

9.2. LAYER STACKING

| OD layer | layer group | subgroup of λ - τ 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:

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

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

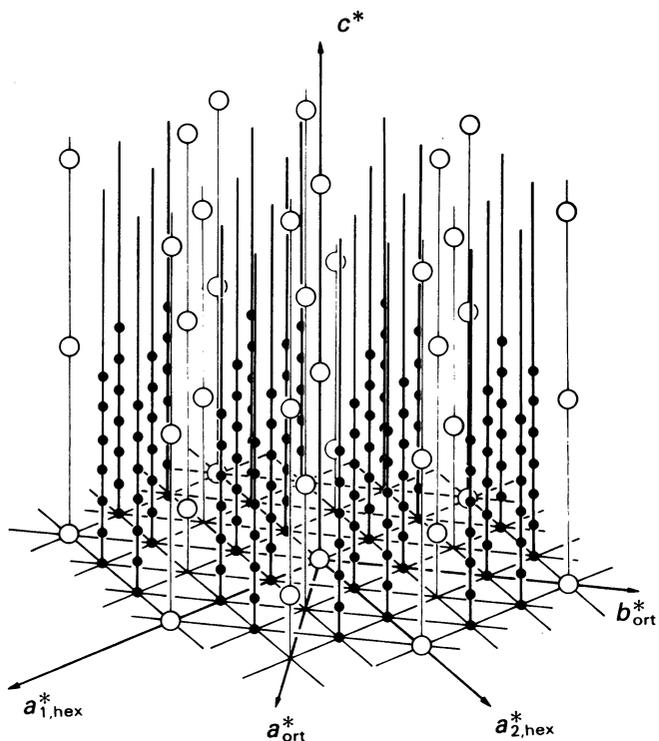


Fig. 9.2.2.15. Clinographic projection of the general scheme of a single-crystal diffraction pattern of hydrous phyllosilicates. Family diffractions are indicated by open circles and correspond in this case to a rhombohedral superposition structure. Only the part with $l \geq 0$ is shown.

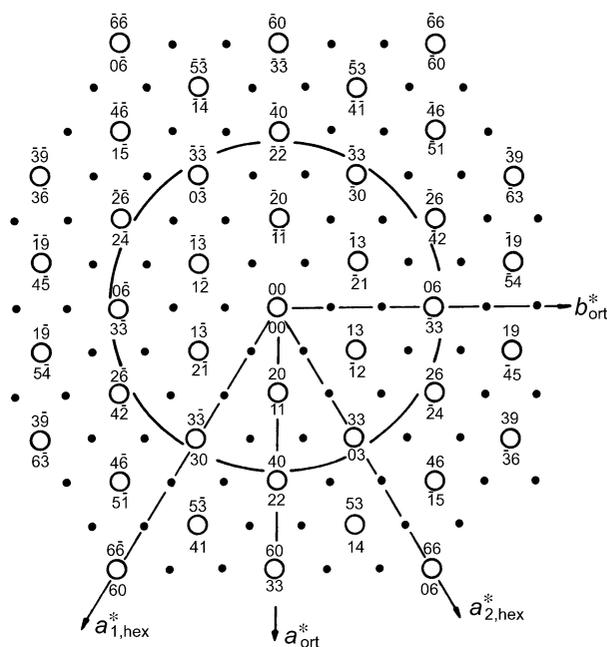


Fig. 9.2.2.16. Normal projection of the general scheme of a single-crystal diffraction pattern of hydrous phyllosilicates. Rows of family diffractions are indicated by open circles; the h, k indices refer to hexagonal (below) and orthogonal (above) axial systems.

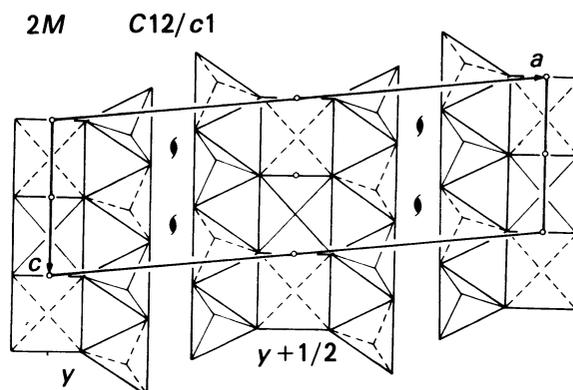


Fig. 9.2.2.17. The structure of stibivanite-2M. The unit cell is outlined and some relevant symmetry operations are indicated (after Merlino *et al.*, 1989).

9. BASIC STRUCTURAL FEATURES

possible positions indicated by the superposition structure. An analysis of the Fourier transform relevant to the above OD groupoid family showed that the Patterson function calculated with coefficients $|\Delta(hkl)|^2 = |F(hkl)|^2 + |F(\bar{h}kl)|^2$ shows interatomic vectors *within* any single OD layer, and it turned out that even a first generalized projection of the function yields the necessary 'yes/no' answer.

The structural principle is shown in Fig. 9.2.2.20.

There are two MDO polytypes in this family. Both are monoclinic (*c* axis unique) and consist of equivalent triples of OD layers. The first, MDO₁, is periodic after two layers and has symmetry $A2/m$. The second, MDO₂, is periodic after four layers, has symmetry $F2/m$ and basis vectors $2a, b, c$. Domains of MDO₁ were present in all crystals (the system of diffuse maxima, mentioned above), but some of them also contained small proportions of MDO₂.

Later, single crystals of pure periodic MDO₁ were also found in specimens prepared hydrothermally (Rabenau, private communication). The results of a structure analysis confirmed the previous results but indicated desymmetrization (Đurovič,

1979). The atomic coordinates deviated significantly from the ideal OD model; the monoclinic angle became 90.5° . Even the family diffractions, which in the disordered crystals exhibited an orthorhombic symmetry, deviated significantly from it in their positions and intensities.

9.2.2.3.4. Remarks for authors

When encountering a polytypic substance showing disorder, many investigators try to find in their specimens a periodic single crystal suitable for a structure analysis by current methods. So far, no objections. But a common failing is that they often neglect to publish a detailed account of the disorder phenomena observed on their diffraction photographs: presence or absence of diffuse streaks, their position in reciprocal space, positions of diffuse maxima, suspicious twinning, non-space-group absences, higher symmetry of certain subsets of diffractions, *etc.* These data should always be published, even if the author does not interpret them: otherwise they will inevitably be lost. Similarly, preliminary diffraction photographs (even of poor quality) showing these phenomena and the crystals themselves should be preserved – they may be useful for someone in the future.

9.2.2.4. List of some polytypic structures

A few examples of some less-common polytypic structures published up to 1994 are listed below:

Minerals: McGillite (Iijima, 1982), tridymite (Wennemer & Thompson, 1984), pyrosmalite (Takéuchi, Ozawa & Takahata, 1983), zirconolite (White, Segall, Hutchison & Barry, 1984), Ti-biotite (Zhukhlistov, Zvyagin & Pavlishin, 1990), diamond (Phelps, Howard & Smith, 1993), scholzite (Taxer, 1992), fiedlerite (Merlino, Pasero & Perchiazzi, 1994), penkvilskite (Merlino, Pasero, Artioli & Khomyakov, 1994), lengebachite – non-commensurate structure (Makovický, Leonardsen & Moelo, 1994).

Inorganic compounds: Borates with general formula $RAI_3(BO_3)_4$, where $R = Y, Nd, Gd$ (Belokoneva & Timchenko,

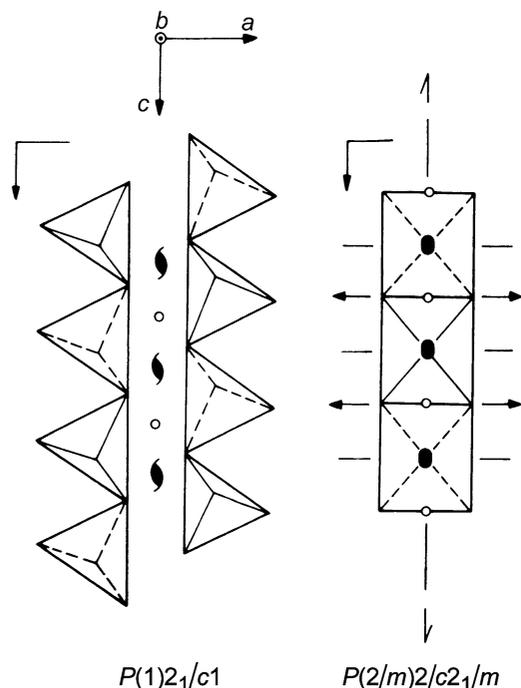


Fig. 9.2.2.18. The two kinds of OD layers in the stibivanite family (after Merlino *et al.*, 1989).

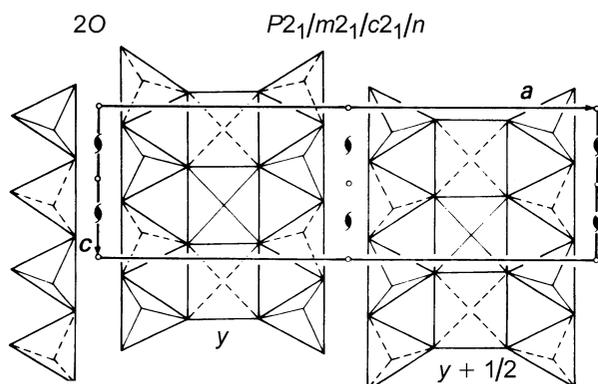


Fig. 9.2.2.19. The structure of stibivanite-2O (after Merlino *et al.*, 1989).

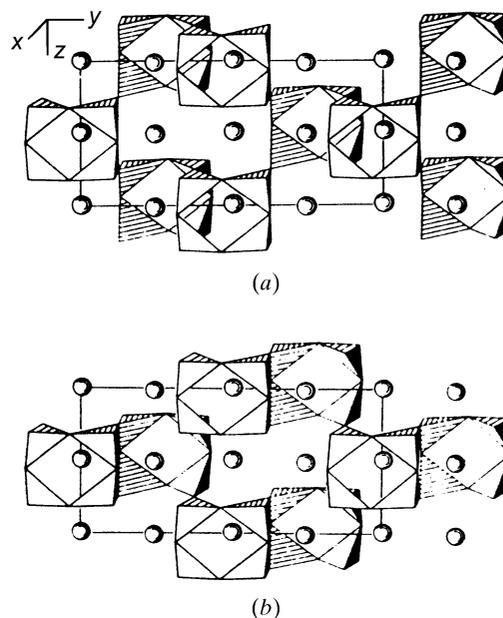


Fig. 9.2.2.20. The structural principle of $\gamma\text{-Hg}_3\text{S}_2\text{Cl}_2$. The shared corners of the pyramids are occupied by the Hg atoms; unshared corners are occupied by the S atoms. A pair of layers, but only the Cl atoms at their common boundary, are drawn. The two geometrically equivalent arrangements (a) and (b) are shown.