

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 (Čísařová, 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;