

9. BASIC STRUCTURAL FEATURES

Not so in OD structures, where any OD layer is by definition situated in a disturbing environment because its symmetry does not conform to that of the entire structure. ‘Antagonistic’ relations between these symmetries are most drastic in pure MDO structures because of the regular sequence of layers. The partial symmetry operations become irrelevant and the OD groupoid degenerates into the corresponding space group.

The more disordered an OD structure is, the smaller become the disturbing effects that the environment exercises on an OD layer. These can be, at least statistically, neutralized by random positions of neighbouring layers so that partial symmetry operations can retain their relevance throughout the structure. This can be expressed in the form of a paradox: the less periodic an OD structure is, the more symmetric it appears.

Despite desymmetrization, the OD theory remains a geometrical theory that can handle properly the *general symmetry pattern* of polytypes (which group theory cannot). It establishes a *symmetry norm* with which deviations observed in real polytypes can be compared. Owing to the high abstraction power of OD considerations, systematics of entire families of polytypes at various degree-of-idealization levels can be worked out, yielding thus a common point of view for their treatment.

9.2.2.2.9. Concluding remarks

Although very general physical principles (OD philosophy, MDO philosophy) underlie the OD theory, it is mainly a geometrical theory, suitable for a *description* of the symmetry of polytypes and their families rather than for an *explanation* of polytypism. It thus does not compete with crystal chemistry, but cooperates with it, in analogy with traditional crystallography, where group theory does not compete with crystal chemistry.

When speaking of polytypes, one should always be aware, whether one has in mind a concrete *real* polytype – more or less in Baumhauer’s sense – or an *abstract* polytype as a structural type (Subsection 9.2.2.1).

A substance can, in general, exist in the form of various polymorphs and/or polytypes of one or several families. Since polytypes of the same family differ only slightly in their crystal energy (Verma & Krishna, 1966), an entire family can be considered as an energetic analogue to one polymorph. As a rule, polytypes belonging to different families of the same substance do not co-exist. $\text{Al}(\text{OH})_3$ may serve as an example for two different families: the bayerite family, in which the adjacent planes of OH groups are stacked according to the principle of close packing (Zvyagin *et al.*, 1979), and the gibbsite-nordstrandite family in which these groups coincide in the normal projection.* Another example is the phyllosilicates (§9.2.2.3.1). The compound $\text{Hg}_3\text{S}_2\text{Cl}_2$, on the other hand, is known to yield two polymorphs α and β (Carlson, 1967; Frueh & Gray, 1968) and one OD family of γ structures (Đurovič, 1968).

As far as the definition of *layer polytypism* is concerned, OD theory can contribute specifications about the layers themselves and the geometrical rules for their stacking within a family (all incorporated in the vicinity condition). A possible definition might then read:

Polytypism is a special case of polymorphism, such that the individual polymorphs (called *polytypes*) may be regarded as arising through different modes of stacking layer-like structural

units. The layers and their stackings are limited by the *vicinity condition*. All polytypes built on the same structural principle belong to a *family*; this depends on the degree of a structural and/or compositional *idealization*.

Geometrical theories concerning rod and block polytypism have not yet been elaborated, the main reason is the difficulty of formulating properly the vicinity condition (Sedlacek, Grell & Dornberger-Schiff, private communications). But such structures are known. Examples are the structures of tobermorite (Hamid, 1981) and of manganese(III) hydrogenbis(orthophosphate) dihydrate (Císařová, Novák & Petříček, 1982). Both structures can be thought of as consisting of a three-dimensionally periodic framework of certain atoms into which one-dimensionally periodic chains and aperiodic finite configurations of the remaining atoms, respectively, ‘fit’ in two equivalent ways.

9.2.2.3. Examples of some polytypic structures

The three examples below illustrate the three main methods of analysis of polytypism indicated in §9.2.2.2.5.

9.2.2.3.1. Hydrous phyllosilicates

The basic concepts were introduced by Pauling (1930*a,b*) and confirmed later by the determination of concrete crystal structures. A *crystallochemical analysis* of these became the basis for generalizations and systemizations. The aim was the understanding of geometrical reasons for the polytypism of these substances as well as the development of identification routines through the derivation of basic polytypes (§9.2.2.2.3). Smith & Yoder (1956) succeeded first in deriving the six basic polytypes in the mica family.

Since the 1950’s, two main schools have developed: in the USA, represented mainly by Brindley, Bailey, and their co-workers (for details and references see Bailey, 1980, 1988*a*; Brindley, 1980), and in the former USSR, represented by Zvyagin and his co-workers (for details and references see Zvyagin, 1964, 1967; Zvyagin *et al.*, 1979). Both these schools based their systemizations on idealized structural models corresponding to the ideas of Pauling, with *hexagonal* symmetry of tetrahedral sheets (see later). The US school uses indicative symbols (Guinier *et al.*, 1984) for the designation of individual polytypes, and single-crystal as well as powder X-ray diffraction methods for their identification, whereas the USSR school uses unitary descriptive symbols for polytypes of all mineral groups and mainly electron diffraction on oblique textures for identification purposes. For the derivation of basic polytypes, both schools use crystallochemical considerations; symmetry principles are applied tacitly rather than explicitly.

In contrast to crystal structures based on close packings, where all relevant details of individual (even multilayer) polytypes can be recognized in the (1120) section, the structures of hydrous phyllosilicates are rather complex. For their representation, Figueiredo (1979) used the concept of *condensed models*.

Since 1970, the OD school has also made its contribution. In a series of articles, basic types of hydrous phyllosilicates have been interpreted as OD structures of $N > 1$ kinds of layers: the serpentine-kaolin group (Dornberger-Schiff & Đurovič, 1975*a,b*), Mg-vermiculite (Weiss & Đurovič, 1980), the mica group (Dornberger-Schiff, Backhaus & Đurovič, 1982; Backhaus & Đurovič, 1984; Đurovič, Weiss & Backhaus, 1984; Weiss & Wiewióra, 1986), the talc-pyrophyllite group (Đurovič & Weiss, 1983; Weiss & Đurovič, 1985*a*), and the chlorite group (Đurovič, Dornberger-Schiff & Weiss, 1983;

* Sandwiches with composition $\text{Al}(\text{OH})_3$ (similar to those in CdI_2) are the same in both families, but their stacking mode is different. This and similar situations in other substances might have been the reason for distinguishing between ‘polytype diversity’ and ‘OD diversity’ (Zvyagin, 1988).

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Weiss & Āuroviĉ, 1983). The papers published before 1983 use the Pauling model; the later papers are based on the model of Radoslovich (1961) with *trigonal* symmetry of tetrahedral sheets. In all cases, MDO polytypes (§9.2.2.3) have been derived systematically: their sets partially overlap with basic polytypes presented by the US or the USSR schools. The OD models allowed the use of unitary descriptive symbols for individual polytypes from which all the relevant symmetries can be determined (Āuroviĉ & Dornberger-Schiff, 1981) as well as of extended indicative Ramsdell symbols (Weiss & Āuroviĉ, 1985b). The results, including principles for identification of polytypes, have been summarized by Āuroviĉ (1981).

The main features of polytypes of basic types of hydrous phyllosilicates, of their diffraction patterns and principles for their identification, are given in the following.

9.2.2.3.1.1. General geometry

Tetrahedral and octahedral sheets are the fundamental, *two-dimensionally periodic* structural units, common to all hydrous phyllosilicates. Any *tetrahedral sheet* consists of $(\text{Si,Al,Fe}^{3+},\text{Ti}^{4+})\text{O}_4$ tetrahedra joined by their three basal O atoms to form a network with symmetry $P(3)1m$ (Fig. 9.2.2.6a). The atomic coordinates can be related either to a hexagonal axial system with a primitive unit mesh and basis vectors $\mathbf{a}_1, \mathbf{a}_2$, or to an orthohexagonal system with a *c*-centred unit mesh and basis vectors \mathbf{a}, \mathbf{b} ($b = \sqrt{3}a$). Any *octahedral sheet* consists of $M(\text{O,OH})_6$ octahedra with shared edges (Fig. 9.2.2.6b), and with cations *M* most frequently $\text{Mg}^{2+}, \text{Al}^{3+}, \text{Fe}^{2+}, \text{Fe}^{3+}$, but also $\text{Li}^+, \text{Mn}^{2+}$ ($r_M < \sim 0.9 \text{ \AA}$), etc. There are three octahedral

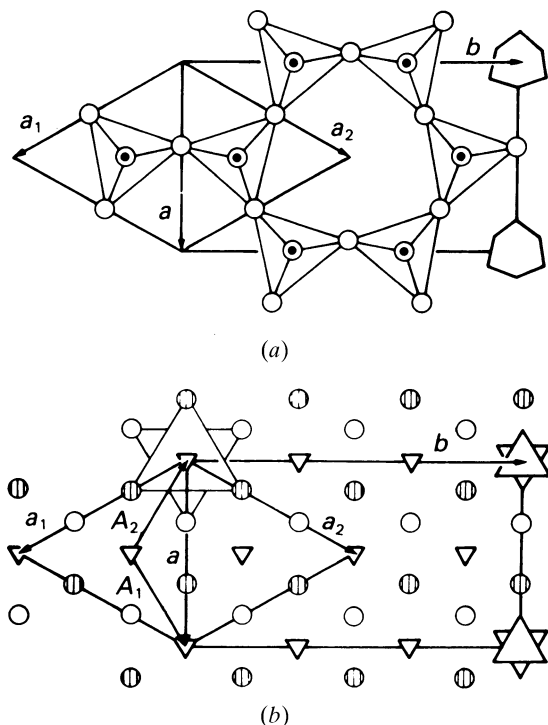


Fig. 9.2.2.6. (a) Tetrahedral sheet in a normal projection. Open circles: basal oxygen atoms, circles with black dots: apical oxygen atoms and tetrahedral cations. Hexagonal and orthohexagonal basis vectors and symbolic figures (ditrigons) for pictorial representation of these sheets are also shown. (b) Octahedral sheet. Open and shaded circles belong to the lower and the upper oxygen atomic planes, respectively; small triangles denote octahedral sites. Triangular stars on the right are the symbolic figures for pictorial representation of these sheets: the two triangles correspond to the lower and upper basis of any octahedron, respectively.

sites per unit mesh $\mathbf{a}_1, \mathbf{a}_2$. Crystallochemical classification distinguishes between two extreme cases: *trioctahedral* (all three octahedral sites are occupied) and *dioctahedral* (one site is – even statistically – empty). This classification is based on a bulk chemical composition. A classification from the symmetry point of view distinguishes between three cases: *homo-octahedral* [all three octahedral sites are occupied by the same kind of crystallochemical entity, *i.e.* either by the same kind of ion or by a statistical average of different kinds of ions including voids; symmetry of such a sheet is $H(3)12/m$];* *meso-octahedral* [two octahedral sites are occupied by the same kind of crystallochemical entity, the third by a different one, in an ordered way; symmetry $P(3)12/m$]; and *hetero-octahedral* [each octahedral site is occupied by a different crystallochemical entity in an ordered way; symmetry $P(3)12$]. The prefixes homo-, meso-, hetero- can be combined with the prefixes tri-, di-, or used alone (Āuroviĉ, 1994).

A tetrahedral sheet (*Tet*) can be combined with an octahedral sheet (*Oc*) either by a shared plane of apical O atoms (in all groups of hydrous phyllosilicates, Fig. 9.2.2.7a), or by hydrogen bonds (in the serpentine-kaolin group and in the chlorite group, Fig. 9.2.2.7b). Two tetrahedral sheets can either form a pair anchored by interlayer cations (in the mica group, Fig. 9.2.2.8a) or an unanchored pair (in the talc-pyrophyllite group, Fig. 9.2.2.8b).

The ambiguity in the stacking occurs at the centres between adjacent *Tet* and *Oc* and between adjacent *Tet* in the talc-pyrophyllite group. From the solved and refined crystal structures it follows that the displacement of (the origin of) one sheet relative to (the origin of) the adjacent one can only be one (or simultaneously three – for homo-octahedral sheets) of the nine vectors shown in Fig. 9.2.2.9.

The number of possible positions of one sheet relative to the adjacent one can be determined by the corresponding *NFZ* relations (§9.2.2.2.1). As an example, the contact (*Tet; Oc*) by shared apical O atoms, and the contacts (*Oc; Tet*) by hydrogen

* A hexagonally centred unit mesh $\mathbf{a}_1, \mathbf{a}_2$ instead of a primitive mesh $\mathbf{A}_1, \mathbf{A}_2$ is used (Fig. 9.2.2.6b).

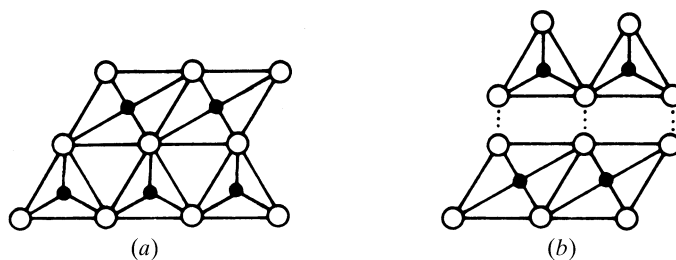


Fig. 9.2.2.7. Two possible combinations of one tetrahedral and one octahedral sheet (a) by shared apical O atoms, (b) by hydrogen bonds (side projection).

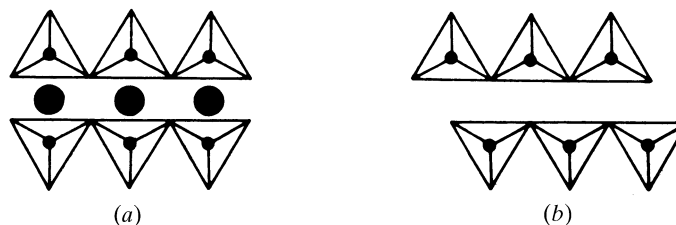


Fig. 9.2.2.8. Combination of two adjacent tetrahedral sheets (a) in the mica group, (b) in the talc-pyrophyllite group (side projection).

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bonds, for a homo-octahedral case, are illustrated in Figs. 9.2.2.10(a) and 9.2.2.10(b),(c), respectively. The two kinds of sheets are represented by the corresponding symbolic figures indicated in Fig. 9.2.2.6. For Fig. 9.2.2.10(a): the symmetry of *Tet* is $P(3)1m$, thus $N = 6$; the symmetry of *Oc* is $H\bar{3}12/m$ and its position relative to *Tet* is such that the symmetry of the pair is $P(3)1m$, thus $F = 6$ and $Z = 1$: this stacking is unambiguous.* But, if the sequence of these two sheets is reversed, $Z = 3$, because $N_{Oc} = 18$ (h centring of *Oc*). For Figs. 9.2.2.10(b) and (c), $Z = 3$. Similar relations can be derived for meso- and hetero-octahedral sheets as well as for the pair (*Tet*; *Tet*) in the talc-pyrophyllite group.

A detailed geometrical analysis shows that the possible positions are always related by vectors $\pm \mathbf{b}/3$. This, together with the trigonal symmetry of the individual sheets, leads to the fact that any superposition structure (§9.2.2.5) is trigonal (also rhombohedral) or hexagonal, and the set of diffractions with $k_{\text{ort}} \equiv 0 \pmod{3}$ has this symmetry too. This is important for the analysis of diffraction patterns.

Some characteristic features of basic types of hydrous phyllosilicates are as follows:

The serpentine-kaolin group: The general structural principle is shown in Fig. 9.2.2.11. The structures belong to category II (§9.2.2.7.2). In the homo-octahedral family, there are 12 non-equivalent (16 non-congruent) MDO polytypes (any two polytypes belonging to an enantiomorphous pair are equivalent but not congruent); in the meso-octahedral family, there are 36 non-equivalent (52 non-congruent) MDO polytypes. These sets are identical with the sets of *standard* or *regular* polytypes derived by Bailey (for references see Bailey, 1980) (trioctahedral) and by Zvyagin (1967) (dioctahedral and trioctahedral). The individual polytypes can be ranged into four groups (subfamilies, which are individual OD groupoid families), each with a characteristic superposition structure.

*If the symmetry of *Tet* is $P(6)mm$ (in the Pauling model), $Z = 2$. This case is common in the literature. However, with the trigonal symmetry of *Tet*, these two possibilities would correspond to Franzini (1969) types *A* and *B*, which are not geometrically equivalent.

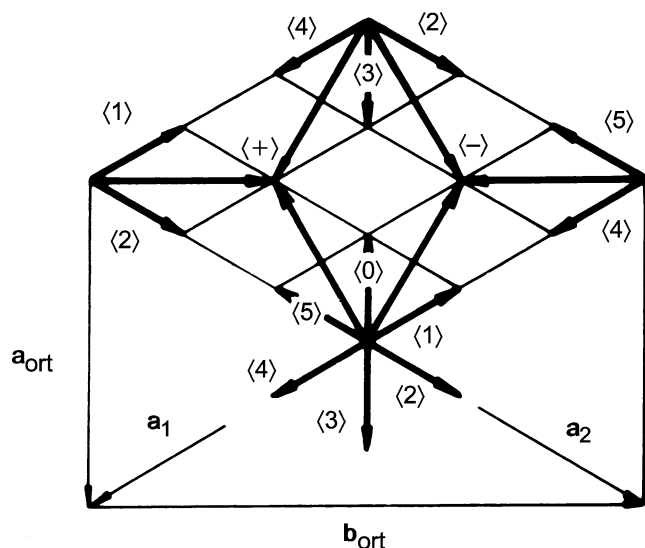


Fig. 9.2.2.9. The nine possible displacements in the structures of polytypes of phyllosilicates. The individual vectors are designated by their conventional numerical characters and the signs +, -. The zero displacement (*) is not indicated. The relations of these vectors to the basis vectors \mathbf{a}_1 , \mathbf{a}_2 or \mathbf{a} , \mathbf{b} are evident.

The mica group: The general structural principle is shown in Fig. 9.2.2.12. The structures belong to category IV. There are 6 non-equivalent (8 non-congruent) homo-octahedral MDO polytypes, 14 (22) meso-octahedral, and 36 (60) hetero-octahedral MDO polytypes. The homo-octahedral MDO polytypes are identical with those derived by Smith & Yoder (1956); meso-octahedral MDO polytypes include also those with non-centrosymmetric 2:1 layers (*Tet*; *Oc*; *Tet*); some of these have also been derived by Zvyagin *et al.* (1979). The individual polytypes can be ranged into two groups (subfamilies). For complex polytypes and growth mechanisms, see Baronnet (1975, 1986).

The talc-pyrophyllite group: The general structural principle is shown in Fig. 9.2.2.13. The structures belong to category I. There are 10 (12) MDO polytypes in the talc family (homo-octahedral) and 22 (30) MDO polytypes in the pyrophyllite family (meso-octahedral); some of these have been derived also by Zvyagin *et al.* (1979). The structures can be ranged into two

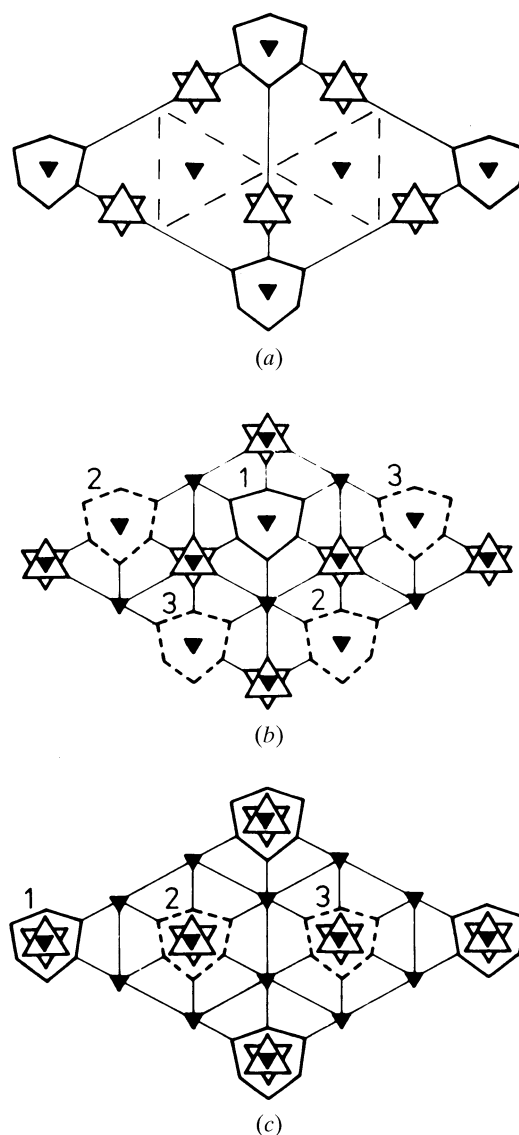


Fig. 9.2.2.10. The NFZ relations (a) for the pair tetrahedral sheet-homo-octahedral sheet (with shared apical O atoms), (b), (c) for the pair homo-octahedral sheet-tetrahedral sheet (by hydrogen bonds). The sheets are represented by their symbolic figures; some relevant symmetry elements are also indicated. One of the possible positions (labelled 1) is drawn by full, the other two (2, 3) by broken lines.

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groups (subfamilies). For more details, see also Evans & Guggenheim (1988).

The chlorite-vermiculite group: There are two kinds of octahedral sheets in these structures: the *Oc* sandwiched between two *Tet* and the *interlayer* (Fig. 9.2.2.14). The structures belong to category IV. Any *Oc* can be independently homo-, meso-, or hetero-octahedral, and thus, theoretically, there are nine families here. Although vermiculites have a crystal chemistry different from chlorites, they can be, from the symmetry point of view, treated together. There are 20 (24) homo-homo-octahedral, 44 (60) homo-meso-octahedral and 164 (256) meso-meso-octahedral MDO polytypes (the first prefix refers to the 2:1 layer, the second to the interlayer); the other families have not yet been treated. Some of these polytypes have also been derived by other authors (for references, see Bailey, 1980; Zvyagin *et al.*, 1979).

In order to preserve a unitary system, some monoclinic polytypes necessitate a 'third' setting, with the *a* axis unique. These should not be transformed into the standard second setting.

9.2.2.3.1.2. Diffraction pattern and identification of individual polytypes

Owing to the trigonal symmetry of the basic structural units and their stacking mode, the single-crystal diffraction pattern of hydrous phyllosilicates has a hexagonal *geometry* and it can be referred to hexagonal or orthohexagonal reciprocal vectors \mathbf{a}_1^* , \mathbf{a}_2^* or \mathbf{a}^* , \mathbf{b}^* , respectively (Figs. 9.2.2.15 and 9.2.2.16). It contains three types of diffractions:

(1) Diffractions $00l$ (or $000l$), always sharp and common to all polytypes of a family including all its subfamilies. They are indicative of the mineral group, but useless for the identification of polytypes.

(2) The remaining diffractions with $k_{\text{ort}} \equiv 0 \pmod{3}$, always sharp and common to all polytypes of the same subfamily.

(3) All other diffractions: sharp only for periodic polytypes, otherwise present on diffuse rods parallel to \mathbf{c}^* . These are characteristic of individual polytypes. Diffractions $0kl$ – if sharp – are common to all polytypes of the family with the same *bc* projection.

From descriptive geometry, it is known that two orthogonal projections suffice to characterize unambiguously any structure and, therefore, the superposition structure (which implicitly contains the *ac* projection) together with the *bc* projection suffice for an unambiguous characterization of any polytype. It also follows that the diffractions with $k \equiv 0 \pmod{3}$ together with the $0kl$ diffractions with $k \not\equiv 0 \pmod{3}$ suffice for its determination (except for homometric structures) (Đurovič, 1981).

From the trigonal or hexagonal symmetry of any superposition structure and from Friedel's law, it follows that the reciprocal

rows $20l$, $13l$, $\bar{1}3l$, $\bar{2}0l$, $\bar{1}\bar{3}l$, and $\bar{1}\bar{3}l$ (Fig. 9.2.2.16) carry the same information. Therefore, for identification purposes, it suffices to calculate the distribution of intensities along the reciprocal rows $20l$ (superposition structure – subfamily) and $02l$ (*bc* projection) for all MDO polytypes. Experience shows (Weiss & Đurovič, 1980) that a mere visual comparison of calculated and observed intensities along these two rows suffices for an unambiguous identification of a MDO polytype. A similar scheme has been presented by Bailey (1988b).

The above considerations are based on the ideal Radoslovich model. Diffraction patterns of real structures may exhibit deviations owing to the distortion of the ideal lattice geometry and/or symmetry of the structure.

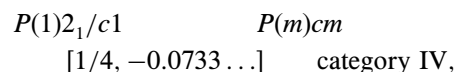
9.2.2.3.2. Stibivanite Sb_2VO_5

The crystal structure of this mineral has been determined by Szymański (1980). It turned out to be identical with that of the compound of the same composition synthesized earlier (Darriet, Bovin & Galy, 1976). The structure is monoclinic with space group $C12/c1$, lattice parameters $a = 17.989$ (6), $b = 4.7924$ (7), $c = 5.500$ (2) Å, $\beta = 95.13$ (3)°.

Structural units are formed of $\text{SbO}_2\text{--O--VO--O--SbO}_2$ extended along *a*, with adjacent units bonded along *c* through Sb--O--Sb and V--O--V bonds. Ribbons are thus formed with no bonding along *b*, and only the Sb--O interactions [2.561 (4) Å] along *a* (Fig. 9.2.2.17). This accounts for the excellent acicular cleavage.

Merlino *et al.* (1989) recognized in this structure sheets of VO_5 square pyramids (*Pyr*) parallel to *bc*, with layer symmetry $P(2/m)2/c2_1/m$ alternating with sheets containing chains of distorted SbO_3 tetrahedron-like pyramids (*Tet*) with layer symmetry $P(1)2_1/c1$ (Fig. 9.2.2.18). Owing to the higher symmetry of *Pyr*, they concluded that there may also exist an alternative attachment of *Tet* to *Pyr*, such that the triples (*Tet*; *Pyr*; *Tet*) will exhibit the layer symmetry $Pmc2_1$, and they will be arranged so that another polytype $2O$ with symmetry $P2_1/m2_1/c2_1/n$ (Fig. 9.2.2.19) is formed [in the original $2M$ polytype, the triples (*Tet*; *Pyr*; *Tet*) have the layer symmetry $P(1)2/c1$]. A mineral with such a structure, with lattice parameters $a = 17.916$ (3), $b = 4.700$ (1), $c = 5.509$ (1) Å, has actually been found.

The polytypism of stibivanite is reflected in its OD character: the two kinds of sheets *Pyr* and *Tet* correspond to two kinds of non-polar layers: their relative position is given by the family symbol:



the *NFZ* relations being

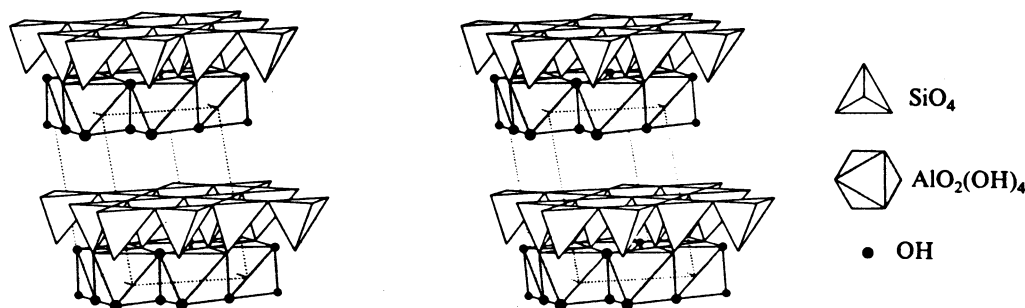


Fig. 9.2.2.11. Stereopair showing the sequence of sheets in the structures of the serpentine-kaolin group (kaolinite-1A, courtesy Zoltai & Stout, 1985).