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Cell Reduction and Lattice Symmetry Determination

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Abstract

Simple inspection of the reduced form of a unit cell can fail to detect the correct lattice symmetry, because of the effects of measurement errors, computer rounding errors and uncertainties in interpretation of almost equal numbers. A procedure which is insensitive to these effects consists of the generation of a list of lattice vectors sorted on length, together with angles between pairs of them. The list includes the edges, face diagonals and body diagonals of the reduced cell, and the sums and differences of any of these which are similar in length. The correct unit cell is easily recognized in the vector list.

Introduction

The determination of the unit cell is an essential first step in a crystal structure determination, once a suitable single crystal has been obtained. With the development of computer-controlled diffractometers, this process has become progressively automated. On many machines it is now possible to mount and centre a crystal, and then leave the control software to locate reflexions and determine a unit cell without any human intervention. That such a use of automatic procedures can lead to the selection of unsuitable unit cells has been recently demonstrated (Marsh & Schomaker, 1979; Ilsley, Albright, Anderson, Glick & Oliver, 1980). Problems arise particularly when the cell is centred or has a very long axis.

Mighell & Rodgers (1980) have proposed that unit cells should be checked routinely by reduction procedures, and the correct Bravais lattice type deduced from the form of the reduced cell. The use of automatic procedures for the recognition and interpretation of the reduced form is, however, dangerous because of the effects of errors in the unit-cell parameters, rounding errors in calculations and the question of equality or inequality of computed non-integral numbers (Ilsley *et al.*, 1980). Small changes in cell dimensions can lead to completely different results for the reduced cell in special cases (Andrews, Bernstein & Pelletier, 1980), making interpretation of the reduced form difficult.

For this reason, we have devised a procedure for checking a unit cell by performing a reduction to a standard form and then generating a list of selected lattice vectors together with the angles between pairs of them. This method is insensitive to the problems of

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imprecise cell parameters and questions of interpretation, and it is easier for the user to recognize the conventional unit cell from the vector list than by direct inspection of the reduced form.

It should be noted that, although the lattice metric symmetry can never be lower than the true symmetry of the crystal structure, it can be higher. Such pseudosymmetry is very common in some classes of materials. Any cell determination procedure based purely on the *geometry* of diffraction will fail to detect the difference between metric and crystal symmetry in such cases. The Laue symmetry must be subsequently investigated by comparison of supposedly equal *intensities*.

Cell reduction

We choose the Niggli reduction, because it gives a unique result and is well documented [*International Tables for X-ray Crystallography* (1969), pp. 530–535; Santoro & Mighell, 1970; Gruber, 1973]. The algorithm given by Křivý & Gruber (1976) is compact and convenient. For each step of the algorithm, as well as making the required changes to the parameters A, B, C, ξ, η and ζ, we also generate a 3×3 transformation matrix describing the new axial vectors in terms of the old, and accumulate these matrices by successive multiplications, so that the overall transformation matrix [*International Tables for X-ray Crystallography* (1969), pp. 15–21] can be printed together with the reduced cell when the reduction procedure is complete. A preliminary transformation must also be made if the original lattice is non-primitive. The required matrices are given in Table 1.

Table 1. *Transformation matrices corresponding to each step of the cell reduction algorithm*

Lattice	Matrix								
I	1	0	0	0	1	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
*R**	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$-\frac{1}{3}$	$-\frac{2}{3}$	$\frac{1}{3}$
F	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	0	$\frac{1}{2}$	$\frac{1}{2}$
A	1	0	0	0	1	0	0	$\frac{1}{2}$	$\frac{1}{2}$
B	$\frac{1}{2}$	0	$\frac{1}{2}$	0	1	0	0	0	1
C	1	0	0	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0	1
Step†	Matrix								
1	0	1	0	1	0	0	0	0	−1
2	−1	0	0	0	0	1	0	1	0
3,4‡	$xs(\xi)$	0	0	0	$xs(\eta)$	0	0	0	$xs(\zeta)$
5	1	0	0	0	1	0	0	$s(\xi)$	1
6	1	0	0	0	1	0	$s(\eta)$	0	1
7	1	0	0	$s(\zeta)$	1	0	0	0	1
8	1	0	0	0	1	0	1	1	1

* Rhombohedral on obverse hexagonal axes; rhombohedral axes are primitive.

† The steps of the Křivý & Gruber (1976) algorithm.

‡ $s(\xi)$ means the sign of ξ (+1 or −1); $x = s(\xi\eta\zeta)$.

Selection of lattice vectors

From the reduced cell, a list of lattice vectors $\mathbf{r}$ is generated, from which the correct Bravais lattice can easily be recognized. Firstly, we generate vectors for the three edges, the six face diagonals and the four body diagonals of the reduced cell, and sort them in order of increasing length.

The list is examined for vectors with approximately equal lengths. If three such are found, and if $\mathbf{r}_1.\mathbf{r}_2$, $\mathbf{r}_2.\mathbf{r}_3$ and $\mathbf{r}_3.\mathbf{r}_1$ are all approximately equal, the four additional vectors $\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3$, $\mathbf{r}_1 - \mathbf{r}_2$, $\mathbf{r}_2 - \mathbf{r}_3$, and $\mathbf{r}_3 - \mathbf{r}_1$ are generated and stored. (This is particularly useful for rhombohedral cells with $c \gg a$ on hexagonal axes.) For all pairs of vectors with almost equal lengths which are not members of such triples, $\mathbf{r}_1 + \mathbf{r}_2$ and $\mathbf{r}_1 - \mathbf{r}_2$ are generated and stored. The generated vectors are then added to the original list of thirteen, which is sorted again.

The output for each vector consists of its length, its components in terms of the edges of both the reduced and original unit cells, and the angles between it and all previous vectors in the list. Angles between 89 and 91° are summarized in an extra table to facilitate the recognition of orthogonal axes. If three vectors are subsequently chosen to describe a cell, the transformation matrix required to generate this cell from the reduced or from the original cell has the relevant vector components as its rows.

Because the cell reduction is only a means to an end, the magnitude of the tolerance which is allowed for the difference of two 'equal' numbers is not important in the reduction step. A generous tolerance for differences in vector lengths and scalar products in the vector generation stage is recommended, to ensure that all potentially interesting vectors are found; the price paid for this is a little extra computing time and output.

Application

The method described here forms a part of the four-circle diffractometer control software in our laboratory as well as being available as a stand-alone program. Unit cells determined on the diffractometer can thus be routinely checked for higher symmetry.

We have tested the method with the cells reported by Marsh & Schomaker (1979) and by Ilsley *et al.* (1980) (parameters both before and after refinement). In each case, the *C*-centred monoclinic cell was easily recognized. Table 2 gives the results for the unrefined cell of Ilsley *et al.* (1980). Although the automatic recognition of the *C*-centred monoclinic cell from the reduced form fails unless generous tolerance limits are allowed, the symmetry axis stands out clearly in the list.

The method also helps in resolving some of the problems to which Santoro, Mighell & Rodgers (1980) have applied their **B**-matrix algorithm. Thus, for

Table 2. *An example of a vector list*

The initial cell is primitive. The correct cell is *C*-centred monoclinic, with $a = 15{\cdot}932$, $b = 15{\cdot}388$, $c = 9{\cdot}494$ Å, $\beta = 93{\cdot}95°$ after refinement (Ilsley *et al.*, 1980). The monoclinic axes are the vectors 9, 8 and 1 respectively.

Initial cell: 14·166 11·088 9·480 93·25 128·94 89·72
Reduced cell: 9·480 11·033 11·088 87·57 86·75 87·00

Niggli matrix:

89·8704	121·7379	122·9437
5·1907	5·9589	5·4664

Transformation matrix, initial to reduced cell:

0·00	0·00	−1·00
−1·00	0·00	−1·00
0·00	1·00	0·00

n	*u*	*v*	*w*	*u'*	*v'*	*w'*	length					
1:	1	0	0	0	0	−1	9·480					
2:	0	1	0	−1	0	−1	11·033					
87·00												
3:	0	0	1	0	1	0	11·088					
86·75	87·57											
4:	1	−1	0	1	0	0	14·166					
51·06	138·06	89·72										
5:	−1	0	1	0	1	1	14·174					
128·64	90·10	41·89	114·62									
6:	1	1	0	−1	0	−2	14·918					
47·61	39·39	86·13	98·67	113·46								
7:	1	0	1	0	1	−1	14·991					
47·60	86·31	39·15	66·36	81·05	61·56							
8:	0	1	−1	−1	−1	−1	15·307					
90·19	46·36	133·93	122·67	122·72	59·45	121·02						
9:	0	1	1	−1	1	−1	15·971					
85·67	43·92	43·65	120·70	58·96	54·50	54·34	90·28					
10:	−1	1	1	−1	1	0	17·947					
117·46	52·16	52·12	141·84	37·94	80·75	80·65	90·15	31·78				
11:	1	1	−1	−1	−1	−2	17·977					
58·37	52·04	124·11	97·36	142·14	37·98	94·77	31·82	87·96	104·20			
12:	1	−1	1	1	1	0	18·032					
58·09	123·94	51·78	37·94	82·50	94·42	37·63	148·28	87·49	103·90			
116·46												
13:	1	1	1	−1	1	−2	19·178					
56·14	51·27	50·91	96·57	83·07	35·23	35·04	90·33	29·53	61·32			
73·21	72·67											
14:	2	−1	−1	1	−1	−1	23·850					
41·89	116·15	116·07	32·70	147·32	81·54	81·62	89·97	127·56	159·35			
66·85	66·99	98·03										
15:	2	1	1	−1	1	−3	25·695					
38·30	60·90	60·56	81·58	98·07	30·87	30·70	90·32	47·37	79·16			
65·85	63·33	17·84	80·19									

Table of right-angles:

1:	8
2:	5
3:	4
4:	3
5:	2
8:	1 9 10 13 14 15
9:	8
10:	8
13:	8
14:	8
15:	8

example, in the case of condelphine hydroiodide (DeCamp, 1976), two vectors of almost equal length appear in the output list, corresponding to the two possible **a** axes. Application to the monoclinic cell of $Rb_2Pb(MnO_2)_2$ clearly demonstrates the close relationship to the rhombohedral cell of $K_2Pb(SO_4)_2$; more significantly, the danger of assigning *C*-centred monoclinic cells to crystals which really are rhombohedral is obviated by use of the vector-generation method, particularly when the hexagonal *c* axis is very long; here, reduction alone can fail to show up the higher symmetry if the monoclinic cell parameters are not very precise.

The routine use of this or a similar method both during structure determination and by referees or editors of crystal structure reports would help to prevent the appearance of incorrect unit cells in the literature.

This method contains, among others, ideas developed from those embodied in programs by Drs R. Taylor and J. E. Davies.

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