International Tables for Crystallography (2006). Vol. C, Section 9.2.2.2.7.1, pp. 764–765.

(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.):

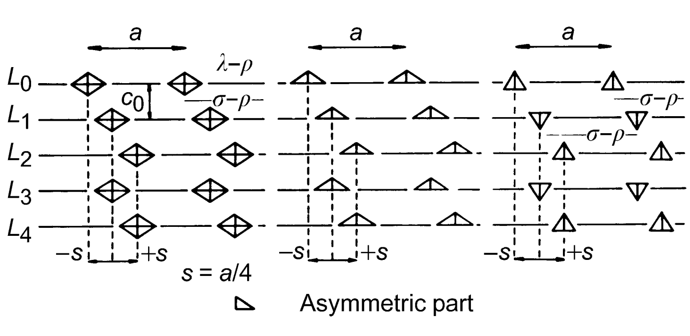

Fig. 9.2.2.3. Schematic examples of the three categories of OD structures consisting of equivalent layers (perpendicular to the plane of the drawing): (*a*) category I – OD layers non-polar in the stacking direction; (*b*) category II – polar OD layers, all with the same sense of polarity; (*c*) category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

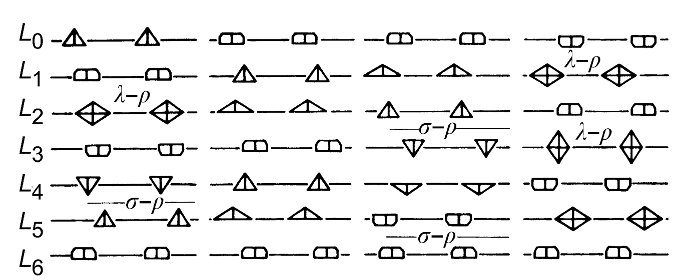

Fig. 9.2.2.4. Schematic examples of the four categories of OD structures consisting of more than one kind of layer (perpendicular to the plane of the drawing). Equivalent OD layers are represented by equivalent symbolic figures. (*a*) Category I – three kinds of OD layers: one kind (L_{2+5n}) is non-polar, 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.

are of two kinds; the origin can be placed in either of them. c_0 is the distance between two nearest ρ planes of the same kind, and slabs of this thickness contain two OD layers. There are three examples for this category known to date: foshagite (Gard & Taylor, 1960), γ-$Hg_3S_2Cl_2$ (Ďurovič, 1968), and 2,2-aziridinedicarboxamide (Fichtner & Grell, 1984).

9.2.2.2.7.2. *OD structures with more than one kind of layer*

If an OD structure consists of $N > 1$ kinds of OD layers, then it can be shown (Dornberger-Schiff, 1964, pp. 64 ff.) that it can fall into one of *four categories*, according to the polarity or non-polarity of its constituent layers and their sequence. These are shown schematically in Fig. 9.2.2.4; the character of the corresponding λ and σ operations is

A slab of thickness c_0 containing the N non-equivalent polar OD layers in the sequence as they appear in a given structure of category II represents completely its composition. In the remaining three categories, a slab with thickness $c_0/2$, the polar part of the structure contained between two adjacent ρ planes, suffices. Such slabs are higher structural units for OD structures of more than one kind of layer and have been called *OD packets*. An OD packet is thus defined as the smallest continuous part of an OD structure that is periodic in two dimensions and which represents its composition completely (Ďurovič, 1974*a*).

The hierarchy of VC structures is shown in Fig. 9.2.2.5.

	category I	category II	category III	category IV
λ operations	τ and ρ (one set) τ ($N-1$ sets)	τ (N sets)	τ (N sets)	τ and ρ (two sets) τ ($N-2$ sets)
σ operations	ρ (one set)	none	ρ (two sets)	none.

Here also category II is the simplest. The structures consist of N kinds of cyclically recurring polar layers whose sense of polarity remains unchanged (Fig. 9.2.2.4*b*). The choice of origin in the stacking direction is arbitrary; c_0 is the projection on this direction of the shortest vector between two τ-equivalent points – a slab of this thickness contains all N OD layers of different kinds. Examples are the structures of the serpentine–kaolin group.

Structures of category III also consist of polar layers but, in contrast to category II, the N-tuples containing all N different OD layers each alternate regularly the sense of their polarity in the stacking direction. Accordingly (Fig. 9.2.2.4*c*), there are two kinds of σ–ρ planes and two kinds of pairs of equivalent adjacent layers in these structures. The origin can be placed in either of the two ρ planes. c_0 is the distance between the nearest two equivalent ρ planes; a slab with this thickness contains $2 \times N$ non-equivalent OD layers. No representative of this category is known to date.

The structures of category I contain one, and only one, kind of non-polar layer, the remaining $N-1$ kinds are polar and alternate in their sense of polarity along the stacking direction (Fig. 9.2.2.4*a*). Again, there are two kinds of ρ planes here, but one is a λ–ρ plane (the layer plane of the non-polar OD layer), the other is a σ–ρ plane. These structures thus contain only one kind of pair of equivalent adjacent layers. The origin is placed in the λ–ρ plane. c_0 is the distance between the nearest two equivalent ρ planes and a slab with this thickness contains $2 \times (N-1)$ non-equivalent polar OD layers plus one entire non-polar layer. Examples are the MX_2 compounds (CdI_2, MoS_2, *etc.*) and the talc–pyrophyllite group.

The structures of category IV contain two, and only two, kinds of non-polar layers. The remaining $N-2$ kinds are polar and alternate in their sense of polarity along the stacking direction (Fig. 9.2.2.4*d*). Both kinds of ρ planes are λ–ρ planes, identical with the layer planes of the non-polar OD layers; the origin can be placed in any one of them. c_0 is chosen as in categories I and III. A slab with this thickness contains $2 \times (N-2)$ non-equivalent polar layers plus the two non-polar layers. Examples are micas, chlorites, vermiculites, *etc.*

OD structures containing $N > 1$ kinds of layers need special symbols for their OD groupoid families (Grell & Dornberger-Schiff, 1982).

9.2.2.2.8. *Desymmetrization of OD structures*

If a fully ordered structure is refined, using the space group determined from the systematic absences in its diffraction pattern and then by using some of its subgroups, serious discrepancies are only rarely encountered. Space groups thus characterize the general symmetry pattern quite well, even in real crystals. However, experience with refined periodic polytypic structures has revealed that there are always significant deviations from the OD symmetry and, moreover, even the atomic coordinates within OD layers in different polytypes of the same family may differ from one another. The OD symmetry thus appears as only an approximation to the actual symmetry pattern of polytypes. This phenomenon was called *desymmetrization* of OD structures (Ďurovič, 1974*b*, 1979).

When trying to understand this phenomenon, let us recall the structure of rock salt. Its symmetry $Fm\bar{3}m$ is an expression of the energetically most favourable relative position of Na^+ and Cl^- ions in this structure – the right angles $\alpha\beta\gamma$ follow from the symmetry. Since the whole structure is cubic, we cannot expect that the environment of any building unit, *e.g.* of any octahedron $NaCl_6$, would exercise on it an influence that would decrease its symmetry; the symmetries of these units and of the whole structure are not 'antagonistic'.

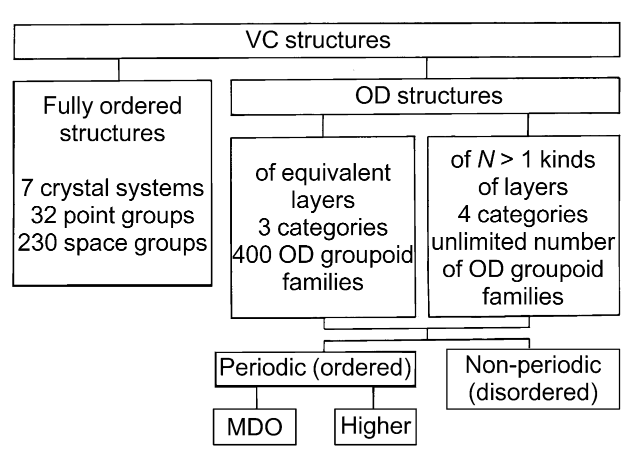

Fig. 9.2.2.5. Hierarchy of VC structures indicating the position of OD structures within it.

references