

## 9.2. LAYER STACKING

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  $\nabla$  of the preceding layer, *or* in all the voids  $\Delta$  – 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  $P(6/m)mm$ ,<sup>†</sup> 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  $\tau$  operations. The remaining 12 operations change any *z* into  $-z$ , thus turning the layer upside down; they constitute a coset. The latter are called  $\rho$  operations. Out of the 12  $\tau$  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  $\tau$  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.

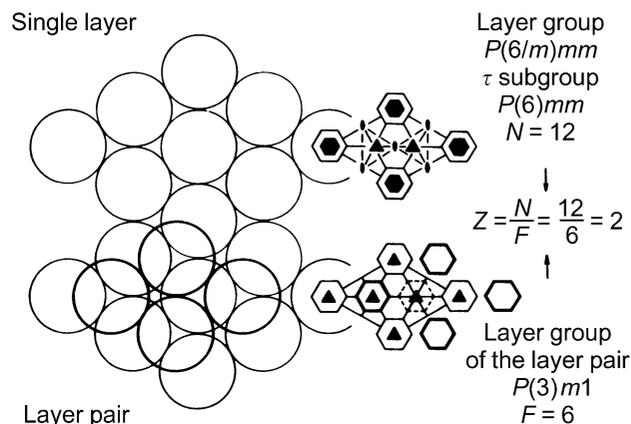


Fig. 9.2.2.1. Symmetry interpretation of close packings of equal spheres. The layer group of a single layer, the subgroup of its  $\tau$  operations, and the number of asymmetric units *N* per unit mesh of the former, are given at the top right. The  $\tau$  operations that have a continuation for the 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.*

<sup>†</sup>The direction in which there is no periodicity is indicated by parentheses (Dornberger-Schiff, 1959).

## 9. BASIC STRUCTURAL FEATURES

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.

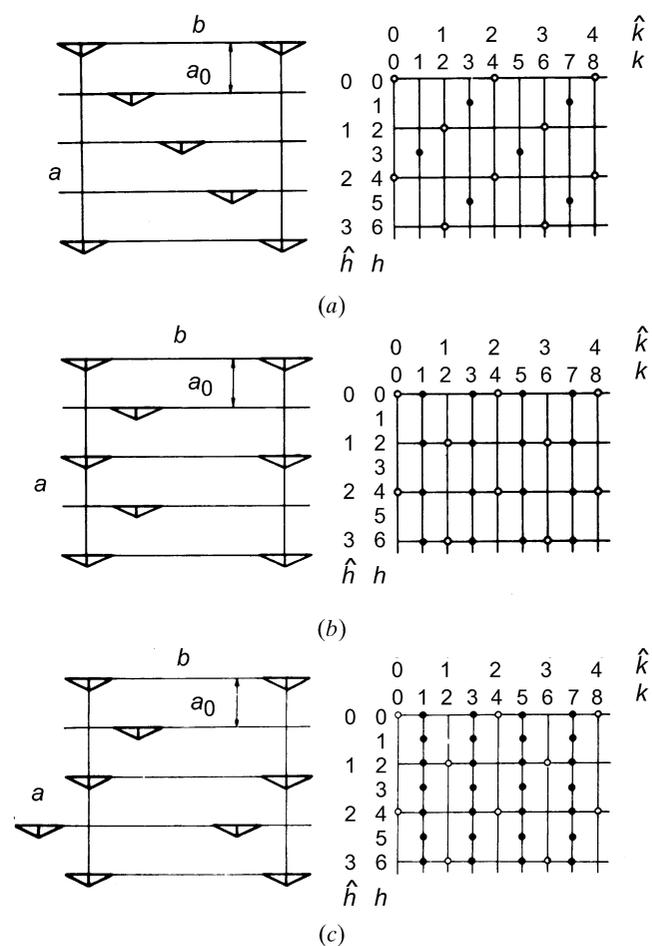


Fig. 9.2.2.2. Schematic representation of three structures belonging to the OD groupoid family *P(1)m1|1*,  $y = 0.25$  (left). The layers are perpendicular to the plane of the drawing and their constituent atomic configurations are represented by isosceles triangles with symmetry *[.m.]*. All structures 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.