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family depends mainly on the idealization and/or abstraction level, *relevant to a concrete purpose*.

This very idealization and/or abstraction process caused the term *polytype* to become also an *abstract notion* meaning a *structural type* with relevant geometrical properties,* belonging to an abstract family whose members consist of layers with identical structure and keep identical bulk composition. Such an abstract notion lies at the root of all systemization and classification schemes of polytypes.

A still higher degree of abstraction has been achieved by Dornberger-Schiff (1964, 1966, 1979) who abstracted from chemical composition completely and investigated the manifestation of crystallochemical reasons for polytypism in the *symmetry of layers* and *symmetry relations between layers*. Her theory of OD (order-disorder) structures is thus a theory of symmetry of polytypes, playing here a role similar to that of group theory in traditional crystallography. In the next section, a brief account of basic terms, definitions, and logical constructions of OD theory will be given, together with its contribution to a geometrical definition of polytypism.

9.2.2.2. Symmetry aspects of polytypism

9.2.2.2.1. Close packing of spheres

Polytypism of structures based on close packing of equal spheres (note this idealization) is explained by the fact that the spheres of any layer can be placed *either* in all the voids ∇ of the preceding layer, *or* in all the voids Δ – not in both because of steric hindrance (Section 9.2.1, Fig. 9.2.1.1).

A closer look reveals that the two voids are *geometrically* (but not translationally) *equivalent*. This implies that the two possible pairs of adjacent layers, say *AB* and *AC*, are geometrically equivalent too – this equivalence is brought about *e.g.* by a reflection in any plane perpendicular to the layers and passing through the centres of mutually contacting spheres *A*: such a reflection transforms the layer *A* into itself, and *B* into *C*, and *vice versa*. Another important point is that the symmetry proper of any layer is described by the layer group $P(6/m)mm$,[†] and that the relative position of any two adjacent layers is such that only some of the 24 symmetry operations of that layer group remain valid for the pair. It is easy to see that 12 out of the total of 24 transformations do not change the *z* coordinate of any starting point, and that these operations constitute a subgroup of the index [2]. These are the so-called τ operations. The remaining 12 operations change any *z* into $-z$, thus turning the layer upside down; they constitute a coset. The latter are called ρ operations. Out of the 12 τ operations, only 6 are valid for the layer pair. One says that only these 6 operations have a *continuation* in the adjacent layer. Let us denote the general multiplicity of the group of τ operations of a single layer by *N*, and that of the subgroup of these operations with a continuation in the adjacent layer by *F*: then the number *Z* of positions of the adjacent layer leading to geometrically equivalent layer pairs is given by $Z = N/F$ (Dornberger-Schiff, 1964, pp. 32 ff.); in our case, $Z = 12/6 = 2$ (Fig. 9.2.2.1). This is the so-called *NFZ relation*, valid with only minor alterations for all categories of OD structures (§9.2.2.2.7). It follows that all conceivable structures based on close packing of equal spheres are built on the same

symmetry principle: they consist of equivalent layers (*i.e.* layers of the same kind) and of equivalent layer pairs, and, in keeping with these stipulations, any layer can be stacked onto its predecessor in two ways. Keeping in mind that the layer pairs that are geometrically equivalent are also energetically equivalent, and neglecting in the first approximation the interactions between a given layer and the next-but-one layer, we infer that all structures built according to these principles are also energetically equivalent and thus equally likely to appear.

It is important to realize that the above symmetry considerations hold not only for close packing of spheres but also for *any conceivable structure* consisting of two-dimensionally periodic layers with symmetry $P(6/m)mm$ and containing pairs of adjacent layers with symmetry $P(3)m1$. Moreover, the OD theory sets a quantitative stipulation for the relation between any two adjacent layers: they have to remain *geometrically equivalent* in any polytype belonging to a family. This is far more exact than the description: ‘the stacking of layers is such that it preserves the nearest-neighbour relationships’.

9.2.2.2.2. Polytype families and OD groupoid families

All polytypes of a substance built on the same *structural principle* are said to belong to the same *family*. All polytypic structures, even of different substances, built according to the same *symmetry principle* also belong to a family, but different from the previous one since it includes structures of various polytype families, *e.g.* SiC, ZnS, AgI, which differ in their composition, lattice dimensions, *etc.* Such a family has been called an *OD groupoid family*; its members differ only in the relative distribution of *coincidence operations** describing the respective symmetries, irrespective of the crystallochemical content. These coincidence operations can be *total* or *partial* (local) and their set constitutes a groupoid (Dornberger-Schiff, 1964, pp. 16 ff.; Fichtner, 1965, 1977). Any polytype (abstract) belonging to such a family has its own stacking of layers, and its symmetry can be described by the appropriate individual groupoid. Strictly speaking, these groupoids are the members of an OD groupoid family. Let us recall that any space group

*A coincidence operation is a space transformation (called also *isometric mapping*, *isometry*, or *motion*), which preserves distances between any two points of the given object.

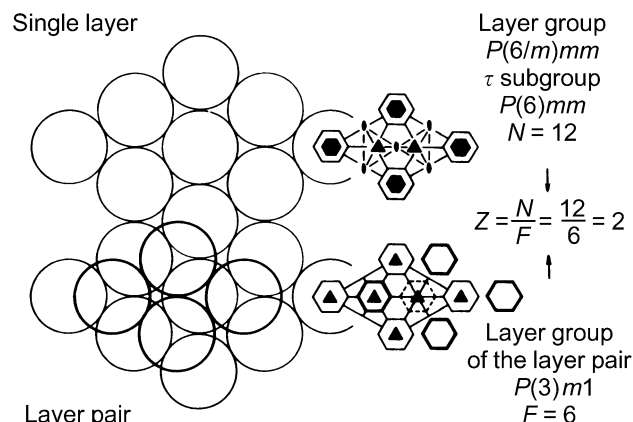


Fig. 9.2.2.1. Symmetry interpretation of close packings of equal spheres. The layer group of a single layer, the subgroup of its τ operations, and the number of asymmetric units *N* per unit mesh of the former, are given at the top right. The τ operations that have a continuation for the pair of adjacent layers, the layer group of the pair, and the value of *F* are indicated at the bottom right.

*This is an interesting example of how a development in a scientific discipline influences semantics: *e.g.* when speaking of a $6H$ polytype of SiC, one has very often in mind a characteristic sequence of Si–C layers rather than deviations from stoichiometry, presence and distribution of foreign atoms, distortion of coordination tetrahedra, *etc.*

[†]The direction in which there is no periodicity is indicated by parentheses (Dornberger-Schiff, 1959).

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consists of total coincidence operations only, which therefore become the symmetry operations for the entire structure.

9.2.2.2.3. MDO polytypes

Any family of polytypes theoretically contains an infinite number of periodic (Ross, Takeda & Wones, 1966; Mogami, Nomura, Miyamoto, Takeda & Sadanaga, 1978; McLarnan, 1981*a,b,c*) and non-periodic structures. The periodic polytypes, in turn, can again be subdivided into two groups, the 'privileged' polytypes and the remaining ones, and it depends on the approach as to how this is done. Experimentalists single out those polytypes that occur most frequently, and call them *basic*. Theorists try to predict basic polytypes, *e.g.* by means of geometrical and/or crystallochemical considerations. Such polytypes have been called *simple*, *standard*, or *regular*. Sometimes the agreement is very good, sometimes not. The OD theory pays special attention to those polytypes in which *all layer triples, quadruples, etc.*, are geometrically equivalent or, at least, which contain the smallest possible number of *kinds* of these units. They have been called polytypes with *maximum degree of order*, or *MDO polytypes*. The general philosophy behind the MDO polytypes is simple: all interatomic bonding forces decrease rapidly with increasing distance. Therefore, the forces between atoms of adjacent layers are decisive for the build-up of a polytype. Since the pairs of adjacent layers remain geometrically equivalent in all polytypes of a given family, these polytypes are in the first approximation also energetically equivalent. However, if the longer-range interactions are also considered, then it becomes evident that layer triples such as *ABA* and *ABC* in close-packed structures are, in general, energetically non-equivalent because they are also geometrically non-equivalent. Even though these forces are much weaker than those between adjacent layers, they may not be negligible and, therefore, under given crystallization conditions either one or the other kind of triples becomes energetically more favourable. It will occur again and again in the polytype thus formed, and not intermixed with the other kind. Such structures are – as a rule – sensitive to conditions of crystallization, and small fluctuations of these may reverse the energetical preferences, creating stacking faults and twinnings. This is why many polytypic substances exhibit non-periodicity.

As regards the close packing of spheres, the well known cubic and hexagonal polytypes *ABCABC...* and *ABAB...*, respectively, are MDO polytypes; the first contains only the triples *ABC*, the second only the triples *ABA*. Evidently, the MDO philosophy holds for a layer-by-layer rather than for a spiral growth mechanism. Since the symmetry principle of polytypic structures may differ considerably from that of close packing of equal spheres, the OD theory contains exact algorithms for the derivation of MDO polytypes in any category (Dornberger-Schiff, 1982; Dornberger-Schiff & Grell, 1982*a*).

9.2.2.2.4. Some geometrical properties of OD structures

As already pointed out, all relevant geometrical properties of a polytype family can be deduced from its symmetry principle. Let us thus consider a hypothetical simple family in which we shall disregard any concrete atomic arrangements and use geometrical figures with the appropriate symmetry instead.

Three periodic polytypes are shown in Fig. 9.2.2.2 (left-hand side). Any member of this family consists of equivalent layers perpendicular to the plane of the drawing, with symmetry $P(1)m1$. The symmetry of layers is indicated by isosceles triangles with a mirror plane $[.m.]$. All pairs of adjacent layers are also equivalent, no matter whether a layer is shifted by $+b/4$

or $-b/4$ relative to its predecessor, since the reflection across $[.m.]$ transforms any given layer into itself and the adjacent layer from one possible position into the other. These two positions follow also from the *NFZ* relation: $N = 2$, $F = 1$ [the layer group of the pair of adjacent layers is $P(1)11$] and thus $Z = 2$.

The layers are all equivalent and accordingly there must also be two coincidence operations transforming any layer into the adjacent one. The first operation is evidently the translation, the second is the glide reflection. If any of these becomes total for the remaining part of the structure, we obtain a polytype with all layer triples equivalent, *i.e.* a MDO polytype. The polytype (a) (Fig. 9.2.2.2) is one of them: the translation $\mathbf{t} = \mathbf{a}_0 + \mathbf{b}/4$ is the total operation ($|\mathbf{a}_0|$ is the distance between adjacent layers). It has basis vectors $\mathbf{a}_1 = \mathbf{a}_0 + \mathbf{b}/4$, $\mathbf{b}_1 = \mathbf{b}$, $\mathbf{c}_1 = \mathbf{c}$, space group $P111$, Ramsdell symbol $1A$,* Hagg symbol $|+|$. This polytype also has its enantiomorphous counterpart with Hagg symbol $|-|$. In the other polytype (b) (Fig. 9.2.2.2), the glide reflection is the total operation. The basis vectors of the polytype are

* According to Guinier *et al.* (1984), triclinic polytypes should be designated A (anorthic) in their Ramsdell symbols.

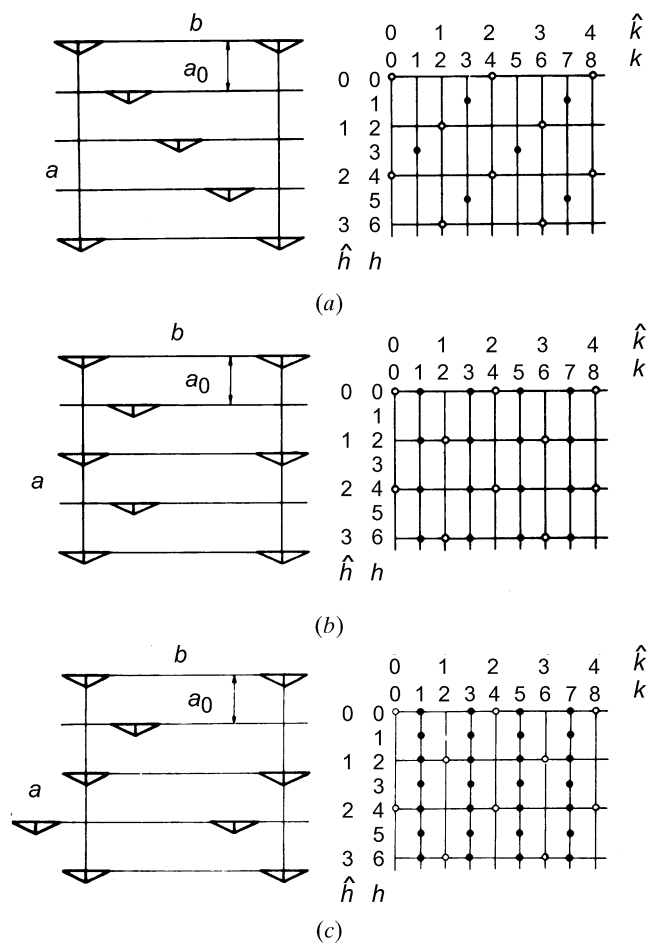


Fig. 9.2.2.2. Schematic representation of three structures belonging to the OD groupoid family $P(1)m1|1$, $y = 0.25$ (left). The layers are perpendicular to the plane of the drawing and their constituent atomic configurations are represented by isosceles triangles with symmetry $[.m.]$. All structures are related to a common orthogonal four-layer cell with $\mathbf{a} = 4\mathbf{a}_0$. The $hk0$ nets in reciprocal space corresponding to these structures are shown on the right and the diffraction indices refer also to the common cell. Family diffractions common to all members of this family ($k = 2\hat{k}$) and the characteristic diffractions for individual polytypes ($k = 2\hat{k} + 1$) are indicated by open and solid circles, respectively.

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$\mathbf{a}_2 = 2\mathbf{a}_0$, $\mathbf{b}_2 = \mathbf{b}$, $\mathbf{c}_2 = \mathbf{c}$, space group $P1a1$, Ramsdell symbol $2M$, Hägg symbol $|+ -|$. The equivalence of all layer triples in either of these polytypes is evident. The third polytype (c) (Fig. 9.2.2.2) is not a MDO polytype because it contains two kinds of layer triples, whereas it is possible to construct a polytype of this family containing only a selection of these. The polytype is again monoclinic with basis vectors $\mathbf{a}_3 = 4\mathbf{a}_0$, $\mathbf{b}_3 = \mathbf{b}$, $\mathbf{c}_3 = \mathbf{c}$, space group $P1a1$, Ramsdell symbol $4M$, and Hägg symbol $|+ - - +|$.

Evidently, the partial mirror plane is crucial for the polytypism of this family. And yet the space group of none of its periodic members can contain it – simply because it can never become total. The space-group symbols thus leave some of the most important properties of periodic polytypes unnoticed. Moreover, the atomic coordinates of different polytypes expressed in terms of the respective lattice geometries cannot be immediately compared. And, finally, for non-periodic members of a family, a space-group symbol cannot be written at all. This is why the OD theory gives a *special symbol* indicating the symmetry proper of individual layers (λ symmetry) as well as the coincidence operations transforming a layer into the adjacent one (σ symmetry). The symbol of the OD groupoid family of our hypothetical example thus consists of two lines (Dornberger-Schiff, 1964, pp. 41 ff.; Fichtner, 1979a,b):

$$\begin{array}{llll} P(1) & m & 1 & \lambda \text{ symmetry} \\ \{(1) & a_2 & 1\} & \sigma \text{ symmetry,} \end{array}$$

where the unusual subscript 2 indicates that the glide reflection transforms the given layer into the subsequent one.

It is possible to write such a symbol for any OD groupoid family for equivalent layers, and thus also for the close packing of spheres. However, keeping in mind that the number of asymmetric units here is 24 (λ symmetry), one has to indicate also 24 σ operations, which is instructive but unwieldy. This is why Fichtner (1980) proposed simplified one-line symbols, containing full λ symmetry and only the rotational part of *any one* of the σ operations plus its translational components. Accordingly, the symbol of our hypothetical family reads: $P(1)m1|1$, $y = 0.25$; for the family of close packings of equal spheres: $P(6/m)mm|1$, $x = 2/3$, $y = 1/3$ (the layers are in both cases translationally equivalent and the rotational part of a translation is the identity).

An OD groupoid family symbol should not be confused with a *polytype symbol*, which gives information about the structure of an individual polytype (Dornberger-Schiff, Āurovič & Zvyagin, 1982; Guinier *et al.*, 1984).

9.2.2.2.5. Diffraction pattern – structure analysis

Let us now consider schematic diffraction patterns of the three structures on the right-hand side of Fig. 9.2.2.2. It can be seen that, while being in general different, they contain a common subset of diffractions with $k = 2\hat{k}$ – these, normalized to a constant number of layers, have the same distribution of intensities and monoclinic symmetry. This follows from the fact that they correspond to the so-called *superposition structure* with basis vectors $\mathbf{A} = 2\mathbf{a}_0$, $\mathbf{B} = \mathbf{b}/2$, $\mathbf{C} = \mathbf{c}$, and space group $C1m1$. It is a fictitious structure that can be obtained from any of the structures in Fig. 9.2.2.2 as a normalized sum of the structure in its given position and in a position shifted by $b/2$, thus

$$\hat{\rho}(xyz) = \frac{1}{2}[\rho(xyz) + \rho(x, y + 1/2, z)].$$

Evidently, this holds for all members of the family, including the non-periodic ones. In general, the superposition structure is obtained by simultaneous realization of all Z possible positions of all OD layers in any member of the family (Dornberger-Schiff, 1964, p. 54). As a consequence, its symmetry can be obtained by completing any of the family groupoids to a group (Fichtner, 1977). This structure is by definition periodic and *common to all members* of the family. Thus, the corresponding diffractions are also always sharp, common, and characteristic for the family. They are called *family diffractions*.

Diffractions with $k = 2\hat{k} + 1$ are characteristic for individual members of the family. They are sharp for periodic polytypes but appear as diffuse streaks for non-periodic ones. Owing to the C centring of the superposition structure, only diffractions with $\hat{h} + \hat{k} = 2n$ are present. It follows that $0kl$ diffractions are present only for $\hat{k} = 2n$, which, in an indexing referring to the actual \mathbf{b} vector reads: $0kl$ present only for $k = 4n$. This is an example of non-space-group absences exhibited by many polytypic structures. They can be used for the determination of the OD groupoid family (Dornberger-Schiff & Fichtner, 1972).

There is no routine method for the determination of the structural principle of an OD structure. It is easiest when one has at one's disposal many different (at least two) periodic polytypes of the same family with structures solved by current methods. It is then possible to compare these structures, determine equivalent regions in them (Grell, 1984), and analyse partial symmetries. This results in an OD interpretation of the substance and a description of its polytypism.

Sometimes it is possible to arrive at an OD interpretation from one periodic structure, but this necessitates experience in the recognition of the partial symmetry and prediction of potential polytypism (Merlino, Orlandi, Perchiazzi, Basso & Palenzona, 1989).

The determination of the structural principle is complex if only disordered polytypes occur. Then – as a rule – the superposition structure is solved first by current methods. The actual structure of layers and relations between them can then be determined from the intensity distribution along diffuse streaks (for more details and references see Jagodzinski, 1964; Sedlacek, Kuban & Backhaus, 1987; Müller & Conradi, 1986). High-resolution electron microscopy can also be successfully applied – see Subsection 9.2.2.4.

9.2.2.2.6. The vicinity condition

A polytype family contains periodic as well as non-periodic members. The latter are as important as the former, since the very fact that they can be non-periodic carries important crystallochemical information. Non-periodic polytypes do not comply with the classical definition of crystals, but we believe that this definition should be generalized to include rather than exclude non-periodic polytypes from the world of crystals (Dornberger-Schiff & Grell, 1982b). The OD theory places them, together with the periodic ones, in the hierarchy of the so-called *VC structures*. The reason for this is that all periodic structures, even the non-polytypic ones, can be thought of as consisting of *disjunct*, two-dimensionally periodic slabs, the *VC layers*, which are stacked together according to three rules called the *vicinity condition* (VC) (Dornberger-Schiff, 1964, pp. 29 ff., 1979; Dornberger-Schiff & Fichtner, 1972):

(α) VC layers are either geometrically equivalent or, if not, they are relatively few in kind;

(β) translation groups of all VC layers are either identical or they have a common subgroup;

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(γ) equivalent sides of equivalent layers are faced by equivalent sides of adjacent layers so that the resulting pairs are equivalent [for a more detailed specification and explanation see Dornberger-Schiff (1979)].

If the stacking of VC layers is unambiguous, traditional three-dimensionally periodic structures result (*fully ordered structures*). *OD structures* are VC structures in which the stacking of VC layers is ambiguous at every layer boundary ($Z > 1$). The corresponding VC layers then become *OD layers*. OD layers are, in general, not identical with crystallochemical layers; they may contain half-atoms at their boundaries. In this context, they are analogous with unit cells in traditional crystallography, which may also contain parts of atoms at their boundaries. However, *the choice of OD layers is not absolute*: it depends on the polytypism, either actually observed or reasonably anticipated, on the degree of symmetry idealization, and other circumstances (Grell, 1984).

9.2.2.2.7. Categories of OD structures

Any OD layer is two-dimensionally periodic. Thus, a unit mesh can be chosen according to the conventional rules for the corresponding layer group; the corresponding vectors or their linear combinations (Zvyagin & Fichtner, 1986) yield the basis vectors parallel to the layer plane and thus also their lengths as units for fractional atomic coordinates. But, in general, there is no periodicity in the direction perpendicular to the layer plane and it is thus necessary to define the corresponding unit length in some other way. This depends on the symmetry principle of the family in question – or, more narrowly, on the *category* to which this family belongs.

OD structures can be built of *equivalent layers* or contain *layers of several kinds*. The rule (γ) of the VC implies that a projection of any OD structure – periodic or not – on the stacking direction is periodic. This period, called *repeat unit*, is the required unit length.

9.2.2.2.7.1. OD structures of equivalent layers

If the OD layers are equivalent then they are either all polar or all non-polar in the stacking direction. Any two adjacent polar layers can be related either by τ operations only, or by ρ operations only. For non-polar layers, the σ operations are both τ and ρ . Accordingly, there are *three categories* of OD structures of equivalent layers. They are shown schematically in Fig. 9.2.2.3; the character of the corresponding λ and σ operations is as follows (Dornberger-Schiff, 1964, pp. 24 ff.):

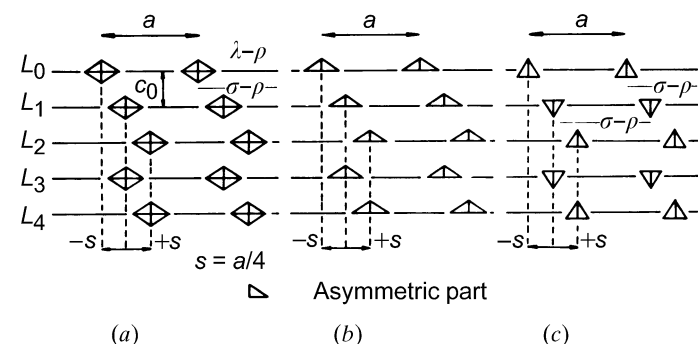


Fig. 9.2.2.3. Schematic examples of the three categories of OD structures consisting of equivalent layers (perpendicular to the plane of the drawing): (a) category I – OD layers non-polar in the stacking direction; (b) category II – polar OD layers, all with the same sense of polarity; (c) category III – polar OD layers with regularly alternating sense of polarity. The position of ρ planes is indicated.

	category I	category II	category III
λ operations	τ and ρ	τ	τ
σ operations	τ and ρ	τ	ρ

Category II is the simplest: the OD layers are polar and all with the same sense of polarity (they are τ -equivalent); our hypothetical example given in §9.2.2.2.4 belongs to this category. The layers can thus exhibit only one of the 17 polar layer groups. The projection of any vector between two τ -equivalent points in two adjacent layers on the stacking direction (perpendicular to the layer planes) is the repeat unit and it is denoted by \mathbf{c}_0 , \mathbf{a}_0 , or \mathbf{b}_0 depending on whether the basis vectors in the layer plane are \mathbf{ab} , \mathbf{bc} , or \mathbf{ca} , respectively. The choice of origin in the stacking direction is arbitrary but preferably so that the z coordinates of atoms within a layer are positive. Examples are SiC, ZnS, and AgI.

OD layers in category I are non-polar and they can thus exhibit any of the 63 non-polar layer groups. Inspection of Fig. 9.2.2.3(a) reveals that the symmetry elements representing the λ - ρ operations (*i.e.* the operations turning a layer upside down) can lie only in one plane called the *layer plane*. Similarly, the symmetry elements representing the σ - ρ operations (*i.e.* the operations converting a layer into the adjacent one) also lie in one plane, located exactly halfway between two nearest layer planes. These two kinds of planes are called ρ planes. The distance between two nearest layer planes is the repeat unit c_0 . Examples are close packing of equal spheres, GaSe, α -wollastonite (Yamanaka & Mori, 1981), β -wollastonite (Ito, Sadanaga, Takéuchi & Tokonami, 1969), $\text{K}_3[\text{M}(\text{CN})_6]$ (Jagner, 1985), and many others.

The OD structures belonging to the above two categories contain pairs of adjacent layers, all equivalent. This does not apply for structures of category III, which consist of polar layers that are converted into their neighbours by ρ operations. It is evident (Fig. 9.2.2.3c) that two kinds of pairs of adjacent layers are needed to build any such structure. It follows that only even-numbered layers can be mutually τ -equivalent and the same holds for odd-numbered layers. There are only σ - ρ planes in these structures, and again they

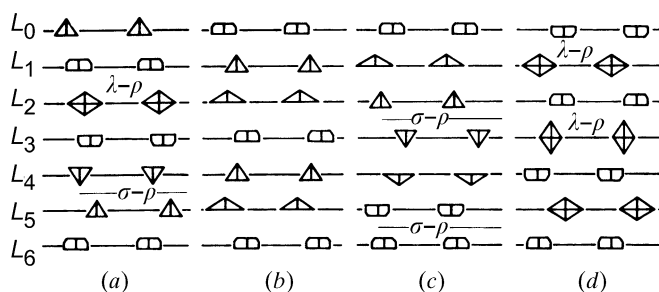


Fig. 9.2.2.4. Schematic examples of the four categories of OD structures consisting of more than one kind of layer (perpendicular to the plane of the drawing). Equivalent OD layers are represented by equivalent symbolic figures. (a) Category I – three kinds of OD layers: one kind (L_{2+5n}) is non-polar, the remaining two are polar. One and only one kind of non-polar layer is possible in this category. (b) Category II – three kinds of polar OD layers; their triples are polar and retain their sense of polarity in the stacking direction. (c) Category III – three kinds of polar OD layers; their triples are polar and regularly change their sense of polarity in the stacking direction. (d) Category IV – three kinds of OD layers: two kinds are non-polar (L_{1+4n} and L_{3+4n}), one kind is polar. Two and only two kinds of non-polar layers are possible in this category. The position of ρ planes is indicated.

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are of two kinds; the origin can be placed in either of them. c_0 is the distance between two nearest ρ planes of the same kind, and slabs of this thickness contain two OD layers. There are three examples for this category known to date: foshagite (Gard & Taylor, 1960), γ -Hg₃S₂Cl₂ (Đurovič, 1968), and 2,2-aziridinedicarboxamide (Fichtner & Grell, 1984).

9.2.2.2.7.2. OD structures with more than one kind of layer

If an OD structure consists of $N > 1$ kinds of OD layers, then it can be shown (Dornberger-Schiff, 1964, pp. 64 ff.) that it can fall into one of *four categories*, according to the polarity or non-polarity of its constituent layers and their sequence. These are shown schematically in Fig. 9.2.2.4; the character of the corresponding λ and σ operations is

	category I	category II	category III	category IV
λ operations	τ and ρ (one set) τ ($N - 1$ sets)	τ (N sets)	τ (N sets)	τ and ρ (two sets) τ ($N - 2$ sets)
σ operations	ρ (one set)	none	ρ (two sets)	none.

Here also category II is the simplest. The structures consist of N kinds of cyclically recurring polar layers whose sense of polarity remains unchanged (Fig. 9.2.2.4b). The choice of origin in the stacking direction is arbitrary; c_0 is the projection on this direction of the shortest vector between two τ -equivalent points – a slab of this thickness contains all N OD layers of different kinds. Examples are the structures of the serpentine-kaolin group.

Structures of category III also consist of polar layers but, in contrast to category II, the N -tuples containing all N different OD layers each alternate regularly the sense of their polarity in the stacking direction. Accordingly (Fig. 9.2.2.4c), there are two kinds of σ - ρ planes and two kinds of pairs of equivalent adjacent layers in these structures. The origin can be placed in either of the two ρ planes. c_0 is the distance between the nearest two equivalent ρ planes; a slab with this thickness contains $2 \times N$ non-equivalent OD layers. No representative of this category is known to date.

The structures of category I contain one, and only one, kind of non-polar layer, the remaining $N - 1$ kinds are polar and alternate in their sense of polarity along the stacking direction (Fig. 9.2.2.4a). Again, there are two kinds of ρ planes here, but one is a λ - ρ plane (the layer plane of the non-polar OD layer), the other is a σ - ρ plane. These structures thus contain only one kind of pair of equivalent adjacent layers. The origin is placed in the λ - ρ plane. c_0 is the distance between the nearest two equivalent ρ planes and a slab with this thickness contains $2 \times (N - 1)$ non-equivalent polar OD layers plus one entire non-polar layer. Examples are the MX_2 compounds (CdI₂, MoS₂, etc.) and the talc-pyrophyllite group.

The structures of category IV contain two, and only two, kinds of non-polar layers. The remaining $N - 2$ kinds are polar and alternate in their sense of polarity along the stacking direction (Fig. 9.2.2.4d). Both kinds of ρ planes are λ - ρ planes, identical with the layer planes of the non-polar OD layers; the origin can be placed in any one of them. c_0 is chosen as in categories I and III. A slab with this thickness contains $2 \times (N - 2)$ non-equivalent polar layers plus the two non-polar layers. Examples are micas, chlorites, vermiculites, etc.

OD structures containing $N > 1$ kinds of layers need special symbols for their OD groupoid families (Grell & Dornberger-Schiff, 1982).

A slab of thickness c_0 containing the N non-equivalent polar OD layers in the sequence as they appear in a given structure of category II represents completely its composition. In the remaining three categories, a slab with thickness $c_0/2$, the polar part of the structure contained between two adjacent ρ planes, suffices. Such slabs are higher structural units for OD structures of more than one kind of layer and have been called *OD packets*. An OD packet is thus defined as the smallest continuous part of an OD structure that is periodic in two dimensions and which represents its composition completely (Đurovič, 1974a).

The hierarchy of VC structures is shown in Fig. 9.2.2.5.

9.2.2.2.8. Desymmetrization of OD structures

If a fully ordered structure is refined, using the space group determined from the systematic absences in its diffraction pattern and then by using some of its subgroups, serious discrepancies are only rarely encountered. Space groups thus characterize the general symmetry pattern quite well, even in real crystals. However, experience with refined periodic polytypic structures has revealed that there are always significant deviations from the OD symmetry and, moreover, even the atomic coordinates within OD layers in different polytypes of the same family may differ from one another. The OD symmetry thus appears as only an approximation to the actual symmetry pattern of polytypes. This phenomenon was called *desymmetrization* of OD structures (Đurovič, 1974b, 1979).

When trying to understand this phenomenon, let us recall the structure of rock salt. Its symmetry $Fm\bar{3}m$ is an expression of the energetically most favourable relative position of Na⁺ and Cl⁻ ions in this structure – the right angles $\alpha\beta\gamma$ follow from the symmetry. Since the whole structure is cubic, we cannot expect that the environment of any building unit, e.g. of any octahedron NaCl₆, would exercise on it an influence that would decrease its symmetry; the symmetries of these units and of the whole structure are not ‘antagonistic’.

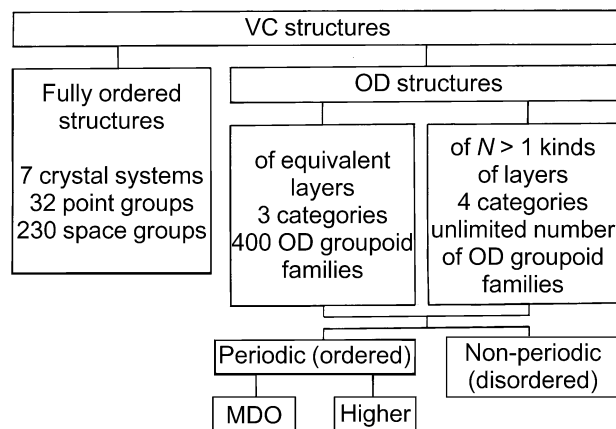


Fig. 9.2.2.5. Hierarchy of VC structures indicating the position of OD structures within it.

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Not so in OD structures, where any OD layer is by definition situated in a disturbing environment because its symmetry does not conform to that of the entire structure. ‘Antagonistic’ relations between these symmetries are most drastic in pure MDO structures because of the regular sequence of layers. The partial symmetry operations become irrelevant and the OD groupoid degenerates into the corresponding space group.

The more disordered an OD structure is, the smaller become the disturbing effects that the environment exercises on an OD layer. These can be, at least statistically, neutralized by random positions of neighbouring layers so that partial symmetry operations can retain their relevance throughout the structure. This can be expressed in the form of a paradox: the less periodic an OD structure is, the more symmetric it appears.

Despite desymmetrization, the OD theory remains a geometrical theory that can handle properly the *general symmetry pattern* of polytypes (which group theory cannot). It establishes a *symmetry norm* with which deviations observed in real polytypes can be compared. Owing to the high abstraction power of OD considerations, systematics of entire families of polytypes at various degree-of-idealization levels can be worked out, yielding thus a common point of view for their treatment.

9.2.2.2.9. Concluding remarks

Although very general physical principles (OD philosophy, MDO philosophy) underlie the OD theory, it is mainly a geometrical theory, suitable for a *description* of the symmetry of polytypes and their families rather than for an *explanation* of polytypism. It thus does not compete with crystal chemistry, but cooperates with it, in analogy with traditional crystallography, where group theory does not compete with crystal chemistry.

When speaking of polytypes, one should always be aware, whether one has in mind a concrete *real* polytype – more or less in Baumhauer’s sense – or an *abstract* polytype as a structural type (Subsection 9.2.2.1).

A substance can, in general, exist in the form of various polymorphs and/or polytypes of one or several families. Since polytypes of the same family differ only slightly in their crystal energy (Verma & Krishna, 1966), an entire family can be considered as an energetic analogue to one polymorph. As a rule, polytypes belonging to different families of the same substance do not co-exist. $\text{Al}(\text{OH})_3$ may serve as an example for two different families: the bayerite family, in which the adjacent planes of OH groups are stacked according to the principle of close packing (Zvyagin *et al.*, 1979), and the gibbsite-nordstrandite family in which these groups coincide in the normal projection.* Another example is the phyllosilicates (§9.2.2.3.1). The compound $\text{Hg}_3\text{S}_2\text{Cl}_2$, on the other hand, is known to yield two polymorphs α and β (Carlson, 1967; Frueh & Gray, 1968) and one OD family of γ structures (Đurovič, 1968).

As far as the definition of *layer polytypism* is concerned, OD theory can contribute specifications about the layers themselves and the geometrical rules for their stacking within a family (all incorporated in the vicinity condition). A possible definition might then read:

Polytypism is a special case of polymorphism, such that the individual polymorphs (called *polytypes*) may be regarded as arising through different modes of stacking layer-like structural

* Sandwiches with composition $\text{Al}(\text{OH})_3$ (similar to those in CdI_2) are the same in both families, but their stacking mode is different. This and similar situations in other substances might have been the reason for distinguishing between ‘polytype diversity’ and ‘OD diversity’ (Zvyagin, 1988).

units. The layers and their stackings are limited by the *vicinity condition*. All polytypes built on the same structural principle belong to a *family*; this depends on the degree of a structural and/or compositional *idealization*.

Geometrical theories concerning rod and block polytypism have not yet been elaborated, the main reason is the difficulty of formulating properly the vicinity condition (Sedlacek, Grell & Dornberger-Schiff, private communications). But such structures are known. Examples are the structures of tobermorite (Hamid, 1981) and of manganese(III) hydrogenbis(orthophosphate) dihydrate (Císařová, Novák & Petříček, 1982). Both structures can be thought of as consisting of a three-dimensionally periodic framework of certain atoms into which one-dimensionally periodic chains and aperiodic finite configurations of the remaining atoms, respectively, ‘fit’ in two equivalent ways.

9.2.2.3. Examples of some polytypic structures

The three examples below illustrate the three main methods of analysis of polytypism indicated in §9.2.2.2.5.

9.2.2.3.1. Hydrous phyllosilicates

The basic concepts were introduced by Pauling (1930*a,b*) and confirmed later by the determination of concrete crystal structures. A *crystallochemical analysis* of these became the basis for generalizations and systemizations. The aim was the understanding of geometrical reasons for the polytypism of these substances as well as the development of identification routines through the derivation of basic polytypes (§9.2.2.2.3). Smith & Yoder (1956) succeeded first in deriving the six basic polytypes in the mica family.

Since the 1950’s, two main schools have developed: in the USA, represented mainly by Brindley, Bailey, and their co-workers (for details and references see Bailey, 1980, 1988*a*; Brindley, 1980), and in the former USSR, represented by Zvyagin and his co-workers (for details and references see Zvyagin, 1964, 1967; Zvyagin *et al.*, 1979). Both these schools based their systemizations on idealized structural models corresponding to the ideas of Pauling, with *hexagonal* symmetry of tetrahedral sheets (see later). The US school uses indicative symbols (Guinier *et al.*, 1984) for the designation of individual polytypes, and single-crystal as well as powder X-ray diffraction methods for their identification, whereas the USSR school uses unitary descriptive symbols for polytypes of all mineral groups and mainly electron diffraction on oblique textures for identification purposes. For the derivation of basic polytypes, both schools use crystallochemical considerations; symmetry principles are applied tacitly rather than explicitly.

In contrast to crystal structures based on close packings, where all relevant details of individual (even multilayer) polytypes can be recognized in the (1120) section, the structures of hydrous phyllosilicates are rather complex. For their representation, Figueiredo (1979) used the concept of *condensed models*.

Since 1970, the OD school has also made its contribution. In a series of articles, basic types of hydrous phyllosilicates have been interpreted as OD structures of $N > 1$ kinds of layers: the serpentine-kaolin group (Dornberger-Schiff & Đurovič, 1975*a,b*), Mg-vermiculite (Weiss & Đurovič, 1980), the mica group (Dornberger-Schiff, Backhaus & Đurovič, 1982; Backhaus & Đurovič, 1984; Đurovič, Weiss & Backhaus, 1984; Weiss & Wiewióra, 1986), the talc-pyrophyllite group (Đurovič & Weiss, 1983; Weiss & Đurovič, 1985*a*), and the chlorite group (Đurovič, Dornberger-Schiff & Weiss, 1983;