

9. BASIC STRUCTURAL FEATURES

(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.):

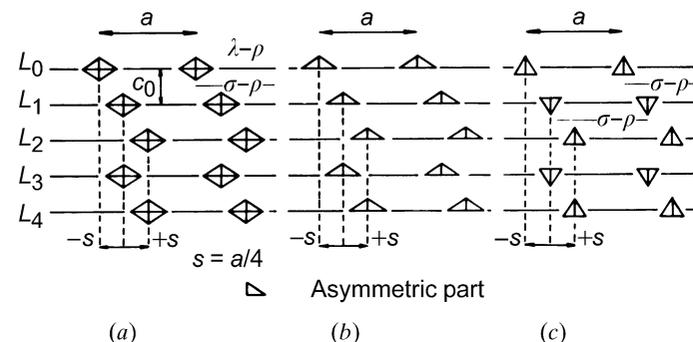


Fig. 9.2.2.3. Schematic examples of the three categories of OD structures consisting of equivalent layers (perpendicular to the plane of the drawing): (a) category I – OD layers non-polar in the stacking direction; (b) category II – polar OD layers, all with the same sense of polarity; (c) category III – 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 \mathbf{ab} , \mathbf{bc} , or \mathbf{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), $\text{K}_3[\text{M}(\text{CN})_6]$ (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. 9.2.2.3c) 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

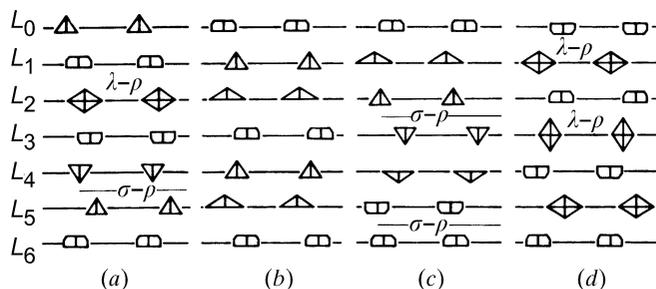


Fig. 9.2.2.4. Schematic examples of the four categories of OD structures consisting of more than one kind of layer (perpendicular to the plane of the drawing). Equivalent OD layers are represented by equivalent symbolic figures. (a) Category I – three kinds of OD layers: one kind (L_{2+5n}) is non-polar,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