

9.2. LAYER STACKING

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’.

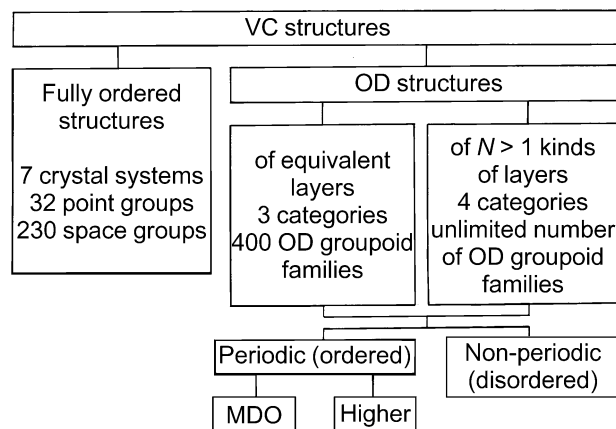


Fig. 9.2.2.5. Hierarchy of VC structures indicating the position of OD structures within it.

9. BASIC STRUCTURAL FEATURES

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 (1930a,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, 1988a; 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, 1975a,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, 1985a), and the chlorite group (Đurovič, Dornberger-Schiff & Weiss, 1983;