A matrix method for lattice symmetry determination.

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Abstract

A general approach for the determination of metric lattice symmetry has been successfully tested on ~30 000 lattices from the National Bureau of Standards Crystal Data File. The central focus of the method is on the determination of matrices relating any primitive cell of the lattice to itself rather than on determining reduced cells or conventional cells. The method can conveniently be used in routine structure work as it readily detects the highest possible metric symmetry within any specified range of cell-parameter errors.

A previous study based on classification according to reduced form has shown that the crystal lattice symmetry and the metric lattice symmetry are usually identical for molecular compounds (Mighell & Rodgers, 1980). Although reduction procedures can reliably be used to determine metric symmetry, there are several non-trivial problems with the method when used automatically without human interaction. Firstly, when calculating the reduced cell, experimental errors cause problems in treating the inequalities inherent in the special conditions for reduction. Occasionally, more than one 'reduced' cell is possible depending on how the errors are treated. Secondly, one must transform an experimentally determined cell to the reduced cell and properly identify the form of the reduced cell matrix. Thirdly, it is difficult to establish all possible pseudo-symmetries when using reduction procedures. Having recognized the problem of experimental error, Clegg (1981) offers an alternative method to obtain the correct Bravais lattice from the reduced cell. However, we recommend a new, general approach to determine metric lattice symmetry. The central focus of the method described herein is on determining matrices that relate any primitive unit cell to itself rather than on obtaining reduced cells and conventional cells.

In a recent paper, it was shown that properties of lattices can be derived from the nature of the transformation matrices relating unit cells in the same or in different lattices (Santoro, Mighell & Rodgers, 1980). An algorithm (**B** matrix) was presented that determines the matrices **B** in the following equation:

$$\mathbf{a}_i = \sum_j B_{ij} \, \mathbf{a}_j \quad (i, j = 1, 2, 3),$$

where $\mathbf{a}_i$ and $\mathbf{a}_j$ define two primitive triplets of noncoplanar translations (a triplet is called *primitive* when it defines a

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primitive cell; *International Tables for X-ray Crystallography*, 1969). We have found that the **B**-matrix algorithm can be used to determine metric lattice symmetry. To determine symmetry using the algorithm, one selects a primitive cell and then determines how many ways it can be transformed into itself to within any specified tolerance of the unit-cell parameters. Only **B** matrices with integer elements and a determinant of +1 are considered. The greater the number of matrices found, the higher the symmetry. Using the algorithm, the number of matrices for the seven lattice metric symmetries are: triclinic, 1; monoclinic, 2; orthorhombic, 4; rhombohedral, 6; tetragonal, 8; hexagonal, 12; and cubic, 24.

In contrast to reduction techniques, one can deduce the lattice symmetry from any primitive cell that has been determined, without transformation to a standard cell. Consider the example of cell *A*, a primitive unit cell which was determined on our diffractometer. The matrix procedure yielded a set of four matrices with integer elements ranging from 0 to ±4. When the original cell was reduced (cell *B*) and analyzed by the matrix procedure, a different set of four integer-only matrices was obtained with elements of 0 and ±1. In each case, the orthorhombic symmetry of the conventional unit cell (cell *C*; *C* centered) was predicted.

Cell *A*:	8·095 (6)	8·096 (6)	30·667 (25) Å
	88·69 (6)	57·95 (5)	87·48 (6)°
Cell *B*:	8·095	8·096	25·996 Å
	90·02	90·19	92·52°
Cell *C*:	11·694 (3)	11·192 (2)	25·961 (5) Å
	89·98 (2)	90·04 (3)	89·97 (3)°.

The most important features of this method are that one can determine the highest possible metric symmetry within a specified tolerance and that pseudo-symmetries are immediately apparent. To ensure that all potentially interesting matrices are generated, a relatively large tolerance for cell-parameter errors should be used (the program execution times are essentially independent of the magnitudes of the tolerances selected). The treatment of experimental error is conceptually simpler than in reduction as one does not need to worry about the inequalities inherent in reduction theory. Our experience shows that even when the experimental error is large, the matrix procedure correctly predicts the metric symmetry.

The matrix method may be used on a problem-to-problem basis to determine symmetry or it can be used to evaluate lattice symmetry critically in large sets of data. In our routine structure work, the matrix procedure has been used to determine symmetry as soon as a refined primitive cell has been obtained; in every case, the method gave the correct symmetry. When the unit cell is highly skewed, one must

Table 1. *Matrices found for a cubic primitive cell*

#										#									
1	−1	0	0	0	−1	0	0	0	1	13	0	0	1	−1	0	0	0	−1	0
2	−1	0	0	0	0	−1	0	−1	0	14	0	0	1	0	−1	0	1	0	0
3	−1	0	0	0	0	1	0	1	0	15	0	0	1	0	1	0	−1	0	0
4	−1	0	0	0	1	0	0	0	−1	16	0	0	1	1	0	0	0	1	0
5	0	−1	0	−1	0	0	0	0	−1	17	0	1	0	−1	0	0	0	0	1
6	0	−1	0	0	0	−1	1	0	0	18	0	1	0	0	0	−1	−1	0	0
7	0	−1	0	0	0	1	−1	0	0	19	0	1	0	0	0	1	1	0	0
8	0	−1	0	1	0	0	0	0	1	20	0	1	0	1	0	0	0	0	−1
9	0	0	−1	−1	0	0	0	1	0	21	1	0	0	0	−1	0	0	0	−1
10	0	0	−1	0	−1	0	−1	0	0	22	1	0	0	0	0	−1	0	1	0
11	0	0	−1	0	1	0	1	0	0	23	1	0	0	0	0	1	0	−1	0
12	0	0	−1	1	0	0	0	−1	0	24	1	0	0	0	1	0	0	0	1

allow the computer program to seek matrices with integer elements as high as ± 10 (typical computer run time of less than 5 s on an UNIVAC 1108). In contrast, when using reduced cells, matrix elements of 0 and ± 1 may be used (typical run time of about 0·03 s). The 24 matrices listed in Table 1 for a primitive cubic cell were output from the computer program used to calculate **B** matrices. Multiplication of the matrices in Table 1 by -1 generates a set of 48 matrices which are identical to those listed for the 48 symmetry operations compatible with a cubic lattice (Rigault, 1980).

Computer analysis of approximately 30 000 lattices from the National Bureau of Standards Crystal Data File has proved that the matrix procedure for metric symmetry determination is fast, efficient and reliable. The method predicts a metric lattice symmetry which, in most cases, is consistent with the reported crystal symmetry. In a relatively low percentage of cases, the matrix procedure predicts a higher symmetry. Our analysis has revealed that many rhombohedral crystals have been incorrectly reported in centered monoclinic or in triclinic space groups. The computer analysis has also shown that many metrically centered orthorhombic crystals have been reported in primitive monoclinic or in triclinic space groups. Further discussions are planned concerning the cases for which the metric symmetry exceeds the reported crystal symmetry.

It has become apparent that metric symmetry, and possibly crystal symmetry, is often missed by techniques employed on modern automated diffractometers. Ideally, the check for metric symmetry should be carried out as soon as a refined unit cell has been determined. Our experience shows that the matrix procedure offers a direct and convenient way to determine the metric lattice symmetry.

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Notes and News

Formation of the British Crystallographic Association

The following note by Professor D. M. Blow, Chairman of the UK National Committee for Crystallography, has been reprinted from the *Royal Society News*, by kind permission of the Royal Society:

For many years the organisation of crystallography at a national level in the UK has been split between a number of scientific societies. The two largest are the Crystallography Group of the Institute of Physics and the Chemical Crystallography Group of the Royal Society of Chemistry, but a number of other societies cover crystallographic aspects of metallurgy, materials science, geology and biophysics. The UK Crystallographic Council provided a loose link between groups of crystallographers but it could not provide a speedy, collective response of UK crystallographers on, for instance, draft Health and Safety Executive legislation or EEC directives. Nor did its structure allow it to undertake activities with financial responsibilities, such as the organisation of a European Crystallographic Meeting in the UK.

The British National Committee for Crystallography, in addition to its duties as corresponding body to the International Union of Crystallography, provided a forum where matters concerning crystallography in the UK could be discussed. But it was not appropriate for it to deal with