

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 $1A$,* Hägg symbol $|+|$. This polytype also has its enantiomorphous counterpart with Hägg 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.

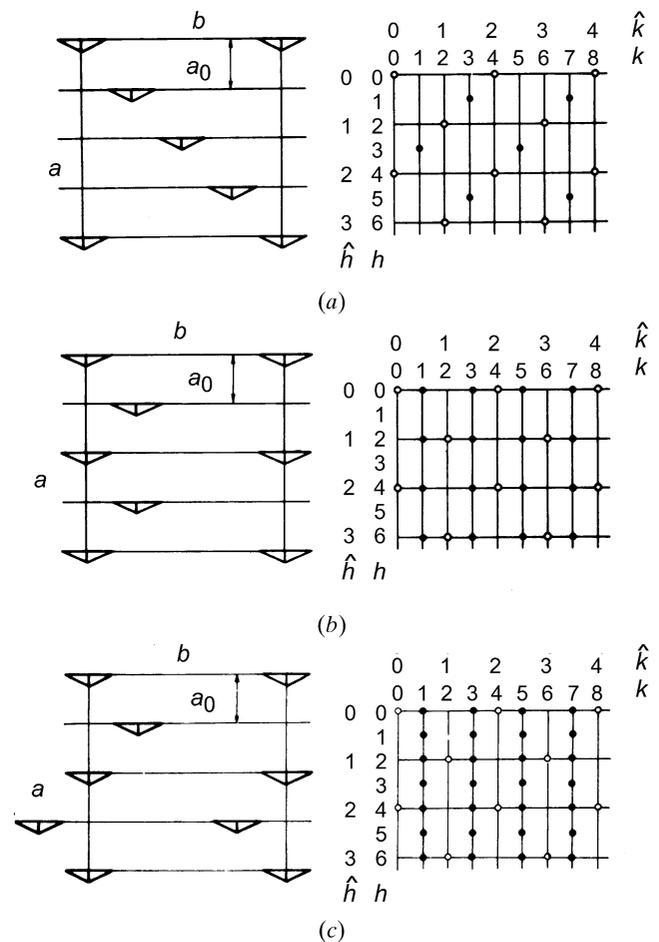


Fig. 9.2.2.2. Schematic representation of three structures belonging to the OD groupoid family $P(1)m1|1$, $y = 0.25$ (left). The layers are perpendicular to the plane of the drawing and their constituent atomic configurations are represented by isosceles triangles with symmetry $[.m.]$. All structures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

9.2. LAYER STACKING

$\mathbf{a}_2 = 2\mathbf{a}_0$, $\mathbf{b}_2 = \mathbf{b}$, $\mathbf{c}_2 = \mathbf{c}$, space group $P1a1$, Ramsdell symbol $2M$, Hagg 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 Hagg 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, urovi & 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; Muller & 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;