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Geometrical and Mathematical Ambiguities Arising in Crystallographic Unit Cell Determination

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Indexing programs often propose several possible cells compatible with the same observed X-ray powder diagram. Two types of ambiguity can be distinguished: one of geometrical origin, in which the crystallographic network remains unchanged, and the other of mathematical origin, giving cells without any physical meaning. A list of these ambiguities is presented and a computer program suitable for their detection is proposed. © 1993 Academic Press, Inc.

Introduction

Many new inorganic compounds are available only in the form of powders, so the indexing of X-ray powder patterns of unknown structures has become a widespread method. Several appropriate computer programs are now available, but they often propose multiple solutions. Besides haphazard cells due to experimental errors, there sometimes exist different cells due to geometrical or mathematical ambiguities, giving exactly the same calculated powder diagram. We compile a list of these ambiguities (probably not exhaustive) and give a simple means of selecting the crystallographic cell. We discuss only ambiguities giving cells whose symmetries are at least monoclinic (any X-ray powder pattern can be indexed with an infinite number of triclinic cells).

Definitions. The reduced cell (Buerger cell) (*1*, *2*) is the primitive cell based on the three shortest noncoplanar vectors. Some compounds can have more than one Buerger cell (*3*, *4*). The Niggli cell (always unique) is the Buerger cell with the greatest angle deviation (deviation = $|\alpha - 90| + |\beta - 90| + |\gamma - 90|$) (*5*). The crystallographic cell belongs to the most symmetric Bravais lattice corresponding to the crystalline network and can contain several lattice points.

Geometrical Ambiguities

These ambiguities arise because a given lattice can be described by different unit cells. Thus, they can occur both in the indexing of powder diagrams and in structure determinations using single crystals (*6–9*). They can be classified according to their respective volumes.

Any high symmetry cell can be indexed with a monoclinic cell with the same volume. In these cases, it is necessary to calculate the different cell choices (as defined in

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the International Tables (*10*)) to put into evidence some particular relationship between the parameters. The *d*-multiplicity test that we propose detects these cases easily.

The problem becomes more complicated when the cells due to geometrical ambiguities and the crystallographic cell do not have the same volume. We now discuss the main possibilities.

Orthorhombic C-Centered System

Any orthorhombic C cell can be indexed using monoclinic *P* cells. Before proposing a monoclinic *P* system, it is necessary first to reduce the cell and then to calculate the two other cell choices (using matrices given in the International Tables (*10*)). If, in one of them, the axial relationship $a = c$ is fulfilled, the compound can be indexed in the orthorhombic *C* system.

Orthorhombic F-Centered System

Any orthorhombic *F* cell can be transformed into three different monoclinic *I* cells and into three different monoclinic *C* cells. We have named these six cells "semicrystallographic cells" as they contain two lattice points, while the crystallographic cell has four and the primitive cell only one. In the monoclinic *I* cell choice, the relationship $a = c$ is fulfilled. So, before proposing a monoclinic *C* system, it is necessary to calculate the corresponding monoclinic *I* cell choice; if $a = c$ the compound can be indexed in the orthorhombic *F* system.

Hexagonal System

Any hexagonal cell can be transformed into an orthorhombic *C* cell, for which the relationship $a = \sqrt{3}b$ is fulfilled.

Rhombohedral System

Any rhombohedral cell can be transformed into a triple hexagonal cell (*10*). A less known ambiguity is transformation into a monoclinic *C* cell. One possible matrix is

$$\begin{pmatrix} 1 & 1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_r \\ \mathbf{b}_r \\ \mathbf{c}_r \end{pmatrix} = \begin{pmatrix} \mathbf{a}_m \\ \mathbf{b}_m \\ \mathbf{c}_m \end{pmatrix}.$$

This matrix does not always give the cell-choice with β closest to 90°; for instance, in the case of $RbSn_2(PO_4)_3$ (a = 9.332 Å, α = 53.00° (*11*)), we obtain a = 16.703, b = 8.328, and c = 9.332 Å, β = 47.74°. The corresponding cell choice with β closest to 90° is *I* centered, a = 9.332, b = 8.328, and c = 12.508 Å, β = 98.74°. In such a case, the detection of rhombohedral symmetry is not obvious. A cell reduction does not give the rhombohedral cell, but two reduced cells with the following parameters:

$a = b = 8.328$ Å, $c = 9.332$ Å, $\alpha = 116.50°$, $\beta = 90.00°$, $\gamma = 120.00°$;

$a = b = 8.328$ Å, $c = 9.332$ Å, $\alpha = 63.50°$, $\beta = 63.50°$, $\gamma = 60.00°$.

In fact, in a rhombohedral system, the primitive crystallographic cell is not reduced when $\alpha < 60°$ or $\alpha > 109.47°$ (*4, 10*).

Cubic Systems

The Niggli cell of crystallographic cubic *I* or *F* cell is rhombohedral (α = 109.47° or 60°, respectively). Therefore, the ambiguities described for the rhombohedral system are also possible. In the case of the cubic *F* system, we can calculate a semicrystallographic cell, tetragonal *I*, with the axial relationship $c = \sqrt{2}a$.

Mathematical Ambiguities

These ambiguities give cells corresponding to a network different from the crystallographic one; in fact, they have no physical meaning. (For example, it is possible to obtain cells with noninteger Z or cells with some apices not corresponding to lattice points!) However, for mathematical reasons, the calculated powder X-ray diagram fits exactly the experimental one. Of course,

these ambiguities cannot occur during structural studies carried out on single crystals. We have found only one systematic work dealing with this problem (Mighell and Santoro (*12*)). They named this effect "geometrical ambiguities." We think this phrase is confusing because, from our point of view, this ambiguity is due to a mathematical rather than to a geometrical cause (the *same* true lattice being cut into cells having different shapes). Thus, we prefer to use the term "mathematical ambiguities."

Cell Identification

1. The elimination of haphazard cells can be performed according to the following criteria:

— low average error on θ (i.e., less than 0.015°)

— low standard deviation on each cell parameter (i.e., less than one-thousandth of the value of the parameter)

— high value of the merit factor F_m (*13*) (it is generally accepted that a true cell must have $F_m > 9$).

These limitations cannot detect any kind of ambiguity.

2. Density measurement is useless in the case of geometrical ambiguity because the Z value of all cells is always an integer. But for mathematical ambiguity, it can help to eliminate cells with a noninteger value of Z.

3. The indexing of several isotypic compositions (solid solutions or pure compounds) provides an additional test, as all samples must be indexed with the same set of *hkl* values.

4. The evolution of the X-ray pattern as a function of temperature is useful in the case of pseudosymmetry as it is likely that not all lattice parameters will change at the same rate.

5. Optical observation under polarized light confirms cubic indexation easily, especially when the cell volume is large, and one may be tempted to look for a smaller unit cell.

6. Finally, the cell must be tested for the existence of some kind of ambiguity.

We list in Table I the main geometrical and mathematical ambiguities. But the problem can be complicated by the fact that the ambiguities can combine with each other. For instance, a powder diagram of a cubic I compound can be indexed using an orthorhombic F cell (mathematical ambiguity) which can itself be transformed into six monoclinic I- or C-centered cells (geometrical ambiguity).

Detection of Ambiguities with Computer Programs

Several programs, or methods suitable for programming, have been proposed in the literature (*14–19*). As discussed by Andrews and Bernstein (*17*), some of these can lack efficiency (especially in the case of pseudosymmetry). The main practical problem is how to take into account the experimental errors on cell parameters, generally not well known by operators (standard deviations given by indexing programs correspond to underestimated experimental errors). These methods are useful for detecting geometrical ambiguities, but *useless in cases of mathematical ambiguity.*

We have developed a program combining several different methods. That the different methods do not have the same sensitivity to experimental errors is a matter of practical interest. The main data to be introduced are the values of the cell parameters, tolerances of the cell parameters and of θ, and the centering type of the proposed cell. We shall now briefly discuss the different options.

Matrices Multiplicity Test

This test, proposed by Himes & Mighell (*14*) to determine the metric symmetry, is

TABLE I

LIST OF KNOWN AMBIGUITIES (–G→, GEOMETRICAL; –M→, MATHEMATICAL)

Proposed cell with special relationship between parameters		*Possible cell of higher symmetry*
Monoclinic P $a = c$ (in one of the cell-choices)	–G→	Orthorhombic C $c_0 = b_m$ $\vec{a}_0 = \vec{a}_m + \vec{c}_m \quad \vec{b}_0 = \vec{a}_m - \vec{c}_m$
Monoclinic P No apparent relationship	–M→	Hexagonal–rhombohedral $a_h = 2b_m$ $c_h = (\sqrt{3} \cdot a_m \cdot c_m \cdot \sin(\beta_m))/(b_m)$
Monoclinic C Transform into monoclinic I; $a = c$	–G→	Orthorhombic F $\vec{a}_0 = \vec{a}_m + \vec{c}_m \quad \vec{b}_0 = \vec{a}_m - \vec{c}_m$ $\vec{c}_0 = \vec{b}_m$
Monoclinic C No apparent relationship	–G→	Hexagonal–rhombohedral $a_h = b_m$ $c_h = (\sqrt{3} \cdot a_m \cdot c_m \cdot \sin(\beta_m))/(b_m)$
Orthorhombic P $a = \sqrt{2} \cdot b = 2c$	–M→	Cubic I $a_c = \sqrt{2}.a_0$
Orthorhombic P $a = \sqrt{3}.b$	–M→	Hexagonal $a_h = 2b_0 \quad c_h = c_0$
Orthorhombic C $a = \sqrt{3}.b$	–G→	Hexagonal $a_h = b_0 \quad c_h = c_0$
Orthorhombic C $a = \sqrt{2}.b = 2\sqrt{2}.c$	–M→	Cubic F $a_c = a_0$
Orthorhombic I $a = \sqrt{2}.b = 3\sqrt{2}.c$	–M→	Cubic F $a_c = a_0$
Orthorhombic F $a = \sqrt{2}.b = 3c$	–M→	Cubic I $a_c = b_0$
Rhombohedral $\alpha = 60°$	–G→	Cubic F $a_c = \sqrt{2}.a_r$
Rhombohedral $\alpha = 109{,}47°$	–G→	Cubic I $a_c = 2a_r/\sqrt{3}$
Hexagonal $a = c/\sqrt{6}$ and nonextinction condition $-h + k + l = 3n$	–G→	Cubic F $a_c = \sqrt{2}.a_h = c_h/\sqrt{3}$
Hexagonal $a = 2\sqrt{2}.c/\sqrt{3}$ and nonextinction condition $-h + k + l = 3n$	–G→	Cubic I $a_c = a_h/\sqrt{2} = 2c_h/\sqrt{3}$
Tetragonal P $a = c/\sqrt{2}$	–M→	Cubic P $a_c = c_t$
Tetragonal P $a = \sqrt{2}.c$	–M→	Cubic I $a_c = 2c_t$
Tetragonal I $a = c/\sqrt{2}$	–G→	Cubic F $a_c = c_t$

Note. a, b, and c represent the unit cell axes moduli. Vector notations have been used only when there was no obvious relationship between vector moduli.

useful only for geometrical ambiguities. Each of the seven lattice systems has a characteristic number of symmetry operations, represented as matrices. Whatever the *primitive* cell proposed, the same number of matrices will transform it into itself. As it

has been pointed out (*17*) that the algorithm used by Himes and Mighell (*19*) could give rise to infinite loops, we use another.

The number of matrices corresponding to each system is 1 (triclinic), 2 (monoclinic), 4 (orthorhombic), 6 (rhombohedral), 8 (tetragonal), 12 (hexagonal), and 24 (cubic). In the case of pseudo-symmetry, the program can also find other values. If this occurs, the operator can change the experimental tolerances. The program also calculates the average cell obtained from the matrices; this is the primitive cell of highest symmetry possible within experimental error.

Niggli Test

This test is useful only in the case of geometrical ambiguities. It calculates the parameters of the Niggli cell and its matrix form, using an algorithm proposed by Gruber (*20*). There are only 44 different types of Niggli cell matrix forms, and calculation of the crystallographic cell is in principle easy (*10, 15*) when the type of Niggli cell is known. Once again, the main practical problem is determining what type the matrix form belongs to, owing to experimental errors (the average cell calculated from the matrix test can be useful for making this choice).

Buerger Test

Starting from the Niggli cell calculated above, this test searches all the other reduced or pseudo-reduced cells (Buerger cells). As some compounds can have more than one reduced cell, a small distortion (within experimental error) could lead the algorithm used during the Niggli test to find a Buerger cell. The matrix form of such a cell could belong to a type not listed in the literature, or not compatible with the other tests performed. If this occurs, the Buerger test will find all the reduced cells possible, including the real Niggli cell. The algorithm is similar to that used in the matrix test.

d-Multiplicities Test

This new test is directly related to the matrix test described above but takes the experimental errors into account in a different way. All the matrices transforming the cell into itself will also transform the *hkl* indices of the reticular planes.

The "*d* multiplicity" is defined as the number of different *hkl* indices corresponding to a given *d* value. It depends on the crystal symmetry and on the *hkl* pattern. The higher the crystal symmetry, the higher the *d* multiplicity.

In case of geometrical ambiguity, the multiplicity corresponding to each *d* value remains the same as that in the true cell. So if a high symmetry crystal powder is indexed in a too-low symmetry cell, the calculated multiplicity of many *d* values will not be compatible with the assumed cell symmetry. The multiplicity values are discussed in Ref. (*21*).

One interest of this *d*-multiplicities test is that it is the only one able to detect the possibility of mathematical ambiguities. In contrast to geometrical ambiguities, the *d* multiplicities are not always the same as those in the true cell, but they lie between the multiplicities predicted by the assumed lattice system and the multiplicities observed in the true crystallographic cell. So, if many *d* values show multiplicities that are too high, it is necessary to search for special relationships between the cell parameters.

Also of practical interest is that this test is the only one in which the operator must assume the experimental tolerance on measured θ. For example, in the case of pseudo-symmetry, the average cell calculated by the matrix test described above would have a too-high symmetry. Using the *d*-multiplicities test, one can see if

this average cell is compatible with the experimental tolerance on θ.

Conclusion

Combining different tests generally allows the calculation of the cell of highest symmetry. However, when possible, the study of some isotypic compositions can provide useful additional information in the indexing of a compound with unknown structure on the basis of an X-ray powder diagram.

A more detailed discussion (*21*) and a listing of our program TESTSYM are available from the authors or from the NAPS.[2]

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[2] See NAPS Document No. 04991 for 63 pages of supplementary materials. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material, $1.50 for postage of any microfiche orders.

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