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 1*A*,* 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

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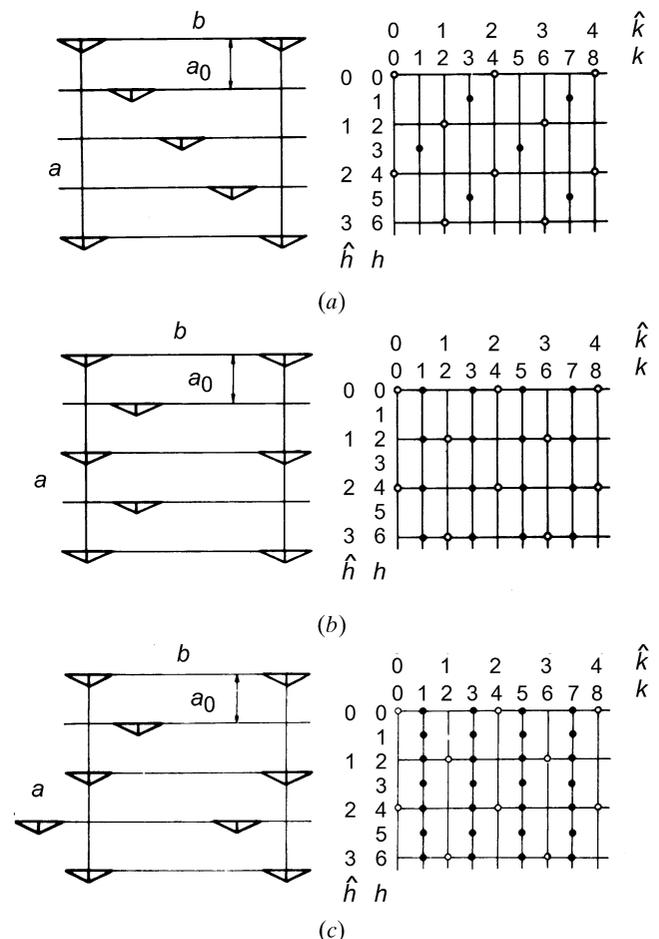

(*a*)

(*b*)

(*c*)

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 $(k = 2k + 1)$ are indicated by open and solid circles, respectively.

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