

Classification, Notation, and Ordering on a Table of Inorganic Structure Types*

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The inorganic structures are classified according to their structural units into five categories: atomic, group, chain, sheet, and framework. Each category is subdivided into homogeneous and heterogeneous, and further subdivisions are based on the constitution and packing of the structural units. A definition of structure type is proposed, and a notation for inorganic structure types is presented that accounts for the coordination of the atoms, the kind and packing of the structural units, and the condensation process of the groups in chains, sheets, and frameworks. Generalized symbols for the stacking sequences of layers also are proposed. A general table including about 800 inorganic structure types is presented, divided along one direction according to the five structural categories and their subdivisions, and along the other direction according to general formulas.

I. Introduction

Because the field embraced by inorganic crystal structures, which involves chemistry, mineralogy, metallurgy, solid state physics, ceramics, etc., is so large, general systematizations have been only outlined and tables have been worked out for only certain groups of structures. This state of affairs obscures the relationship among structures in different domains, e.g., alloys and minerals, the recognition of structure types common to different fields, and consequently, the possibility of reducing the number of fundamental structural arrangements of atoms, and the search for general structural principles and rules. Therefore, the systematization of the many crystal structures that have been determined since the advent of X-ray diffraction has become an imperative necessity.

The concept of structure type, although widely and commonly used, is not well defined and has different meanings according

to each author. This was clearly concluded at a meeting organized by the authors, where a few crystallographers discussed this subject.¹ It is also clear that there is a lack of a convenient and generally adopted notation to deal with structure types, and the greater the number of known structures, the more necessary becomes the use of such notation. On the other hand, some general classifications of inorganic structure types have been outlined, but not applied systematically.

Therefore, in order to obtain an appropriate systematization of inorganic structures, we must define the concept of structure type, establish a general structural classification and adopt a convenient notation. The aim of this work is to present a basis for such a systematization and to present a general table of inorganic structure types.

¹ Informal meeting on inorganic structure types, Lisbon, Portugal, May 1968. Attendants: M. J. Buerger, A. L. Loeb and P. Schlichta (United States); F. Laves (Switzerland); W. B. Pearson (Canada); M. O. Figueiredo, J. Lima-de-Faria, and A. Lopes Vieira (Portugal).

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I. General Structural Considerations

A crystal structure is a definite arrangement and linkage of atoms in a periodic, orderly array. Each individual structure can be described by the chemical nature and the relative positions of the atoms within the unit cell, their coordination, and the kind, strength, and length of the bonds between them.

It is best not to regard a crystal structure as merely a geometric arrangement of atoms since the way the interatomic bonds are distributed also plays an important role. The bonding arrays define the so-called structural units, which range from isolated atoms through tightly linked groups of atoms with increasing degree of dimensional condensation, up to a three-dimensional linkage. These structural units tend to pack together as efficiently as possible, the remaining atoms accommodating in the interstices between them.

The simplest structural units, isolated atoms, occur mostly when there is a predominance of nondirectional forces. In these structures the larger atoms (structural units) pack together as closely as possible, giving rise to various sorts of close packings, and the smaller atoms occupy the interstices. In structures where directional forces are dominant, certain atoms may associate in finite groups, in infinite chains, in infinite sheets, or in three-dimensional networks or frameworks. Groups, chains, or sheets of atoms will also tend to pack together as efficiently as possible, the remaining atoms occupying the interstices. The directional character of the bonds constrains these structures to less dense arrays of atoms. Frameworks, especially, have the important characteristic of being open forms, with large interstices that may accommodate interstitial units, either atoms or groups.

When one considers the packing of structural units, it is clear that their shapes and sizes are important characteristics. The packing efficiency of the structural units will be hampered by the interaction between the structural units themselves or by the satisfaction of a particular coordination of the interstitial atoms, and the resulting structure will be the balance between these interactions and the tendency for the densest packing.

Moreover, important properties of a structure, such as cleavage, polymorphism, isomorphism, exsolution, and gliding, are primarily dependent on the shape and size of the structural units and their type of packing. These considerations make it clear that it is not the nature of the bonds between the atoms that is more important in a crystal structure, but the distribution of the relative strength of such bonds, defining the structural and the interstitial units.

The possibility of substitution for atoms in a structure, beyond the nature of bonds, is intimately related to their coordination and size. Therefore, size and coordination of the atoms are also important structural factors (1).

III. Definition of Structure Type

As we have already mentioned, the concept of structure type has been vaguely defined and, as a consequence, has had different meanings for different authors. This requires a more precise definition, and recently, a few such attempts have been presented (2-5).

It is clear that to elaborate a definition of structure type, we have to consider the main structural features already discussed, and accordingly, we propose the following definition.

Two structures are isotypic, i.e., they belong to the same structure type if:

(1) The symmetry (space group) is the same, and corresponding atoms are placed in the same set, or sets, of equivalent positions. These are either fully occupied by corresponding atoms ($C^o[Th]^c$ and $Na^o[Cl]^c$) or by different atoms randomly distributed ($\underline{Sn^tZn^t}[As_2]^c$ and $Zn^t[S]^c$), or partially occupied at random by the same or different atoms ($\underline{Ga_2^t}\square^t[S_3]^c$, $Zn_2^t\underline{Ge^t}\square^t[S_4]^c$ and $Zn^t[S]^c$). In the case of certain assemblages of atoms in which some atoms are not completely localized (rotating molecules, hydrogen in OH and H₂O, etc.), these assemblages are considered to behave structurally as isolated atoms; therefore, $Li^o[I(H_2O)_3]^h$ and $Ni^o[CsCl_3]^h$ are isotypic. This means that what is specific to the structure type are the

sets of equivalent positions and not the number of atoms per unit cell.

(2) The coordination of the corresponding atoms, the structural units, and their packing are the same. Different values of the axial parameters, of the positional parameters, and of the relative size of the atoms, can give rise to differences on the structural characteristics mentioned above. Examples of pairs of structures which, although satisfying condition one, correspond to distinct structure types are: $\text{Al}_2^p[\text{Th}]^{7s}$ and $[\text{UHg}_2]R_{2y}^{21}$; $\text{Li}^o\text{Ni}^o[\text{O}_2]^c$ and $\text{Na}^o[\text{H}^2\text{F}_2]_{33}^{11c}$; $\text{Li}_2^f[\text{O}]^c$ and $\text{Ca}^{cb}[\text{F}_2]^{2s}$.

We can condense the above definition in the following way. Two structures are isotypic if (i) they have the same symmetry (space group), (ii) they involve the same sets of equivalent positions occupied by corresponding atoms (or assemblages of atoms) with the same coordination, and (iii) they are formed by the same structural units packed in the same way.

IV. Classification of Inorganic Crystal Structures

As we have already emphasized, the structural units play an important role in the constitution of crystal structures because they express the bonding array of the structure and their kind and packing are determinant with respect to most properties.

A classification based on structural units was first applied with success to the silicates by Machatschki (6). He replaced the old chemical classification by a structural one based on the types of structural units of silica tetrahedra, and Bragg (7) developed these ideas, which lead to the known categories of group-, ring-, chain-, sheet-, and framework-silicates. This classification explained many physical and chemical properties of the silicates.

Structural classifications based on similar grounds have been proposed for other groups of compounds, such as aluminosilicates (8, 9), fluoaluminates (10), borates (11, 12), germanates (13, 14), phosphates (15, 16), orthophosphate hydrates (17), tellurium oxosalts (18), sulfosalts (19–23) and sulfates (24).

Moreover, Machatschki (25) and Povarennykh (26) developed chemical-structural classifications for the wide domain of minerals, and various authors (27–35) have outlined general classifications of structures based on the types of structural units.

It was apparent from all these studies that a classification based on structural units would be the most appropriate. Therefore, we propose to group the inorganic crystal structures first by the category of their structural units, which may be isolated atoms, finite groups, and infinite chains, sheets, or frameworks. In structures containing more than one category of structural units, the packing will be determined by the structural unit of highest dimension, and they are grouped according to this unit. Consequently, only five categories of structures need to be considered: *atomic*, *group*, *chain*, *sheet*, and *framework*.

Structures involving one type (category, shape, and size) or different types of structural units are called *homogeneous* or *heterogeneous*, respectively. For instance, the structure of Na_2O_2 , where Na atoms pack together with O_2 groups, and the structure of $(\text{NO}_2)_2\text{S}_3\text{O}_{10}$ built of the linear NO_2 group and the tetrahedral group S_3O_{10} , are both heterogeneous group structures. Atomic structures are heterogeneous whenever the packing is made up with atoms of different sizes.

Many structural units can be imagined to be subdivided into smaller units, called building units, which can be dimers (the linear linkage between two atoms), polygons, or polyhedra of atoms. If structural units are built up with a single building unit, they are called simple; if they are built up with different kinds of building units, they are called composite. Structures based on simple structural units are called *simple* and those having composite structural units are called *composite*. For instance the diopside structure is based on chains of silica tetrahedra and is therefore a simple structure. But, for example, calciborite, which is built up of chains of triangles and tetrahedra of boron and oxygen atoms, and fairfieldite, which is built up of chains of tetrahedra and octahedra, are, by definition, composite structures.

Structures can be further subdivided into *linear*, *polygonal*, *polyhedral*, and *mixed* if their structural units are built of dimers, polygons, polyhedra, or mixtures thereof, respectively.

We have been considering the possibility of characterizing structures in terms of the constitution of their structural units, and we shall now consider the second important aspect, which is the packing of these units. The problem of filling space with structural units is a three-dimensional one, but in most cases it can be formally decomposed into a two- plus one-dimensional problem, that is, the building up of layers and the way they stack together. This is very convenient because it very much simplifies the description and correlation of different packings.

In the case of atomic structures, we consider that the ideal layers are close-packed and have a certain structural character, which is emphasized by phase transformation mechanisms and by plastic deformation and polytypism properties. The structures whose packings can be described in this way, that is, by defining layers and characterizing their stacking, are called *layered* structures. The structures for which this description is not possible are called *nonlayered*. Most of the atomic structures are layered, but some are non-layered. An example of a nonlayered simple atomic structure is the garnet structure, where the oxygen atoms occupy one set of 96 equivalent positions, forming a special close packing that cannot be decomposed into layers.

Chart I represents the scheme of this classification of inorganic structures. In

certain cases it may be a difficult problem to distinguish which atoms form the structural units. Even in pure ionic structures, it is often possible to distinguish certain atoms that are clustered but without forming, as a whole, any structural unit of higher dimension. This is the case for certain group, chain, or sheet configurations that are a consequence of the stable distribution of certain proportions of the interstitial atoms within the packing of the larger atoms. If such structures fit a dense close packing emphasizing the nondirectional character of the bonds, they will be considered as atomic. Examples are $\text{Mg}_2^{\circ}\text{Si}^{\text{I}}[\text{O}_4]^{\text{h}}$ (olivine), $\text{Si}^{\text{I}}[\text{S}_2]^{\text{c}}$ and $\text{Cd}^{\circ}[\text{I}_2]^{\text{h}}$, which are atomic and not group, chain, or sheet structures, respectively. However, when these configurations lead to a marked distortion of the packing, giving rise to well-defined structural units, the structure is no longer an atomic one, and it will be classified under the corresponding category. For instance, CoGeO_3 is an atomic structure, but diopside, $\text{CaMgSi}_2\text{O}_6$, which has a parental chain configuration of the tetrahedral cations, is a chain structure.

Some heterogeneous atomic structures, like Cr_3O , do not possess layers in the structural sense mentioned above and they behave as three-dimensional assemblages. However, they can still admit a planar description in successive planes of atoms, stacked in a certain way, some planes being purely geometrical with atoms very far apart from each other. Although it may be convenient to use such a planar description, they are not considered here to be layered, but just "planar" structures (36, 37).

Certain structures can be imagined derived

CHART I. Scheme of the classification of inorganic structures.

Main category of structural units	Composition of the bonding array ^a	Constitution of structural units ^b	Shape of building units	Packing of structural units
Atomic	Homogeneous	Simple	Linear	Layered — (2D + 1D) — Type of layers and stacking sequence
Group			Polygonal	
Chain			Polyhedral	
Sheet	Heterogeneous	Composite	Mixed	Non-layered — 3D
Framework				

^a Equal or different structural units.

^b Equal or different building units.

from packings with regularly distributed vacancies, and their representation is simplified greatly if we use a normal packing description and the symbol \square for the vacant packing positions. These vacancies give rise, in general, to interstitial coordinations that do not exist in the corresponding normal packings. An example of a "defect layered structure" is $\text{Cd}_2^{\text{cb}}\text{Ta}_2^{\text{6}}[\text{O}_7\square]^{\text{qs}}$.

When classifying individuals one always has to deal with intermediate cases. It is a characteristic inherent to any classification, since a classification is an abstraction and simplification imposed on the complexity of nature. What seems important is to classify the well-defined cases, say, the extreme and typical cases. When an intermediate case is considered one has to decide to which extreme it is more similar and classify it according to this similarity.

V. Notation

(a) Structural Formulas

Several notations have been proposed for structural formulas, and among them we shall distinguish those of Niggli (28) and of Machatschki (38).

A notation must be as simple and self-explanatory as possible, and it should be kept as close as possible to the way the chemists write the formulas in order to facilitate the transfer from chemical to crystallochemical nomenclature. On the other hand, in order to obtain appropriate structural formulas, not too overloaded but containing sufficient information, one must select the most relevant structural characteristics, and these have to be inferred from the definition of structure type and from the structural classification already proposed.

Although symmetry may account for certain physical properties, it is not necessarily an expression of the arrangement of atoms, since slight changes in the positions of the atoms may give rise to quite different symmetries. Conversely, the same symmetry and equivalent positions may comply with quite different arrangements of atoms. Therefore, if we want to express mainly the atomic arrangement of the atoms in a structure, we can avoid an

indication of the symmetry in the structural formulas. However, the coordination of the atoms, the composition, and the category of the structural units, their kind and the way they pack together, are important structural features which must be figured out in the structural formulas.

To express the coordination, we use superscripts placed on the right-hand side of the chemical symbol of the element. For regular or quasi-regular coordination polyhedra we use small letters like *tr* (triangular), *π* (trigonal pyramidal), *t* (tetrahedral), *o* (octahedral), *sq* (square), *p* (trigonal prismatic), \bar{p} (trigonal antiprismatic), *cb* (cubic), \bar{cb} (anticubic), *do* (dodecahedral), *co* (cubo-octahedral), *ic* (icosahedral). In the other cases, the coordination number is used, and in complicated situations, as for large packing atoms where the same element may have different environments, the coordination will be omitted.

Two main kinds of atoms may build up a crystal structure: those that form the structural units, and those (interstitial atoms) that are located in the interstices left by the packing of such units. The atoms that constitute the structural units have been indicated within brackets by several authors, the square brackets being the most used. Square brackets are also adopted here to embrace the atoms building up the structural units, and parentheses are used to express groups of atoms like (OH), (NH₄), etc., which may behave crystallochemically as a single atom. In composite structures, it may be convenient to emphasize certain subunits that form the structural units and these will be placed within vertical bars. In heterogeneous structures, the various types of structural units packing together will be placed within braces.

The category of the structural unit will be indicated by a symbol following the square brackets: ∞ for group, $\infty 1$ for chain, $\infty 2$ for sheet, $\infty 3$ for framework, the absence of symbol meaning atomic. The symbol ∞ has been widely used for infinite structural units; for groups we propose the symbol ∞ because it looks like part of the symbol infinite, suggesting in this way the condensation of groups to form infinite higher dimensional structural units.

The writing of structural formulas starts with the interstitial atoms, then the atoms forming the structural unit, and finally the symbol for its category. This way of writing the structural formula brings it closer to the chemical formula and avoids possible misinterpretation of the meaning of the numerical part of some category symbols.

The next step is to characterize the structural units by figuring out their kind and the way they pack together, and for this we use superscripts on the right-hand side of the square brackets embracing the structural unit.

Groups can be imagined as formed by the condensation of atoms, which may further condense in infinite chains, in infinite sheets, and finally in frameworks. A composite symbology is used to express this condensation process, which appears to be an important structural feature (8, 39, 40).

A group is specified by a Roman numeral, corresponding to the number of building units involved, and an Arabic numeral as a superscript is used to distinguish among groups with the same number of building units. For instance, there are several topologically distinct groups corresponding to the formula A_2X_7 , formed by two tetrahedra sharing a corner, which are denoted by II^1 , II^2 , II^3 , etc. The shape of the building unit is indicated within the structural unit by the coordination of the central atom. However, when the building units forming the group are not centered, their shape is indicated by a superscript placed on the left-hand side of the chemical symbol of the element or of the straight lines enclosing the subunits. Examples are $[^{\circ}S_6]_6^{\circ}$ and $[^{\circ}BCl_4]_4^{\circ b}$.

A chain will be considered as deriving from the group which, by translation or screw rotation, except the diad, may generate such an infinite chain. Therefore, with the exception of the screw rotation cases, the group corresponds to the repeat unit of the chain. The chain symbol will then be composed of the group symbol plus another order number, which may distinguish among chains derived from the same group. For instance, the K_2CuCl_3 and the $AgPO_3$ chain structures both derive from the tetrahedral group I^1 and their chain symbols are I^{11} and I^{14} , respectively.

The sheets can be considered as derived either by condensation of chains or derived directly by condensation of groups, and no restrictions are imposed on their condensation process. In the first case, another order number is added to the chain symbol; in the second case, a zero and an order number are added to the group symbol, to maintain uniformity on the sheet symbology. For instance, the sheet in sanbornite, $BaSi_2O_5$, can be considered to derive by condensation of II^{21} chains and its symbol is II^{211} , and the sheet in muscovite can be imagined to be derived from the two-dimensional condensation of a group of two tetrahedra II^1 , and its symbol is II^{101} .

Framework structures can be derived by condensation of sheets or derived directly from chains or even groups. Whenever possible, sheets will be preferred as connected infra-units, and they may be of the two types mentioned above. There is no need to add to the symbols of those units any other order number to specify the framework in which they condense because the distinction between related frameworks will be made by the symbol for the connectivity of such infra-units.

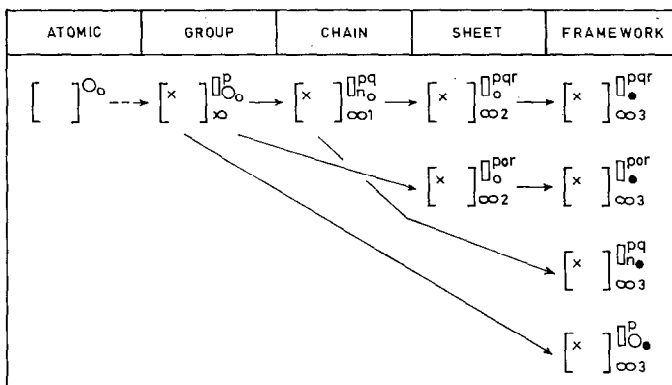
Chart II presents schematically the notation for the structural units. In some particular cases it may be convenient to consider the structural units derived from intermediate infra-units, and the number of these infra-units is also indicated. For instance, the amphibole chains are normally considered as double chains derived by the connectivity of two pyroxene chains of symbol II^{11} , and the amphibole chain symbol will be $2-II^{11}$.

We have described the notation for the structural units and we shall now consider the symbology for the packing.

As already mentioned, whenever a reasonably dense and planar layer direction exists in a structure we decompose the three-dimensional problem of describing the spatial arrangement of the structural units in a $2D$ plus $1D$ problem, thus describing such a layer and characterizing its stacking mode.

The layers may be of two fundamental types: either both crystallographic dimensions in the plane are equivalent, N -type layers, or they are not, R -type layers.

CHART II. Scheme of the notation for the structural units. ○ kind of layer or set of layers of atoms or groups; ○ stacking of layers or sets of layers; ● connectivity of connected units in frameworks; □ number of building units constituting the group (Roman numerals); p , order number of group within the category with same number of building units; g , order number of chain derived from group \square^p ; n , order number of layer formed by the packing or the arrangement of chains \square^{pq} ; r , order number of R - or N -type sheet derived from chain \square^{pq} or group \square^p , respectively; x , coordination of the central atom of each building unit or its shape if not centered.



The densest layers that may be formed by the simplest structural units, the atoms, belong to the first type. The centers of the packing atoms in the closest-packed layers form a triangular net, labeled T , which is one of the three regular tessellations. The other two, the square net 4^4 and the hexagonal net 6^3 , which also occur in atomic packings, are also N -type layers, and are labeled Q (from quadrangular) and H , respectively. A few of the semiregular tessellations also receive special symbols, like the kagomé network of triangles and hexagons, a N -type layer labeled K , but most of them are symbolized according to the general notation as N or R layers.

The layer parallel to the (110) plane of the body centered cubic packing may be considered as a special case of deformation intermediate between T and Q layers, in whose meshes only angles of 60° and 90° are involved, respectively. The mesh of such a network is a rhombus with an angle of $70^\circ 32'$ and a centered unit cell. This is a R -type layer and is labeled B to suggest the packing in which it occurs.

In networks with different kinds of polygons, the need for expressing the kind and number of such polygons becomes clear. Therefore, even in atomic structures, the

general layer symbol is a compound one and expresses the layer type by the letters N and R followed by a set of numerical superscripts that are a sort of simplified topological description. They represent the kind of polygons involved in the network ordered by increasing edge multiplicity (3 for triangle, 4 for square, and so on) and as a superscript the number of such polygons necessary to characterize and generate the network. For instance the semiregular tessellation 3^2434 (Schläfli symbol) found in certain alloy phases like CuAl_2 has the symbol $N^{3^24^1}$, that is, two triangles and one square are sufficient to characterize the network, and the 3^34^2 tessellation with one ribbon of triangles alternating with one ribbon of squares, is symbolized as $R^{3^14^1}$. In the most common cases of networks formed exclusively by triangles and squares, a simplification is still made: the numerical symbols 3 and 4 for the polygons are suppressed and only their number is figured out. Therefore, the above-mentioned tessellations have the simplified symbols N^{2^1} and R^{1^1} . Whenever the enumeration of such polygons leads to a structural formula that is too long, they are indicated in a generic way as m/n , this meaning a certain combination of m triangles and n squares. Several authors (36, 41-43) have already proposed layer

notations based on similar grounds, but confined to families of intermetallic compounds.

The heterogeneous atomic layers, that is, layers formed by atoms of different sizes, can be imagined as deriving from homogeneous layers by a complex substitution process. The same capital letters are used for corresponding networks, but complemented with special symbols to express simple, double (by pairs), or simple + double substitution, respectively (\cdot , \odot , \circ). Also, when the layer is slightly puckered, as in the case of the Friauf-Laves phases, the symbol \sim is placed over the capital letter denoting the layer type.

Heterogeneous atomic structures also may be formed by the stacking of homogeneous layers, differing either in metrics and kind, or only in metrics. Such metrical difference is expressed by superscripts indicating the number of polygons covered by the supercell common to the layers stacked together. For instance, the ThCu_2Si_2 structure is written $\text{Si}_2^8\{[\text{Cu}_2][\text{Th}]^{(Q^2Q^1)}\}_f$, where Q^2 denotes the square layer of the smaller Cu atoms containing two squares per supercell, and Q^1 denotes the square layer of Th atoms with larger mesh corresponding to one square per cell.

For the description of certain nonlayered atomic structures, the so-called planar structures, with networks formed by atoms quite separate apart from each other, we use the symbols for the atomic close-packed layers displaying the same geometrical arrangement, but placed within angular brackets.

We shall now consider the stacking modes of equal layers, and for this we shall treat first the notation for the stacking of the simplest and most symmetrical layers and then extend it to the general cases of N and R layers. Small letters will be applied to denote the stacking sequences, in contrast with the capital letters used for the layers.

For the closest-packed T layers, there are three main and regular ways of stacking: the closest stacking, with three possible positions for the layers giving rise to the well-known cubic and hexagonal sequences, denoted by c and h respectively, and mixtures thereof, c/h , all resulting in coordination number (CN) 12,

with one atom located over the void between three atoms in the layer below; the stacking of one atom over the valley between two atoms in the layer below, corresponding to CN 10, with four possible stacking positions giving rise to three pure sequences denoted by b (from body-centered), v (from valley), and d (from diamond glide planes); finally, the simple superposition of layers, CN 8, with one atom in every layer touching only another atom in the layer below, corresponding to the stacking possibility denoted by s (from superposition). The T_b arrangement is called tetragonal close packing (44), and the T_s arrangement is called simple hexagonal packing (Fig. 1).

For the Q layers, the closest stacking corresponds to one sole possibility denoted by f (from face-centered) giving rise to the cubic closest packing. Q_f is clearly equivalent to T_c , and we shall use T_c for cubic close-packed sequences and Q_f only in mixed stacking sequences, as will be explained latter. The stacking over valleys (CN 8) may give rise to two pure sequences denoted by b and d , by analogy to the similar stackings of the T layers. The Q_b packing is equal to T_s , and again the first symbol is only used in mixed stacking sequences. The superposition of Q layers (CN 6) also receives the symbol s , and the Q_s arrangement is called simple cubic packing.

The B layers are very special in the sense that they have a centered unit cell and they are

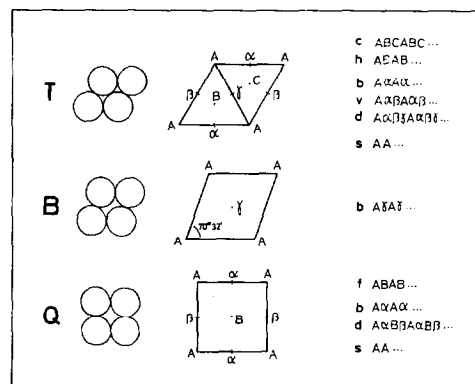


FIG. 1. Stacking symbols for the simplest atomic layers; T , closest-packed layer; B , body centered cubic close-packed layer parallel to (110) planes; Q , square layer.

involved in body centered cubic packing. This packing corresponds to the stacking of the *B* layers in such a way that one atom goes over the valley between two atoms that do not contact each other. As the number of contacts of one atom with the atoms in the layer below is still two, such stacking is denoted by *b*, the symbol already used for the parallel situation in *T* and *Q* layers.

When extending this symbology to layers of general type *N*, the idea of number of contacts as a main guide to the definition and characterization of the stacking modes must be modified because in the stacking of such layers more than one kind of contact is generated in general for atoms within the same layer. An alternative may be to consider the relative positions of homologous points in successive layers connected by a stacking vector. Consequently, to define the sequences we use a primitive unit cell of the layer and the projection of the stacking vector reported to the origin. The stacking symbols of the *T*- and

Q-type layers are generalized for the corresponding modes of the *N*-type layers in the way summarized in Fig. 2.

In the *R*-type layers, the distinction between the two main directions must become apparent, *x* referring to the direction of the ribbons of polygons, and *y* to the other direction in a primitive unit cell of the layer, and whenever the stacking vectors are along these directions, *x* or *y* is added to the stacking symbols. Two new symbols are introduced to account for stacking vectors along general directions or of magnitudes different from one-third or one-half of the unit cell sides or of the diagonal. If the situation is parallel to *h*, that is, the stacking involves two positions exclusively, the symbol is *o* (from orthorhombic), and if the situation is parallel to *c*, then the symbol is *m* (from monoclinic). To avoid ambiguities, it is postulated that the projection of the stacking vector must fall within the unit cell of the layer, and that the angle at the origin of the primitive cell is $\geq 90^\circ$ (Fig. 2).

Type of layer	Pure stacking sequences
N	
R	

FIG. 2. Generalized stacking symbols; *x* and *y* do not necessarily refer to crystallographic axes.

Certain structures are built up of only one type of layer following a mixture of stacking modes. Whenever it is possible to distinguish in these mixtures a set of layers obeying the same stacking sequence and stacked over an identical set in a different way, it is convenient to describe first the layers and their stacking within the set, and next, the stacking sequence of the sets considered as packing entities. In such cases, the symbols for the set of layers are placed within parentheses, followed by the stacking symbol for the sets. An illustrative example is AsFe_2 , a homogeneous atomic structure, built up of superimposed sets of three square layers Q stacked in f . The corresponding packing symbol is $(3Q_f)$.

Most of the heterogeneous atomic structures exhibit analogous situations and they are treated in the same way. For instance, the Friauf-Laves phases can be described by the close stacking of pairs of layers composed of a puckered heterogeneous triangular layer \bar{T} and a homogeneous kagomé layer K . If we consider the densest way of stacking of these layers, K can only be stacked on \bar{T} in one position, but \bar{T} can be placed over K in two positions. Consequently for the set $\bar{T}K$, as a unit, there are three possible positions, thus giving rise to the possibility of c/h sequences, the c , h , and ch sequences being represented by the Cu_2Mg , Zn_2Mg , and Ni_2Mg structures, respectively. In the case of heterogeneous atomic structures formed by two kinds of layers that are constrained to stack in a well-defined way (the densest), the packing symbol only needs to express the kinds of layers. An example is $\{[\text{Cu}_5][\text{Ca}]\}^{TK}$.

The symbology presented here for the packing in atomic structures deals with a few definitions and a small set of numbers and letters, and when dealing with complex layers of the kind found in the packing of group, chain, and sheet structures, we preferred to extend and generalize the meaning of such symbols rather than introducing new ones.

To describe the packing in group structures, we therefore consider the array of the geometrical centers of the groups and deal with them by directly applying the symbology for the atomic packings. However, for groups whose shape is not approximately spherical,

an uncertainty still remains regarding the orientation relatively to the plane of the layers, and the same packing description may correspond to various possibilities of arranging the groups.

In chain structures, it is necessary to choose first the plane direction along which the chains are packed with the highest density. This direction defines the layer whose stacking is to be described, and, because different layers may be generated by the same chains packed in different ways, an order number for such layers is added on the bottom right-hand side of the chain symbol. For instance pyroxenes have the same chains of tetrahedra as the CrO_3 structure, but the way they pack together to form the layers is different. In chain structures, the layers are always of R -type, with x along the chain axis, and the symbology developed for the stacking of atomic R layers is extended to them.

The sheets can be of type R or N , depending on whether they derive from a one-dimensional condensation of chains or a two-dimensional condensation of groups. The symbology for the stacking sequences of the atomic layers is extended to them and applied according to the type of sheet we are dealing with.

In framework structures, where the structural units extend in three dimensions, the concept of packing has no sense. The packing of the structural units is replaced by the connectivity of connected units, but the symbology is the same as used for the other categories of structures according to the possibility of considering a framework derived from the connectivity of sheets, chains or groups.

Heterogeneous structures, with the exception of atomic ones, have complicated arrangements, and consequently, their packings may be figured out only in the simplest cases. Also, no symbology is proposed here for the packing or connectivity in nonlayered structures, which is only denoted by an asterisk, except in the cases already considered for the planar structures.

The same structural formula, in the way we have described, may correspond to more than one polymorph of a certain compound. This may happen only when the symmetry and/or

the distribution pattern of the interstitial atoms vary in the structures. In such cases, the designation of the particular form has to be included in the structural formula in order to avoid the ambiguity. Examples are the α and β forms of Po, and the δ' and δ'' forms of NM_2O .

As a matter of convenience, a few simplifications are adopted in the notation. Because cubic and hexagonal close packings are so common in atomic and group structures, we use the symbols c and h instead of Tc and Th , respectively. Also, for the body centered cubic packing, we use b instead of Bb , the other packings with b stacking, like Tb and Qb , being written in their complete form. Two other simplifications are still made: the symbol I^1 in group structures is omitted in the cases where no ambiguity is present, and the order number for the packing layers in chain structures is only figured out for orders higher than one.

(b) Structure Type Symbol

A general notation for structure types was first proposed by Ewald and Hermann in 1931 (45). This notation is not very widespread, possibly due to its lack of structural information, and structure types are frequently referred to, or represented, by the best known substance having that structure type. The American Society for Testing Materials (46) proposed a nomenclature for alloy phases, which expresses the chemical formula of a representative substance followed by the number of atoms per unit cell, and the Bravais lattice type codified in a literal symbol. Improvements of this nomenclature were proposed by Schubert (47) for elements and binary compounds, and by Pearson (48) for metals and alloys. Although this symbology is simple and useful, especially for ordering structure types in a list for structure determination purposes, it is not intended to emphasize the relationships between crystal structures.

A more structural nomenclature has been attempted by Hellner (49) and by Donnay, Hellner, and Niggli (50), ascribing descriptive symbols based on the lattice complexes to crystal structure types.

Giving still more importance to the atomic

arrangement than to the symmetry characteristics, Lima-de-Faria (51) proposed a symbology for close-packed structure types based on general structural formulas. For instance, the NaCl structure type, with symbol $B1$ in Ewald-Hermann notation, was represented by the symbol $A^{\circ}X^c$, where X^c means a large packing atom in cubic close packing, and A° means an interstitial atom in an octahedral void. However, this notation needed the addition of superscripts to distinguish among structure types with the same general structural formula.

To solve this ambiguity one can use the structural formula of a certain substance instead of the general structural formula. Such symbology, in addition to its own descriptive value, also would have the advantage of being in agreement with the generalized use of compounds for the representation of structure types. Consequently, we adopt the structural formula of a representative substance as the symbol for the corresponding structure type, the $B1$ structure type being therefore represented by the symbol $\text{Na}^{\circ}[\text{Cl}]^c$.

VI. Ordering of Inorganic Structure Types on a General Table

The ordering of inorganic structure types in tables has already been considered for certain groups of structures (2, 4, 33, 52-56). A suggestion of a general table has been advanced by Lima-de-Faria (51), and a sketch of such a general table has been presented by the authors at the Symposium on the "Geometry and Systematics of Crystal Structures," organized by A. L. Loeb, and held at Lexington, Massachusetts in August 1969.

Considering that a rectangular shape is more appropriate for a table, two main entries or directions will be available, and relevant structural features must be selected to guide the ordering along these two directions. It is clear that after having proposed a structural classification of inorganic structure types, and having chosen the structural formulas as their symbols, the structural divisions and the general formulas are naturally the relevant features to be adopted.

This way of devising the table will enable us to answer two important crystallochemical questions:

(a) Given a certain general formula, what are the possible structure types?

(b) Given a certain structure type, what are the related structure types?

For convenience of space distribution, we chose the horizontal direction for the structural divisions, and the vertical direction for the general formulas, placing them by increasing complexity, X , AX , XY , etc.

By general formula we mean the formula obtained by clearing the structural information, replacing the symbols of the chemical elements by capital letters, and simplifying the chemical indices on the structural formula of a compound; when there is a random distribution of elements in certain structural positions (equipoints) it is the whole proportion of the structural positions and not of the elements alone that should be considered. Accordingly, to $\text{Na}^{\circ}[\text{Cl}]^{\circ}$, $\text{Nb}_3^{\circ}[\text{O}_3\Box]^{\circ}$, $\text{Sn}^{\circ}\text{Zn}^{\circ}[\text{As}_2]^{\circ}$ and $\text{Ga}_2^{\circ}[\Box]^{\circ}[\text{S}_3]^{\circ}$ corresponds the same general formula AX . The letters will emphasize the relative differences in the sizes of the atoms, similar sizes being represented by consecutive letters in the alphabet, and larger sizes by higher order letters. General chemical formulas could look apparently identical to general formulas, in this structural sense, but there is an important difference concerning the information on the atoms that are crystallochemically different and their relative sizes. For instance, the compound TlSe of general chemical formula AB has the general formula ARX_2 because Tl occupies two different structural positions, half of the atoms having tetrahedral coordination and half anticubic coordination, the corresponding structure type symbol being $\text{Tl}^{\circ}\text{TI}^{\circ\text{cb}}[\text{Se}_2]^{\circ\text{N}^{\circ}\text{I}^{\circ}}$.

As a matter of convenience, and to embrace several general formulas corresponding to the same number and proportions of crystallochemically different atoms, we also used the simplified general formulas A_mB_n , $A_pB_qC_r$, etc., where the letters have no relative size meaning. On the other hand, in order to represent families of structure types we also may consider general structural formulas, where the

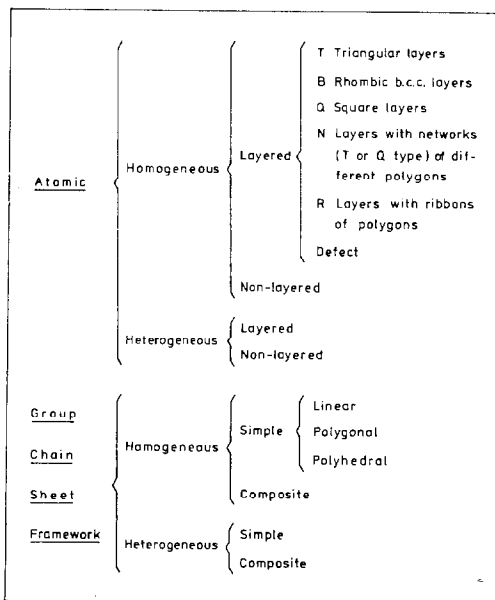
structural information is retained. An example is $\text{A}_2^{\circ}[\text{X}_3]^{\circ}$ which includes $\text{Al}_2^{\circ}[\text{O}_3]^{\circ}$ and $\text{Cr}_2^{\circ}[\text{S}_3]^{\circ}$.

The application of the classification principles to the domain of known inorganic structures leads to the structural divisions presented in Chart III. In atomic structures, the structural units (atoms) cannot be subdivided into building units, and therefore, the homogeneous and heterogeneous atomic structures are directly subdivided into layered and non-layered structures.

In the general table, we have split into two columns some very overloaded subdivisions like the tetrahedral chains, sheets, or frameworks, where we have placed in one column the structures related with groups I and II, and in another those related to groups higher than II. On the other hand, we have grouped under the same column some less populated subdivisions in order to save space.

If structure types displaying essentially the same atomic arrangement were listed together, the table would not show clearly the main different structural arrangements. In fact, the same whole arrangement, but with minor distortions, may be found in structural types

CHART III. Categories of inorganic structures and their subdivisions.



with different symmetries and/or slight changes in atomic coordination. Therefore, we placed separately, under the designation of distortion derivatives, the structure types related in this way to certain ones mentioned in the main table, and those related to the same structure type were linked by a dash.

To enable the easy identification of most of the minerals, we found it useful to add their names to the structure type symbols, but, for the sake of saving space, this procedure was restricted to those having complicated formulas or to particularly interesting ones.

According to the definition of heterogeneous structures, no such structures can correspond to general formulas X , $X_m Y_n$, and $X_p Y_q Z_r$, and the respective spaces are marked with a solid line. Moreover, other spaces on the table are empty, and this may be a consequence either of incompleteness, or of certain structural reasons, whose search will constitute one of the goals of the systematic derivation of structure types.

To organize a general table of inorganic structure types, a considerably large number and variety of structures had to be considered, in order to select representative examples for the main categories of structures. However, although the table had to be as representative as possible it could not be too large in order to be handled easily. Therefore the present general table,² containing about 800 structure types, is a compromise between the number of representative examples and its size.

Structure determination studies have been usually confined to the determination of atomic positions, coordinations, and interatomic distances. Nowadays, other structural features, such as length and nature of the bonds, packing characteristics, etc., are more commonly discussed, but there is still a lack of a more complete structural information, which

could possibly be obtained through methods other than X-ray or neutron diffraction. As a consequence, a few structure types that could not be characterized completely were nevertheless included in the table because of their representativeness. On the other hand, it is probable that in the future some structure types will have to change their place in the table when more detailed structural information is available.

The classification and the notation proposed here enable a simple characterization and relation of the structure types, but it is through the table that the structural relationships become more apparent. The table enables the easy establishment of many kinds of relations, namely, between structure types and their derivatives, either distortion, substitution, or stuffed, between those reflecting different condensation processes of the same infraunits, and between those with the same structural units but displaying different arrangements.

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² See NAPS Document No. 02554 for 16 pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. Remit in advance for each NAPS accession number \$1.50 for microfiche or \$5.00 for photocopies up to 30 pages, \$0.15 for each additional page. Make checks payable to Microfiche Publications. Outside of the United States and Canada, postage is \$2.00 for a photocopy or \$0.50 for a fiche.

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