

9.2. LAYER STACKING

OD layer	layer group	subgroup of $\lambda-\tau$ oper.	N	F	Z
L_{2n+1}	$P(2/m)2/c2_1/m$	$P(2)cm$	4		1
			↘		↗
				2	
L_{2n}	$P(1)2_1/c1$	$P(1)c1$	2		2.
			↗		↘

Both polytypes are slightly desymmetrized. Since the shift between the origins of *Pyr* and *Tet* is irrational, stibivanite has no superposition structure and thus the diffraction patterns of its polytypes have no common set of family diffractions. Another remarkable point is that the recognition of these structures as OD structures of layers has nothing to do with their system of chemical bonds (see above).

9.2.2.3.3. γ - $Hg_3S_2Cl_2$

Among about 40 investigated crystals synthesized by Carlson (1967), not one was periodic. All diffraction patterns exhibited a common set of family diffractions, but the distribution of intensities along diffuse streaks varied from crystal to crystal (Đurovič, 1968). The maxima on these streaks indicated in some cases a simultaneous presence of domains of three periodic polytypes – one system of diffuse maxima was always present and it was referred to a rectangular cell with $a = 9,328(5)$, $b = 16.28(1)$, $c = 9.081(6)$ Å with monoclinic symmetry. All crystals were more or less twinned, sometimes simulating orthorhombic symmetry in their diffraction patterns.

The superposition structure with $A = a$, $B = b/2$, $C = 2c$ and space group $Pbmm$ was solved first. Here, a comparison of the family diffractions with the diffraction pattern of the α

modification (Frueh & Gray, 1968) proved decisive. It turned out that only one kind of Hg atom contributed with half weight to the superposition structure. This means that only these atoms repeat in the actual structure with periods $b = 2B$ and $c = 2C$. All other atoms (in the first approximation) repeat with the periods of the superposition structure and thus do not contribute to the diffuse streaks.

The symmetry of the superposition structures is compatible with the OD groupoid family determined from systematic absences:

$$\begin{matrix} A(2) & m & m \\ \{(b_{1/2} & 2_{1/2} & 2\} \\ \{(b_{1/2} & 2_{1/2} & 2\} & \text{category III,} \end{matrix}$$

where the subscripts 1/2 indicate translational components of $b/4$ (Dornberger-Schiff, 1964, pp. 41 ff.).

The solution of the structural principle thus necessitated only the correct location of the ‘disordered’ Hg atom in one of two

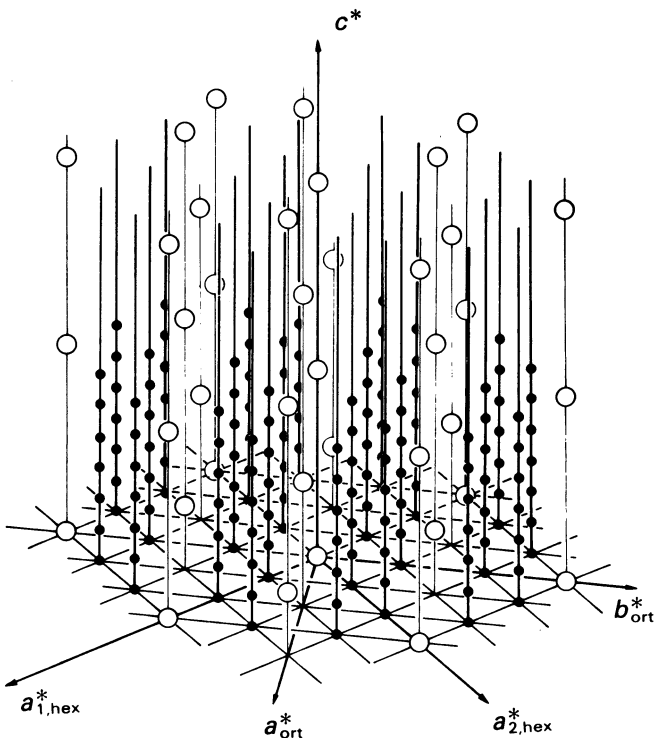


Fig. 9.2.2.15. Clinographic projection of the general scheme of a single-crystal diffraction pattern of hydrous phyllosilicates. Family diffractions are indicated by open circles and correspond in this case to a rhombohedral superposition structure. Only the part with $l \geq 0$ is shown.

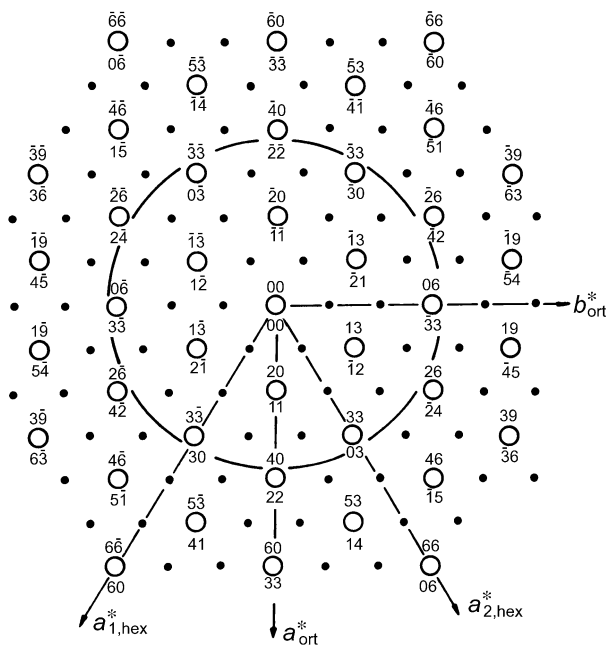


Fig. 9.2.2.16. Normal projection of the general scheme of a single-crystal diffraction pattern of hydrous phyllosilicates. Rows of family diffractions are indicated by open circles; the h, k indices refer to hexagonal (below) and orthogonal (above) axial systems.

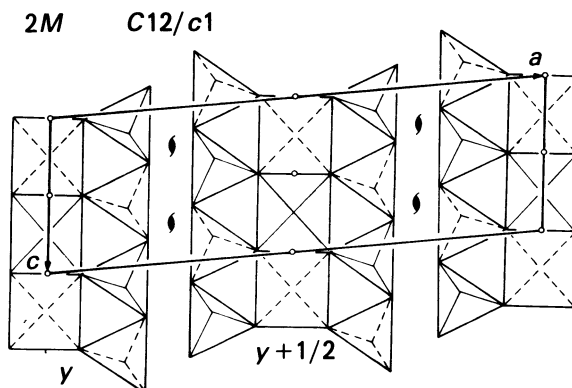


Fig. 9.2.2.17. The structure of stibivanite-2M. The unit cell is outlined and some relevant symmetry operations are indicated (after Merlino *et al.*, 1989).