International Tables for Crystallography (2006). Vol. C, Section 9.2.2.2.6, pp. 763–764.

$\mathbf{a}_2 = 2\mathbf{a}_0$, $\mathbf{b}_2 = \mathbf{b}$, $\mathbf{c}_2 = \mathbf{c}$, space group $P1a1$, Ramsdell symbol $2M$, Hägg 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 Hägg 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, 1979*a*,*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, Ďurovič & 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

$$\hat{\rho}(xyz) = \tfrac{1}{2}[\rho(xyz) + \rho(x, y + 1/2, z)].$$

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 $0\hat{k}\hat{l}$ 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; Müller & 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, 1982*b*). 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;

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(γ) equivalent sides of equivalent layers are faced by equivalent sides of adjacent layers so that the resulting pairs are equivalent [for a more detailed specification and explanation see Dornberger-Schiff (1979)].

If the stacking of VC layers is unambiguous, traditional three-dimensionally periodic structures result (*fully ordered structures*). *OD structures* are VC structures in which the stacking of VC layers is ambiguous at every layer boundary ($Z > 1$). The corresponding VC layers then become *OD layers*. OD layers are, in general, not identical with crystallochemical layers; they may contain half-atoms at their boundaries. In this context, they are analogous with unit cells in traditional crystallography, which may also contain parts of atoms at their boundaries. However, *the choice of OD layers is not absolute*: it depends on the polytypism, either actually observed or reasonably anticipated, on the degree of symmetry idealization, and other circumstances (Grell, 1984).

9.2.2.2.7. *Categories of OD structures*

Any OD layer is two-dimensionally periodic. Thus, a unit mesh can be chosen according to the conventional rules for the corresponding layer group; the corresponding vectors or their linear combinations (Zvyagin & Fichtner, 1986) yield the basis vectors parallel to the layer plane and thus also their lengths as units for fractional atomic coordinates. But, in general, there is no periodicity in the direction perpendicular to the layer plane and it is thus necessary to define the corresponding unit length in some other way. This depends on the symmetry principle of the family in question – or, more narrowly, on the *category* to which this family belongs.

OD structures can be built of *equivalent layers* or contain *layers of several kinds*. The rule (γ) of the VC implies that a projection of any OD structure – periodic or not – on the stacking direction is periodic. This period, called *repeat unit*, is the required unit length.

9.2.2.2.7.1. *OD structures of equivalent layers*

If the OD layers are equivalent then they are either all polar or all non-polar in the stacking direction. Any two adjacent polar layers can be related either by τ operations only, or by ρ operations only. For non-polar layers, the σ operations are both τ and ρ. Accordingly, there are *three categories* of OD structures of equivalent layers. They are shown schematically in Fig. 9.2.2.3; the character of the corresponding λ and σ operations is as follows (Dornberger-Schiff, 1964, pp. 24 ff.):

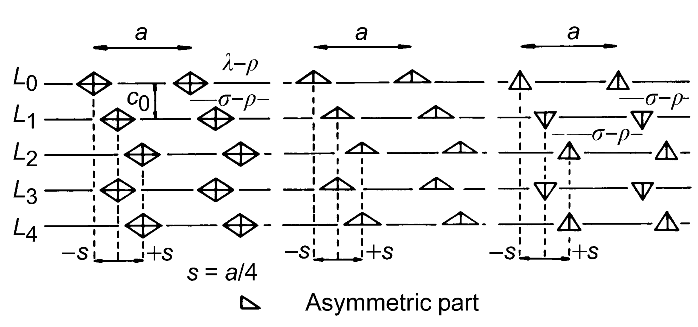

Fig. 9.2.2.3. Schematic examples of the three categories of OD structures consisting of equivalent layers (perpendicular to the plane of the drawing): (*a*) category I – OD layers non-polar in the stacking direction; (*b*) category II – polar OD layers, all with the same sense of polarity; (*c*) category III – polar OD layers with regularly alternating sense of polarity. The position of ρ planes is indicated.

	category I	category II	category III
λ operations	τ and ρ	τ	τ
σ operations	τ and ρ	τ	ρ

Category II is the simplest: the OD layers are polar and all with the same sense of polarity (they are τ-equivalent); our hypothetical example given in §9.2.2.2.4 belongs to this category. The layers can thus exhibit only one of the 17 polar layer groups. The projection of any vector between two τ-equivalent points in two adjacent layers on the stacking direction (perpendicular to the layer planes) is the repeat unit and it is denoted by $\mathbf{c}_0$, $\mathbf{a}_0$, or $\mathbf{b}_0$ depending on whether the basis vectors in the layer plane are **ab**, **bc**, or **ca**, respectively. The choice of origin in the stacking direction is arbitrary but preferably so that the z coordinates of atoms within a layer are positive. Examples are SiC, ZnS, and AgI.

OD layers in category I are non-polar and they can thus exhibit any of the 63 non-polar layer groups. Inspection of Fig. 9.2.2.3(*a*) reveals that the symmetry elements representing the λ–ρ operations (*i.e.* the operations turning a layer upside down) can lie only in one plane called the *layer plane*. Similarly, the symmetry elements representing the σ–ρ operations (*i.e.* the operations converting a layer into the adjacent one) also lie in one plane, located exactly halfway between two nearest layer planes. These two kinds of planes are called ρ planes. The distance between two nearest layer planes is the repeat unit c_0. Examples are close packing of equal spheres, GaSe, α-wollastonite (Yamanaka & Mori, 1981), β-wollastonite (Ito, Sadanaga, Takéuchi & Tokonami, 1969), $K_3[M(CN)_6]$ (Jagner, 1985), and many others.

The OD structures belonging to the above two categories contain pairs of adjacent layers, all equivalent. This does not apply for structures of category III, which consist of polar layers that are converted into their neighbours by ρ operations. It is evident (Fig. 9.2.2.3*c*) that two kinds of pairs of adjacent layers are needed to build any such structure. It follows that only even-numbered layers can be mutually τ-equivalent and the same holds for odd-numbered layers. There are only σ–ρ planes in these structures, and again they

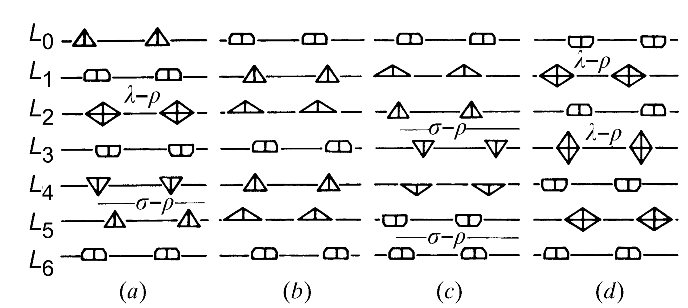

Fig. 9.2.2.4. Schematic examples of the four categories of OD structures consisting of more than one kind of layer (perpendicular to the plane of the drawing). Equivalent OD layers are represented by equivalent symbolic figures. (*a*) Category I – three kinds of OD layers: one kind (L_{2+5n}) is non-polar, the remaining two are polar. One and only one kind of non-polar layer is possible in this category. (*b*) Category II – three kinds of polar OD layers; their triples are polar and retain their sense of polarity in the stacking direction. (*c*) Category III – three kinds of polar OD layers; their triples are polar and regularly change their sense of polarity in the stacking direction. (*d*) Category IV – three kinds of OD layers: two kinds are non-polar (L_{1+4n} and L_{3+4n}), one kind is polar. Two and only two kinds of non-polar layers are possible in this category. The position of ρ planes is indicated.

references