry reduction.

Analysis of determinants. In the tetragonal system, there are six ways to combine two twofold axes with a fourfold axis. Similarly, in the hexagonal system, there are 15 ways to combine two twofold axes with a sixfold axis. For each combination, assemble a 3×3 matrix of directions. The three directions to be used for the cell edges are found directly from the values of the determinants of these matrices. In the tetragonal system, one of the six determinants will be twice the others. Assume that the four possible twofold axes are labeled 1,2,3,4. If the combination of 1 and 2 with a fourfold axis gives a determinant twice the rest, then the vectors 3 and 4 should be selected as directions for the conventional cell edges. In the hexagonal system, there will be nine combinations with a determinant of ±1, three combinations with a determinant of ±2, and three combinations with a determinant of ±3. If the six possible twofold axes are labeled $1,\ldots,6$, and the combinations of 1-2, 1-3 and 2-3 give determinants of ±3, then the directions for any two of the twofold axes 4, 5 or 6 may be used as cell edges. Comparison of the values of determinants provides a second way to analyze the dependency relations between the symmetry elements. For example, in the tetragonal system, the one basis with a determinant twice the others may be compared to relabeling the **a** and **b** axes of a conventional tetragonal cell so that they lie along the cell diagonals. However, the determinant method greatly simplifies the analysis based on symmetry because data is analyzed with respect to *any* orientation without having to view it, either visually or mathematically, from a standard basis.

Similarity. The values of the elements in each B matrix depend on the kind and orientation of each symmetry operation with respect to the coordinate system chosen. As a result, the group of symmetry matrices generated from a skewed unit cell will be different from the group of symmetry matrices generated from either a standard cell or a second skewed cell. Since any two cells defining the lattice belong to the same Bravais class, there exists a homogeneous linear transformation which will transform one lattice into the other and will transform the holohedry of one lattice into the holohedry of the other. Suppose the transformation of cell 1 to cell 2 is represented by the equation

$$\begin{pmatrix} a_2 \\ b_2 \\ c_2 \end{pmatrix} = S \begin{pmatrix} a_1 \\ b_1 \\ c_1 \end{pmatrix}$$

and the holohedry for cells 1 and 2 is defined by $H_1=\{B_1\}$ and $H_2=\{B_2\}$ respectively, where B_1 and B_2 are the groups of B matrices. The relationships between the symmetry groups is given by the equation $H_2=SH_1S^{-1}$. This equation defines the effect a change of basis has on the matrix of a linear operator. By definition, two matrices representing the same linear operator with respect to different bases are similar. An explanation of the similarity equation is given in §5.5 of Anton (1984).

Discussion and examples

Metric symmetry and pseudosymmetry

When determining the metric symmetry for an unknown crystal, one must be particularly careful that the unit-cell parameters and errors have been properly determined and interpreted. In many cases, it appears that the reported experimental error (as indicated by e.s.d.'s) is too optimistic, even for unit-cell parameters refined by least-squares analysis using modern diffractometry. High precision cannot always be used as an indication of accuracy. Independent unit-cell determinations of β-clopenthixol illustrate this point. The X-ray crystal structure of β-clopenthixol has been reported in the literature (Jones, Sheldrick & Horn, 1981). A crystalline sample of β-clopenthixol had earlier been obtained from one of these authors (AH) and the unit-cell parameters were determined using both powder (Morris, McMurdie, Evans, Paretzkin, Hubbard & Carmel, 1980) and single-crystal diffraction techniques.

Single-crystal cell (Jones *et al.*, 1981)	Single-crystal cell determined at NBS	Powder cell (Morris *et al.*, 1980)
$a=$ 6·493(2) Å	6·4978(7) Å	6·518(4) Å
$b=$ 7·758(3)	7·7701(8)	7·773(3)
$c=$21·881(8)	21·871(2)	21·939(11)
$\alpha=$90·11(2)°	90·011(8)°	90·06(4)°
$\beta=$91·48(2)	91·501(9)	91·60(5)
$\gamma=$92·81(2)	93·129(9)	93·06(4)

The unit-cell parameters agree reasonably well. However, depending on which values are used, the γ angles for the two cells refined with single-crystal diffractometer data differ by approximately 16 to 35 estimated standard deviations (e.s.d.'s). Thus, especially when working with cells prior to the final cell, one should assume rather large experimental errors whenever the highest possible symmetry is

sought. Experience has shown that the matrix procedure correctly predicts the metric symmetry even when the experimental error is large.

The mineral chabazite provides an example where the assessment of the experimental error plays an integral role in the determination of metric symmetry. Lattice parameters for chabazite were determined using a natural sample from Wasson's Bluff, Nova Scotia, Canada:

$a = 9{\cdot}3799(14)$, $b = 9{\cdot}3926(14)$, $c = 9{\cdot}3918(14)$ Å,
$\alpha = 94{\cdot}263(12)$, $\beta = 94{\cdot}408(12)$, $\gamma = 94{\cdot}469(12)°$.

Analysis of this primitive cell (=reduced cell) using the matrix procedure gave a set of six symmetry matrices when program limits of 1·0 and 6·0 were used for the cell edges and angles, respectively (Table 1). Suppose the limit for a reasonable experimental error is chosen to be equal to 5 e.s.d.'s of the lattice parameters. With this constraint, the metric symmetry for chabazite would be monoclinic. When the tolerance matrices for matrices 1 and 6 are averaged and applied to the initial cell, the calculated lattice parameters are:

$a = 9{\cdot}3799$, $b = 9{\cdot}3922$, $c = 9{\cdot}3922$ Å,
$\alpha = 94{\cdot}2630$, $\beta = 94{\cdot}4385$, $\gamma = 94{\cdot}4385°$.

This cell may be transformed by the matrix (0 1 1 / 0 −1 1 / 1 0 0) to a *C*-centered monoclinic unit cell with lattice parameters

$a = 12{\cdot}779$, $b = 13{\cdot}767$, $c = 9{\cdot}380$ Å,
$\alpha = 90{\cdot}00$, $\beta = 96{\cdot}53$, $\gamma = 90{\cdot}00°$.

Although all six tolerance matrices are relatively small, the tolerance matrices for matrices 1 and 6 are considerably less than those for matrices 2, 3, 4 and 5. With the current definition of a reasonable experimental error (*i.e.* 5 e.s.d.'s), the matrix procedure indicates that chabazite is monoclinic with rhombohedral pseudosymmetry. The knowledge of metric pseudosymmetry is extremely useful as it means that there exist distinct, but metrically similar, unit cells in the lattice. Three metrically similar monoclinic cells were found for chabazite and refined on a diffractometer. If chabazite is assumed to be monoclinic with rhombohedral pseudosymmetry, the three C-centered cells presented in Table 2 would index differently the same set of diffraction data. Of the three cells, note that the refined lattice parameters for cell 2 are closer to having exact monoclinic metric symmetry than are those for cells 1 and 3.

A second interpretation is that the average of all six tolerance matrices from Table 1 corresponds to reasonable experimental errors and that chabazite has rhombohedral metric symmetry. When the error matrix (=averaged tolerance matrix) is applied to the refined primitive cell, the resulting unit cell has lattice

Table 1. *Symmetry matrices and tolerance matrices found for chabazite*

(1)	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0{\cdot}0000 & -0{\cdot}0008 & 0{\cdot}0008 \\ 0{\cdot}0000 & 0{\cdot}0610 & -0{\cdot}0610 \end{pmatrix}$
(2)	$\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0{\cdot}0127 & -0{\cdot}0127 & 0{\cdot}0000 \\ 0{\cdot}1450 & -0{\cdot}1450 & 0{\cdot}0000 \end{pmatrix}$
(3)	$\begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0{\cdot}0119 & 0{\cdot}0000 & -0{\cdot}0119 \\ 0{\cdot}2060 & 0{\cdot}0000 & -0{\cdot}2060 \end{pmatrix}$
(4)	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0{\cdot}0119 & -0{\cdot}0127 & 0{\cdot}0008 \\ 0{\cdot}2060 & -0{\cdot}1450 & -0{\cdot}0610 \end{pmatrix}$
(5)	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0{\cdot}0127 & -0{\cdot}0008 & -0{\cdot}0119 \\ 0{\cdot}1450 & 0{\cdot}0610 & -0{\cdot}2060 \end{pmatrix}$
(6)	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0{\cdot}0000 & 0{\cdot}0000 & 0{\cdot}0000 \\ 0{\cdot}0000 & 0{\cdot}0000 & 0{\cdot}0000 \end{pmatrix}$

Table 2. *The three C-centered monoclinic cells of chabazite which reduce to a common cell*

Cell 1	Cell 2	Cell 3
$a = 12{\cdot}7465(20)$ Å	12·7794 (17) Å	12·7533 (20) Å
$b = 13{\cdot}7816(20)$	13·7674 (22)	13·7743 (20)
$c = 9{\cdot}3918(14)$	9·3799(14)	9·3926(14)
$\alpha = 89{\cdot}905(12)°$	89·959 (13)°	90·136 (12)°
$\beta = 96{\cdot}392(12)$	96·532 (12)	96·433 (12)
$\gamma = 89{\cdot}922(12)$	90·004 (12)	90·073 (12)
$\begin{pmatrix} 0{\cdot}5 & -0{\cdot}5 & 0 \\ 0{\cdot}5 & 0{\cdot}5 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 0{\cdot}5 & -0{\cdot}5 & 0 \\ 0{\cdot}5 & 0{\cdot}5 & 0 \end{pmatrix}$	$\begin{pmatrix} 0{\cdot}5 & 0{\cdot}5 & 0 \\ 0 & 0 & 1 \\ 0{\cdot}5 & -0{\cdot}5 & 0 \end{pmatrix}$

$a = 9{\cdot}380$ $b = 9{\cdot}393$ $c = 9{\cdot}392$ Å
$\alpha = 94{\cdot}26$ $\beta = 94{\cdot}41$ $\gamma = 94{\cdot}47°$

parameters

$a = 9{\cdot}3881$, $b = 9{\cdot}3881$, $c = 9{\cdot}3881$ Å,
$\alpha = 94{\cdot}380$, $\beta = 94{\cdot}380$, $\gamma = 94{\cdot}380°$.

This calculated cell differs from the refined cell by a maximum of approximately 10 e.s.d.'s. The matrix procedure yields all possible lattice symmetries within

Table 3. *Symmetry matrices found for* $C_{56}H_{60}Cu_5N_{22}$

Program limits of 1·0 and 6·0 were used for the cell edges and angles, respectively.

$$(1)\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix}\quad(2)\begin{pmatrix}-1&0&0\\0&1&0\\0&0&-1\end{pmatrix}\quad(3)\begin{pmatrix}0&-1&0\\-1&0&0\\0&0&-1\end{pmatrix}$$

$$(4)\begin{pmatrix}0&-1&0\\1&0&0\\0&0&1\end{pmatrix}\quad(5)\begin{pmatrix}0&1&0\\-1&0&0\\0&0&1\end{pmatrix}\quad(6)\begin{pmatrix}0&1&0\\1&0&0\\0&0&-1\end{pmatrix}$$

$$(7)\begin{pmatrix}1&0&0\\0&-1&0\\0&0&-1\end{pmatrix}\quad(8)\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$$

Table 4. $C_{56}H_{60}Cu_5N_{22}$: *symmetry matrices calculated from a skewed cell*

Program limits of 1·0 and 6·0 were used for the cell edges and angles, respectively.

$$(1)\begin{pmatrix}-3&0&2\\-8&1&4\\-5&0&3\end{pmatrix}\quad(2)\begin{pmatrix}-3&0&2\\-4&-1&4\\-4&0&3\end{pmatrix}\quad(3)\begin{pmatrix}-1&0&0\\-4&1&0\\0&0&-1\end{pmatrix}$$

$$(4)\begin{pmatrix}-1&0&0\\0&-1&0\\-3&0&1\end{pmatrix}\quad(5)\begin{pmatrix}1&0&0\\4&-1&0\\3&0&-1\end{pmatrix}\quad(6)\begin{pmatrix}3&0&-2\\4&1&-4\\5&0&-3\end{pmatrix}$$

$$(7)\begin{pmatrix}3&0&-2\\8&-1&-4\\4&0&-3\end{pmatrix}\quad(8)\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$$

a specified tolerance. The actual selection of the highest possible symmetry of the lattice is dependent on the assessment of the experimental error. An advantage of using the matrix procedure to determine metric lattice symmetry is that the method enables a direct comparison of the calculated errors with the experimental errors determined for the primitive unit cell. Chabazite (from north-east Azerbaijan, Iran) has been reported in the literature as having rhombohedral symmetry, space group $R\bar{3}m$ and unit-cell parameters $a = 9{\cdot}421(4)$ Å, $\alpha = 94{\cdot}20(1)°$ (Calligaris, Nardin, Randaccio & Chiaramonti, 1982).

Laue symmetry and conventional cell determination

A primitive unit cell with

$a = 13{\cdot}8102(21)$, $b = 13{\cdot}8091(22)$, $c = 16{\cdot}6620(28)$ Å,

$\alpha = 89{\cdot}994(13)$, $\beta = 89{\cdot}993(13)$, $\gamma = 89{\cdot}980(13)°$

was determined for the complex $C_{56}H_{60}Cu_5N_{22}$. The group of B matrices generated from this unit cell is given in Table 3. The metric lattice symmetry is tetragonal since eight symmetry matrices were found. When evaluating symmetry using the matrix method, the experimentalist need not rely solely on metric information. The group of B matrices may be viewed as sets of equivalent (h, k, l)'s represented in matrix form. Once a reflection has been found on the diffractometer, the equation

$$\left[\begin{pmatrix}h\\k\\l\end{pmatrix}_{eq}\right]_i = B_i\begin{pmatrix}h\\k\\l\end{pmatrix}$$

may be used to generate sets of reflections that should have equivalent intensities if the metric and crystal symmetry agree. Substitution of the B matrices from Table 3 into the above equation, where $i = 1, \ldots, 8$ for the tetragonal system, generates the following set of (h, k, l)'s:

$(-h, -k, l)$ $(-h, k, -l)$ $(-k, -h, -l)$ $(-k, h, l)$
$(k, -h, l)$ $(k, h, -l)$ $(h, -k, -l)$ (h, k, l).

This is the familiar set used for the tetragonal system since the primitive cell used to generate the symmetry matrices reflected the conventional metric conditions consistent with the highest possible symmetry of the lattice (*i.e.* in the tetragonal system, a cell with $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$ as opposed to a primitive cell with $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90°$). For sets of general (h, k, l)'s, it was found that the intensities for all eight reflections in the sets were equivalent, indicating $4/mmm$ Laue symmetry for the complex. This observation was confirmed by a full structure determination (Himes, Mighell & Siedle, 1981).

With the matrix approach, the Laue symmetry and any pseudosymmetry, metric or crystal, may be determined from any cell defining the lattice. A second unit cell was determined for the complex $C_{56}H_{60}Cu_5N_{22}$ and refined on a diffractometer:

$a = 19{\cdot}5263(27)$, $b = 42{\cdot}4583(59)$, $c = 30{\cdot}8742(45)$ Å,

$\alpha = 29{\cdot}242(13)$, $\beta = 18{\cdot}442(13)$, $\gamma = 23{\cdot}106(12)°$.

As expected, the matrix procedure predicted tetragonal symmetry since eight B matrices were generated (Table 4). The group of matrices used to determine the metric symmetry was also used to evaluate the Laue symmetry from this skewed unit cell. For example, when the (5,6,7) reflection was multiplied by each of the B matrices from Table 4, the following set of (h, k, l)'s was predicted, and subsequently found, to have equal intensities:

$(-1, -6, -4)$ $(-1, 2, 1)$ $(-5, -14, -7)$ $(-5, -6, -8)$
$(5, 14, 8)$ $(1, -2, 4)$ $(1, 6, -1)$ $(5, 6, 7)$.

Once the symmetry has been evaluated, these same matrices may be used to obtain a transformation matrix to a conventional or standard cell. For this example the lattice approach is used to analyze the symmetry matrices and to derive a transformation matrix, while the analysis of determinants is employed to choose the directions to be used as cell edges. Even for a skewed unit cell, the spatial distribution of all the symmetry operations of the lattice may

be obtained by a simple analysis of the symmetry matrices. Calculation of the determinant (always +1) and the trace for each matrix indicates that matrices 1 and 6 correspond to fourfold axes (trace = +1), matrices 2, 3, 4, 5, 7 correspond to twofold axes (trace = −1), and matrix 8 corresponds to the identity operation (trace = +3). The direction of each axis is given by the solutions of an equation of the form $(B-\mathbf{1})\mathbf{q}=0$. Thus, to calculate the direction of the twofold axis represented by matrix 2, the following equation is solved:

$$\begin{pmatrix}-4 & 0 & 2\\ -4 & -2 & 4\\ -4 & 0 & 2\end{pmatrix}\begin{pmatrix}a\\ b\\ c\end{pmatrix}=0.$$

Since $a=\frac{1}{2}c$ and $b=c$, the direction of the twofold axis is given by (1, 2, 2). From similar calculations, it can be found that matrices 1, . . . , 7 correspond to the (0, 1, 0), (1, 2, 2), (0, 1, 0), (0, 0, 1), (2, 4, 3), (0, 1, 0), (1, 2, 1) directions respectively. The next step in determining a matrix to a conventional cell is to select the three symmetry directions to be used as the cell edges. In this case, the direction of a fourfold axis is taken as c and the directions for two of the four twofold axes represented by matrices 2, 4, 5, 7 are selected for the cell edges a and b. The 3×3 matrix of directions represented by matrices 4-5-1,

$$\begin{pmatrix}0 & 2 & 0\\ 0 & 4 & 1\\ 1 & 3 & 0\end{pmatrix},$$

has a determinant of +2 whereas the matrices of directions for the combinations 2-4-1, 2-5-1, 2-7-1, 4-7-1 and 5-7-1 have determinants of +1 or −1. Thus the symmetry directions represented by matrices 2-7-1 should be chosen as directions for conventional cell edges. The task of obtaining a transformation matrix from the skewed cell to a conventional cell may now be viewed as a change-of-basis problem. When the augmented matrix of directions

$$\left(\begin{array}{ccc|cc|ccc}1 & 1 & 0 & 0 & 2 & 1 & 0 & 0\\ 2 & 2 & 1 & 0 & 4 & 0 & 1 & 0\\ 2 & 1 & 0 & 1 & 3 & 0 & 0 & 1\end{array}\right),$$

is reduced to row echelon form,

$$\left(\begin{array}{ccc|cc|ccc}1 & 0 & 0 & 1 & 1 & -1 & 0 & 1\\ 0 & 1 & 0 & -1 & 1 & 2 & 0 & -1\\ 0 & 0 & 1 & 0 & 0 & -2 & 1 & 0\end{array}\right),$$

the familiar relationships between the symmetry operations is defined by the first five columns of the matrix, while the last three columns give a transformation matrix to a conventional cell.

The compound basic beryllium acetate provides a second illustration of the matrix approach to

Table 5. *Basic beryllium acetate: symmetry matrices calculated from a skewed primitive cell*

Program limits of 1·0 and 6·0 were used for the cell edges and angles, respectively. Asterisks are used to define one of the two sets of matrices that may be used to calculate sets of equivalent (h, k, l)'s for $m3$ Laue symmetry.

(1)* $\begin{pmatrix}-3 & 0 & 2\\ -9 & -1 & 9\\ -4 & 0 & 3\end{pmatrix}$ (9) $\begin{pmatrix}-1 & 1 & -1\\ -1 & 0 & 3\\ 0 & 0 & 1\end{pmatrix}$ (17)* $\begin{pmatrix}1 & 2 & -5\\ 1 & 9 & -21\\ 0 & 4 & -9\end{pmatrix}$

(2)* $\begin{pmatrix}-3 & 1 & 0\\ -10 & 1 & 5\\ -4 & 0 & 3\end{pmatrix}$ (10)* $\begin{pmatrix}-1 & 3 & -6\\ 0 & 9 & -20\\ 0 & 4 & -9\end{pmatrix}$ (18)* $\begin{pmatrix}2 & -3 & 6\\ 9 & -10 & 18\\ 4 & -4 & 7\end{pmatrix}$

(3) $\begin{pmatrix}-3 & 2 & -3\\ -10 & 9 & -15\\ -4 & 4 & -7\end{pmatrix}$ (11) $\begin{pmatrix}0 & -3 & 7\\ -1 & -9 & 21\\ 0 & -4 & 9\end{pmatrix}$ (19) $\begin{pmatrix}2 & 1 & -4\\ 9 & 1 & -9\\ 4 & 0 & -3\end{pmatrix}$

(4) $\begin{pmatrix}-3 & 3 & -5\\ -9 & 10 & -18\\ -4 & 4 & -7\end{pmatrix}$ (12) $\begin{pmatrix}0 & -1 & 3\\ 1 & -1 & 4\\ 0 & 0 & 1\end{pmatrix}$ (20)* $\begin{pmatrix}3 & -3 & 5\\ 10 & -9 & 15\\ 4 & -4 & 7\end{pmatrix}$

(5)* $\begin{pmatrix}-2 & -1 & 4\\ -9 & 0 & 7\\ -4 & 0 & 3\end{pmatrix}$ (13)* $\begin{pmatrix}0 & 1 & -3\\ 1 & 0 & -3\\ 0 & 0 & -1\end{pmatrix}$ (21)* $\begin{pmatrix}3 & -2 & 3\\ 9 & -9 & 16\\ 4 & -4 & 7\end{pmatrix}$

(6) $\begin{pmatrix}-2 & 3 & -6\\ -9 & 9 & -16\\ -4 & 4 & -7\end{pmatrix}$ (14)* $\begin{pmatrix}0 & 3 & -7\\ -1 & 10 & -22\\ 0 & 4 & -9\end{pmatrix}$ (22) $\begin{pmatrix}3 & -1 & 0\\ 9 & 0 & -7\\ 4 & 0 & -3\end{pmatrix}$

(7) $\begin{pmatrix}-1 & -2 & 5\\ 0 & -9 & 20\\ 0 & -4 & 9\end{pmatrix}$ (15) $\begin{pmatrix}1 & -3 & 6\\ 1 & -10 & 22\\ 0 & -4 & 9\end{pmatrix}$ (23) $\begin{pmatrix}3 & 0 & -2\\ 10 & -1 & -5\\ 4 & 0 & -3\end{pmatrix}$

(8)* $\begin{pmatrix}-1 & 0 & 0\\ -1 & 1 & -4\\ 0 & 0 & -1\end{pmatrix}$ (16)* $\begin{pmatrix}1 & -1 & 1\\ 0 & -1 & 0\\ 0 & 0 & -1\end{pmatrix}$ (24) $\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}$

symmetry. A primitive unit cell with

$a=19{\cdot}2600(9)$, $b=63{\cdot}8825(62)$, $c=27{\cdot}2394(27)$ Å,
$\alpha=5{\cdot}7696(134)$, $\beta=19{\cdot}4709(129)$, $\gamma=17{\cdot}2952(126)°$

was refined on a diffractometer. The metric lattice symmetry is cubic since 24 matrices were found (Table 5). The error matrix,

$$\begin{pmatrix}0{\cdot}0027 & 0{\cdot}0048 & 0{\cdot}0023\\ -0{\cdot}0014 & 0{\cdot}0003 & -0{\cdot}0001\end{pmatrix},$$

indicates that the refined cell parameters must be changed by less than $1\frac{1}{2}$ e.s.d.'s in order to reflect exact cubic metric symmetry. The B matrices were next used to calculate sets of 24 (h, k, l)'s which were examined on the diffractometer. Rather than observing one group of 24 equivalent intensities, two sets of 12 equivalent intensities were found, indicating $m3$ Laue symmetry. It is both the nature and the direction of the observed axes that defines the symmetry. [The symmetry is *not* hexagonal even though sets of 12 intensities were found to be equivalent since different sets of (h, k, l)'s would be equivalent for the hexagonal system and there are no matrices

corresponding to sixfold axes.] Calculation of the determinant (+1) and trace for each symmetry matrix reveals that matrices 2, 5, 14, 17, 20 and 21 correspond to fourfold axes (trace = +1), matrices 4, 6, 9, 11, 12, 15, 19, 22 correspond to threefold axes (trace = 0) and, with the exception of the identity matrix, 24, the remaining symmetry matrices correspond to twofold axes (trace = −1). Since the symmetry was found to be cubic, the directions of the fourfold axes may be used as directions for conventional cell edges. When the object method is used to obtain a transformation matrix to a conventional cell, the directions of the axes are calculated from the transposes of the inverses of the symmetry matrices. Matrices 2, 5 and 17 correspond to fourfold axes in the (0, 2, −5), (2, −2, 3) and (2, 0, −1) directions, respectively. A transformation matrix is obtained simply by writing these directions for the fourfold axes as rows in a matrix. This matrix should be assembled so that it has a positive determinant, ensuring the definition of a right-handed coordinate system. Since the determinant of the transformation matrix,

$$\begin{pmatrix} 2 & -2 & 3 \\ 0 & 2 & -5 \\ 2 & 0 & -1 \end{pmatrix},$$

is +4, the conventional cell will be *F*-centered. When this matrix is applied to the refined primitive cell, the resulting unit cell will not reflect the exact cubic symmetry. The observed differences are due to experimental errors. However, it must be remembered that the cell calculated in this way is just one of 24 metrically similar cells in the lattice. Thus, in certain cases, this practice can lead to a misevaluation of the cell parameters and errors. The matrix approach provides an ideal way to calculate the conventional cell taking into account the metric deviations of all the symmetrically equivalent cells in the lattice. The error matrix is used to calculate an ideal cell reflecting exact metric symmetry ($a = 19{\cdot}2627$, $b = 63{\cdot}8873$, $c = 27{\cdot}2417$ Å, $\alpha = 5{\cdot}7682$, $\beta = 19{\cdot}4712$, $\gamma = 17{\cdot}2951°$). When the transformation matrix is applied to the idealized primitive cell, a conventional unit cell with $a =$ 15·728 Å is obtained. The group of matrices defining the holohedry of the conventional cell may also be calculated from any cell defining the lattice using the similarity equation $H_2 = SH_1 S^{-1}$. For example, substitution of matrix 1 from Table 5 into the equation gives matrix 1 in Table 6:

$$\begin{pmatrix} 2 & -2 & 3 \\ 0 & 2 & -5 \\ 2 & 0 & -1 \end{pmatrix}\begin{pmatrix} -3 & 0 & 2 \\ -9 & -1 & 9 \\ -4 & 0 & 3 \end{pmatrix}\begin{pmatrix} -\frac{1}{2} & -\frac{1}{2} & 1 \\ -\frac{5}{2} & -2 & \frac{5}{2} \\ -1 & -1 & 1 \end{pmatrix}$$
$$= \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

Table 6. *Basic beryllium acetate: symmetry matrices defining the holohedry of the conventional cell*

These matrices were calculated by hand by analyzing the symmetry matrices for the skewed unit cell (Table 5).

(1) $\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$ (2) $\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$ (3) $\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$ (4) $\begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix}$ (5) $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$ (6) $\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$ (7) $\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$ (8) $\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

(9) $\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix}$ (10) $\begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$ (11) $\begin{pmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix}$ (12) $\begin{pmatrix} 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix}$ (13) $\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$ (14) $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$ (15) $\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$ (16) $\begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$

(17) $\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ (18) $\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$ (19) $\begin{pmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$ (20) $\begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$ (21) $\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ (22) $\begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{pmatrix}$ (23) $\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ (24) $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

Thus the similarity equation provides one way to illustrate theoretically that the observed equivalent intensities correspond to $m3$ Laue symmetry.

As illustrated by the previous examples, the *B* matrices may be used both theoretically and practically to analyze symmetry from any cell defining the lattice. The *B*-matrix algorithm generates the matrices relating the lattice to itself to within any specified tolerance of the unit-cell parameters. In practice, the program tolerances are routinely set to relatively large values, providing a menu of all possible symmetries. When used in combination with experimental data, the Laue symmetry and any group–subgroup relationships (such as pseudosymmetry) are immediately apparent. These same matrices may be used to calculate a transformation matrix to a standard cell or even a second skewed cell. With use of the similarity relationship, the symmetry matrices for the transformed basis may also be calculated.

Concluding remarks

In sharp contrast to other methods which focus on the consequences of symmetry (such as dot products, *d* spacings *etc.*), the matrix approach deals with symmetry in its most abstract form – represented as

matrices. Matrices provide an ideal mathematical notation for conceptualizing and analyzing symmetry. The mathematics and algorithms used to analyze symmetry become extremely simple since they are based on manipulating integers and simple rational numbers using elementary linear algebra. More importantly, the ability to abstract the symmetry from a problem and to represent it as a group of matrices leads to numerous practical and theoretical applications. In crystallography, for example, we have shown that the symmetry matrices may be used in practice to define the metric symmetry, the directions of the symmetry axes, the Laue symmetry, group–subgroup relationships, and conventional or standard cells. By providing the conceptual and practical framework required to perform experimental procedures in a logical and general manner, the matrix method should revolutionize the automation of diffractometers. Although evolving from research in lattices in crystallography, the matrix approach to symmetry is not limited to this discipline. Because of its fundamental nature, the matrix approach should provide the basis for further experimental and theoretical advances in symmetry and symmetry-related topics in crystallography as well as in chemistry, physics and mathematics.

Program availability

A Fortran program, *NBS*LATTICE*, has been written to analyze lattice relationships and is available for distribution by the NBS Crystal Data Center. The present version of *NBS*LATTICE* performs several functions including the determination of metric lattice symmetry, the identification of unknown materials using lattice–formula matching techniques, the calculation of the reduced cell of the lattice, and the calculation and reduction of specified derivative supercells and/or subcells.

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A Joint Probability Distribution of Invariants for all Space Groups

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Abstract

A probability distribution is derived in the form of an infinite sum of cosine phase invariants between any number of structure factors and is applicable to any space group. No approximations are made. With the use of only the first-order terms, and the assumption that the reflection magnitudes are small and that all atoms are equal, the distributions reduce to the known invariant distribution forms. The effect of neighbourhood reflections is implicit in the form of the distribution.

1. Introduction

Joint probability distributions (j.p.d.'s) have been derived by many authors, *e.g.* Hauptman & Karle (1953), Klug (1958), Naya, Nitta & Oda (1965), Tsoucaris (1970), Hauptman (1974, 1975), Fortier & Hauptman (1977), Heinerman, Krabbendam & Kroon (1979), Giacovazzo (1974, 1975, 1976) and more recently Shmueli & Weiss (1985). Each of these treatments is applicable to a particular set of phases or a particular space group. The distribution described in this paper is general and is intended to serve as the starting point for the derivation of a specific formula, rather than deriving the distributions for each case of interest. The expressions presented have the advantage of separating the notational complexity of the derivation of distributions into two distinct areas. The first is the calculation of integral coefficients. The second is the search for a set of integers that satisfy the phase-invariant relationships.

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