The Determination of the Relationship Between Derivative Lattices

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Abstract

Derivative lattices are related to one another by transformation matrices having rational elements. A simple algorithm for finding these matrices consists in testing if the scalar products of the vectors defining two arbitrary primitive cells of two lattices can be exactly or approximately related by equations with rational coefficients. A rational relationship indicates that two or more lattices have a number of geometrical features in common such as common superlattices, sublattices, *etc.* The algorithm can, therefore, be applied to a variety of crystallographic problems such as the study of twinning, the indexing of powder patterns, single-crystal diffractometry and the critical evaluation of crystal data. Five examples are discussed in detail.

Introduction

In the study of crystalline materials, it is often necessary to find the relationship between two or more crystal lattices, either identical or different from one another. Typical cases in which a knowledge of lattice relationships are required occur, for example, in the critical evaluation of data to be included in major compilations such as the Crystal and Powder Data Files, in the analysis of twinning and coincidence-site lattices, in the study of inter-related structures, in the evaluation of the results obtained from powder-indexing procedures, in single-crystal diffractometry, and in many other areas of crystallography.

The method commonly employed to study how two lattices are related is based on converting an arbitrary cell into a standard one, such as the Delaunay cell (Delaunay, 1933), the reduced cell (Santoro & Mighell, 1970), the *Crystal Data* cell (Donnay & Ondik, 1972), or the cell used in *International Tables for X-ray Crystallography* (1969, p. 7). This method is particularly suitable to classify crystalline materials, to establish symmetry, and to recognize if two cells describe the same lattice. It has, however, one serious

disadvantage in that it does not allow one to determine easily if the two lattices are derivative of each other, *i.e.* if one is the super-, sub-, or composite-lattice of the other (these lattices are defined by Santoro & Mighell, 1972). This is unfortunate because many of the crystallographic problems mentioned previously stem from the derivative character of lattices. For example: (i) twinning by reticular merohedry takes place because a superlattice of the crystal lattice has elements of symmetry beyond those of the crystal lattice; (ii) the solutions obtained in the indexing of a powder pattern are commonly derivative lattices; (iii) cell determinations carried out with automated four-circle diffractometers not infrequently yield lattices which are derivative of the true lattice of the crystal.

This shortcoming can be circumvented by devising practical procedures to determine the matrices relating arbitrary cells of two or more lattices. The relevant properties of the lattices can then be derived from the nature of the transformation matrices. A method based on such an approach is described in the following sections.

Theory

Let us consider two lattices A and A' defined by the primitive triplets of noncoplanar translations $\mathbf{a}_i$ and $\mathbf{a}'_i$ ($i = 1, 2, 3$). As the metric properties of a lattice are completely specified by any primitive triplet, $\mathbf{a}_i$ and $\mathbf{a}'_i$ can be chosen arbitrarily. Let us assume that A and A' have a common origin in a node, but arbitrary mutual orientation. The two lattices are then related by the transformation

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

The elements B_{ij} of matrix $\mathbf{B}$ can be any real numbers.

Let us suppose, however, that they are all rational. In this case we have:

Theorem. If two lattices A and A' are related by a transformation matrix $\mathbf{B}$ having rational elements B_{ij},

the two lattices have a superlattice Γ in common, and conversely.

If the B_{ij}'s are rational, we may write

$$B_{ij} = N_{ij}/n_{ij} = v_{ij}/\mu_i, \tag{2}$$

where N, n, v and μ are integers and μ_i is the smallest common multiple of n_{i1}, n_{i2} and n_{i3}. Substituting in (1), we have

$$\mathbf{a}_i = \sum_j \frac{v_{ij}}{\mu_i} \mathbf{a}_j'$$

or

$$\mu_i \mathbf{a}_i = \sum_j v_{ij} \mathbf{a}_j' = \mathbf{s}_i. \tag{3}$$

Since μ_i and v_{ij} are integers, the translations $\mu_i \mathbf{a}_i$ define a superlattice of Λ† and the translations $v_{ij} \mathbf{a}_j'$ and $\sum_j v_{ij} \mathbf{a}_j'$ superlattices of Λ'. It follows that the translations $\mathbf{s}_i$ define a lattice Γ which is a superlattice of both Λ and Λ'.

To prove the converse, let us suppose that Λ and Λ' have a common superlattice Γ defined by the translations $\mathbf{s}_i$. We may write

$$\mathbf{s}_i = \sum_j R_{ij} \mathbf{a}_j = \sum_j R_{ij}' \mathbf{a}_j', \tag{4}$$

where the elements R_{ij} and R_{ij}' are integers. Comparing with (1), we obtain

$$\mathbf{B} = \mathbf{R}^{-1} \mathbf{R}' \tag{5}$$

in which the elements B_{ij} are rational.

From the above results, it follows that:

Theorem. If two lattices Λ and Λ' have a superlattice Γ in common, they also have in common the derivative lattices Δ of Γ.

According to definitions given elsewhere (Santoro & Mighell, 1972), the derivative lattices Δ of Γ are all the lattices obtained from Γ with the transformation

$$\mathbf{d}_i = \sum_j L_{ij} \mathbf{s}_j, \tag{6}$$

where the primitive triplet of translations $\mathbf{s}_i$ define Γ and the elements L_{ij} are rational numbers. From (6) and (4), we obtain

$$\mathbf{d}_i = \sum_j L_{ij} \sum_k R_{jk} \mathbf{a}_k = \sum_j L_{ij} \sum_l R_{jl}' \mathbf{a}_l' \quad (k, l = 1, 2, 3). \tag{7}$$

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† The traditional definitions are followed in this paper. Given an original lattice, a superlattice is built on a multiple cell, from which all centering nodes are omitted, and a sublattice is built on a submultiple cell, the cell volumes becoming, respectively, larger or smaller than that of the original primitive cell. In some publications (*e.g.* Cassels. 1971) a superlattice is called 'sublattice' (of the original lattice) where the term 'subgroup' is meant.

The lattices Δ, therefore, are common to Λ and Λ' and can be obtained from $\mathbf{a}_i$ and $\mathbf{a}_i'$ by means of the matrices $\mathbf{LR}$ and $\mathbf{LR}'$, respectively.

If Λ and Λ' have a superlattice in common, matrix $\mathbf{B}$ can be expressed by means of (5). If we generate the superlattice from Λ by means of a matrix $\mathbf{Q}$ such that the elements Q_{ij} are integers and $\mathbf{Q}$, in addition, is upper triangular with

$$0 \leq Q_{ij} < Q_{jj} \quad \text{with} \quad i < j \tag{8}$$

(Santoro & Mighell, 1973; especially the Appendix), then (5) can be written

$$\mathbf{B} = \mathbf{Q}^{-1} \mathbf{P}, \tag{9}$$

where the elements P_{ij} are also integers. Equation (9) has been used to find the common superlattice with the smallest cell volume and the common sublattice with the largest cell volume consistent with any given rational matrix $\mathbf{B}$.

If not all the elements B_{ij} are rational, the lattices Λ and Λ' are not related to each other in a specialized manner, *i.e.* the two lattices do not have common geometric properties or features. The previous treatment shows that the rational solutions of (1) are the only ones of crystallographic interest.

These can be found with the following procedure. Setting

$$A_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j, \quad A_{ij}' = \mathbf{a}_i' \cdot \mathbf{a}_j', \tag{10}$$

from (1), we obtain

$$A_{ij} = \left(\sum_k B_{ik} \mathbf{a}_k'\right) \cdot \left(\sum_l B_{jl} \mathbf{a}_l'\right) = \sum_k \sum_l B_{ik} B_{jl} A_{kl}'$$

$$(k, l = 1, 2, 3). \tag{11}$$

Rational solutions of (11) can be found, if they exist, by substituting for the unknown elements B_{ik} and B_{jl} rational numbers to be generated systematically in some convenient way, *e.g.* by writing

$$B_{ij} = N_{ij}/n_{ij}$$

and by assigning to N_{ij} and n_{ij} all possible integral values. In many practical applications these integers can be limited to a small interval, for example $(-5, 5)$, because the relationships of crystallographic interest usually involve simple rational numbers.

If two lattices are not related exactly, (11) becomes

$$\sum_k \sum_l B_{ik} B_{jl} A_{kl}' - A_{ij} = S_{ij}. \tag{12}$$

The rational relationship between the two lattices will be acceptable or unacceptable depending on the magnitude of the values of S_{ij} that can be tolerated in a given problem.

Applications

(a) Ambiguities in determining unit cells from powder data

In the automatic indexing of powder patterns with the program of Visser (1969), the output consists of four candidate unit cells. The algorithm described in the previous section has been used to relate these cells with one another and with the correct unit cell, if known. Not uncommonly, two or more of the four lattices were found to be in a derivative relationship with each other and/or with the true lattice of the crystal.

An example has been encountered in the indexing of chromium phosphate hydrate, $CrPO_4.6H_2O$. From a set of observed d spacings, the best solution found by the indexing method was

$$a = 6.030, \, b = 11.471, \, c = 11.711 \text{ Å};$$

$$\alpha = 94.72, \, \beta = 97.72, \, \gamma = 99.49°.$$

A single-crystal analysis carried out with a Syntex automated diffractometer, on the other hand, showed that the correct cell is

$$a' = 6.003, \, b' = 6.007, \, c' = 23.389 \text{ Å};$$

$$\alpha' = 97.04, \, \beta' = 92.61, \, \gamma' = 110.16°.^*$$

Both these cells are reduced, and one must therefore conclude that they define different lattices. The B-matrix algorithm, applied to the two cells, established that they are related by the transformation

$$\mathbf{a}'_i = (-100/\tfrac{1}{2}\tfrac{1}{2}0/-\tfrac{1}{2}-\tfrac{1}{2}-2) \, \mathbf{a}_i \quad (i = 1, 2, 3).$$

Since the determinant of the transformation matrix is unity and since there are fractional elements, the two lattices bear a composite relationship to each other.

This example shows that in certain cases the lattice determined by the indexing program is related to the correct one by a rational matrix. In this case the two lattices are in a composite relationship and have many d spacings in common. Therefore, the observed diffraction lines, because of accidental absences, are consistent almost equally well with cell $\mathbf{a}_i$ and $\mathbf{a}'_i$.

(b) Relationship between cells determined from different crystals of the same species

There are lattices in which two or more unit cells are dimensionally similar. This may cause problems in single-crystal work whenever it is necessary to use two or more individuals of the same material to collect a complete set of data. An example of such a lattice has

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* The lattice defined by this cell is monoclinic A-centered. The refined parameters are $a = 23.473$, $b = 6.890$, $c = 9.882$ Å, $\beta = 99.42°$ (Morris, McMurdie, Evans, Paretzkin, deGroot, Weeks & Newberry, 1978, p. 27).

been reported by DeCamp (1976) and is summarized below.

In a study of the structure of condelphine hydroiodide, two experimenters, using different crystals, described the crystal lattice by means of two different cells:

$$a = 9.34, \, b = 17.39, \, c = 9.10 \text{ Å};$$

$$\alpha = 94.85, \, \beta = 119.15, \, \gamma = 88.57°$$

and

$$a' = 9.32, \, b' = 17.45, \, c' = 9.09 \text{ Å};$$

$$\alpha' = 94.84, \, \beta' = 118.83, \, \gamma' = 86.50°.$$

The differences in lattice parameters were ascribed, at first, to experimental errors, especially absorption. Subsequent work revealed this not to be the case, because intensities of corresponding reflections differed far more than the experimental errors would justify. The application of the B-matrix algorithm immediately established the relation between the two cells

$$\mathbf{a}'_i = (101/0\bar{1}0/00\bar{1}) \, \mathbf{a}_i.$$

In the original paper, reduction theory was used to show that the two cells describe the same lattice and to find the relation between them. The present method, however, is to be preferred in problems of this type, not only because it is more direct, but especially because there could be in the lattice more than two cells with similar parameters, which would be revealed immediately by the B-matrix algorithm, but could not be detected by the reduction procedure.

(c) Relation between different unit cells of the same crystal determined by an automated four-circle diffractometer

In determining the unit cell of a crystal with a four-circle diffractometer, there are cases in which accidental or systematic extinctions (as well as other causes) may lead to the choice in reciprocal space of a superlattice of the correct one. An example of this type of error was encountered in the study of the structure of (3-chloro-2-hydroxy-5-nitrophenyl) (2'-chlorophenyl)iodonium hydroxide, inner salt ($C_{12}H_6Cl_2$-INO_3).

The solution of this structure was initially attempted by using the data collected on the basis of the monoclinic lattice described by the cell

$$a = 13.595, \, b = 4.638, \, c = 10.321 \text{ Å}, \quad \beta = 98.28°.$$

In the last stages of refinement, however, it was found that two different models refined equally well to an R of about 8%. This result could be ascribed to disorder in the structure or to an incorrect procedure in collecting the data. By mounting the crystal a second time, the following cell was determined:

$$a' = 15.928, \, b' = 4.623, \, c' = 18.271 \text{ Å}, \quad \beta' = 105.58°$$

(Hubbard, Himes, Mighell & Page, 1980). The B-matrix algorithm immediately revealed that the two cells are related by the transformation

$$\mathbf{a}'_i = \begin{pmatrix} \bar{1} & 0 & \bar{1} \\ 0 & 1 & 0 \\ 1 & 0 & \bar{1} \end{pmatrix} \mathbf{a}_i.$$

This matrix shows that by using the first cell, only half of the data were collected and used in the structure determination. With the second cell, the structure was successfully solved and refined.

(d) Studies of related structures

In many problems of crystal chemistry it is important to establish the relationship between two or more structures. In this area the B-matrix algorithm is particularly useful, as the following example illustrates.

The compound $Rb_2Pb(MnO_2)_2$ is structurally related to palmierite, $K_2Pb(SO_4)_2$, and, on the basis of chemical considerations and values of the ionic radii, one could predict a rhombohedral lattice with parameters (in hexagonal axes)

$$a = 6{\cdot}058, c = 21{\cdot}73 \text{ Å}.$$

The powder pattern of the Rb compound, however, although similar to that of palmierite, could not be indexed in terms of the hexagonal cell and was found to be consistent with a C-centered monoclinic cell of parameters

$$a = 14{\cdot}905 \text{ (5)}, b = 6{\cdot}070 \text{ (3)}, c = 10{\cdot}477 \text{ (3) Å},$$

$$\beta = 103{\cdot}55° \text{ (3)}$$

(Morris, McMurdie, Evans, Paretzkin, deGroot, Weeks & Newberry, 1978, p. 63). The corresponding reduced form (No. 39, *International Tables for X-ray Crystallography*, 1969, p. 530),

$$\begin{pmatrix} \mathbf{a.a} & \mathbf{b.b} & \mathbf{c.c} \\ \mathbf{b.c} & \mathbf{a.c} & \mathbf{a.b} \end{pmatrix} \equiv \begin{pmatrix} 36{\cdot}845 & 64.751 & 109{\cdot}768 \\ -18{\cdot}294 & 0 & -18{\cdot}422 \end{pmatrix},$$

shows that $\mathbf{c.c} \simeq 3\mathbf{a.a}$ and $\mathbf{b.c} \simeq \mathbf{a.b}$, *i.e.* there is more specialization than the one required by a monoclinic C-centered cell, indicating that the lattice has derivative lattices of symmetry higher than monoclinic.

The B-matrix algorithm showed that a primitive cell of the monoclinic lattice can be obtained from a primitive cell of the rhombohedral lattice with the transformations

$$(101/011/002) \quad (200/010/001) \quad (100/020/001).$$

This indicates that the monoclinic lattice can be oriented in space in three different ways with respect to the hexagonal lattice, *i.e.* it is possible mutually to orient three monoclinic individuals so that a common

hexagonal sublattice extends from one to the others with little or no disturbance. These are the conditions required for twinning (Santoro, 1974). The existence of twins in $Rb_2Pb(MnO_2)_2$ is, therefore, quite possible, and anyone working on the compound by single-crystal methods should be aware of it.

(e) Studies of the geometrical properties of lattices

It has been shown (Santoro & Mighell, 1970) that in some lattices more than one cell is based on 'the shortest three' noncoplanar translations. Gruber (1973) has shown that, at most, five different cells of this type may exist in the same lattice. For identification purposes, it is necessary to describe a crystal in terms of only one of these cells and the special conditions of reduction theory provide a way to make such a selection.

On the other hand, there are cases in which it is useful to find all five of the cells and relate them to one another, and the B-matrix algorithm represents a simple procedure to study this type of problem. As an example, let us consider the triclinic lattice studied by Gruber (1973) and described by the cell

$$a = 2, b = 4, c = 4 \text{ Å},$$

$$\alpha = 60° \, 00', \beta = 79° \, 12', \gamma = 75° \, 31'.$$

As we require only the equality of cell edges, only the equations

$$A_{ll} = \sum_k \sum_l B_{lk} B_{ll} A_{kl} \quad (k, l, i = 1, 2, 3)$$

need to be satisfied and the required values of the

Table 1. *The five unit cells based on the shortest noncoplanar translations of the lattice of example (e)*

In the columns are shown the transformation matrices for obtaining cells 2, 3, 4 and 5 from cell 1, the axial lengths (Å) and the interaxial angles.

Matrix			Lengths	Angles
1	0	0	$a = 2$	$\alpha = 60° \, 00'$
0	1	0	$b = 4$	$\beta = 79° \, 12'$
0	0	1	$c = 4$	$\gamma = 75° \, 31'$
$\bar{1}$	0	0	$a = 2$	$\alpha = 60° \, 00'$
0	$\bar{1}$	0	$b = 4$	$\beta = 86° \, 24'$
0	$\bar{1}$	1	$c = 4$	$\gamma = 75° \, 31'$
$\bar{1}$	0	0	$a = 2$	$\alpha = 120° \, 00'$
0	0	1	$b = 4$	$\beta = 93° \, 36'$
0	1	$\bar{1}$	$c = 4$	$\gamma = 100° \, 48'$
1	0	0	$a = 2$	$\alpha = 117° \, 57'$
$\bar{1}$	1	0	$b = 4$	$\beta = 93° \, 36'$
0	$\bar{1}$	1	$c = 4$	$\gamma = 104° \, 28'$
$\bar{1}$	0	0	$a = 2$	$\alpha = 113° \, 58'$
1	$\bar{1}$	0	$b = 4$	$\beta = 100° \, 48'$
0	0	1	$c = 4$	$\gamma = 104° \, 28'$

elements B_{ij} are restricted to integers for which $|\mathbf{B}| = 1$. The algorithm yields the five cells given in Table 1.

Conclusions

In the previous section only a few examples of the application of the algorithm have been illustrated. Many more could have been given. The method represents a practical tool to study inter- and intra-lattice relationships and, for this reason, is particularly suited to carry out research on published crystallographic data. Applications of the procedure, underway or planned, comprise cross-referencing of the single-crystal and powder data files, routine identification and registration procedures, and a systematic study of twinning, especially to clarify the relationship between the geometrical and structural aspects of twins.

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The Expected Values of Triplet Invariants. Acentric Case

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Abstract

A formula for the expected values of triplet phase invariants is derived in the acentric case from third-order determinantal joint probability distributions. Theoretical calculations based on this and earlier formulae are compared with expected values observed for a roughly equal-atom structure and one containing a heavy atom.

Introduction

The expected value of a triplet phase invariant is affected by the knowledge of the magnitudes of appropriate structure factors. It is possible to obtain expressions for such expected values from joint probability distributions involving the triplet invariants of interest and certain associated structure-factor magnitudes. A general joint probability distribution function has been derived recently (Karle, 1978) that is based on the determinants that provide the necessary and sufficient conditions that a Fourier series representing a crystal structure be non-negative (Karle & Hauptman, 1950). These determinantal joint probability distributions have already been applied in the fourth order (Karle, 1979, 1980) to obtain conditional distributions for the triplet invariants $\varphi_{\mathbf{k}_1-\mathbf{k}_2} + \varphi_{-\mathbf{k}_1+\mathbf{k}_3} + \varphi_{\mathbf{k}_2-\mathbf{k}_3}$, given the structure-factor magnitudes $|\mathscr{E}_{\mathbf{k}_1-\mathbf{k}_2}|$, $|\mathscr{E}_{-\mathbf{k}_1+\mathbf{k}_3}|$, $|\mathscr{E}_{\mathbf{k}_2-\mathbf{k}_3}|$ and many sets of $|\mathscr{E}_{\mathbf{k}_1}|$, $|\mathscr{E}_{\mathbf{k}_2}|$, $|\mathscr{E}_{\mathbf{k}_3}|$.

The third-order determinants and determinantal joint probability distributions give the main formulae for phase determination, $\sum_2$ and the sum of angles formula. One question of interest is how well the new distributions represent the expected values of the triplet phase invariants, $\varphi_{\mathbf{k}_1} + \varphi_{-\mathbf{k}_2} + \varphi_{-\mathbf{k}_1+\mathbf{k}_2}$, given the three magnitudes $|\mathscr{E}_{\mathbf{k}_1}|$, $|\mathscr{E}_{-\mathbf{k}_2}|$, $|\mathscr{E}_{-\mathbf{k}_1+\mathbf{k}_2}|$. Such expected values have been investigated in some detail previously (Karle, 1972; Karle & Gilardi, 1973) in connection with other forms for the appropriate joint probability