

Lattices and Reduced Cells as Points in 6-Space and Selection of Bravais Lattice Type by Projections

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Abstract

A characterization of crystallographic unit cells as vectors in a Euclidean six-dimensional space (E^6 in the usual mathematical notation; here termed G^6) is introduced, in which the non-triclinic Bravais lattice types form one-, two-, three- and four-dimensional linear subspaces. This formalism makes the determination of the 'best' Bravais lattice (or lattices) for a particular experimentally determined cell a process of determining Euclidean distances in G^6 from the cell to its projections into the subspaces of the lattice types. The elements of vectors in the space are drawn from the Niggli matrix with the unsymmetrical elements doubled. A cell is first reduced and all its nearly Buerger-reduced cells are used in the distance determinations. Thus the smallest distance provides information about both the propriety of the lattice type selection and the instability of the cell reduction.

Introduction

The formal setting in which a problem is specified often foretells the first method that will be used to solve that problem.

(Blahut, 1985)

Besides merely being a finite set of rules which gives a sequence of operations for solving a specific type of problem, an algorithm has five important features: . . . Finiteness, . . . Definiteness, . . . Input, . . . Output, . . . Effectiveness.

(Knuth, 1973)

The concept of the reduced cell in crystallography has a long history, and a number of papers concerning the uses of reduced cells have been published in recent years. An important use is the assignment of the correct Bravais lattice of a crystal. The use of the reduced-cell formalism suffers from mathematical instabilities (Andrews, Bernstein & Pelletier, 1980); even the correct determination of the Bravais lattice is not ensured. The recent publication of several techniques which attempt to determine the correct Bravais lattice is an indication that the problem is not yet

solved [for example, Katayama (1986) states 'none of the programs is satisfactory enough to find the Bravais lattice automatically']. In this paper, we describe a modified formulation of unit-cell description and reduction, and we describe its use in several applications, including determination of the Bravais lattice.

New method

The method we propose is built on five observations. The first concerns the work of Gruber (1973). Table 2 of his paper lists the transformations which will generate all Buerger-reduced cells when the Niggli-reduced cell is known. The transformations generate alternate unit-cell choices for the lattice from which the Niggli cell was chosen. Any nearly reduced basis for which the base lengths differ by only small amounts from those of the Niggli basis will be found by use of these transformations and by the interchange of nearly equal-length axes and sign interchanges of near zeros. In this work, the metric tensor in the Euclidean space of six dimensions (E^6 in the usual mathematical notation, here termed G^6 to acknowledge the contributions of Gruber in this field) is assumed to be a unit tensor.

If two of the reduced-cell base vectors or the base vectors of a nearly Buerger-reduced cell are nearly equal in length, then the search must include that basis and the bases generated by interchanging the two vectors of near-equal length. If all three base vectors are of similar length, then all six permutations of the three axes must be examined. The determination of axes that are nearly equal should be based on the measured standard deviations.

Thirdly, if one of the unsymmetrical scalars is nearly zero, then it is necessary to consider the possibility that its sign is incorrectly determined. In such cases, the rules about converting the reduced cells to standard presentation so that the angles are all acute or all obtuse must be relaxed for the near-zero scalar [conversion to standard presentation is termed 'normalization' by Gruber (1973) and by Křivý & Gruber (1976)].

The fourth observation concerns the mathematical form used to represent lattices and the operations for transforming from one unit cell of the lattice to another. The Niggli matrix is not a simple device for visualizing comparisons of lattices. Instead of treating the description of a lattice as a matrix, we will write it explicitly as a vector in the space G^6 (the six-dimensional space of real numbers). All the operations for transforming from centered to primitive representations, for cell reduction, and for searching for similar cells in a single lattice are linear operations in G^6 in this representation. This formulation leads to a simple natural metric for comparing lattices, for searching a database, for determining the best cell for each type of Bravais lattice, and for determining which Bravais lattice is probably best.

The last observation is that each of the 42 non-triclinic lattice types is a linear subspace in the space G^6 . This linearity means that the point in each subspace which is nearest to any experimentally determined cell (a single point in G^6) can be found by simply generating a perpendicular line from the point which represents the reduced basis of the experimental cell to the linear form.

Review of older methods

The recent literature contains at least six computational methods for determining the correct Bravais lattice of an experimentally determined unit cell.

Roof (1969) and Mighell & Rodgers (1980) discuss comparison of the Niggli matrix of a reduced cell with the 44 standard forms. Zimmermann & Burzlaff (1985) describe an analogous method using the 24 forms of the Delaunay reduction. These papers do not describe how such a comparison should be made or what the measure of correctness should be. As stated, these methods lack definiteness, and it is not clear that they are effective. An important problem is the lack of an appropriate metric for the necessary comparisons.

Himes & Mighell (1987) proposed the use of B matrices to determine which symmetry axes are present in a lattice. No metric is described which would indicate how close the test lattice is to a lattice of a particular type. 'Distances' from a Bravais form are found by examining averaged 'tolerance matrices'. It is clear that the method is not applicable to other purposes for which unit-cell reduction is used (such as for comparing two cells or for searching a database).

Ferraris & Ivaldi (1982) describe a procedure which attempts to determine the multiplicities of the lengths of the vectors in the lattice. For lattices which are close to the type which is sought, the method will work. However, there is no metric proposed, and such wording as 'might produce an apparent higher symmetry' and 'careful inspection of the list of vectors'

indicates that the method lacks definiteness. It is not hard to imagine cases where the multiplicity might be ambiguous. The method is probably not easily extended to other problems since vector spaces of infinite dimension do not have metrics.

Clegg (1981) describes a method which searches in the list of vectors in the lattice for those special vectors which are symmetry axes. Again, no general method of choosing an appropriate tolerance for the search is given, and the method is not suitable for problems other than Bravais lattice determination.

Andrews, Bernstein & Pelletier (1980) used a new description of lattices which is useful for problems other than Bravais lattice determination. They describe a least-squares technique for finding the 'best' Bravais lattice of each type. The occurrence of false minima in searches for correct Bravais lattices and the presence of limit points for $\alpha = \beta = \gamma = 90^\circ$ makes the method difficult to apply in some cases. These limit points cause the algorithm to be less sensitive to differences in angles than to edge lengths.

Le Page (1982) describes a program which determines the Bravais lattice by searching for possible twofold axes and by examining their spatial distribution. The method seems only to be suited to Bravais lattice determination.

Today, the term 'reduced cell' is often used as a synonym for the reduced cell defined by Niggli (1928). Niggli's definition is based on certain mathematical considerations of the properties of matrices; the rules for performing this reduction are described by Burzlaff, Zimmermann & de Wolff (1983), and by Křivý & Gruber (1976), and below in this work. Buerger (1957) attempted to give a more geometric definition. He defined the reduced cell as that which uses as base vectors the three shortest non-coplanar vectors of the lattice. Gruber (1973) has shown that there may be up to five Buerger-reduced cells which can be chosen from a single lattice. The relationships between such cells are not simply the alternate choice of the three shortest vectors and their inverses. Andrews, Bernstein & Pelletier (1980) addressed exactly this ambiguity. Much of the confusion about reduced cells and their use arises from this ambiguity, and it is the most important reason that the assignment of the correct Bravais lattice to an experimentally determined cell is a problem for which there was no previous general solution based on reduced cells.

When more than one Buerger-reduced cell can be found in a lattice, the Niggli-reduced cell is one of the Buerger-reduced cells. If a lattice has only one cell that meets the Buerger reduction criterion, then it is the Niggli-reduced cell. The other commonly used reduced cell is that of Delaunay (1933). The Delaunay-reduced cell is based upon geometrical criteria about the distances of nearby lattice points from a central one. If the Niggli-reduced cell has all obtuse angles, then it is identical to the Delaunay-

reduced cell. If the Niggli-reduced cell has all acute angles, then two of the unit-cell edges are also edges of the Delaunay-reduced cell. Gruber (1978) has suggested that in those cases where more than one Buerger-reduced cell exists in a lattice that the one with the smallest surface area be chosen as 'the reduced cell'. On the other hand, Zimmermann & Burzlaff (1985) choose the Buerger-reduced cell with maximal surface area, and they state that this choice is consistent with the Niggli rules. Other criteria can be found to select any of the Buerger-reduced cells as the one to consider as 'the reduced cell'. It is important to choose algorithms which are not sensitive to particular choices of reduced cell in those cases where more than one choice exists (Andrews, Bernstein & Pelletier, 1980). Further, it is important to allow for experimental error and to be able to determine that two lattices are only slight distortions of each other. Neither of these problems has been fully discussed in the literature.

Common implementations using the Niggli or Delaunay formalisms are sensitive to experimental error. The approach presented here avoids such a sensitivity by considering all the alternate approximately reduced cells.

Representation of a unit cell as a point in G^6

In the study of reduced cells, a conventional representation of a lattice is a matrix of six elements in two rows (the Niggli matrix):

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

The first row is often called the symmetrical scalars, and the second is called the unsymmetrical scalars. The operations for transforming between unit cells are conventionally represented as 3×3 matrices (really tensors) which operate on the base vectors of the lattice (represented as a vector of three vectors) and therefore only indirectly on the Niggli matrix. The problems with this formalism are that the operators do not operate directly on the Niggli matrix representation, that there is no concept of a metric for comparing two lattices, and that the Niggli matrix has no easily visualized meaning. In an alternate formulation, the operations are performed directly on the Niggli matrix entries; this representation also does little to aid in a physical understanding of the process.

It is clear that six parameters are required to describe unit cells. The representation of lattices as vectors in a six-dimensional space leads to a system which is simpler to understand. In the space G^6 (the

Euclidean space of six dimensions), the vectors are

$$\mathbf{g} = \begin{pmatrix} \mathbf{a} \cdot \mathbf{a} \\ \mathbf{b} \cdot \mathbf{b} \\ \mathbf{c} \cdot \mathbf{c} \\ 2\mathbf{b} \cdot \mathbf{c} \\ 2\mathbf{a} \cdot \mathbf{c} \\ 2\mathbf{a} \cdot \mathbf{b} \end{pmatrix} = \begin{pmatrix} |\mathbf{a}|^2 \\ |\mathbf{b}|^2 \\ |\mathbf{c}|^2 \\ 2|\mathbf{b}||\mathbf{c}|\cos(\alpha) \\ 2|\mathbf{a}||\mathbf{c}|\cos(\beta) \\ 2|\mathbf{a}||\mathbf{b}|\cos(\gamma) \end{pmatrix} = \begin{pmatrix} g_1 \\ g_2 \\ g_3 \\ g_4 \\ g_5 \\ g_6 \end{pmatrix}.$$

This representation follows Gruber (1973) by including the factor of two in the unsymmetrical scalars. If that factor is included, then the numerical range of the 'unsymmetrical' scalars is the same as that of the 'symmetrical' ones. Inclusion of the principal diagonal of the first orthant within the region of space that contains valid unit cells means that permutations of the axes of reduced cells fill the first orthant instead of leaving an 'impossible' region surrounding that diagonal. In addition, there are fewer factors of two and of one-half in the transformations shown below.

The above representation leads to a simpler system of operations and to simpler interpretation than does the conventional dual system of representations (cells and Niggli matrices). The operators are simple 6×6 matrices which transform one vector in G^6 into another, rather than tensors which operate on vector triples which must then be transformed into the Niggli matrix or sets of operations on Niggli matrices whose geometrical meaning is not simple. The required operators are those for converting representations in centered lattices into the corresponding primitive ones, those for performing cell reduction, and those for searching for nearly reduced bases.

In addition, linear operations give the representation of best cell of each Bravais lattice type. The orientation of the base vectors is lost in the process of representing a lattice in G^6 . As pointed out by Křivý & Gruber (1976), more than one series of transformations may be found to convert from an arbitrary basis to a reduced basis. Because the path is not unique, the loss of orientation information is not important; the base vectors in 3-space can be determined later. Perhaps the most important advantage of representing lattices as points in a metric space rather than as matrices is that a distance measure is available.

Operators for transforming from centered lattices to primitive lattices

The transformation of a lattice from a centered representation to a primitive representation must precede cell reduction. The transformations in G^6 are given in Table 1. As an example, one possible transformation for a centered lattice is derived.

Let the original body-centered cell be represented by base vectors in 3-space \mathbf{a}_1 , \mathbf{b}_1 , and \mathbf{c}_1 and by the

Table 1. Operations in G^6 for converting representations of centered lattices to the corresponding primitive lattice

For lattice type R the transformation is for rhombohedral lattices written as hexagonal.

$$\mathbf{g}_P = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ 0 & 1 & 0 & \frac{1}{2} & 0 & \frac{1}{2} \\ 1 & 0 & 0 & 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \mathbf{g}_I$$

$$\mathbf{g}_P = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & 0 & 0 \\ 0 & 1 & 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \mathbf{g}_A$$

$$\mathbf{g}_P = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ \frac{1}{4} & \frac{1}{4} & 0 & 0 & 0 & \frac{1}{4} \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & \frac{1}{2} \end{pmatrix} \mathbf{g}_C$$

$$\mathbf{g}_P = \begin{pmatrix} \frac{1}{4} & \frac{1}{4} & 0 & 0 & 0 & \frac{1}{4} \\ \frac{1}{4} & 0 & \frac{1}{4} & 0 & \frac{1}{4} & 0 \\ 0 & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ 0 & \frac{1}{2} & 0 & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ \frac{1}{2} & 0 & 0 & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \end{pmatrix} \mathbf{g}_F$$

$$\mathbf{g}_P = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ \frac{1}{4} & 0 & \frac{1}{4} & 0 & \frac{1}{4} & 0 \\ 0 & 0 & 0 & \frac{1}{2} & 0 & \frac{1}{2} \\ 1 & 0 & 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \mathbf{g}_B$$

$$\mathbf{g}_P = \begin{pmatrix} \frac{4}{9} & \frac{4}{9} & \frac{4}{9} & \frac{2}{9} & \frac{2}{9} & \frac{4}{9} \\ \frac{1}{9} & \frac{1}{9} & \frac{1}{9} & \frac{1}{9} & -\frac{1}{9} & -\frac{1}{9} \\ \frac{1}{9} & \frac{4}{9} & \frac{1}{9} & -\frac{2}{9} & -\frac{1}{9} & -\frac{2}{9} \\ \frac{1}{9} & \frac{4}{9} & \frac{2}{9} & -\frac{1}{9} & 0 & \frac{1}{9} \\ -\frac{2}{9} & -\frac{4}{9} & \frac{2}{9} & -\frac{1}{9} & 0 & \frac{1}{9} \\ -\frac{4}{9} & -\frac{8}{9} & \frac{2}{9} & 0 & \frac{1}{9} & -\frac{6}{9} \\ -\frac{4}{9} & \frac{4}{9} & \frac{2}{9} & \frac{3}{9} & \frac{1}{9} & 0 \end{pmatrix} \mathbf{g}_R$$

corresponding G^6 vector \mathbf{g}_I . One choice for the base vectors of the primitive lattice is $\mathbf{a}_P = \mathbf{a}_I$, $\mathbf{b}_P = \mathbf{b}_I$ and $\mathbf{c}_P = (\mathbf{a}_I + \mathbf{b}_I + \mathbf{c}_I)/2$. Computing the vector \mathbf{g}_I from these equations gives the equations

$$\mathbf{a}_P \cdot \mathbf{a}_P = \mathbf{a}_I \cdot \mathbf{a}_I$$

$$\mathbf{b}_P \cdot \mathbf{b}_P = \mathbf{b}_I \cdot \mathbf{b}_I$$

$$\mathbf{c}_P \cdot \mathbf{c}_P = (\mathbf{a}_I \cdot \mathbf{a}_I + \mathbf{b}_I \cdot \mathbf{b}_I + \mathbf{c}_I \cdot \mathbf{c}_I + 2\mathbf{a}_I \cdot \mathbf{b}_I + 2\mathbf{a}_I \cdot \mathbf{c}_I + 2\mathbf{b}_I \cdot \mathbf{c}_I)/4$$

$$2\mathbf{b}_P \cdot \mathbf{c}_P = \mathbf{b}_I \cdot \mathbf{b}_I + (2\mathbf{a}_I \cdot \mathbf{b}_I + 2\mathbf{b}_I \cdot \mathbf{c}_I)/2$$

$$2\mathbf{a}_P \cdot \mathbf{c}_P = \mathbf{a}_I \cdot \mathbf{a}_I + (2\mathbf{a}_I \cdot \mathbf{b}_I + 2\mathbf{a}_I \cdot \mathbf{c}_I)/2$$

$$2\mathbf{a}_P \cdot \mathbf{b}_P = 2\mathbf{a}_I \cdot \mathbf{b}_I$$

Table 2. Operations in G^6 for permuting axes of a cell

$$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}$$

Expressed as a matrix/vector equation, these equations are the transformation from a body-centered to a primitive representation in G^6 given in Table 1. The inverse transformation may be used to go from a primitive representation to one that is body-centered.

Cell reduction – part I: conversion to standard presentation

At each step during the cell reduction process, the current choice of base vectors is relabeled such that $\mathbf{a} \cdot \mathbf{a} < \mathbf{b} \cdot \mathbf{b} < \mathbf{c} \cdot \mathbf{c}$. This choice is arbitrary, and any of the permutations $\mathbf{a} \cdot \mathbf{a} < \mathbf{c} \cdot \mathbf{c} < \mathbf{b} \cdot \mathbf{b}$, $\mathbf{b} \cdot \mathbf{b} < \mathbf{a} \cdot \mathbf{a} < \mathbf{c} \cdot \mathbf{c}$, $\mathbf{b} \cdot \mathbf{b} < \mathbf{c} \cdot \mathbf{c} < \mathbf{a} \cdot \mathbf{a}$, $\mathbf{c} \cdot \mathbf{c} < \mathbf{a} \cdot \mathbf{a} < \mathbf{b} \cdot \mathbf{b}$, $\mathbf{c} \cdot \mathbf{c} < \mathbf{b} \cdot \mathbf{b} < \mathbf{a} \cdot \mathbf{a}$ could be used. In G^6 these six permutations are related by the symmetry operations resembling $m\bar{3}$ in the space E^3 . The operations relating the G^6 representations of the permutations are given in Table 2.

Any one convention can be converted to another by applying an appropriate operation. In this sense, conversion to standard presentation is only the choice of the correct (arbitrarily chosen) asymmetric unit of the G^6 point group representing the unit cells. If $|\mathbf{a}| = |\mathbf{b}|$ or $|\mathbf{b}| = |\mathbf{c}|$ or $|\mathbf{a}| = |\mathbf{b}| = |\mathbf{c}|$, then another arbitrary decision must be made: how to decide to which asymmetric unit a point should be assigned. A number of rules exist for deciding which permutation of the axes to choose in these cases. If the methodology is stable to perturbation, the choice does not need to be made (Andrews, Bernstein & Pelletier, 1980; Le Page, 1982); any choice should yield a correct answer. If the methodology is not perturbation stable then the choice is crucial, and a further choice of degree of accuracy during cell reduction must be made (Mighell, 1976). How this choice is to be made has not been described in the literature. Although making this choice may aid in determining the correct Bravais lattice in some cases, it will invariably lead to cases where the assignment will be incorrect and to cases where two nearly identical unit cells have very different reduced cells. Database searching will

be misleading because matches between nearly identical cells will fail.

Cell reduction – part II: reduction

Cell reduction is the process of finding a unique primitive basis which has the shortest vectors subject to certain conditions. If at any step in cell reduction the cell is not reduced, then a new choice of a base vector is made. The new vector may be chosen as the shortest among the face and body diagonals of the current cell. Krivý & Gruber (1976) have given a set of four operations for performing each step for which general or special conditions are not satisfied. Their algorithm, rewritten in G^6 (and modified so that the general conditions are always satisfied before the special conditions are tested) is described in the next section.

Algorithm

The algorithm is divided into two parts: conversion to standard presentation (steps SP1 through SP4) and reduction (steps R5 through R14). The term ‘conversion to standard presentation’ is introduced here as a replacement for the term ‘normalization’ used by Gruber (1973) and Krivý & Gruber (1976) in order to allow the unambiguous use of normalization in its conventional mathematical meaning (for vectors) of conversion to unit length. A function, sign , is defined such that

$$\begin{aligned}\text{sign}(x) &= +1 \text{ if } x > 0; \\ \text{sign}(x) &= -1 \text{ if } x < 0.\end{aligned}$$

SP1. If $(g_1 > g_2)$ or $(g_1 = g_2 \text{ and } |g_4| > |g_5|)$, then interchange the a and b axes.

$$\mathbf{g}' = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \mathbf{g}.$$

SP2. Else if $(g_2 > g_3)$ or $(g_2 = g_3 \text{ and } |g_5| > |g_6|)$, then interchange the b and c axes.

$$\mathbf{g}' = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \mathbf{g}.$$

SP3. Else if $g_4 g_5 g_6 > 0$, then set g_4, g_5, g_6 positive.

$$\mathbf{g}' = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \text{sign}(g_4) & 0 & 0 \\ 0 & 0 & 0 & 0 & \text{sign}(g_5) & 0 \\ 0 & 0 & 0 & 0 & 0 & \text{sign}(g_6) \end{pmatrix} \mathbf{g}.$$

SP4. Else (where $g_4 g_5 g_6 \leq 0$, always), then set g_4, g_5 and g_6 negative.

$$\mathbf{g}' = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\text{sign}(g_4) & 0 & 0 \\ 0 & 0 & 0 & 0 & -\text{sign}(g_5) & 0 \\ 0 & 0 & 0 & 0 & 0 & -\text{sign}(g_6) \end{pmatrix} \mathbf{g}.$$

Endif (end of conversion to standard presentation).

R5. If $|g_4| > g_2$, then
 $s = \text{sign}(g_4)$

$$\mathbf{g}' = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & -s & 0 & 0 \\ 0 & -2s & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -s \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \mathbf{g}.$$

R6. Else if $|g_5| > g_1$, then
 $s = \text{sign}(g_5)$

$$\mathbf{g}' = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & -s & 0 \\ 0 & 0 & 0 & 1 & 0 & -s \\ -2s & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \mathbf{g}.$$

R7. Else if $|g_6| > g_1$, then
 $s = \text{sign}(g_6)$

$$\mathbf{g}' = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 & -s \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & -s & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ -2s & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \mathbf{g}.$$

R8. Else if $g_1 + g_2 + g_4 + g_5 + g_6 < 0$, then

$$\mathbf{g}' = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & 1 \\ 0 & 2 & 0 & 1 & 0 & 1 \\ 2 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \mathbf{g}.$$

R9. Else if ($g_2 = g_4$ and $2g_5 < g_6$) or ($g_2 = -g_4$ and $g_6 < 0$), then same operations as R5.

R10. Else if ($g_1 = g_5$ and $2g_4 < g_6$) or ($g_1 = -g_5$ and $g_6 < 0$), then same operations as R6.

R11. Else if ($g_1 = g_6$ and $2g_4 < g_5$) or ($g_1 = -g_6$ and $g_6 < 0$), then same operations as R7.

R12. Else if ($g_1 + g_2 + g_4 + g_5 + g_6 = 0$ and $2g_1 + 2g_5 + g_6 > 0$), then same operations as R8.

R13. Otherwise exit from looping, because the cell is Niggli reduced.

R14. Go to step SP1.

Searching for nearly reduced cells

Gruber (1973) dealt with the problem of determining whether several cells which are Buerger reduced can be found in a lattice. When a lattice has several Buerger-reduced cells, there can be special problems (for instance, for cell comparison or database searching); these were solved by Andrews, Bernstein & Pelletier (1980) who used an algorithm which works but which has difficulties due to limit points (in the sense of conformal mapping) whenever an interaxial angle is near 90° . Mighell & Himes (1986) describe the difficulties that these lattices cause in database searches, and they promise to publish a program to solve the problem. Andrews, Bernstein & Pelletier (1980) have published one solution using a seven-parameter representation (reduced cell lengths, reduced reciprocal-cell lengths and the cell volume). These lattices also cause problems in the determination of the correct Bravais lattice. For example, face-centered cubic lattices have two Buerger-reduced cells. Only one of these is Niggli reduced. However, a small distortion of the lattice can cause the other Buerger-reduced cell to become the Niggli-reduced cell and the previously Niggli-reduced cell to become non-reduced [for examples, see Andrews, Bernstein & Pelletier (1980)]. Since the cells have quite different shapes, programs for Bravais lattice identification may fail to find the correct Bravais lattice in these cases.

Gruber (1973) enumerated the 24 transformations of a lattice which must be searched in order to seek alternative Buerger-reduced cells. This is the same set of transformations which is used here to search for nearly Buerger-reduced cells. The original purpose was only to seek bases which have base vectors of

the same lengths as those of the Niggli-reduced basis. Gruber (1973) limited the transformations to those that generate cells on the border of the region of reduced cells. Unlike the purpose of Gruber (1973), a perturbation-stable search may need cells which are not in adjacent asymmetric units. The 24 transformations are applied recursively to any nearly Buerger-reduced cells that are found as well as to those of the Niggli-reduced cell until no new nearly Buerger-reduced cells are found. In addition, axes which are nearly equal in length must be interchanged (using the operators in Table 2). If near-zeros of the unsymmetrical scalars occur, then the all-acute all-obtuse rule must be relaxed. In a sense, this is like the *B*-matrix search of Himes & Mighell (1982), but only a finite number of iterations is required, because the starting point is a reduced cell. The transformation matrices in G^6 are given in Table 3.

Bravais lattice determination

The 42 non-triclinic lattice types are listed in many places. The enumerations of Roof (1969) and of Burzlaff, Zimmermann & de Wolff (1983) are convenient because they list the Niggli matrix restrictions for each lattice. If the Niggli matrix exactly matches one of the matrices for one of the 42 types, then the choice may be fairly simple. However, some allowance for errors in measurement must be made [discussed by Andrews, Bernstein & Pelletier (1980)]. Problems arise from the determination of a single best choice; for instance, a cell may be exactly orthorhombic, but a sufficiently large error allowance will produce a tetragonal or cubic cell. Zimmermann & Burzlaff (1985) and Le Page (1982) have reported programs which produce multiple indications of possible Bravais lattices.

In G^6 the problem of Bravais lattice determination is simple. Each of the 42 non-triclinic lattice types is a linear subspace (hyperplane) which intersects the origin. The cubic cells are linear subspaces of order 1 (lines), the tetragonal, hexagonal, and rhombohedral cells are order 2 (planes), the orthorhombic cells are order 3, and monoclinic cells are order 4 (triclinic cells are order 6, that is they may occur anywhere in G^6 that represents a valid cell). The specifications of the subspaces of the 42 types are listed in Table 4.

Example: simple cubic, $a = a_P$

$$\mathbf{g}_{P\text{-cubic}} = a_P^2 \begin{pmatrix} 1 \\ 1 \\ 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}.$$

Table 3. Operations in G^6 for searching for nearly Buerger-reduced cells

Example: primitive orthorhombic, $a = a_0, b = b_0, c = c_0$

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

$$\mathbf{g}_{P\text{-ortho}} = \begin{pmatrix} a_0^2 \\ b_0^2 \\ c_0^2 \\ 0 \\ 0 \\ 0 \end{pmatrix}.$$

The simple cubic cells all occur on the line $g_1 = s, g_2 = s, g_3 = s, g_4 = 0, g_5 = 0, g_6 = 0$, where s is an arbitrary parameter. The primitive tetragonal cells (c unique) all occur on the plane $g_1 = s, g_2 = s, g_3 = t, g_4 = 0, g_5 = 0, g_6 = 0$, where s and t are arbitrary parameters.

For a given cell, the perpendicular projection of the G^6 point which represents the reduced basis or the projection of one of the nearly Buerger-reduced bases onto each of the 42 hyperplanes gives 42 'best' cells of the lattice types. These are 'best' cells in the least-squares sense in G^6 . The distance of the determined point from each hyperplane is the measure of how good the fit of that lattice type is for the cell being examined. Propagation of the errors of the original cell constants can produce a measure in standard deviations of the fit. In keeping with actual measurement, there is never a single best lattice type; the agreement of each lattice type is simply determined.

Example

What is the best simple cubic cell for the primitive orthorhombic cell $a = 4.9, b = 5.0, c = 5.1 \text{ \AA}$?

In G^6 the base vector of the simple cubic cells is

$$\mathbf{b} = (\sqrt{3}/3) \begin{pmatrix} 1 \\ 1 \\ 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}.$$

For the orthorhombic cell,

$$\mathbf{g}_0 = \begin{pmatrix} 24.01 \\ 25.00 \\ 26.01 \\ 0 \\ 0 \\ 0 \end{pmatrix}.$$

The projection of \mathbf{g} onto \mathbf{b} is the dot product of \mathbf{g} and \mathbf{b} times \mathbf{b} .

Example: face-centered cubic, $a = a_F$

$$\mathbf{g}_{F\text{-cubic}} = a_F^2 \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}.$$

Dot product = $(\sqrt{3}/3) \times 75.02$.

$$\mathbf{g}_{\text{best-cubic}} = (1/3) \begin{pmatrix} 75.02 \\ 75.02 \\ 75.02 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 25.0067 \\ 25.0067 \\ 25.0067 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\mathbf{g}_{\text{best-cubic}} - \mathbf{g}_0 = \begin{pmatrix} 0.9967 \\ 0.01 \\ -1.0033 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\text{Error} = [0.9967^2 + (-1.0033)^2 + 0.01^2]^{1/2} = 1.41426$$

$$|\mathbf{g}_{\text{best-cubic}}| = (\sqrt{3})a^2 = 43.3 \pm 1.414$$

$$a = 5.002 \pm 0.082.$$

To produce a set of base vectors in G^6 for any of the 42 lattice types, it is only necessary to produce four random vectors in G^6 which meet the requirements of the lattice type. The four vectors are then converted to a basis set by Gram-Schmidt orthonormalization [Chow (1983) or standard books on linear algebra]. If the lattice type is of order less than four, then the Gram-Schmidt process will find only the appropriate number of non-zero base vectors. The conditions (except for normalization to unit length) that the base vectors must obey are listed in Table 4.

In order to determine possible Bravais lattices, the reduced cell and all the nearly Buerger-reduced cells of a lattice must be determined. Then the G^6 representations of each of those cells are projected onto the linear subspace of each Bravais lattice type to find which is the closest to the hyperplane of that lattice type. The distance of the closest cell to each linear subspace is the measure of goodness of fit for that type of lattice.

Comparison of two lattices

The first step in comparing two experimental lattice (unit-cell) determinations in order to see if they are different is to reduce the cells. If the reduced cells are the same, then the process is finished. In G^6 , the cells are the same if the distance between them is small (perhaps in the sense of a small number of standard deviations). If the cells differ, but g_1 , g_2 and g_3 are similar in magnitude, then there may be a nearly Buerger-reduced cell of one cell that nearly matches the reduced cell of the other. One of the two original cells is chosen, and its nearly Buerger-reduced cells (if any) are compared with the other cell to see if any near match exists.

Table 4. *The linear subspaces in G^6 describing each of the 42 nontriclinic Bravais lattice types*

The column headings refer to the designations of Roof (1969) and of Burzlaff, Zimmermann & de Wolff (1983). The symbols r , s , t and u may be chosen to have arbitrary values. Any random selection of values will be included in the appropriate linear subspace, but it may not be a physically meaningful unit cell. For instance, no actual unit cell will have a negative unit-cell edge length or an angle with a cosine larger than 1.00. To make a set of basis vectors, the vectors need to be normalized to unit length in G^6 .

Lattice type	Roof's label	International Tables	Linear subspace
<i>cP</i>	44A	3	$(r, r, r, 0, 0, 0)$
<i>cI</i>	44B	5	$(r, r, r, -2r/3, -2r/3, -2r/3)$
<i>cF</i>	44C	1	(r, r, r, r, r, r)
<i>tP</i>	45A	11	$(r, r, s, 0, 0, 0)$
	45B	21	$(r, s, s, 0, 0, 0)$
<i>tI</i>	45C	15	$(r, r, s, -r, -r, 0)$
	45D	6	$(r, r, r, -r-s, -r-s, 2s)$
	45D	7	$(r, r, r, 2s, -r-s, -r-s)$
	45E	18	$(r, s, s, r/2, r, r)$
<i>hP</i>	48A	12	$(r, r, s, 0, 0, -r)$
	48B	22	$(r, s, s, -s, 0, 0)$
<i>hR</i>	49B	9	(r, r, s, r, r, r)
	49C	2	(r, r, r, s, s, s)
	49D	4	(r, r, r, s, s, s)
	49E	24	$(r, s, s, -s + (r/3), -r, -r)$
<i>oP</i>	50C	32	$(r, s, t, 0, 0, 0)$
<i>oS</i>	50A	36	$(r, s, t, 0, -r, 0)$
	50B	38	$(r, s, t, 0, 0, -r)$
	50D	13	$(r, r, s, 0, 0, t)$
	50E	23	$(r, s, s, t, 0, 0)$
	50F	40	$(r, s, t, -s, 0, 0)$
<i>oF</i>	51A	16	$(r, r, s, t, t, -2r-2t)$
	51B	26	$(r, s, t, r/2, r, r)$
<i>oI</i>	52A	8	$(r, r, r, s, t, -2r-s-t)$
	52B	19	(r, s, s, t, r, r)
	52C	42	$(r, s, t, -s, -r, 0)$
<i>mP</i>	53A	33	$(r, s, t, 0, u, 0)$
	53B	35	$(r, s, t, u, 0, 0)$
	53C	34	$(r, s, t, 0, 0, u)$
<i>mS</i>	54A	39	$(r, s, t, u, 0, -r)$
	54B	41	$(r, s, t, -s, u, 0)$
	54C	37	$(r, s, t, u, -r, 0)$
	55A	10	(r, r, s, t, t, u)
	55A	14	(r, r, s, t, t, u)
	55B	20	(r, s, s, t, u, u)
	55B	25	(r, s, s, t, u, u)
	56A	28	$(r, s, t, u, r, 2u)$
	56B	30	$(r, s, t, s, u, 2u)$
	56C	29	$(r, s, t, u, 2u, r)$
	57A	43	$(r, s, t, -s-u, -r-u, 2u)$
	57B	17	$(r, r, s, t, u, -2r-t-u)$
	57C	27	(r, s, t, u, r, r)

Searching a database of unit-cell parameters

There are two ways to organize a search within a database of known unit cells. Either the database keyset may be kept small, with a corresponding increase in search time, or the database may be enlarged with an increase in the time to set it up initially.

1. Increased search time with a smaller database

The reduced cells are computed for all the entries in the database. The six parameters of the cell in G^6 are used as the keys. When the database is to be searched for an unknown, the Niggli-reduced cell of

the unknown is computed, and so are all the nearly Buerger-reduced cells. The G^6 representation of each of these cells is used to search in the database with some specified tolerance. Any database entry within some user-specified distance in G^6 is reported as a match.

II. Decreased search time with a larger database

The reduced cells and all of the nearly Buerger-reduced cells of each of the experimental cells are computed for all entries in the database. All these G^6 vectors are loaded into the database. The reduced cell and the nearly Buerger-reduced cells for any entry should all point to a single item; in this way, only the key size is increased. When an unknown is sought in the database, only the representation of its Niggli-reduced cell is needed for the search. The tolerance specifications are as before except that a tolerance limit is also needed for deciding whether to include any particular nearly Buerger-reduced cell.

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APPENDIX

A referee has requested a more complete description of the calculations relating to the hyperplanes representing the lattice types (the generation of the base vector set for a lattice type and the determination of the distance from a hyperplane). Although slightly tedious, the computations for any given case can be performed by hand, and they are easily done on some hand calculators. The entire computation except for reduction and orthonormalization is shown for one case. For hand calculations, the orthonormalization and the subsequent arithmetic can be greatly simplified in most cases by choosing the random numbers to be 0's and 1's (being sure to get a linearly independent set of starting vectors).

Generation of a set of base vectors

For this particular example, the base vectors will be computed for the rhombohedral cells with α greater than 109.49° (*International Tables* designation 24). The generic form for the base vectors (from Table 4) is

$$(r, s, s, -s + (r/3), -2r/3, -2r/3).$$

Two base vectors will be needed because there are two variables. For each of the base vectors, we generate two random numbers; one we call r and the other s . Computation of the other G^6 components to make vectors of the generic form gives

$$\begin{pmatrix} 0.17 \\ -0.25 \\ -0.25 \\ 0.30 \\ -0.11 \\ -0.11 \end{pmatrix} \begin{pmatrix} 0.31 \\ -0.62 \\ -0.62 \\ 0.73 \\ -0.21 \\ -0.21 \end{pmatrix}.$$

Performing a Gram-Schmidt orthonormalization [Chow (1983) or any standard book on linear algebra] on the above set produces the following pair of orthonormal (that is, unit-length and with null dot product) base vectors:

$$\begin{pmatrix} 0.32277 \\ -0.47908 \\ -0.47908 \\ 0.58667 \\ -0.21518 \\ -0.21518 \end{pmatrix} \begin{pmatrix} -0.63660 \\ -0.33182 \\ -0.33182 \\ 0.11962 \\ 0.42440 \\ 0.42440 \end{pmatrix}.$$

Any linear combination of these vectors is also an acceptable set of base vectors. To generate a G^6 basis set orthogonal to this pair, choose four random six-element vectors and (without modifying them to fit the current case) continue the Gram-Schmidt process, starting with the above two vectors.

Determination of a 'best cell'

Start with the primitive cell $a = b = c = 10 \text{ \AA}$ and $\alpha = 112$, $\beta = 112.5$ and $\gamma = 112.9^\circ$. The corresponding G^6 vector is $(100, 100, 100, -74.9, -76.5, -77.8)$ where each element has the units of \AA^2 . The reduced cell is $a = 8.41$, $b = 10$, $c = 10 \text{ \AA}$, $\alpha = 112$, $\beta = 106.3$, $\gamma = 106.8^\circ$. The reduced G^6 vector is $(70.7, 100, 100, -74.9, -47.3, -48.5)$. Next the dot products of the reduced vector with the two base vectors are computed; they are -96.3 and -161.0 respectively. Multiplying the base vectors by their respective dot products gives the projections of the reduced vector onto the base vectors. Adding the two projections gives the best least-squares fit (in the space G^6) to case 24.

$$\begin{pmatrix} 71.39 \\ 99.57 \\ 99.57 \\ -75.77 \\ -47.60 \\ -47.60 \end{pmatrix} = \begin{pmatrix} -31.09 \\ 46.15 \\ 46.15 \\ -56.51 \\ 20.73 \\ 20.73 \end{pmatrix} + \begin{pmatrix} 102.48 \\ 53.42 \\ 53.42 \\ -19.26 \\ -68.32 \\ -68.32 \end{pmatrix}.$$

Note that the determined best fit is independent of the particular pair of base vectors. The resulting vector meets the requirements of case 24. The result vector is converted to the reduced cell (8.45, 9.98, 9.98, 112.4, 106.4, 106.4) which is the best least-squares fit of the original cell to case 24. The corresponding unreduced rhombohedral cell has $a = 9.98 \text{ \AA}$, $\alpha = 112.4^\circ$.

The error of the fit can be computed in two ways: either the reduced vector can be projected onto a set of G^6 base vectors normal to the base vectors of the particular case (the length of the sum of the projections being the error), or the length of the difference between the best-fit vector and the G^6 vector before projection can be computed. The latter difference is

$$\begin{pmatrix} -0.69 \\ 0.43 \\ 0.43 \\ 0.87 \\ 0.30 \\ -0.90 \end{pmatrix} = \begin{pmatrix} 70.70 \\ 100.00 \\ 100.00 \\ -74.90 \\ -47.30 \\ -48.50 \end{pmatrix} - \begin{pmatrix} 71.39 \\ 99.57 \\ 99.57 \\ -75.77 \\ -47.60 \\ -47.60 \end{pmatrix}$$

with a length of 1.6 \AA (from the reduced vector to the best fit in case 24). In practice, this length should be compared with the error computed from the determination of the unit-cell parameters. For small molecules, diffractometers normally produce error vectors with lengths in the range 0.05 to 0.4 \AA^2 . On the basis of this rule of thumb, the proposal that the original cell is rhombohedral should probably be rejected in the absence of other evidence. Certainly the differences in the original angles are outside the usual error bounds for diffractometers.

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The Use of E -Magnitude Filters in Direct Methods

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Abstract

In direct methods difficulties can be experienced in solving structures in situations where data of high resolution are being used very early in the phasing process; in real space, this tends to build too much atomic detail before the molecular outline is fully

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