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## Proper Layer Description and Standard Representation of Inorganic Layered Structure Types\*

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### Abstract

A standard representation is proposed for layered structure types (broadly speaking, those that are decomposable in layers), based on a layer description along plane directions. As an example, this standard representation is applied to simple structure types based on cubic closest packing, complemented by an appropriate notation.

### Introduction

The aim of this paper is to help establish a certain order and simplicity in the representation of structures, that are decomposable in any kind of layers and not just certain types of layers (e.g. Wells, 1975, p. 29). A standard representation is proposed based on the layer description along the most suitable plane directions, and which is inspired by the condensed-model technique (Lima-de-Faria, 1965*a*). This standard representation has been applied to many close-packed structure types; however, only a group of structure types of simple binary compounds, based on cubic closest packing, will be presented here.

### Notation

For a more complete description of the structures we need to include, not only the type of packing layers and

their stacking, but also the kind of configuration of the packing atoms in minor proportion and that of the interstitial atoms, *i.e.* their distribution patterns and the way these distribution patterns are superposed within the structures.

The notation used here for the distribution patterns of either packing or interstitial atoms, and their sequences, is an extension of the symbology already used for the description of the layers and their stackings in the general table of inorganic structure types (Lima-de-Faria & Figueiredo, 1976).

The distribution patterns are symbolized by a capital letter indicating the shape of the plane unit cell of their patterns, using *T* for hexagonal (triangular net), *Q* for square (quadrangular net), and *R* for rectangular or oblique shape, and an upper symbol indicating the occupancy of the atoms in the possible sites within this unit cell. For instance  $Q^{5^2}$  means a distribution pattern of the type *Q* with a proportion of occupancy of  $\frac{2}{3}$ . In the particular cases of proportions of occupancy of  $\frac{1}{2}$ ,  $\frac{1}{3}$ ,  $\frac{1}{4}$ , ... the number one is omitted, for reasons of simplicity, and  $Q^2$  corresponds to a proportion  $\frac{1}{2}$ ;  $Q^0$  corresponds to zero occupancy. In the case of layers with mixed composition the distribution pattern normally refers to the atoms in smaller proportion in the layer, because it generally leads to the simplest description.

The sequence of the distribution pattern either of the packing atoms in minor proportion or of interstitial atoms is indicated by a superscript near the symbol of the distribution pattern, which represents the translation and/or the rotation of the distribution pattern necessary to reproduce its successive positions within

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the structure (Fig. 1). For instance in the case of a structure with packing layers of mixed composition like  $[\text{AuCu}_3]^c$ , the complete structural formula would be  $[\text{Au}^{Q^2 Q^0} \text{Cu}_3]^c$  ( $c$  for c.c.p. of Au and Cu packing atoms, the square brackets emphasizing the packing,  $Q^2$  and  $Q^0$  for the types of distribution patterns formed by the Au atoms, and  $s$  for the sequence of the  $Q^2$  distribution pattern). In the case of an interstitial structure, for instance anatase,  $\text{Ti}^o[\text{O}_2]^c$ , the complete structural formula would be  $\text{Ti}^{oQ^2}[\text{O}_2]^c$  ( $c$  for c.c.p. of the oxygen packing atoms,  $o$  for the octahedral coordination of the titanium interstitial atoms,  $Q^2$  for the kind of distribution pattern they form, and  $d$  for its sequence). More details of this notation are presented with this publication as deposited material.\*

This symbology is apparently similar to that used by Figueiredo (1979) when considering the stacking of different commensurable layers, but in fact it has a

\* See deposition footnote.

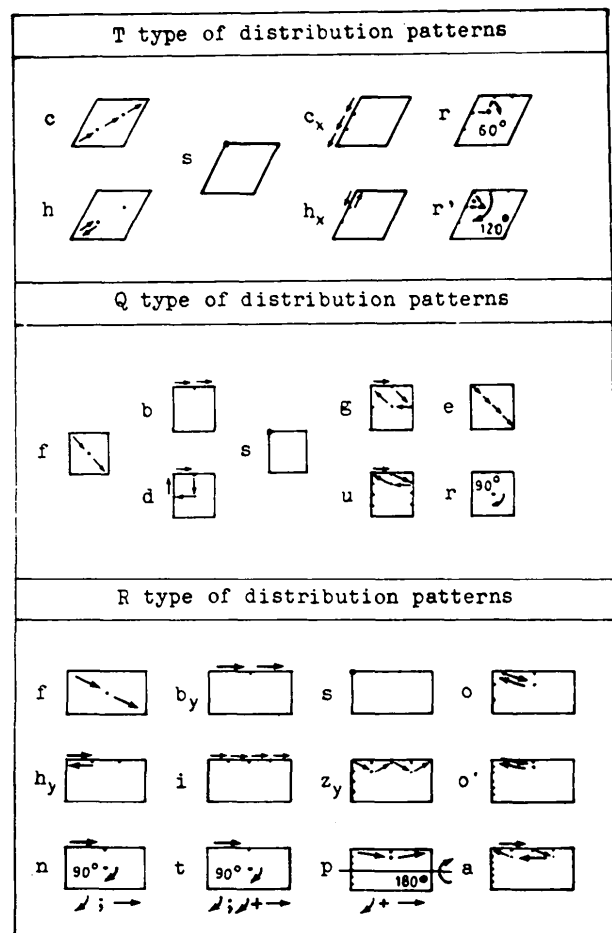


Fig. 1. Translations (projected vectors) and/or rotations indicating the sequences of the distribution patterns mentioned in Figs. 3, 4, 5 and 6.

different meaning. In the latter case it expresses the commensurability and indicates the rank of the commensurate multiple cell (or the number of points per unit cell with reference to a supercell). Our notation expresses the occupancy within the unit cell and does not refer to any other unit cell.

**Proper layer description**

Most of the inorganic structures can be decomposed into layers (Lima-de-Faria, 1965b; Lima-de-Faria & Figueiredo, 1976), and the superposition of the layers obeys certain simple rules (Lima-de-Faria, 1978). However, some structures permit more than one

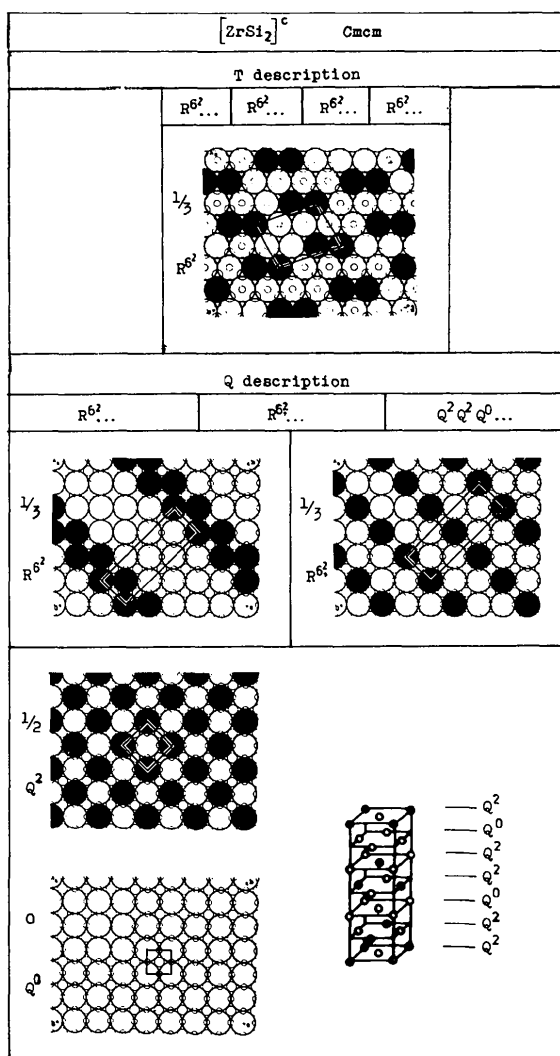


Fig. 2. The seven possible layer descriptions and the four different ones permitted by the  $[\text{ZrSi}_2]^c$  structure type. The standard representation based on the proper layer description  $Q^2 Q^2 Q^0 \dots$  is also shown.

description in terms of layers, and a search for the simplest or 'proper' one is necessary.

An important group of structures permitting several layer descriptions is that based on the exact or approximate cubic closest packing of large atoms with or without small atoms in octahedral or tetrahedral interstices. These structures permit seven layer descriptions: four along the closest-packed layers, and three along the quadrangular layers, perpendicular to the fourfold axes of the cubic closest packing. This can be illustrated by the structure  $[\text{ZrSi}_2]^c$ , which is orthorhombic, space group  $Cmcm$ . It permits a single description along the four closest-packed layer directions ( $T$  description, referred to the c.c.p. alone), and which correspond to the sequence of equal layers  $R^{6^2}$ , with a not very symmetrical distribution pattern of the packing atoms in these layers (Fig. 2). Along the quadrangular layer directions ( $Q$  description, referred to the c.c.p. alone), this structure permits three different descriptions: two corresponding to sequences of equal layers but with not very symmetrical distribution patterns,  $R^{6^2}$  and  $R^{6^2}$ , and a further description involving two simple layers,  $Q^2$  and  $Q^0$ , with occupancy  $\frac{1}{2}$  and zero respectively, in the sequence  $Q^2 Q^2 Q^0 \dots$ . This last description is the simplest and therefore the 'proper' layer description of the  $[\text{ZrSi}_2]^c$  structure (Fig. 2). The two different distribution patterns  $R^{6^2}$  and  $R^{6^2}$  (Fig. 2) correspond to the same type of unit-cell pattern  $R$ , and the same proportion of occupancy  $\frac{2}{6}$ ; the dash is used to distinguish them, and  $\frac{2}{6}$ , instead of  $\frac{1}{3}$ , to indicate the multiplicity 6 of the unit cells.

#### The standard representation of inorganic layered structure types

The layers we have considered are constructive layers and not only packing layers (Lima-de-Faria, 1978). The packing layers are only built by the packing atoms, the larger atoms, normally the anions; a constructive layer is made up of the packing layer and the interstitial atoms situated in between it and the upper adjacent packing layer. Constructive layers when stacked together completely generate the crystal structure. These layers correspond to the transparent sheets of the condensed models. In the condensed-model technique a structure is sliced into layers, and these layers are represented by transparent plastic sheets, which are placed over one another in an appropriate supporting rack (Lima-de-Faria, 1965a). To draw the layers and the complete unit cell of a structure type we only need to consider that part of the condensed model which is included within the unit cell, and represent it in perspective. The drawing of the constructive layer or layers (if different), corresponding to the proper description, and the drawing of their superposition, give

a simple and satisfactory representation of a structure type, and is proposed to be called 'standard' representation. In some cases, however, the exact drawing of the superposition of the layers may give rise to a certain overlapping of the layers, causing confusion. To avoid this difficulty the unit cell is then slightly expanded, particularly in the direction perpendicular to the layers. This procedure produces some distortion of the unit cell, but this is not relevant in most cases.

#### The proper layer description and the standard representation of $[X_m Y_n]^c$ , $A_m^o[X_n]^c$ and $A_m^t[X_n]^c$ structure types

If we apply the proper layer description and the standard representation to the structure types of general formulae  $[X_m Y_n]^c$ ,  $A_m^o[X_n]^c$  and  $A_m^t[X_n]^c$ , with  $m$  and  $n \leq 4$ , we obtain the results shown on Figs. 3, 4 and 5. On the left-hand side of these figures, the proper constructive layers necessary to build all these structure types are represented, and the interstitial sites are indicated by small circles of two sizes ( $o$  and  $t$ ), dashed when not occupied, and filled when occupied. On the right-hand side are shown the drawings of part of the constructive layers, or their subdivisions, contained within the unit cell of these structure types, and the corresponding structural information.

In the drawings of the superposition of layers of structure types without interstitial atoms, the packing atoms are represented by small circles, black or white according to the kind of atom they represent. In structure types with interstitial atoms, the interstitial atoms are represented by small black circles, the unoccupied interstices by small squares (a widely used symbol for vacancies), and the packing atoms are represented by dots, because it is the configuration of the interstitial atoms which changes and which it is important to emphasize, the packing being well defined and always the same for all these structures. It is this device that makes this description so simple (Figs. 4 and 5).

When the plane of the interstitial atoms does not coincide with the plane of the packing atoms, I have subdivided the constructive layers into two different levels, in order to achieve a more exact representation. This happens with  $A_m^t[X_n]^c$ , and with the  $A_m^o[X_n]^c$  structure types when described along closest-packed layers. However, in considering this process extended to more complex cases, such as those involving two types of interstitial atoms (octahedral and tetrahedral), e.g. the olivine structure,  $\text{Mg}_2^o\text{Si}^t[\text{O}_4]^h$ , this subdivision would very much distort the unit cell and complicate the drawing, and therefore it is advisable to represent each constructive layer on only one plane.

For reasons of simplicity, and to facilitate the relationship among structure types, the structural

information is presented here (Figs. 3, 4 and 5) in a different way from that explained in the section on notation. For instance, instead of  $[\text{AuCu}_3]^c$ ,  $[\text{AuCu}_3]^c$  is written with  $Q^2 Q^0$  underneath.

It can be seen that these constructive layers have in general very simple and symmetrical patterns. It will also be realized that many structure types are built of equal layers, or by alternate sequences of simple layers.

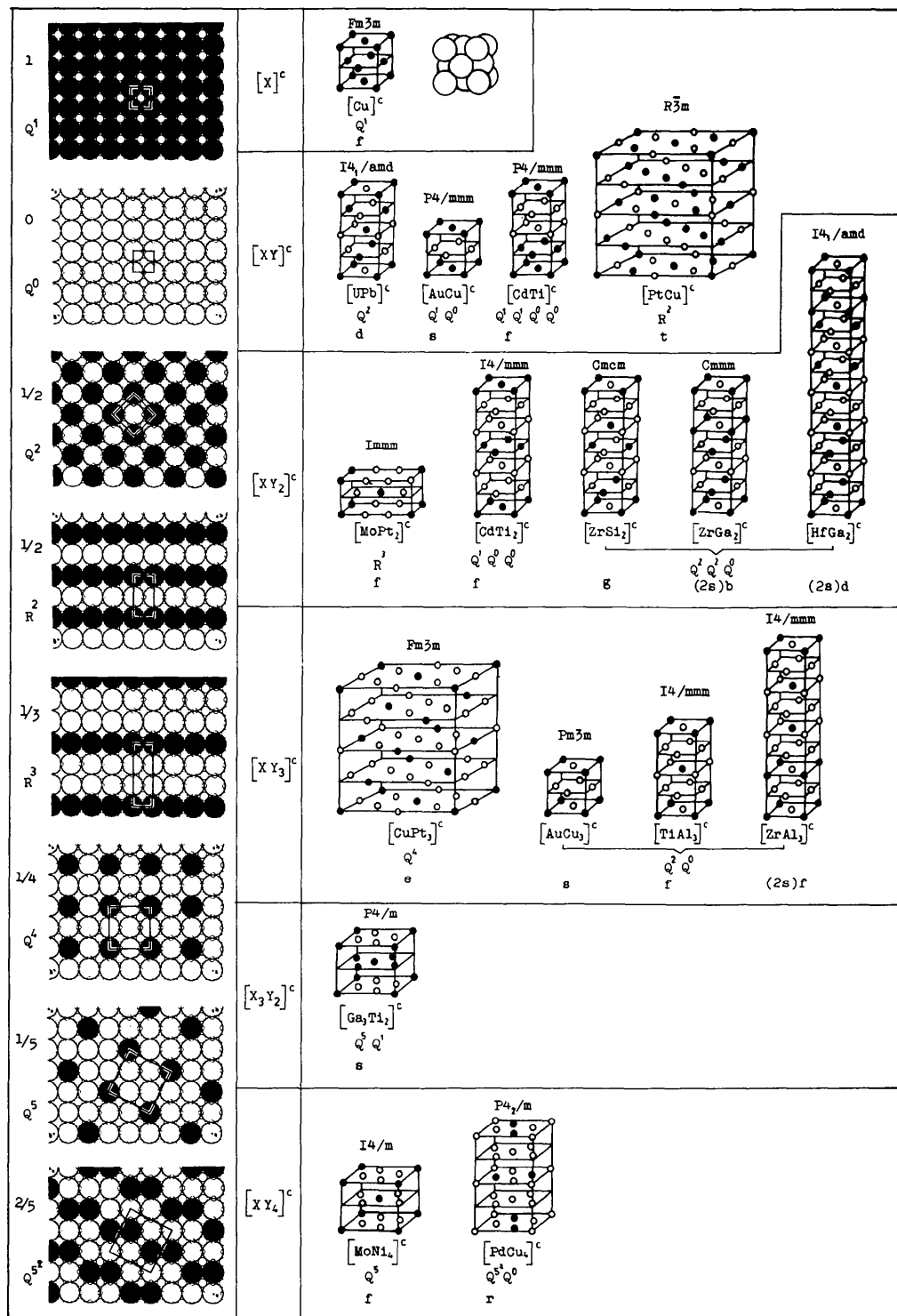


Fig. 3. The standard representation of layered inorganic structure types of general formula  $[X_m Y_n]^c$  with  $m, n \leq 4$ .

For instance the  $[XY_2]^c$  structure types are built either by equal  $R^3$  layers, or by the sequence of layers  $Q^1 Q^0 Q^0 \dots$ , or  $Q^2 Q^2 Q^0 \dots$

It is also apparent from these figures that the same way of superposition of the distribution patterns is adopted by several different structure types, and that

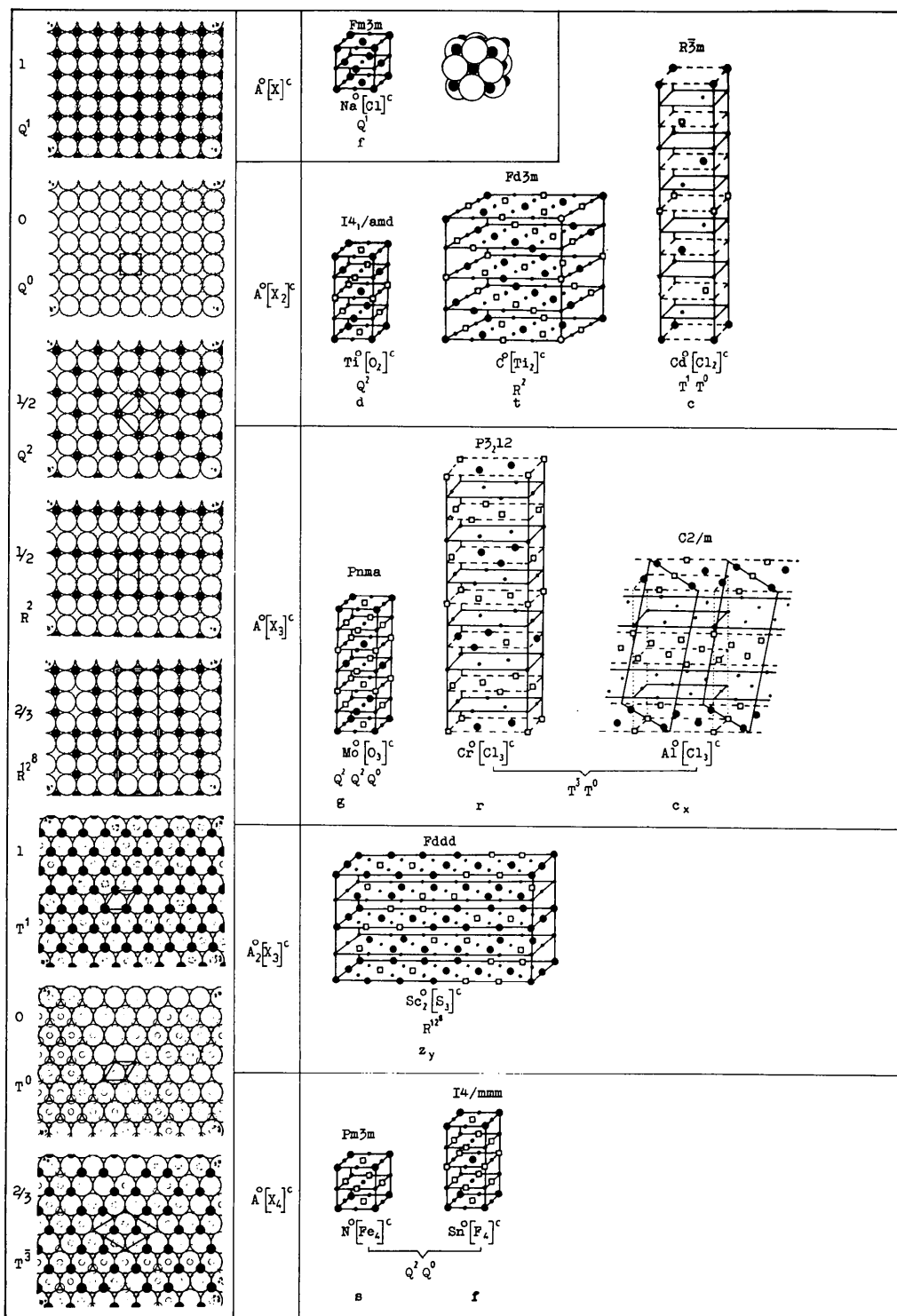


Fig. 4. The standard representation of layered inorganic structure types of general formula  $A_m^o[X_n]^c$ , with  $m, n \leq 4$  ( $o$  means octahedral interstitial atoms).

few types of sequences are found among so many different structure types. It is also remarkable that many of these sequences of the distribution patterns coincide with the ones already observed for the

constructive layers of a large number of inorganic structure types (Lima-de-Faria & Figueiredo, 1976), and that only a few new symbols for the sequences have had to be introduced (Fig. 1).

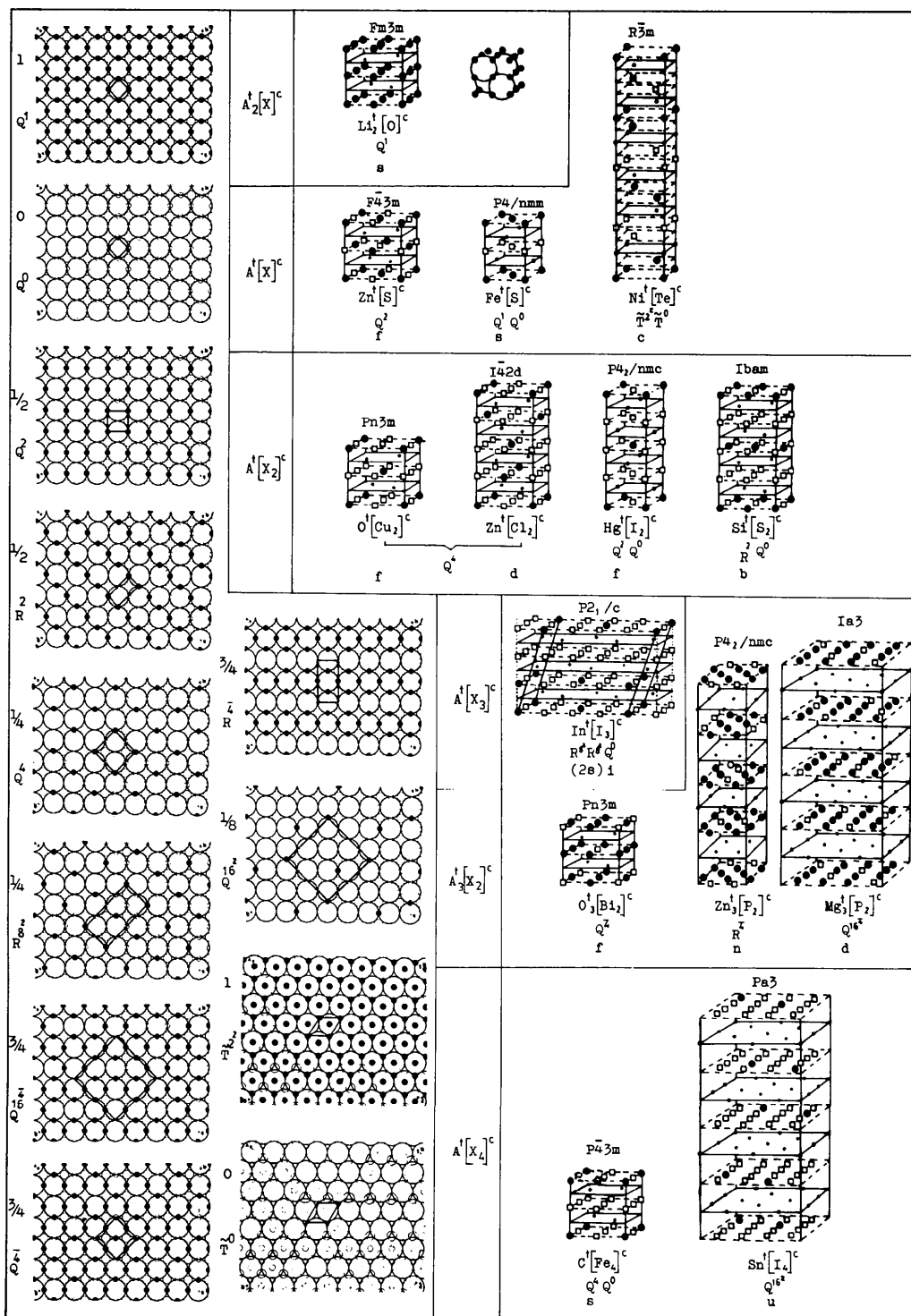


Fig. 5. The standard representation of layered inorganic structure types of general formula  $A_m^t[X_n]_c^c$ , with  $m, n \leq 4$  ( $t$  means tetrahedral interstitial atoms).

Another interesting feature has come out of these figures. If one compares  $[X_m Y_n]^c$  with  $A_m^o[X_n]^c$  structure types, some of them show identical distributions of atoms, the drawings differing only in the replacement of open circles by squares, that is, of atoms by vacancies (Fig. 6). This emphasizes the important role that vacancies may play in structure stability, which has already been pointed out in relation to other structures by Figueiredo & Lima-de-Faria (1979), and also the tendency for atoms, either packing or interstitial, to form very symmetrical three-dimensional stable distributions.

There is also a certain analogy between  $[X_m Y_n]^c$  structure types and some of the  $A_m^t[X_n]^c$  structure types, like the relation between  $\text{Hg}^t[\text{I}_2]^c$  and  $[\text{TiAl}_3]^c$ , and between  $\text{Fe}^t[\text{S}]^c$  and  $[\text{AuCu}]^c$ , but this analogy is much more pronounced between  $[X_m Y_n]^c$  and  $A_m^o[X_n]^c$  structure types, which is possibly related to the identity of the three-dimensional arrangement of the packing atoms and of the octahedral voids in the cubic closest packing, allowing the same kind of spatial distribution for the various proportions of atoms.

The analogy among proper layers of the  $[X_m Y_n]^c$ ,  $A_m^o[X_n]^c$  and  $A_m^t[X_n]^c$  structure types, with very similar patterns  $Q^1$ ,  $Q^0$ ,  $Q^2$ ,  $R^2$ , etc., also shows the tendency for a certain stability in two dimensions, which may be related to the crystal-growing process.\*

\* Detailed information on the notation and additional considerations on this standard representation have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38319 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

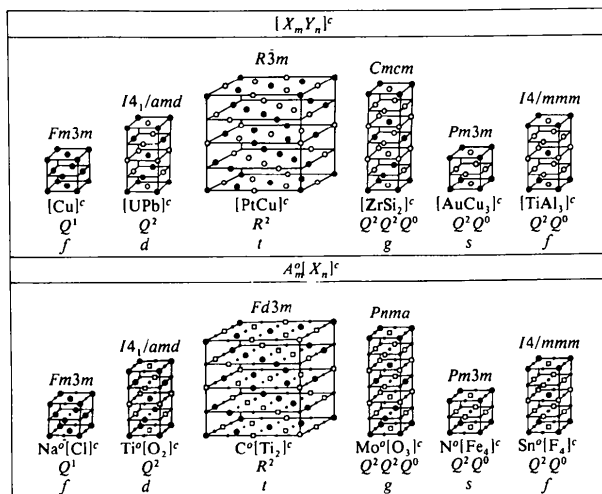


Fig. 6. Some of the structure types represented in Figs. 3 and 4 show a strong analogy to the three-dimensional distributions of the packing atoms and the octahedral interstitial atoms, which is revealed by their standard representation. The difference in space groups in two pairs of these structure types results from slight distortions of the ideal packing structures.

### Final remarks

The standard character of this representation is justified by the fact that most inorganic structure types are layered structure types, even those of complex silicates, as has already been shown in the general table of inorganic structure types (Lima-de-Faria & Figueiredo, 1976).

This standard representation is apparently similar to certain types already used by other authors. However, there are important differences: in some cases certain atoms are not represented for reasons of clarity (Wadsley, 1964; Flahaut, 1972; Pearson, 1972; Sadanaga, Takeuchi & Morimoto, 1978; Katada & Herber, 1980; Wakihara, Hinode, Abe & Taniguchi, 1981), in other cases the representation is sometimes not confined to the unit cell (Bokii, 1954; Shpynova, Belov & Mel'nik, 1980), and it is always restricted to a small number of structure types.

To find out the several different layer descriptions of each of the structure types studied here, in order to choose the proper layer description, I have used their condensed models, and want to call attention to the fact that without these aids, and based only on the drawings available in the literature, it would certainly have been very difficult to undertake such a study.

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