novelty in this application is in using these methods as an aid to recognizing structures; normally they are used to represent structures once they have been determined. However we feel that our application is not a trivial one since the examination of masses of E-map output had become a major stumbling block in the structure – solving process – especially for non-centrosymmetric structures. Now, on average, 30 minutes of perusal of the graphical displays together with the numerical supplementary information relating to bond lengths and angles is sufficient to find the structure. We have now reached the stage of development where for the vast majority of moderately complex structures no human judgement is required between setting a crystal on an automatic diffractometer to the point of examining the graphical output.

Since they became available some two years ago about 300 structures have been solved by the LSAM and MULTAN programme packages. The availability of the graphical search routines should make these programmes even more attractive to those who wish to solve moderately complex crystal structures without being too intimately concerned with the method of solution so that it becomes just one more technique for

examining materials albeit a little more complicated than ESR or NMR.

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Tessellations and Plane Symmetry Groups as Applied to the Derivation of Closest-Packed Binary Layers

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A method is described for the derivation of binary closest-packed layers of a given composition with the condition that the atoms of the minor component should be crystallographically equivalent. The method is based on the theory of derivatives of space groups developed by Buerger, which is here applied to those multiple cells that may be regarded as tessellations drawn over a basic triangular net. The results are presented for a set of compositions, in order to illustrate the method of derivation.

Introduction

In preceeding work concerning the systematic derivation of close-packed structure types (Lima-de-Faria & Figueiredo, 1969), a method was developed in which the rules for derivation followed directly from the conditions for structural stability already discussed (Lima-de-Faria, 1965). Appropriate layers were so deduced for the generation of ordered binary close-packed structures, under the previous statement of crystallographic equivalency for the atoms of the minor component.

The fact that this method applied to the majority of known structures in the area investigated proved its efficacy in deriving the most probable patterns. However, it was not established that all the appropriate layers had been derived. On the other hand, a small proportion were found to have no corresponding appropriate layer; if proved, and not merely a consequence of the simplifications involved in that derivation technique, this circumstance has interesting structural implications. The aim of the present work is to verify these results by applying an exhaustive method to the derivation of these binary close-packed layers.

Statement of the problem

The essential problem is to find all the two-dimensional patterns built up with symmetrically equivalent points as a result of partially filling the nodes of a triangular net.

The two designations, triangular net and hexagonal lattice, will be used below to refer to the regular tessellation we are dealing with, whose Schläfli symbol is {3,6}; the geometrical aspect is implied with the first designation while the second applies to the crystallographic point of view.

The proportion of the triangular net filled will be given by the ratio of the number of occupied nodes in a multiple cell considered over the fundamental net to the total number of nodes covered by this cell. The occupied nodes must be symmetrically equivalent, as stated above, and thus they will belong to a single set of equivalent positions, either general or special, of the plane symmetry group or groups, compatible with the two-dimensional cell used. The groups analysed are restricted to those involving symmetry elements consistent with those already found in the original lattice, and consequently the groups containing fourfold rotation points are excluded. Also, when considering the distribution of one sole component, as is the case here, the general position in $p1$ corresponds to a monoclinic primitive lattice (Burzlaff, Fischer & Hellner, 1968). Therefore, only 13 of the 17 two-dimensional space groups have to be taken into account.

The proposed question appears then to be split into two distinct problems : (a) to find the subarrays or multiple cells that are compatible with the triangular net; (b) to search for the distinct configurations built up with equivalent points that those cells could originate.

Tessellations and the subdivision of the triangular net

The particular case of subdividing the nodes of a triangular net into hexagonal subarrays has already been treated in the literature in relation to other topics (Iida, 1957; Morris & Loeb, 1960; Loeb, 1962, 1964, 1968). In every instance, the hexagonal subarray corresponds to a compound tessellation with general symbol {3,6} [n{3,6}] (Takeda & Donnay, 1965), where n is the multiplicity of the larger cell, that is, the total number of nodes contained in it. However, this particular case is here included under the general treatment of subdivision into subarrays of all possible symmetries.

As a consequence of the symmetry of the hexagonal lattice itself, oblique, rectangular and hexagonal multiple cells are possible, while square cells are not. Such cells define subarrays that may be regarded as tessellations (Coxeter, 1961, p. 52), whose faces are parallelograms, rectangles and rhombs respectively. For any tessellation, provided a sufficiently large circle is considered, the number of lattice points equals the number of faces (Coxeter, 1961, p. 53). Crystallographically

speaking, this means that the multiplicity of a general cell is given by the area ratio A/α, where A is the area of the multiple cell and α is the area of the rhomb constituting the elementary cell of the hexagonal lattice.

In the same kind of treatment, given by Loeb (1964) to subdivision into hexagonal subarrays, vector algebra was used to express A in terms of α for any kind of regular subdivision of the triangular net. Starting from a node taken as origin, let $\mathbf{a}_1$ and $\mathbf{a}_2$ be the elementary vectors characterizing the elementary cell of the hexagonal lattice, whose area is α (Fig. 1). $\mathbf{A}_1$ and $\mathbf{A}_2$ are the vectors defining the multiple cell of area A; expanding them in terms of $\mathbf{a}_1$ and $\mathbf{a}_2$ we have

$$\mathbf{A}_1 = k\mathbf{a}_1 + l\mathbf{a}_2$$
$$\mathbf{A}_2 = u\mathbf{a}_1 + v\mathbf{a}_2$$

where k, l, u and v are integers.

For all the cases to be considered, it is sufficient to keep β, the angle between $\mathbf{A}_1$ and $\mathbf{A}_2$, between 60 and 90°. Therefore, the parameters defining these vectors must be positive integers, and to avoid duplication arising from different orientations of the same cell, it is postulated that only u may assume the value zero. So, the conditions are

$$60° \le \beta \le 90°$$
$$k,l,v > 0, \quad u \ge 0.$$

The vector and scalar products of vectors $\mathbf{A}_1$ and $\mathbf{A}_2$ provide the main equations relating the area ratio A/α and the angle β with the free parameters k, l, u, v:

$$A/\alpha = kv - lu \tag{1}$$

$$\cot \beta = \frac{v(2l - k) + u(2k - l)}{\sqrt{3}(kv - lu)}. \tag{2}$$

For hexagonal cells expression (1) assumes a simple form (Loeb, 1964) because $\beta = 60°$ and the defining vectors $\mathbf{A}_1$ and $\mathbf{A}_2$ have the same magnitude
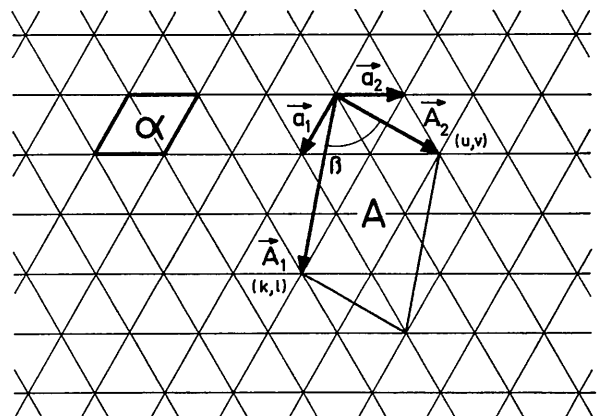
$$A/\alpha = k^2 - kl + l^2. \tag{3}$$

Fig. 1. General cell and defining vectors and parameters.

For rectangular cells, as $\cot \beta = 0$, a simplified form can also be obtained, but for the case of oblique cells there is no substantial simplification to be made.

Therefore, by giving values to k, l, u and v in equations (1) and (2), the solution of the first question is obtained, that is these equations allow for the search of the multiple cells with a given multiplicity that are compatible with the triangular net.

Plane symmetry groups and the derivation of homogeneous configurations

According to the intrinsic symmetry of the hexagonal lattice, the two-dimensional symmetry group ascribed to the elementary cell of area α is $p6m$; to any multiple cell of area A a derivative (Buerger, 1947, 1967) of $p6m$ will be the highest permissible symmetry group.

The derivatives of a given space group consist of all its subgroups in the widest sense, and these will belong to different categories, depending on whether their translation groups are different or the same as that of the space group concerned (Buerger, 1967). As we are dealing with multiple cells, the subgroups involved here have different translation groups; this relates only to the cell dimensions when considering hexagonal cells, but concerns also the lattice type for rectangular and oblique cells.

The space groups dealt with here are two-dimensional, and so the nomenclature is that of *International Tables for X-ray Crystallography* (1952). A slight change is introduced because the word 'point' when referred to a rotation centre (n-fold point) could cause confusion, since the nodes of the triangular net are often referred to as points (lattice points); therefore preference is given to the designation 'rotocentre' (Le Corbeiller & Loeb, 1967).

Three distinct ways of reducing the overall symmetry and deriving the complete set of subgroups of a given space group are possible (Buerger, 1967). These reduction processes are applied either separately or together, and are the following:

(i) change in translation multiplicity;

(ii) lowering of symmetry to another element involving the same kind of transformation, direct or opposite (sixfold rotocenters to three- and twofold rotocentres, mirror lines to glide lines);

(iii) reduction to a simple translation of the same or different multiplicity.

For deriving the two-dimensional space groups compatible with a given multiple cell, the reduction processes first mentioned are made to operate over the symmetry elements inherent in the hexagonal lattice; they are distributed as follows: sixfold rotocentres coinciding with the nodes; threefold rotocentres located at the centres of the triangular meshes; twofold rotocentres over the middle of the edges; mirror-reflexion lines containing the nodes and being either coincident with the rows of nodes or perpendicular to them; glide-reflexion lines containing the middle points

of the edges, that is the twofold rotocentres, and lying parallel to the mirror lines.

Among the multiple cells derived through the previous equations for a given multiplicity it is necessary first to select those to which these derivative groups will be applied, in order to obtain the homogeneous configurations with a certain filling proportion. This choice is determined in the way explained below by the multiplicities of the available sets of equivalent positions in two-dimensional groups.

The proportion of nodes filled is represented by p/q and refers to the minor component in binary layers. All the atoms of this component must be kept equivalent, as stated above, and the patterns obeying this statement are said to be homogeneous. To achieve this homogeneity condition, such atoms must occupy those nodes of the fundamental triangular net that are crystallographically equivalent positions in the unit cell of the multiple array. Let us now multiply the filling proportion p/q by s, a positive integer which we shall call the multiplicity factor of the configuration. In this way, sp is the number of nodes that must correspond to a single set of symmetrically equivalent points, and sq equals the total number of nodes covered by the multiple cell, that is, the multiplicity of this cell. However, for a homogeneous configuration to be extracted from a multiple cell of sq total nodes, it is necessary that a symmetry group containing at least one set of positions with multiplicity sp should be applicable to this cell. As a consequence, s may assume only certain values, depending on the available sets of equivalent positions in all the space groups permissible for the proportion of filling considered. The available set multiplicities are distributed over the fundamental symmetries in the following way:

> oblique cells: 1, 2
> rectangular cells: 1, 2, 4, 8
> hexagonal cells: 1, 2, 3, 6, 12 .

Cells with the same multiplicity will frequently exist with different symmetries; but it may happen that the symmetry of the available cells with a given multiplicity (sq) does not permit the covering, with a single set of equivalent positions, of all the nodes that might be kept equivalent (sp), even for the lowest multiplicity factor ($s=1$). For such a filling proportion p/q, any pattern that one might conceive would be non-homogeneous.

Application to a certain set of filling proportions

Triangular nets may be used for the description of crystal structures based on close packings of large atoms, with different degrees of filling of the interstices (Smirnova, 1956; Iida, 1957; Wells, 1954, 1958; Morris & Loeb, 1960; Gehman, 1963; Loeb, 1964; Lima-de-Faria, 1965; Beck, 1967, 1968; Lima-de-Faria & Figueiredo, 1969). They are applied either to the closest-packed layers or to the layers of interstitial

atoms, octahedral and tetrahedral, when considering separately the upper and lower tetrahedral voids.

The present paper derives from an earlier paper. The method now described was first applied in the exhaustive derivation of the possible homogeneous configurations for the filling proportions dealt with there.

These proportions are listed in Table 1, first column. They correspond to the minor component in close-packed structures of formulae X_mY_n and A_mX_n, where X and Y refer to the atomic species building the close packed array and A to the atomic species occupying the octahedral voids of this packing, always with $m,n \leq 4$. Two possible sequences were considered for generating these structures: equal layers and alternate layers.

Table 1 lists the cell multiplicities (sq) that are required by such a range of filling proportions according to the multiplicities available for the sets of equivalent positions in two-dimensional symmetry groups. This Table distinguishes these set multiplicities and also lists the symmetries containing them.

The multiple cells existing for every fundamental symmetry and their orientation relative to the triangular net are derived through the mathematical expressions established above [equations (1) and (2), when giving values to k, l, u and v, until $A/\alpha \leq 60$]. The analysis of the possible cells derived in this way shows that not all those cells listed in Table 1 exist with a convenient symmetry to account for the necessary set multiplicities. Conversely, some multiplicities are realized with various cell outlines and orientations, and also several distinct configurations are obtained when applying all the permissible space groups to the same cell, or even when giving the permissible values to the free parameters of one set of equivalent positions. As a result there is great variation in the total number of distinct configurations obtained for each one of the filling proportions, as can be seen from Table 2, which contains all the homogeneous configurations derived for the filling proportions listed in Table 1.

To explain in detail the application of this derivation method, the study of the filling proportions $\frac{6}{7}$ and $\frac{3}{7}$ is presented here.

Both proportions are realized for the same cell multiplicities $(7s)$, and the multiplicities of the sets of positions to be filled in such cells are respectively $(6s)$ and $(3s)$. Because their multiplicities are multiples of 6 and 3, these sets may only be found under hexagonal symmetry; as the equivalent positions under this symmetry are grouped in sets of one, two, three, six and twelve, as already mentioned, the permissible values for the multiplicity factor s are 1 and 2 for $\frac{6}{7}$ and 1, 2 and 4 for $\frac{3}{7}$, and consequently the necessary cell multiplicities are 7, 14 and 28 (see Table 1). The survey of the total number of nodes covered by cells with hexagonal shape as a result of giving values to k and l in equation (3), reveals that there is one multiple cell with seven points, none with 14 points and one with 28 points.

The multiple cell covering seven points is located over the original hexagonal lattice in such a way that the actual symmetry elements are reduced to rotocentres exclusively, the highest applicable symmetry group being $p6$ (Fig. 2). The only way to group the seven nodes covered by this cell under $p6$ is to ascribe the equivalent position $1(a)6*$ to one node (taken as the origin), and $6(d)1$ to the remaining six nodes; one homogeneous configuration is therefore obtained for $\frac{6}{7}$, and another for $\frac{1}{7}$, but no attention is called to this pattern as its filling proportion lies out of the range of p/q values selected to illustrate the method of derivation. Now, two ways are possible for reducing the symmetry of this cell to a subgroup of $p6$. One may reduce the sixfold rotocentre to threefold – consequently eliminating the twofold rotocentres – and the group $p3$ is obtained (Fig. 2); obviously, the set of general positions under $p6$ is here split, and the six points are grouped into two sets of three points each; therefore, the filling proportion $\frac{3}{7}$ is attained, but only one distinct pattern is obtained because both groups of nodes corresponding to the set $3(d)1$ under $p3$ lead to the same configuration. This is not always the case for different ways of grouping the nodes satisfying the same set of equivalent positions, as may be seen in Table 2 for the symmetry group $p2$ when applied to large cells. Also, three distinguishable sets of threefold rotocentres were generated when lowering the sixfold rotocentres to threefold, but this fact does not lead to distinct patterns in the present case. To lower the symmetry of this multiple cell even more, one may reduce the sixfold rotocentres to twofold and thus obtain the space group $p2$;

Table 1. *Number of symmetrically equivalent nodes filled in the cells with the multiplicities (sq) required by the domain of filling proportions (p/q) chosen to illustrate the application of the derivation method*

In the last line the symmetries are indicated that contain sets of equivalent positions with the multiplicities considered under each sq value. H, hexagonal; R, rectangular; O, oblique.

p/q \ sq	2	3	4	5	6	7	8	9	10	12	14	15	16	18	20	24	28	30	32	36	40	48	60
6/7						6					12												
4/5				4					8			12											
3/4			3				6						12										
2/3		2			4			6		8				12									
1/2	1		2		3		4			6			8			12							
3/7						3					6						12						
2/5				2					4			6			8			12					
1/3		1			2			3		4				6		8				12			
1/4			1				2			3			4			6			8			12	
1/5				1					2			3			4			6			8		12
Possible symmetries	H R O	H R O	H R O	H R O	H R O	H R	H R O	H	H R O	H R O	H	H	H R	H	H	H R	H R	H	H	R	H	H R	H

as it is oblique, for the reasons mentioned before, this group cannot be used to derive homogeneous configurations corresponding to the proportions $\frac{3}{7}$ and $\frac{6}{7}$, but only $\frac{1}{7}$ or $\frac{2}{7}$.

The multiple cell covering 28 nodes bears the same orientation relationship with the fundamental hexagonal lattice as does the cell with multiplicity seven. Thus, the highest applicable symmetry group is also $p6$, whose highest set multiplicity is six; the configuration arising from filling this set [general position $6(d)$] would correspond to the proportion $p/q = \frac{3}{14}$. Therefore, no homogeneous configuration can be obtained for $\frac{3}{7}$ with this cell.

In conclusion, only two homogeneous patterns are obtained for the proportions $\frac{6}{7}$ and $\frac{3}{7}$, and both with hexagonal symmetry and a multiplicity factor one.

Table 2. *Homogeneous configurations derived for the set of filling proportions listed in Table* 1

The configurations are ordered by increasing multiplicity factor (s), and for each s by decreasing filling proportion p/q (top left). The symmetry (space group) is indicated and an order number is given to each pattern (bottom left).

Table 2 (*cont.*)

Table 2 (*cont.*)

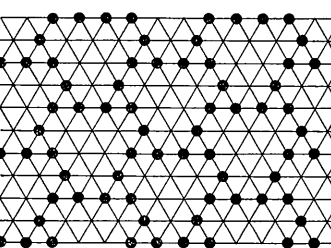| s=2 $\frac{1}{5}$ pmg 39	s=2 $\frac{1}{5}$ pmg 40
s=2 $\frac{1}{5}$ p2 41	s=2 $\frac{1}{5}$ p2 42
s=2 $\frac{1}{5}$ p2 43	s=2 $\frac{1}{5}$ p2 44
s=2 $\frac{1}{5}$ p2 45	s=2 $\frac{1}{5}$ p2 46
s=2 $\frac{1}{5}$ p2 47	s=2 $\frac{1}{5}$ p2 48
s=3 $\frac{1}{3}$ p3m1 49	s=3 $\frac{1}{4}$ p6m 50
s=3 $\frac{1}{4}$ p31m 51	s=4 $\frac{1}{3}$ pmg 52

Table 2 (*cont.*)

s = 4, 1/3, pmg, 53	s = 4, 1/4, cmm, 54
s = 4, 1/4, cmm, 55	s = 4, 1/5, pgg, 56
s = 4, 1/5, pgg, 57	s = 4, 1/5, pmg, 58
s = 4, 1/5, pmg, 59	s = 6, 1/2, p6m, 60
s = 6, 1/2, p31m, 61	s = 8, 1/4, cmm, 62
s = 12, 1/3, p6m, 63	s = 12, 1/4, p6m, 64

Conclusions

One of the important features of Table 2 is the absence of homogeneous configurations for the proportion $\frac{4}{7}$, a fact that had already been noticed (Lima-de-Faria & Figueiredo, 1969). This also implies that any pattern with filling proportion $\frac{4}{7}$ is non-homogeneous with respect to the predominant chemical component.

Another feature to notice is the derivation of only one configuration each for the proportions $\frac{3}{4}$, $\frac{6}{7}$ and $\frac{3}{7}$ (Table 2, numbers 2, 1 and 5). The first was also derived in the preceeding work, but the other two were not. The reason for this may now be understood: the pattern for $\frac{3}{7}$ implies the close location of the three occupied nodes, a situation which clearly disagrees with one of the structural-stability conditions (Lima-de-Faria, 1965) from which the simplified technique emerged; and the choice of the most distant position, being made on adjacent rows in that technique, prevents the derivation of the $\frac{6}{7}$ pattern.

According to the structural-stability conditions already mentioned, the configurations presenting a high probability of being found in real structures are among the most symmetrical, with lowest multiplicity, and presenting the highest degree of regular and uniform filling of nodes over the fundamental triangular net.

Symmetry has a directly available expression and multiplicity is a measurable quantity. The third characteristic is closely related with the space-filling principle (Laves, 1956), or its alternative, the vector-equilibrium principle, stated by Loeb (1967, 1970) in the following way: 'crystal structures tend to assume configurations in which a maximum number of identical atoms or ions are equidistant from each other; if more than a single type of atom or ion are present, then each atom or ion tends to be equidistant from as many as possible of each type of atoms or ions' (sic). The mathematical concept of Dirichlet domains in a two-dimensional space would perhaps allow for a quantified expression of this homogeneity condition, but this suggestion requires further study. Configurations that are equally possible from the viewpoint of symmetry because they have been derived exclusively through symmetry considerations may not be equally probable when considered using a criterion with a physical background, such as the one mentioned above.

The method developed throughout this work appears to be a general tool for the purpose of deriving patterns for binary layers. It is possible to adapt and extend it to plane networks other than the triangular net by dealing properly with the symmetry of the involved network and its metrical characteristics. Regular tes-
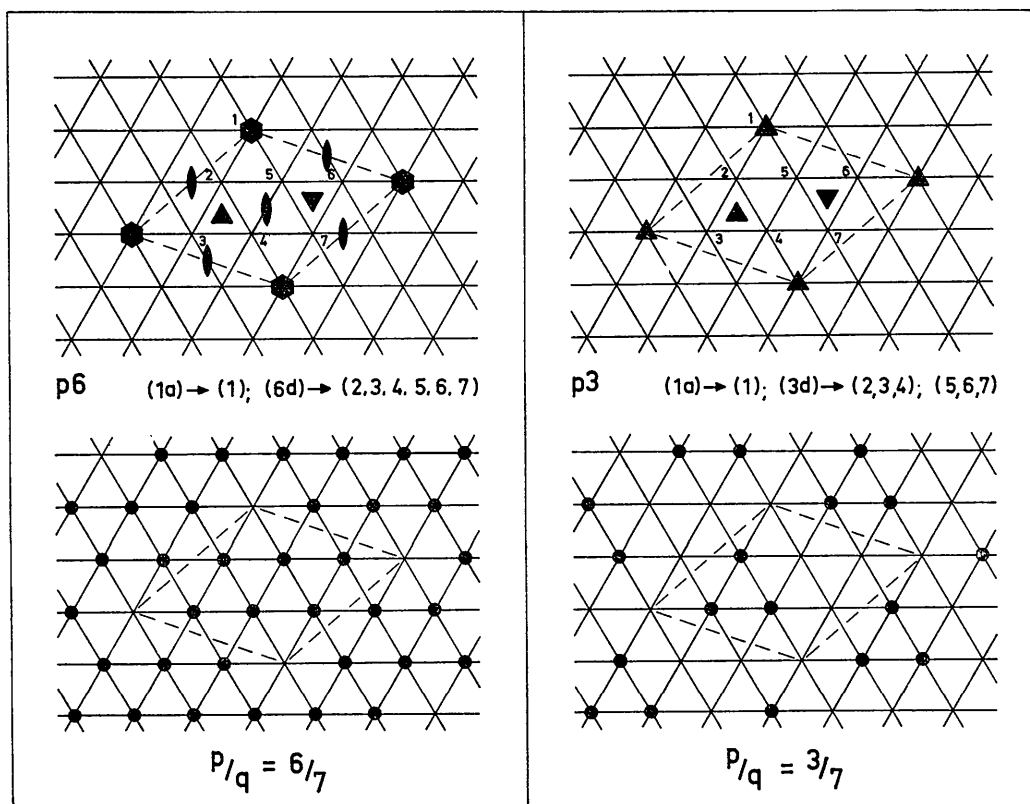

Fig. 2. Multiple cell covering seven points. Possible ways of grouping these points under the plane groups $p6$ and $p3$, and resulting homogeneous configurations for filling proportions $\frac{6}{7}$ and $\frac{3}{7}$.

sellations would be handled more easily, but even binary layers based on the homogeneous circle packings recently studied (Fischer, 1968) could be derived by an extension of this method.

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Relations between the DO_9 (ReO3) Structure Type and Some 'Bronze' and 'Tunnel' Structures

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A number of the 'bronze' and 'tunnel' structures are derived from the DO_9 type by a simple geometrical operation: examples given are the tetragonal tungsten bronze and related structures, and Mo_5O_{14} and $LiNb_6O_{15}F$. They are seen to form families of crystallographic shear structures of a new type.

Introduction

In the DO_9/ReO3 structure type $[MO_6]$ octahedra are united by common vertices [Fig. 1(a)]. Projection down one of the cubic axes [Fig. 1(b)] emphasizes the empty 'tunnels' of square cross-section within the structure. (They are in fact strings of cuboctahedra sharing square faces.) In the $E2_1$/perovskite structure type sites at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ (cuboctahedra centres), which are empty in DO_9, are occupied by the A cations, e.g. by Ca in $CaTiO_3$ [Fig. 1(c)]. In some tungsten bronzes A_xWO_3 these same sites are fractionally occupied by alkali metal or other cations.

But there are other bronze structures which also contain sites of high coordination number partly occupied by A cations. One is the tetragonal tungsten bronze (TTB) structure in which these sites are in pentagonal as well as square tunnels in an array of corner-connected $[WO_6]$ octahedra (Magnéli, 1949a). Examples of TTB-related structures are legion, particularly in the system $Nb_2O_5 + WO_3$ (Stephenson, 1968). A number of binary, ternary and quaternary oxides and oxide-fluorides have related structures but definite stoichiometries: Mo_5O_{14} (Kihlborg, 1963), Ta_3O_7F (Jahnberg & Andersson, 1967) and the closely similar $LiNb_6O_{15}F$ (Lundberg, 1965), and $NaNb_6O_{15}F$ (and $NaNb_6O_{15}OH$)