

## 9.2. LAYER STACKING

are of two kinds; the origin can be placed in either of them.  $c_0$  is the distance between two nearest  $\rho$  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),  $\gamma$ -Hg<sub>3</sub>S<sub>2</sub>Cl<sub>2</sub> (Đurovič, 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  $\lambda$  and  $\sigma$  operations is

	category I	category II	category III	category IV
$\lambda$ operations	$\tau$ and $\rho$ (one set) $\tau$ ( $N - 1$ sets)	$\tau$ ( $N$ sets)	$\tau$ ( $N$ sets)	$\tau$ and $\rho$ (two sets) $\tau$ ( $N - 2$ sets)
$\sigma$ operations	$\rho$ (one set)	none	$\rho$ (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. 9.2.2.4b). The choice of origin in the stacking direction is arbitrary;  $c_0$  is the projection on this direction of the shortest vector between two  $\tau$ -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. 9.2.2.4c), there are two kinds of  $\sigma$ - $\rho$  planes and two kinds of pairs of equivalent adjacent layers in these structures. The origin can be placed in either of the two  $\rho$  planes.  $c_0$  is the distance between the nearest two equivalent  $\rho$  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. 9.2.2.4a). Again, there are two kinds of  $\rho$  planes here, but one is a  $\lambda$ - $\rho$  plane (the layer plane of the non-polar OD layer), the other is a  $\sigma$ - $\rho$  plane. These structures thus contain only one kind of pair of equivalent adjacent layers. The origin is placed in the  $\lambda$ - $\rho$  plane.  $c_0$  is the distance between the nearest two equivalent  $\rho$  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<sub>2</sub>, MoS<sub>2</sub>, 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. 9.2.2.4d). Both kinds of  $\rho$  planes are  $\lambda$ - $\rho$  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).

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  $\rho$  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 (Đurovič, 1974a).

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

## 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 (Đurovič, 1974b, 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<sup>+</sup> and Cl<sup>-</sup> 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<sub>6</sub>, would exercise on it an influence that would decrease its symmetry; the symmetries of these units and of the whole structure are not ‘antagonistic’.

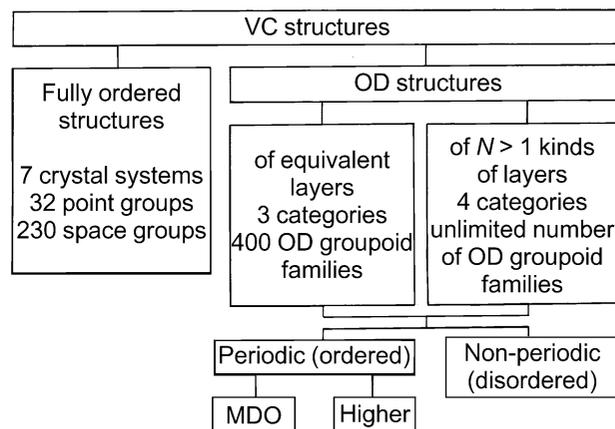


Fig. 9.2.2.5. Hierarchy of VC structures indicating the position of OD structures within it.