

## POLYTYPIISM OF CRYSTAL STRUCTURES

B. B. ZVYAGIN

Institute of Ore Mineralogy (IGEM), U.S.S.R. Academy of Sciences, Staromonetny 35,  
Moscow 109017, U.S.S.R.

**Abstract**—Polytypism occupies a singular position in the structural crystallography uniting features of polymorphism and diversity of crystal structure built of definite units. In the structural systematics the polytype structures are considered in relation to fragmentary, interstratified, hybrid (both commensurate and incommensurate), order-disorder (OD) and modulated structures. The polytype diversity includes close packings of identical and different atoms, stackings of tetrahedral, octahedral and prismatic sheets, phyllosilicates and complex silicates having a wide variety of relative positions and/or orientations of the building units, combinations of structural units periodic in two and one dimensions or having finite dimensions, as well as purely chain-ribbon structures. Different polytypes require a variety of individual approaches in their consideration and symbolic description using symbols of the structural units, of their positions-displacements, orientations-rotations, or of the symmetry operations relating them. As a versatile notion polytypism presents an important crystallochemical phenomenon, a means to perceive crystalline substances not as isolated objects but as sets of interrelated members of united systems, and a cognition method effective in the solution of theoretical as well as applied problems.

### 1. INTRODUCTION

The notion of polytypism is versatile. Its different aspects were elucidated in the fundamental book of Verma and Krishna [1]. Additional new materials are given in the Volume "*Polytype Structures*" edited by Krishna [2]. This article is therefore not dealing with such problems as physical chemistry and thermodynamics, crystal growth and transformation, properties and practical use of polytypes. These items were considered in detail in these publications and are nevertheless still open for further studies. An attempt is made here to bring together and to conceive the structural aspect of polytypism, the specific structural, symmetry and diffraction features of polytypes that are establishing special possibilities of understanding and description, as well as theoretical deduction and experimental identification of polytype structures.

### 2. THE NOTION OF POLYTYPIISM AND THE POSITION OF POLYTYPES IN THE STRUCTURAL SYSTEMATICS OF CRYSTALLINE SUBSTANCES

The notion of polytypism combines features of two crystallochemical phenomena. On the one hand polytypism is a particular case of polymorphism as it implies a diversity of crystal structures of the same composition built of some common for them structural units (layers, rods, blocks) of one or several kinds. On the other hand, just because the polytype structures consist of the same structural units but differ in their disposition they belong to a wide variety of crystal substances which may be imagined as composed of a definite set of structural blocks (moduli). Thus, Pauling has presented all the phyllosilicates (micas, chlorites, kaolinites, etc.) as being composed of gibbsite-brucite and tridymite sheets [3]. Blocks of different substances are forming polysomatic series from brucite to olivine  $[\text{Mg}(\text{OH})_2 \cdot n\text{Mg}_2\text{SiO}_4, n = 0, 1, 2, \dots, \infty]$  [4-6], from pyroxene-amphibole to mica-talc (biopyriboles) [7, 8], etc.

The combination of features of both phenomena (polymorphism and fragmentary composition) restricts substantially the diversity of polytype structures by conditions of an equal alternation order of structural units (if they are of several kinds) and existence of definite crystallochemical or geometrical rules for the possible relative positions of adjacent units [9, 10]. The absence of the first restriction is characteristic for mixed-layered structures [11], the absence of the second one for hybrid structures [12, 13], although it should be mentioned that there are no distinct boundaries between these three kinds of structures. A complete and unambiguous understanding of the relationship between polytypes and allied kinds of structures as well as between the respective notions has not been achieved as yet. It is appropriate to consider this problem for the simplest and best studied case of structures composed of units periodical in two dimensions. Hereafter

these units will be called layers even when they are not isolated but are joined together into three-dimensional frameworks. Such a consideration may also have a general significance for structures built of other kinds of units or their combinations.

Two cases are to be distinguished for layer structures: that of more than one layer kind and that of one layer kind.

#### *Layers of several kinds*

When there are no restriction on the sequence order and relative positions of the layers, the corresponding structures are qualified as mixed-layer or interstratified. The layer alternation may be completely random or subjected to some statistical or strict rules.

Mixed-layer structures having an unequivocal layer sequence order (i.e. excluding sequences of the type AAB permitting both A and B layers to follow layer A) are forming a more narrow quantity of hybrid structures [12, 13]. Initially the latter term was used for structures containing hydroxide (brucite-like) layers as one kind of layers [12]. According to the direct meaning of the word "hybrid" the notion of hybrid structures is applicable to all cases where the layers of each kind are separately characteristic for original compounds which may be of essentially different nature. This was the case for the classical examples of such substances—valleriite and tochilinite [12–14]. However, the term may be extended to all cases when the layers of different kind alternate in a definite unequivocal order sequence, even if the individual structures composed of some particular kinds of layers are not known.

Hybrid structures may be imagined as superpositions of several structures inserted one into another. Having common basal repeats along the normal to the layers characterized by a single set of the reciprocal lattice points  $00l$  they may differ in the two-dimensional cells in the basis plane parallel to the layers. In particular cases these cells may be equal or rationally related by means of linear equations with integer coefficients and are thus commensurate. On the contrary, the relations may be irrational and cells incommensurate. In principle the substructures of the hybrid structures are also independent without respect to the periodicity in the direction of the layer alternation. They may have both equal and different strict periods (if their directions coincide there is then a strict period which is an integer multiple of the particular periods), or there may be not strict periods at all for some particular substructures as well as for all substructures. The absence of strict periodicities may correspond to semirandom structures which are periodic up to certain shifts (e.g.  $\pm b/3$ ) or in certain projections (e.g. on the plane  $XOZ$ ). Such structures have sharp reflexions  $hkl$  besides of  $00l$  for definite indices  $hk$  (e.g. with  $k = 3n$ ,  $h - k = 3n$ , etc.). In the limiting case hybrid structures as well as mixed-layer structures in general, may be turbostratic, representing a one-dimensional sequence of two-dimensional lattices.

If the adjacent layers of the hybrid structures are stacked according to definite rules defining several crystallochemically equivalent variants the respective structures are polytypes forming thus a part of the hybrid structures. The existence of more than one variant for the layer stacking that are compatible with these rules and restrictions is the reason for the polytype diversity. Depending on the distribution of these variants over the consecutive layer pairs homogeneous and inhomogeneous polytypes are distinguished. The homogeneity condition may be in general understood as equivalence of the relative position of each layer among the others and equivalence of transition from the preceding layer to the next one for all layers of a given kind. If, for instance, the layer positions are characterized by their azimuthal orientations and relative displacements, homogeneity implies either identical consecutive rotations and displacements of the respective layers or a regular alternation of rotations and/or displacements having equal absolute values but opposite signs. Inhomogeneous polytypes involve distortions of the regular alternation of the stacking variants. These distortions may be of a different degree depending on the number of distortions and of the set of variants present in the structure. In extreme cases this set may be limited by two alternative variants or include all variants. Whereas homogeneous polytypes have only a limited number of relatively short strict periods the inhomogeneous polytypes may be both periodic (without any limitations on the number of layers per period) and aperiodic. Respectively they are called ordered and semirandom. Fully random polytypes are impossible since the limited set of distortions excludes arbitrary rotations and displacements of the layers.

The fixed layers of the maximum thickness compose all the structures of a polytype family. The

layer pairs of these structures are formed according to crystallochemical laws and are established experimentally by means of structure analysis methods. If such pairs are not only crystallochemically but also symmetrically equivalent that is a distinguishing feature of order–disorder (OD) structures [15]. In the OD-structures the pairs are related by partial symmetry operations converting the pairs into themselves but not obligatory valid for all the structure as a whole. Under such conditions peculiar forms of OD are possible in the arrangement of the structural units. Structures with a maximum degree of order (MDO-structures) having strict repeats are of course polytypes but that does not mean that polytypes are always OD (MDO)-structures. With the choice of layers having maximum dimensions the polytype diversity is wider than the OD-diversity if not all polytype layer pairs are symmetrically equivalent. The polytypes are subdivided into as many groups of OD-structures as many symmetrically nonequivalent kinds of layer pairs exist with more than one variant for the position of one layer relative to the other. According to the well-known criterion of the OD-theory [15–17]  $Z = N/F$ , where  $Z$  is the number of OD-equivalent variants of the positions of one structural unit relative to the neighbouring one,  $N$  is the order of the symmetry group of the initial structural unit and  $F$  the order of the symmetry group of the pair of adjacent structural units.

The extension of the OD-diversity in order to bring it into coincidence with the polytype diversity may be attained at another choice of layers being some parts of the maximum layers permanently present in all polytype structures and hence being of smaller dimensions and more kinds [16, 17]. These layers are supplied with symmetry properties which are not evident and are to be accepted as a sequence of rather than a reason for the resulting structure. This is done in order to ensure an unequivocal formation of layers having maximum dimensions and not to increase the polytype diversity beyond the actual one. Such an approach is justified only if it leads to some useful sequences and serves to the solution of problems otherwise unsolvable. In all cases the choice of layers having maximum dimensions and common for all polytype structures is of principle importance. They are expressing the specificity of the structures and are in correspondence with conditions of their formation and existence. Some variations of composition and structure of these layers are permissible being both consequences and conditions for the realization of the respective polytypes.

Depending on the polarity–nonpolarity of the layers and on the number of their kinds the OD-structures are subdivided into four categories [15, 16]. The same categories might be valid for polytype structures built of different kinds of layers since the surfaces of polytype layers usually behave as OD layers.

#### *Layers of one kind*

The systematics of respective structures depends only on the rules of relative disposition of adjacent layers separated by a unique interlayer distance. Three cases are to be distinguished:

- (i) there are no distinct rules or they are not known;
- (ii) there are several crystallochemically equivalent variants;

and

- (iii) the variants are symmetrically equivalent.

These cases correspond to three sets of structures. The first one is in the extreme case turbostratic, the second contains polytypes and the third, OD-structures, the third quantity being a part of the second one. Depending on the distribution of the layer stacking variants the OD-structures and polytypes may be either strictly periodic [both homogeneous (MDO-) and inhomogeneous] or aperiodic, semirandom at different extent. OD-structures, and apparently, polytypes are subdivided in this case into three categories [15]. The first quantity of structures is separated from the second one by some intermediate area which is characterized by the presence of stacking distortions both belonging and not belonging to the polytype set of variants.

The inhomogeneous strictly periodic polytype structures represent an alternation of layer sequence orders characteristic for different homogeneous structures. Therefore, they may be considered as peculiar “solid solutions” of homogeneous structures and are called also complex polytypes. In particular linear sequences, series, are possible having two homogeneous structures as end members. Likewise polytypes and OD-structures without a strict repeat of the layer

alternation may be considered as a "solid solutions" and series leading from one homogeneous structure to another through semirandom structures with a statistic distribution of permitted variants of the layer stacking. These "solid solutions" and series are particular displaying of sequences of crystal substances with variable structure features in the system of mixed-layer and polysomatic series in general where both composition and structure are changing.

The notion of polytypism is connected also with the notion of modulated structures [18] in which the main periodicity is modulated by some function influencing the atomic positions and their occupancies. The modulation periods may be in rational as well as in irrational relations with the periods of the main structure, so that the respective superlattice and lattice may be either commensurate or incommensurate. For polytypes one should distinguish between modulations which are parallel to the layers and to the direction of layer alternation. Layer modulations are quite natural; it is easy to imagine them and they are well-known for many examples (minerals antigorite, cymrite, greenalite). They may be one- or two-dimensional, commensurate or incommensurate. In principle one may imagine similar modulations for the direction of the layer alternation as variations of composition and structure of consecutive layers. However, when the layers are autonomous and the interlayer bonds are weaker than intralayer bonds it is difficult to find physical reasons for such features. It is more reasonable to associate the polytype modulations taking place in the third dimension relative to the main periodicity of the structural projection on the normal to the layers. Such modulations have two characteristics: one quantitative and one qualitative. The first is given by the number  $n$  of layers per repeat, the second concerns the layer stacking differences at one and the same repeat. In particular for  $n = 1$  the possible modulations have the same repeat at the projection on the normal and differ qualitatively by the disposition of layers.

### 3. POLYTYPE STRUCTURES

The world of polytype structures is very diverse. The simplest form of polytypism is the diversity of closest packing of identical spheres, characteristic for many metals and alloys [5, 19–22]. The structural units are layers of close packed atoms lying in a plane. The layer is imaged as a network of triangles having two alternative orientations and representing the bases of possible tetrahedral and octahedral voids (Fig. 1). The polar subgroups of symmetry for a single layer  $P(6)mm$  and layer pairs  $P(3)1m$  and the above mentioned formula  $Z = N/F$  [15] give the value  $Z = 2$  which coincides with only two possibilities for positioning the next layer over the preceding one in closest packings and this substantiates the symmetry equivalence of these possibilities.

The ideas of closest packings are a basis for a wide variety of polytype structures composed of different atoms. The polytypes of SiC are the classical example which opened the era of polytypism [23]. The SiC polytypes as well as those of ZnS are formed by tetrahedral layers having one kind

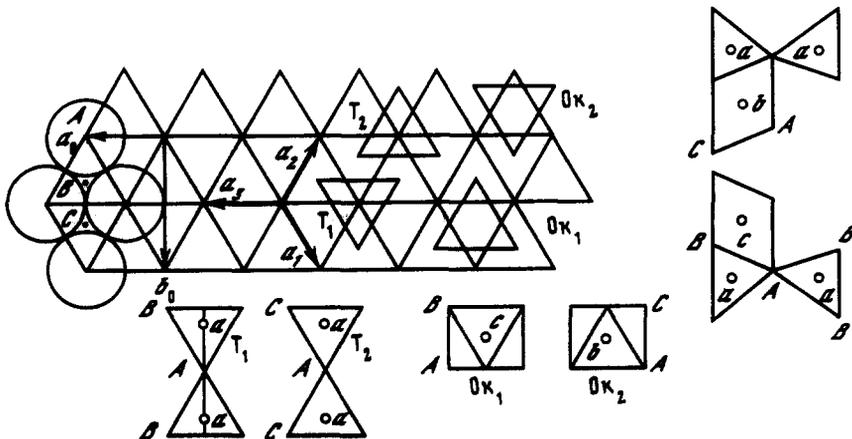


Fig. 1. The scheme of a close packed atomic plane and possible positions of octahedral and tetrahedral voids [9].

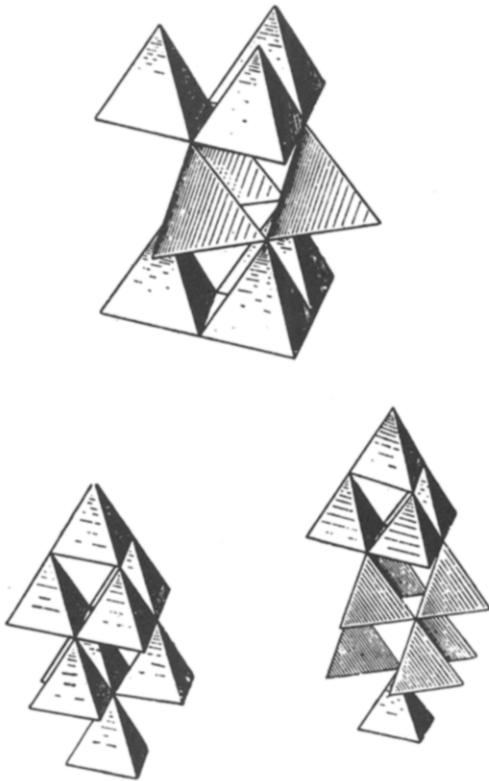


Fig. 2. Polytype structures composed of close packed tetrahedral layers: (a) wurtzite ( $2H$ ); (b) sphalerite ( $3R = 3C$ ), carborundum III ( $4H$ ) [5].

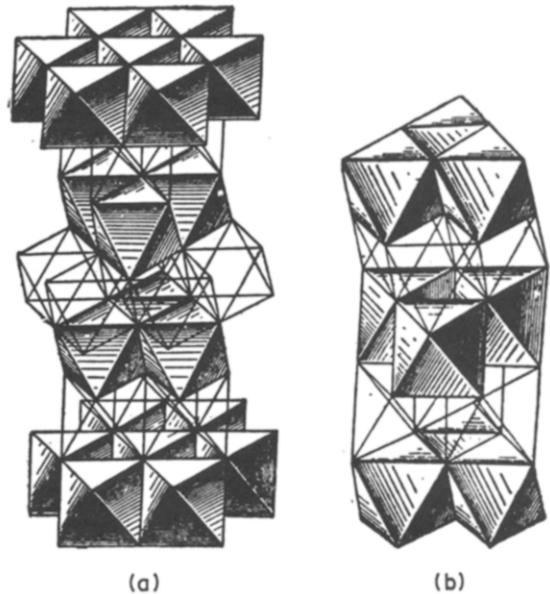


Fig. 3. Polytype structures composed of close packed octahedral layers: (a)  $6H$ - (ramsayite) and (b)  $4H$ - (topaz) close packings [5].

of atoms (C, S) in the apices and another (Si, Zn) in the centers [1, 5] (Fig. 2). According to the same principles the structures of diamond and lonsdaleite are built from carbon atoms only [24].

Polytypes composed of close packed octahedral layers (Fig. 3) are characteristic of the halogenides of cadmium and lead, oxides and hydroxides of di- and trivalent metals [1, 5, 25–28]. For some of them the octahedral cavities are occupied totally or partially over all storeys, others have alternating storeys of occupied and vacant octahedra. In the case of  $\text{Al}(\text{OH})_3$  polytypes, dioctahedral layers (having  $2/3$  of octahedra occupied by Al) alternate with vacant interlayers but it is only in one of the polytypes (bayerite) that the hydroxyls (OH) bordering the interlayers are close packed. In the other two (gibbsite and norstrandite) the hydroxyls of the interlayers lie one over another violating the closest packing, so that layers of occupied octahedra alternate with interlayers of vacant trigonal prisms [5, 6, 9, 26, 27] (Fig. 4). It is clear that in this case even the hydroxyl planes of adjacent octahedral layers of bayerite and gibbsite cannot be considered as OD-layers so that the polytype diversity is of a purely crystallochemical nature.

Similar violations of the closest packing but taking place inside occupied layers are peculiar for disulfides of molybdenum (molybdenite), rhenium and tungsten, diselenides of niobium and tantalum, the polytypes of which are composed of close packed layers of occupied trigonal prisms separated by interlayers of vacant octahedra and tetrahedra (Fig. 5) [1, 9, 29]. Some polytypes ( $\text{TaSe}_2$ ) contain both octahedral and prismatic occupied layers.

Layers of trigonal prisms occupied by pairs of metal atoms of the type  $\text{X-M-M-X}$  (Fig. 6) are forming the polytype structures of GaS, GaSe, InSe (Fig. 7) [30].

A remarkable case is presented by the polytypes of  $\text{ZnIn}_2\text{S}_4$ . Under conditions of the closest packing of S atoms there are three-storey layers. The middle storey is a sheet of octahedra occupied by In, the two outer storeys are sheets of tetrahedra sharing common apices with octahedra. One of them is occupied also by In, the other by Zn. The layers are separated by interlayers of one storey of vacant octahedra and tetrahedra (Fig. 8) [31]. The structural variations may be associated with packing changes of S-atomic planes both inside and between the layers. This may be treated

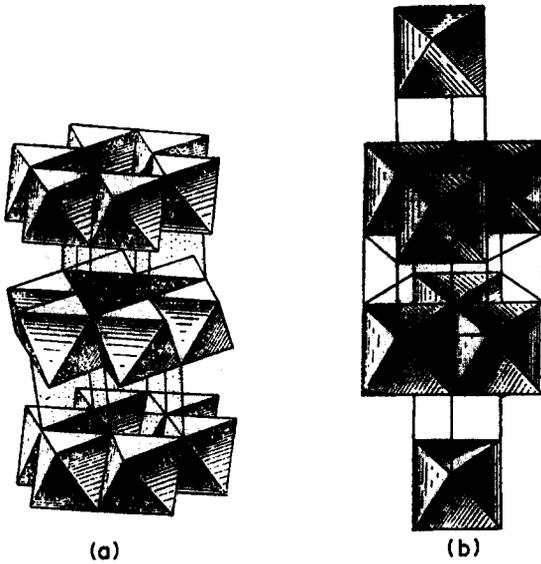


Fig. 4. Polytype structures composed of octahedral layers and prismatic interlayers: (a) gibbsite ( $2H$ ) and (b) norstrandite ( $3R$ ) [5].

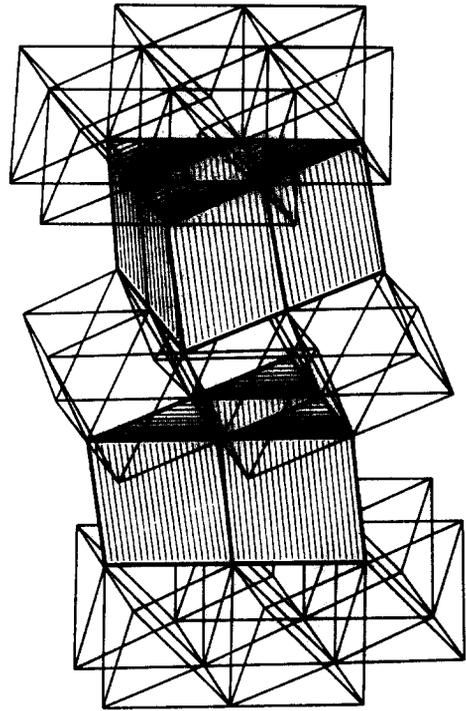


Fig. 5. One of the molybdenite polytype structures  $2H$  composed of prismatic layers with octahedral interlayers [9].

as a two-stage polytypism: polytypism of layers consisting of one-storeyed sheets and polytypism of structures consisting of three-storeyed layers. According to Ref. [31] it is only the packing of sheets inside layers that is varied while the boundary S-atomic planes are neighbouring relative to the adjacent S planes in a definite way being in the hexagonal position. Thus only the first stage of polytypism is realized. Another subject of variation is the polar distribution of In and Zn among the tetrahedral sheets.

For all these structures, from  $\text{MoS}_2$  to  $\text{ZnIn}_2\text{S}_4$ , the symmetries of separate layers and layer pairs are of equal order and the number of symmetrically equivalent layer stacking variants  $Z = 1$ . This clearly indicates that here is a pure polytype diversity and but not an OD.

Graphites are another remarkable example of polytypism. Graphite layers are single planes of carbon atoms that, however, are not close packed (Fig. 9) [1, 32]. The C atoms form a network of noncentred hexagons so that the three positions  $000$ ;  $2/3 \ 1/3 \ 0$  and  $1/3 \ 2/3 \ 0$  along the large

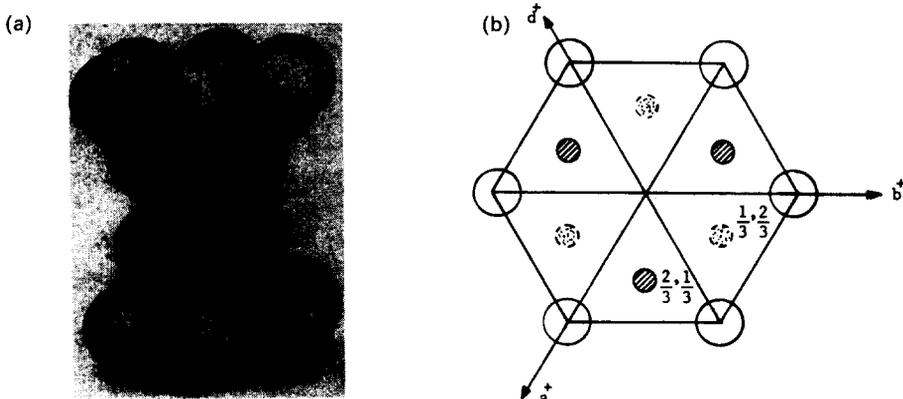


Fig. 6. Model (a) and projection scheme (b) of a prismatic layer XMMX [29].

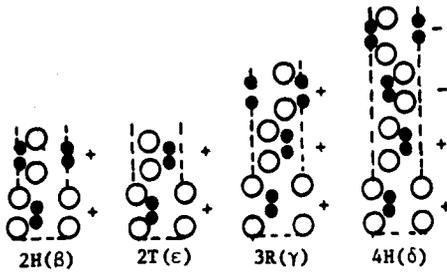


Fig. 7. Polytypes 2H, 2T, 3R and 4H built of prismatic layers XMMX in projection on the plane (11 $\bar{2}$ 0) [29].

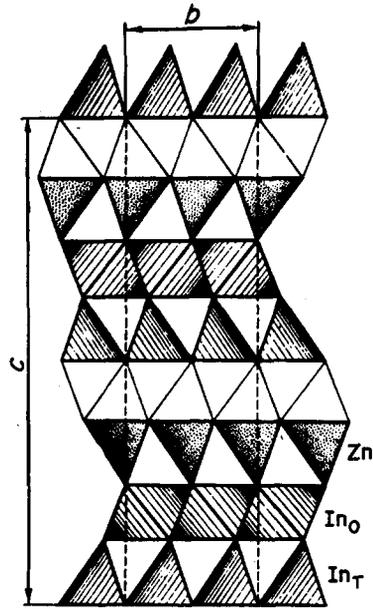


Fig. 8. The structural scheme of a two-layer polytype  $ZnIn_2S_4$  [30].

diagonal of the hexagonal unit cell are occupied consecutively by two carbons and one vacant hexagon centre. Different polytypes are characterized by the sequence of the positions of the hexagon centres for the consecutive layers projecting into the same points of the basis diagonal. It is worth noting that under conditions of an infinite number of layer sequence possibilities only two polytypes have been observed for sure: one two-layer hexagonal and one three-layer rhombohedral.

One of the most important examples of polytypism is the case of phyllosilicate structures containing two-dimensional sheets of Si-O-tetrahedra with admission of some isomorphous substitutions. The phyllosilicates are important minerals of the earth's crust that permanently participate in various processes taking place at different stages of its formation and development. The phyllosilicates consist of physically distinct layers which are formed by different combinations of an octahedral sheet with tetrahedral sheets composed of tetrahedral hexagons facing in one direction relative to the common plane of the tetrahedral bases (Fig. 10). Combinations of one octahedral sheet and one tetrahedral sheet (1:1-layers, Fig. 11) compose the structure of dioctahedral kaolinites and trioctahedral serpentines. Three-storeyed 2:1-layers (combinations of one inner octahedral sheet and two outer tetrahedral sheets sharing with the former common apices

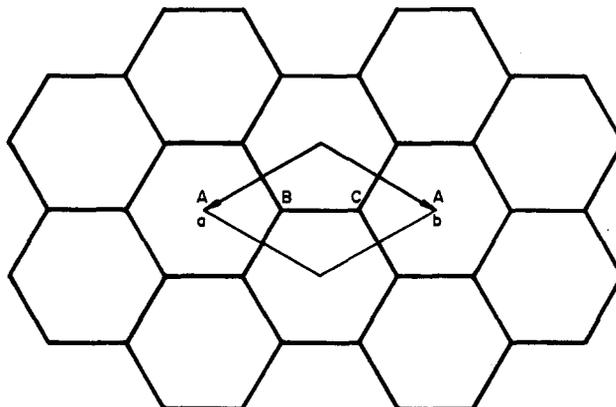


Fig. 9. Scheme of the graphite atomic layer with indication of the unit cell and layer positions A, B, C [32].

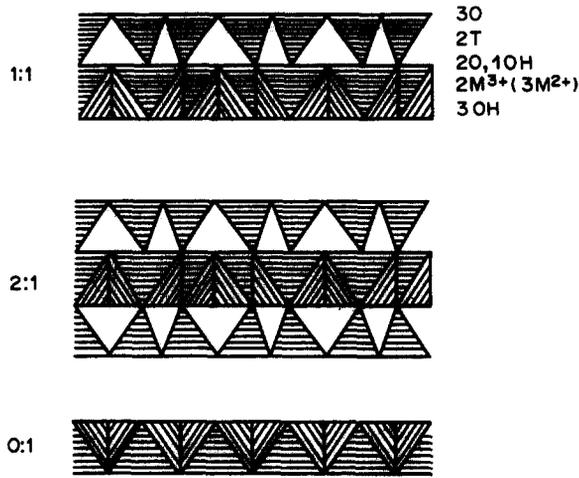


Fig. 10. Scheme of the phyllosilicate layers.

and facing thus in opposite directions) are present in the structure of mica, pyrophyllite and talc, and smectites. In chlorite structures the 2:1-layers regularly alternate with single octahedral sheets (0:1-layers) [3, 5, 9, 33, 34].

It is most simple and clear to describe the structure of all phyllosilicates operating with the tetrahedral and octahedral sheets as structural units. One may also use combinations of sheets (1:1, 2:1 and 2:1 + 0:1) which represent the one kind of layers characteristic for separate groups of phyllosilicates. The mutual disposition of these structural units is much more diverse than in the above mentioned structures. In general these units may have 6 azimuthal orientations and 9 relative displacements subjected, however, to certain limitations and obeying to definite rules [33]. Therefore the phyllosilicates may serve as a model example permitting to get a more complete and general insight into the polytypism phenomenon [9].

Apart from phyllosilicates, there are layer silicates in which the octahedral sheets are intermediate links joining together into three-dimensional frameworks the two-dimensional structural units formed by Si-tetrahedra (sometimes in combination with other polyhedra). Tetrahedra reversed in opposite directions and occupying several levels (2, 3 or 4) are forming a variety of 3-, 4-, 5-, 6-, 8-, 9- or 12-member rings (Figs 12-17) [35]. The structures are formed by two kinds of

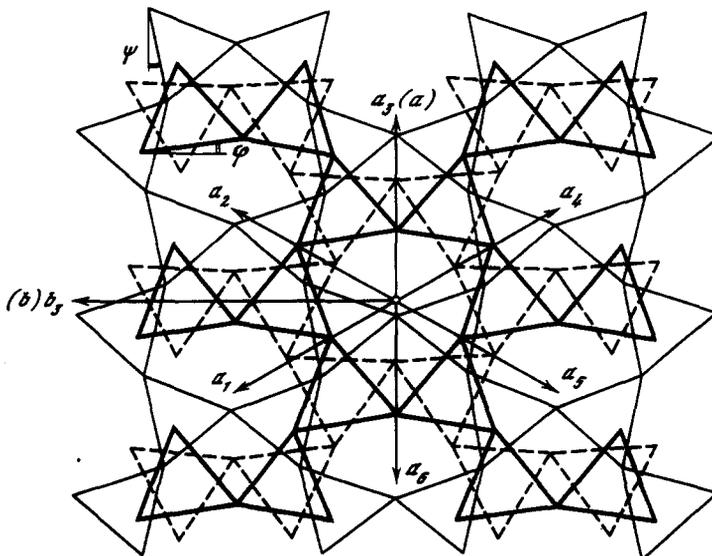


Fig. 11. Scheme of the 1:1 kaolin layer in the normal projection on the plane *ab* [9].

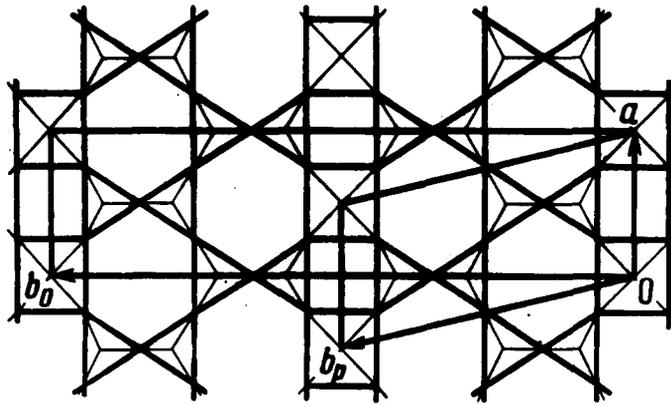


Fig. 12. The astrophyllite T-layer [9].

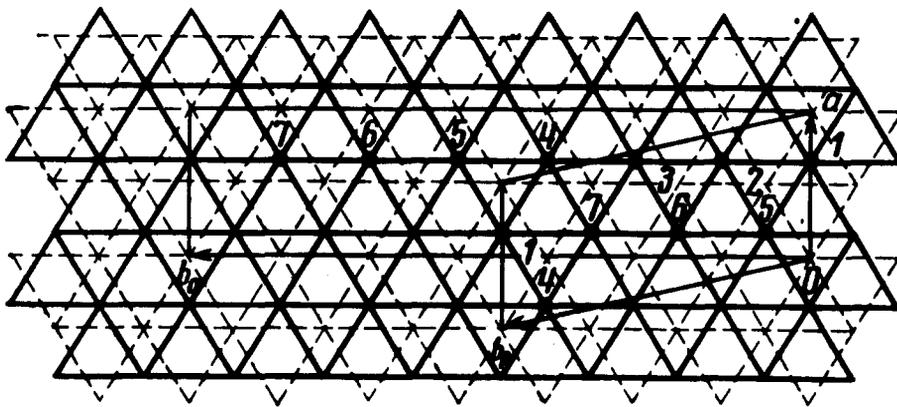


Fig. 13. The astrophyllite O-layer [9].

layers designated as O- and T-, these layers, however, not being isolated. The O- and T-layers may have two opposite azimuthal orientations but the main factor of the polytype diversity is the relation between the cells of the layers. Thus the cells of the T-layers of astrophyllite, zussmanite, pyrosmalite and stilpnomelane contain 7, 13, 16 and 48 cells of the O-layer, respectively (Fig. 18) [9, 36–40]. Displacements of the T-layer relative to the O-layer by translations of the O-layer that are not being translations of the T-layer give undistinguishable pairs of T- and O-layers but result in essentially different pairs of successive T-layers (separated by an intermediate O-layer) [35].

The example of astrophyllite has revealed the possibility of a special case of polytypism in which the basis unit cell of the polytypes does not coincide with the cells of separate layers [36]. In general this is possible when the structure is formed by at least two kinds of layers, one of them having rotation axes 4, 3 or 6 that are absent in the other [36, 41]. If the latter layers are translationally

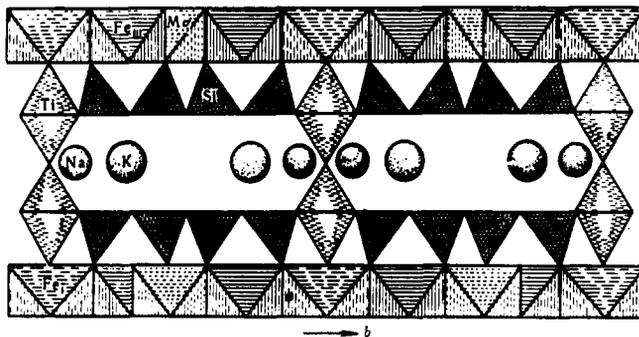


Fig. 14. The combination of astrophyllite T- and O-layers [47].

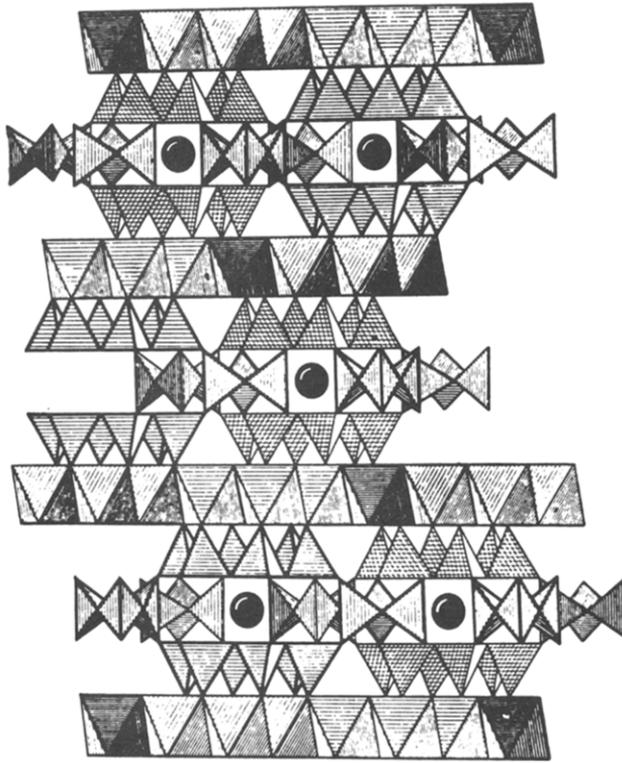


Fig. 15. The combination of zussmanite T- and O-layers [47].

identical their cell is at the same time the basis of the polytype three-dimensional cells. If these layers are rotated at angles permitted by axes 4, 3 or 6 of the adjacent layers the polytypes have a tetragonal or hexagonal supercell basis containing  $n$  cells of the layers without rotation axes. The supercell multiplicity  $n$  is equal to the multiplicity of the layers without the indicated rotation axes relative to the cells of the layers having these axes [36, 41]. In the astrophyllite case  $n = 7$  (Fig. 19). If there are only pseudo-axes 4, 3 or 6 the polytypes may not have a common cell basis at all, so that they are described by several lattices with different cell bases as though enclosed one into another. This feature relates them to hybrid structures.

Sometimes polytype units have such peculiar features that their origins concern some not clearly defined structural positions and hence the use of displacements and orientations for polytype characterization becomes problematic. The symmetry relations become of primary importance.

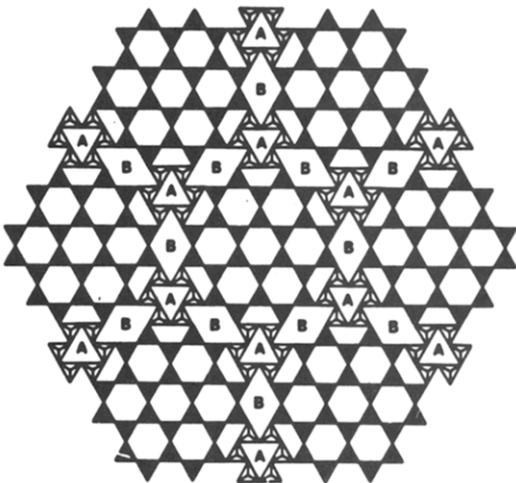


Fig. 16. The T-layer of stilpnomelane [40].

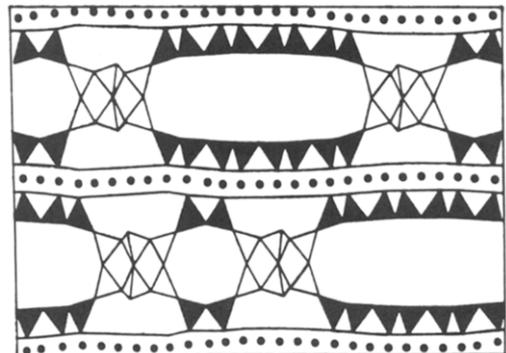


Fig. 17. The combination of stilpnomelane O- and T-layers [40].

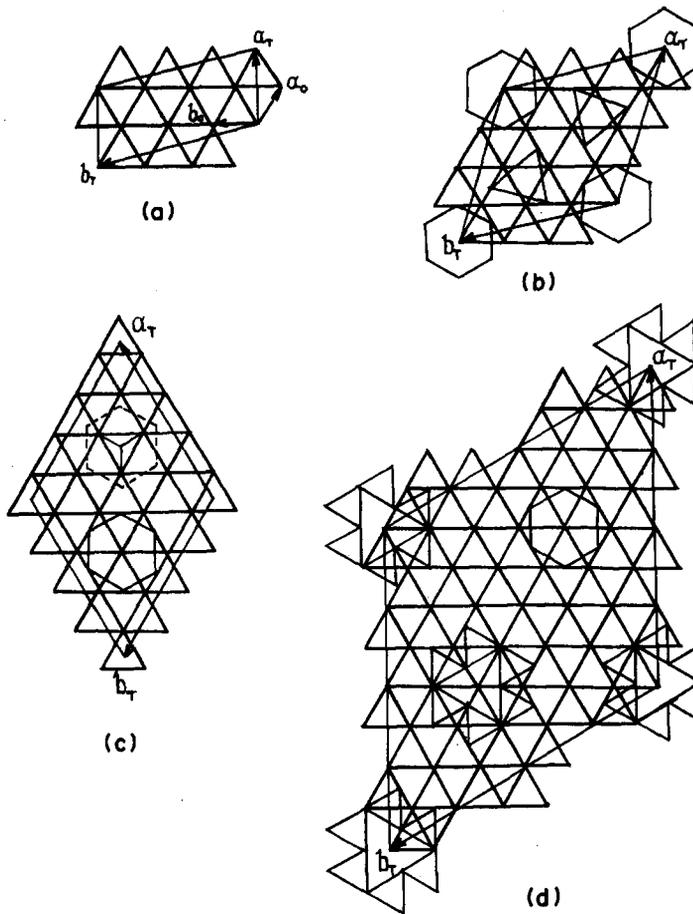


Fig. 18. The relations between the unit cells of the O- and T-layers in astrophyllite (a), zussmanite (b), pyrosmalite (c) and stilpnomelane (d) [34].

That was the case for the rare-earth borates  $RA_3(BO_3)_4$  ( $R = Y, Nd, Gd$ ) composed of two kinds of two-dimensional structural units built of Al-octahedra, R-deformed trigonal prisms and B-triangles (Fig. 20) [42]. The units are joined into a three-dimensional framework through some common edges of Al-octahedra. The polytype diversity results from the multiplicity differences of the symmetries of the units:  $C_{12/m}$  and  $C_{12i}$ . The symmetry  $C_{12/m}$  provides two positions for

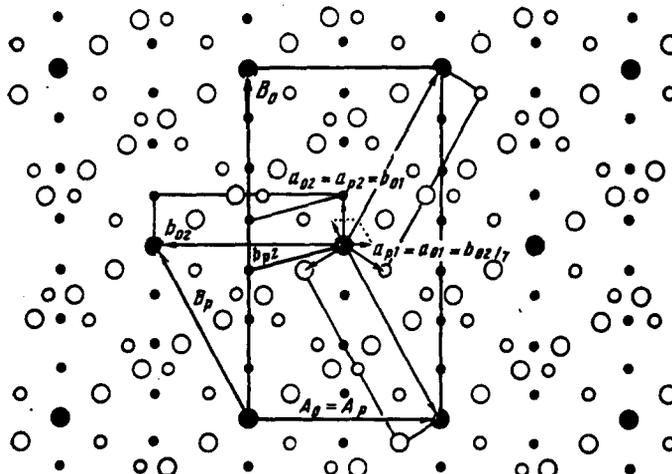


Fig. 19. The layer cells and supercell of the superposition of astrophyllite T-layers having different azimuthal orientations [36].

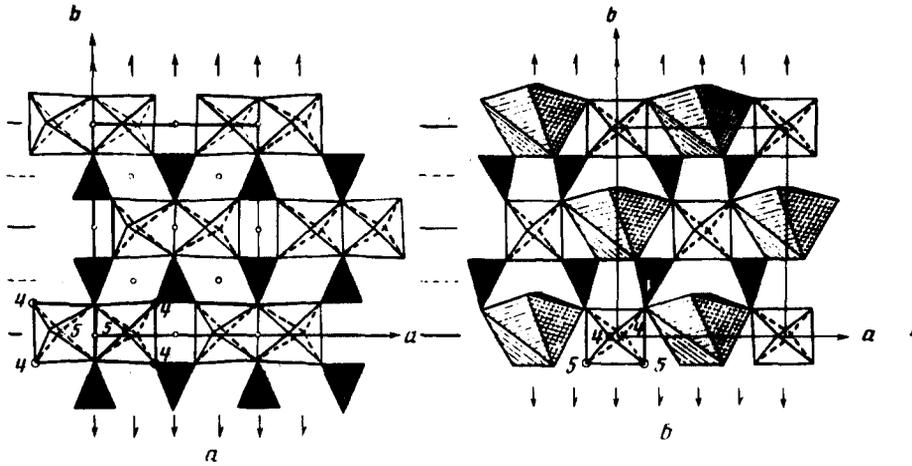


Fig. 20. Two layer kinds forming the polytypes of the rare-earth borates: (a)  $\text{Al}_2\text{B}_2\text{O}_{10}$ , symmetry  $C_{12/m}(1)$ , (b)  $\text{RAlB}_2\text{O}_{10}$ , symmetry  $C_{12}(1)$  [42].

the successive unit equivalent to the position of the preceding one related to its by either the rotation axis 2 or by inversion  $\bar{1}$ .

Apart from layers, structural units of other kinds and their combinations may compose the polytype structures. Thus, two-dimensional tetrahedral sheets are combined with octahedral ribbons in the structures of palygorskite and sepiolite. The sheets are themselves a result of condensation of double and triple chain tetrahedral ribbons alternatively reversed in opposite directions with respect to the plane formed by their bases linked through shared apices (Fig. 21). The ribbons may be of two configurations containing closed and open tetrahedra hexagons [13] (Figs 21 and 22). Hence the sheets may be of two kinds thus representing two polymorphs of

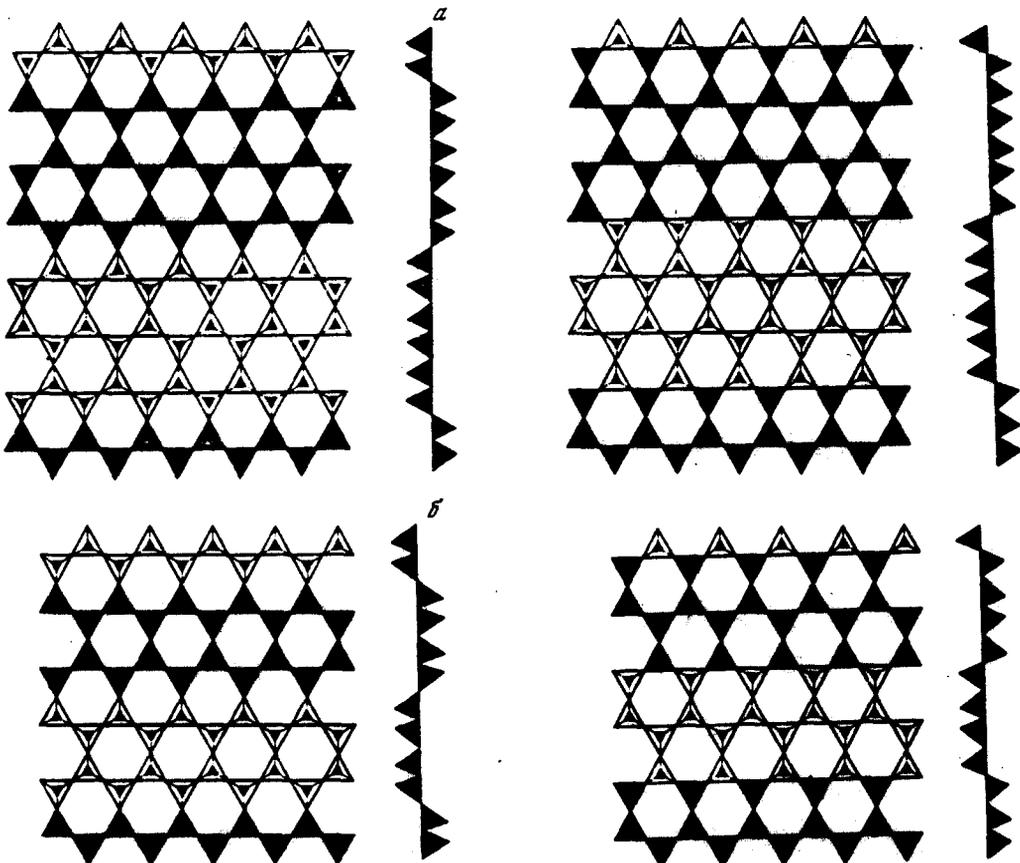


Fig. 21. Two kinds of T-layers: in sepiolite (a) and palygorskite (b) [13].

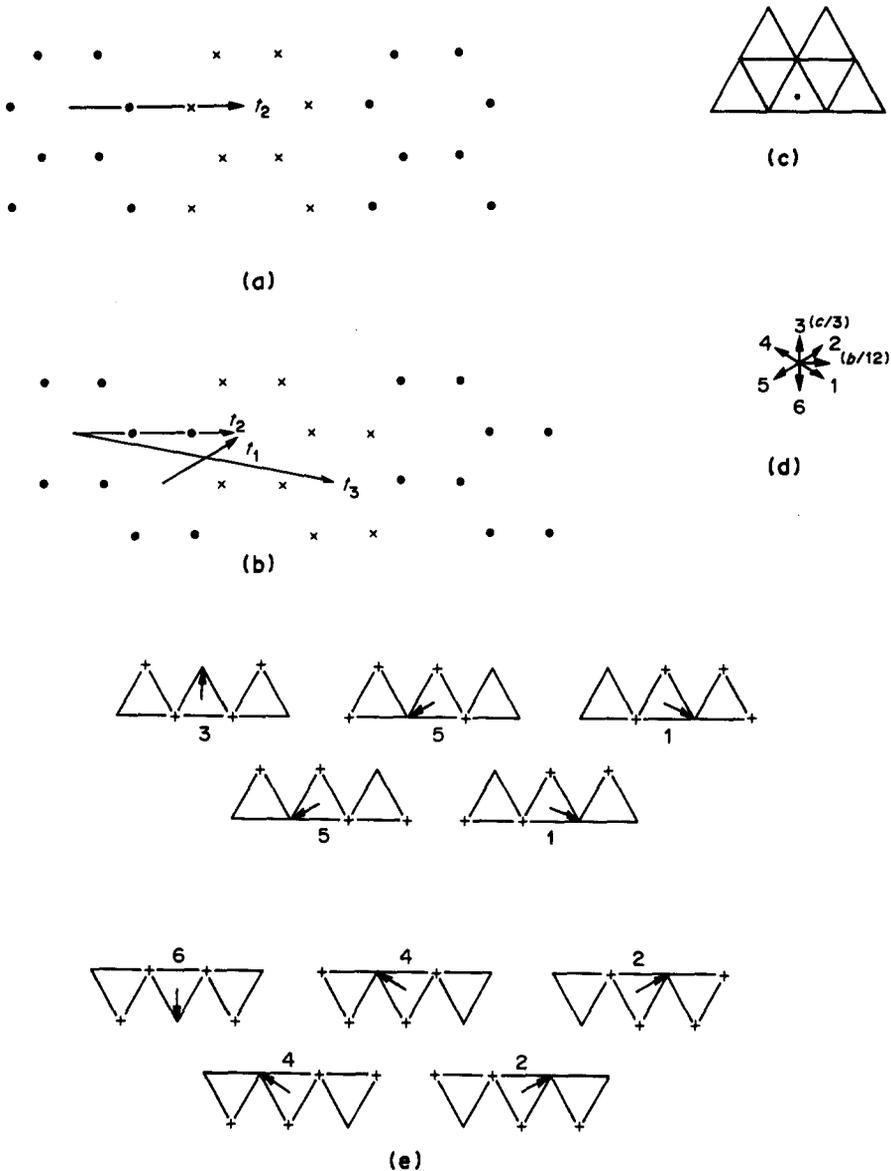


Fig. 22. Structural elements of palygorskite and inter- and intra-rod displacements: (a) and (b) two kinds of the T-layers and intra-layer displacements  $t$  of the oppositely reversed T-ribbons; (c) the repeating part of the O-ribbon and its origin, (d) vectors of the intra-rod displacements; (e) relation between the intra-rod displacements, the kind of T-ribbons and the orientation of the O-ribbon; (in projection on the plane  $bc$ ) [43].

two-dimensional structures (or to be more precise—two-dimensional polytypes built of one-dimensional units). The polytype diversity may be associated with orientation variations of the octahedral ribbons in different storeys of the structure, as well as with relative displacements of tetrahedral sheets joined by the octahedral ribbons (having the same values as in the phyllosilicate structures) and with intrasheet displacements of the ribbons (Fig. 22). Combinations of two T-ribbons with one intermediate O-ribbon may be considered as 2:1-rods. For palygorskites built of equivalent rods two subfamilies are possible differing in the structure of the T-sheets containing respectively 4 and 2 groups, 18 and 8 polytypes [43].

The structure of carlosturanite [44] is a combination of octahedral layers and tetrahedral ribbons. The same was initially supposed for ganophyllite [45]. As in phyllosilicates, the tetrahedral units joined through intermediate octahedra have definite relative displacements. In addition the adjacent tetrahedral ribbons may have the following relative displacements: 0,  $b/2$  accompanied with a change of the ribbon width in carlosturanite (Fig. 23) and 0,  $\pm a/3$  in ganophyllite (Fig. 24) (the

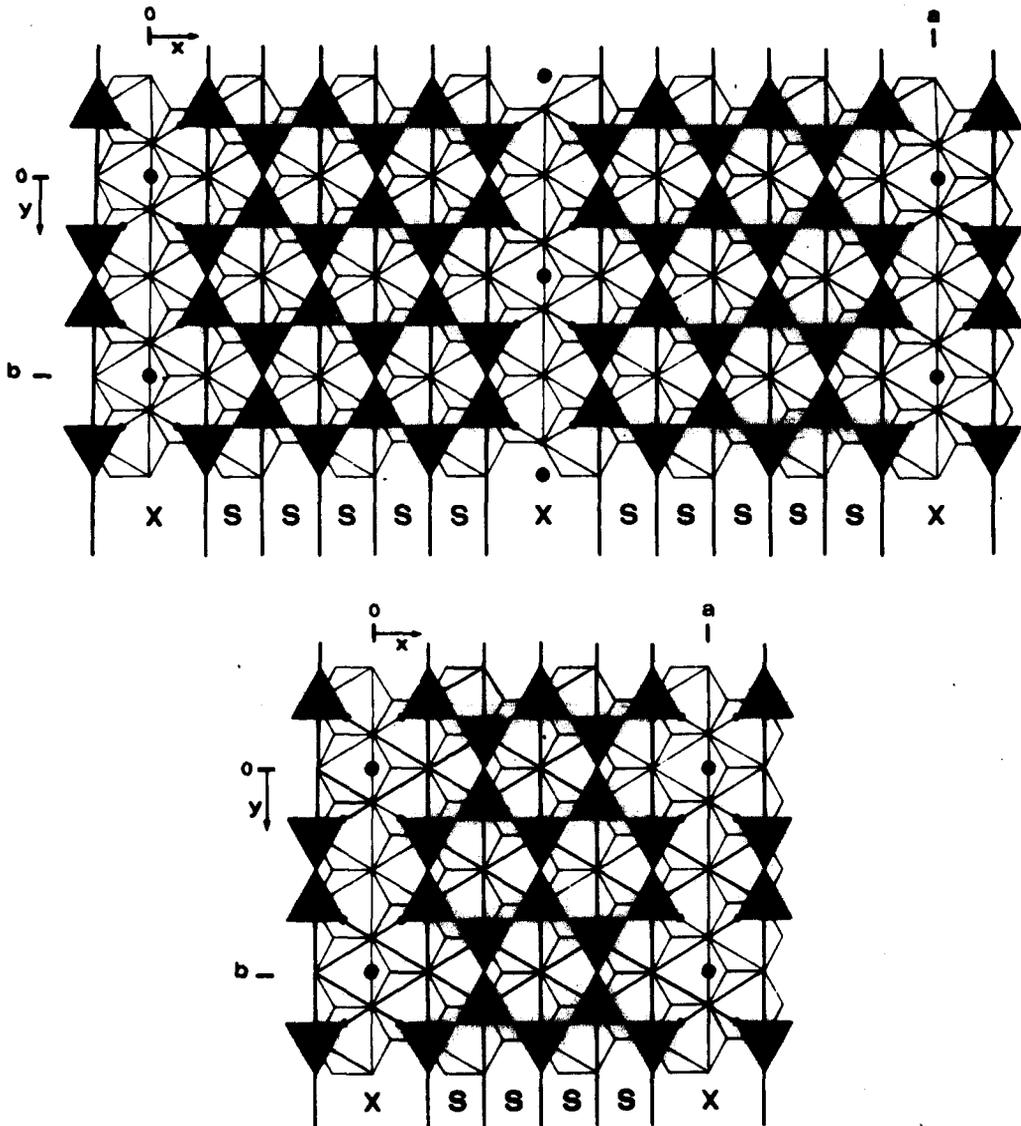


Fig. 23. The combination of O-layers and T-ribbons in carlosturanite structures presented as polysomatic series composed of blocks  $S$  [serpentine  $M_2T_2O_5(OH)_4$ ] and  $X$  [ $M_6T_2O_5(OH)_{14}$ ] [44].

ribbon directions relative to the octahedral sheet of these minerals are mutually perpendicular). This determines a possibility of polytypism for two-dimensional structures built of one-dimensional units combined with the polytypism of the three-dimensional structure. The refinement of the ganophyllite structure has shown that the tetrahedral ribbons lying both in one and the same storey as well as in adjacent storeys bordering the successive octahedral sheets are linked through inverted tetrahedra into four-storeyed tetrahedral layers (Fig. 25) [46]. The above mentioned relative displacements of the ribbons result in variations of layer structure, i.e. in a sort of polymorphism of the four-storeyed layer. At regular distributions of the possible displacements of the T-ribbons the T-layers may have either orthogonal one-chain orthogonal two-chain, or oblique-angled one-chain cells. It is remarkable that different "polymorphs" of the T-layers are met at different storeys of one ganophyllite polytype structure (Fig. 24).

The structures of pyroxenes, amphiboles and other biopyriboles are composed solely of one-dimensional structural units [7, 8]. They consist of 2:1-rods (Fig. 26) the width of which is defined by the number  $n$  of pyroxene rods composing them which, in their turn, are composed of one zig-zag octahedral chain and two tetrahedral chains linked to the opposite octahedral bases sharing common apices. The rods are joined into a three-dimensional structure in such a way that

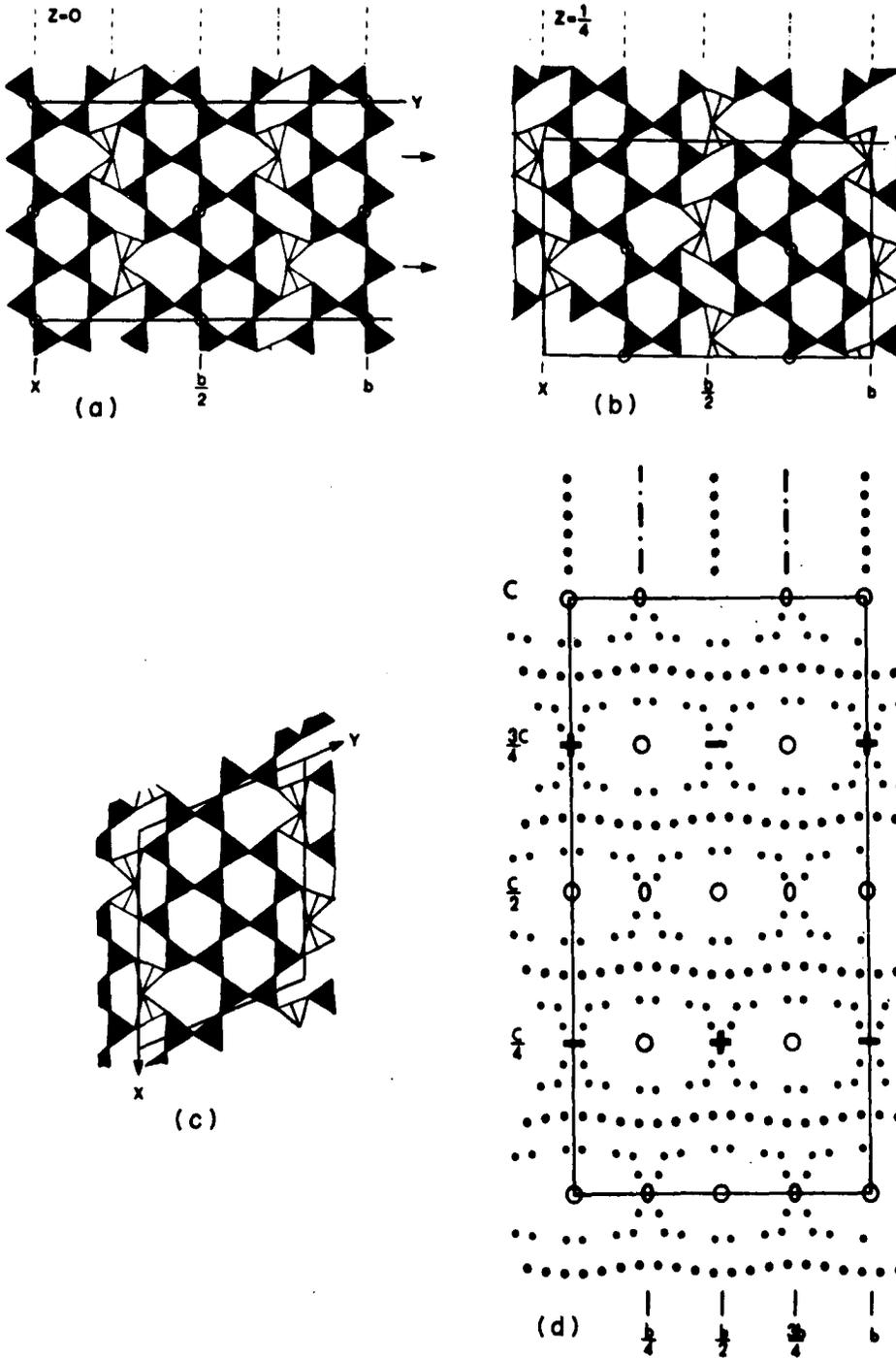


Fig. 24. The structural schemes of ganophyllite: a, b, c— T-layers, d— the structural projection along the a-axis, symbols 0, +, - indicating displacements of the T-ribbons [45].

the peripheral T-apices of one rod are also peripheral O-apices of the adjacent rods and vice versa (Fig. 27). At the one and the same positions of three apices the lying up and down octahedral bases and the octahedral ribbons as a whole may have two opposite orientations (along and counter the *c*-axis, Fig. 28). Sharing common T- and O-apices the adjacent rods may be displaced in opposite directions of the *c*-axis (Fig. 29) with an accompanied rotation of the T-bases at angles  $\psi$  and a simultaneous change of edge length from  $l\sqrt{3}/2$  at  $\psi = 0$  to  $l$  at  $\psi = \pm 30^\circ$  ( $l$  is length of the octahedral edge) [8].

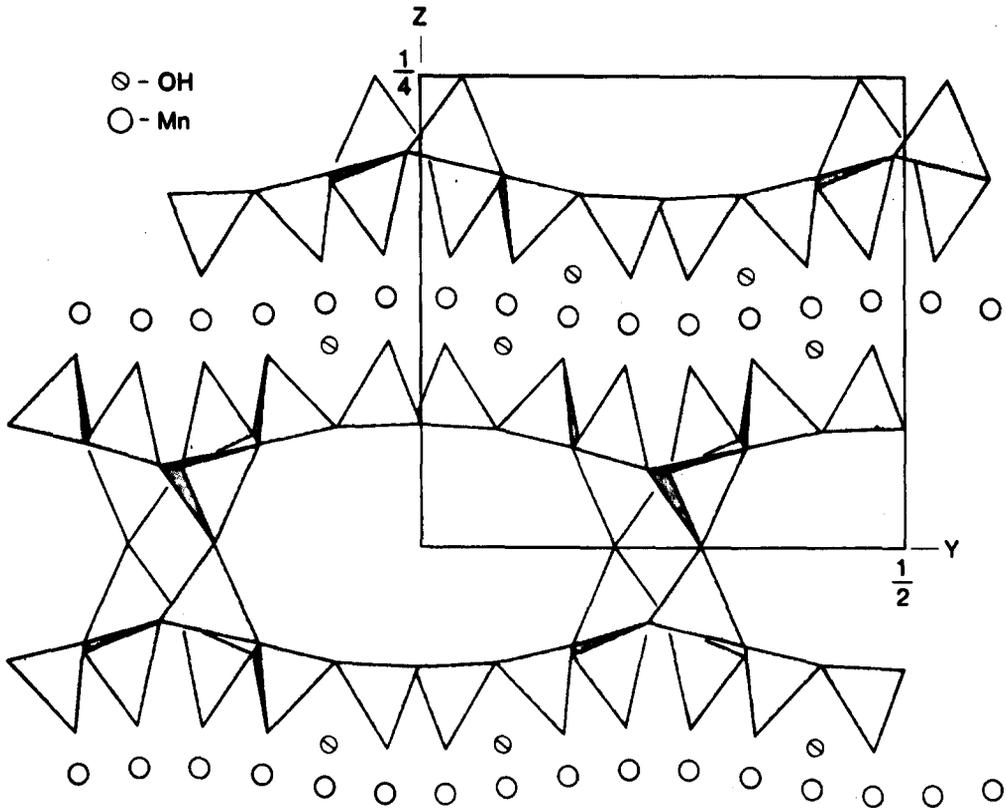


Fig. 25. The four-storeyed T-layer of ganophyllite [45].

The polytypes of pseudowollastonite  $\text{CaSiO}_3$  and isostructural with it  $\text{SrSiO}_3$  and  $\text{SrGeO}_3$  [10, 47] are presenting another peculiar example of a combination of different kind structural units. Layers of Ca- or Sr-octahedra sharing common edges are alternating with storeys of isolated three-member rings (islands) of Si- or Ge-tetrahedra linked to the  $1/3$  of the tetrahedral cavities of the octahedral layer (Fig. 30).

#### 4. POLYTYPE SYMBOLIC NOTATIONS

The possibility of a symbolic description of structures is an outstanding feature of the polytypes representing simple and accessible means to distinguish individual structures and to operate with

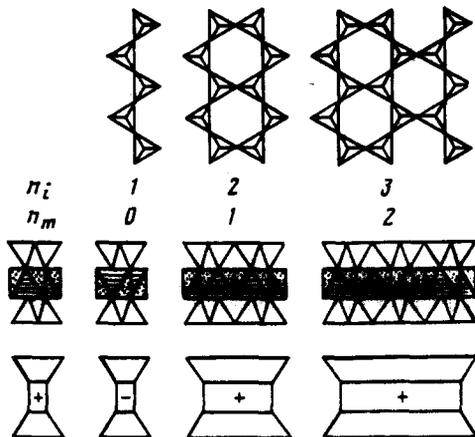


Fig. 26. The 2:1 rods of biopyriboles [8].

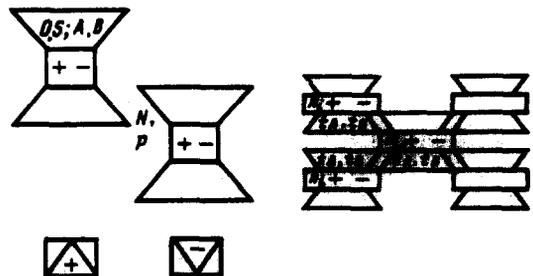


Fig. 27. The linkage of 2:1 rods in biopyribole structures [8].

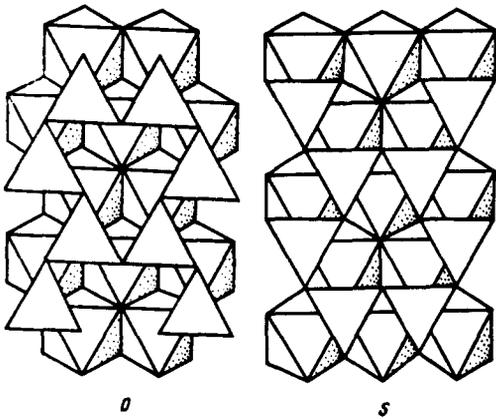


Fig. 28. Two relative orientations, — opposite (O) and same (S), of the T- and O-ribbons in the 2:1 rods of the biopyriboles [8].

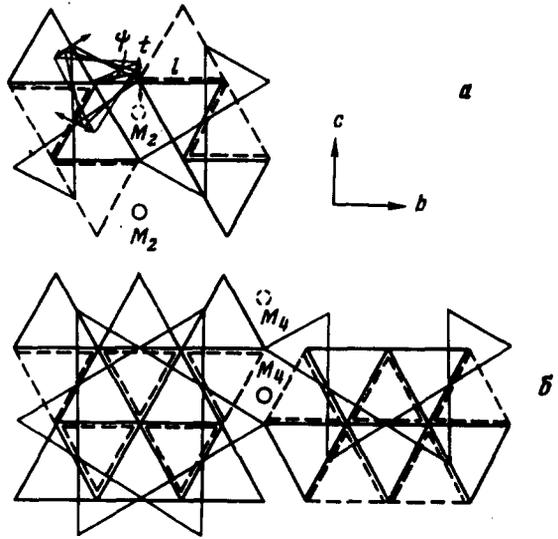


Fig. 29. Scheme of the relative displacements  $t$  of the 2:1 rods resulting from tetrahedra rotations at angles  $\psi$  in pyroxenes (a) and amphiboles (b) [8].

them in practice of investigations. There are symbols of two kinds: short indicative (Ramsdell) symbols designating such general characteristics as the number of structural units per repeat and symmetry, and fully descriptive symbols that specify the exact sequence of structural units, allow structure simulation and calculation of diffractive characteristics.

In the simplest case of closest packing the polytype structures are described by the layer positions  $A, B, C$ , symbols  $h$  and  $c$  of hexagonal and cubic stacking of adjacent layers, or symbols  $+$  and  $-$  of direct and reverse orders in the letter cyclic sequences  $ABC$  or  $ACB$  [1, 5, 19–21]. The closest packings exclude direct sequences of equal positions such as  $AA$  and there are only two alternative variants  $+$  or  $-$  for the position of the next layer over the the preceding one. Under such conditions one may use Zhdanov symbols denoting numbers of successive “pluses” and “minuses” which are especially effective for description of long period polytype [47]. The same principles are

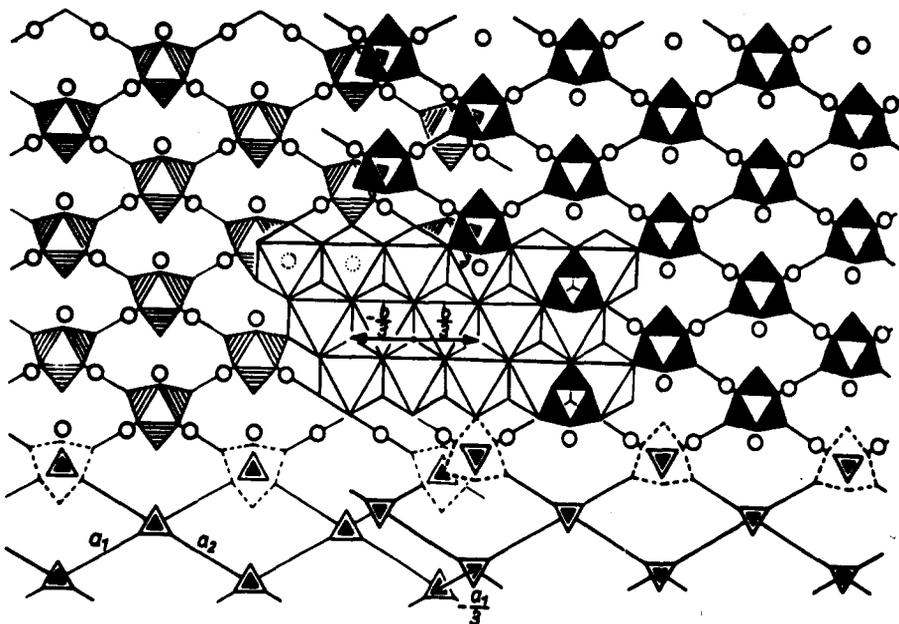


Fig. 30. Combination of O-layers with T-rings [10].

applied to structures composed of different close packed atoms, some of which occupy the main positions  $A, B, C$  while the others are in the octahedral and tetrahedral cavities denoted by similar letters  $a, b, c$  or  $\alpha, \beta, \gamma$ .

By means of symbols it is easier to give an account of the fundamental polytype features. Thus, for instance, the closest packings of identical atoms and the tetrahedral structures have only two polytypes with a homogeneous alternation of layers:  $ccc\dots$  and  $hhh$ , or  $+++ \dots$  and  $+ - + - \dots$ , or using Zhadanov's symbols— $\infty, 0$  and  $1, 1$ . Such are in particular the minerals  $ZnS$ —sphalerite and wurtzite having indicative symbols  $3C$  and  $2H$  respectively. The other polytypes containing in the notations both symbols  $c$  and  $h$  without a single rule for the alternation of the signs  $+$  and  $-$  are inhomogeneous. They are characterized by the degree of hexagonality or cubicity according to the ratios  $N_h/(N_h + N_c)$  "or  $N_c/(N_h + N_c)$ ," where  $N_h$  and  $N_c$  are the relative numbers of the symbols  $h$  and  $c$  in the structure notations. Such polytypes may have very long periods (e.g.  $400H$  and  $1200R$  [1]).

The occupied layers and vacant interlayers of the octahedral structures have respective notations like  $AcB$  and  $AB$ . Violations of the closest packing by positioning adjacent atoms along the normals to the layers to form prismatic polyhedra is written as sequences of equal letters ( $BB, CC, AA$ ). Such violations are absent in the  $Al(OH)_3$ —polytype  $AcBACB$  (bayerite) but are present in  $AcBBcA$  (gibbsite) and  $AcBBaCCbA$  (norstrandite) [9] as well as in the polytypes of  $MoS_2$   $AbABA B$  ( $2H, P6_3/mmc$ ),  $AbABcBCaC$  ( $3R, R3m$ ),  $TaSe_2$ ,— $AcBAcABcABcB$  ( $4H, P6_3/mmc$ ),  $NbSe_2$ ,— $AbABcBAbACbC$  ( $4H, P\bar{6}m2$ ) [1] and  $GaS, GaSe, InSe$ , e.g.  $AbbABaaB$  ( $2H, P6_3/mmc$ ),  $AbbABccB$  ( $2T, P\bar{6}m2$ ),  $AbbABccBCaaC$  ( $3R, R3m$ ) (Fig. 7) [30].

By means of closest packing symbols the simplest polytype of  $ZnIn_2S_4$  having one 2:1-layer per repeat and symmetry  $P3m1$  is described as  $AbBcAaBA\dots$  [31].

If the above mentioned three positions in the common basis of the graphite structures which divide the long basis diagonal into 3 equal parts are designated also as  $A, B, C$  (although they have another meaning) the two known graphite polytypes will have symbols:  $AB\dots$  ( $2H, P6_3/mmc$ ) and  $ABC\dots$  ( $3R, R3m$ ) [1, 39]. The positions of the carbon atoms along the normals to the atomic nets passing through  $A, B, C$  do not satisfy the closest packing rules. In graphite  $2H$  they are disposed in succession along one normal and alternate with hexagon centres along the two others, an atom  $C$  on one normal being at the same level that a hexagon centre on the other normal. In graphite  $3R$  two carbons and one hexagon centre alternate along each normal but the hexagon centres occupy different levels on different normals. Similar features are known for the cation positions in the structures of corundum  $Al_2O_3$  and  $LiJO_3$  [5, 32].

Six orientations and six displacements characteristic for phyllosilicates related to a hexagonal or orthogonal basis-centred layer cell with  $b = a\sqrt{3}$  are defined by vectors related to the vector  $a/3$  by rotations multiple of  $60^\circ$ . In addition, there is also a zero displacement and two displacements  $\pm b/3$  (Fig. 31). No more than six from the total number of nine displacements are possible for any given pair of layers depending on the relative orientations of the layers [33]. Similar displacements and/or orientations are met in other polytype substances and may be used for their description.

The six rotationally related orientations are enumerated anticlockwise from 1 to 6 the number 3 designating the vectors  $a/3$ ; the other 3 vectors are designated as 0, +, - [9]. These ciphers and signs (characters) and their combinations and sequences are used as symbols both for single layers

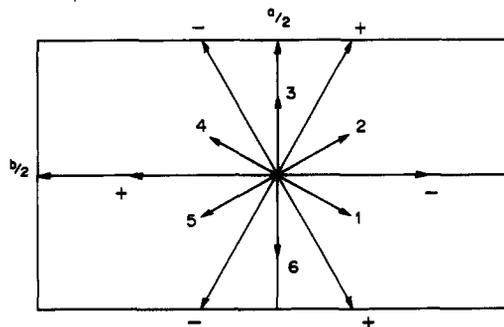


Fig. 31. Vectors characterizing the displacements and orientations of the phyllosilicate layers [9].

and for polytype structures. There are simple rules of their transformation accompanying symmetry operations to which the structures are subjected. Using these rules it is easy to establish the equivalence of structures described in different settings and coordinate systems, to choose unit cells and construct models of polytype structures [49].

There are several different symbolisms for phyllosilicate polytypes depending on the authors view and peculiarities of the particular structures. Some of them are widely accepted because of the significant results obtained by the authors, the chlorite notations of Bailey being a good example [34]. In order to unify the polytype symbolism special Committees of the International Mineralogical Associations and of the International Union of Crystallography have recommended to use for a full description polytype symbols written in a two-line form with orientation characters in the upper and displacement characters in the lower line [10, 50, 51]:  $i_j k_1 m_n \dots$ . The character values depend on the choice of structural units and their origins. In principle instead of orientations one may use orientation differences (rotations), and instead of displacements—origin positions.

If there is an interrelation between the two kinds of characters, only one line may be left in the symbol:  $ikm \dots$  or  $jln \dots$ . Thus in micas the surface of adjacent 2:1-layers are fixed by interlayer cations and the respective tetrahedral sheets have a zero relative displacement. If the 2:1-layers are centrosymmetrical they are designated by pairs of intralayer displacements of the tetrahedral sheets  $ii, kk, mm$  which define layer orientations  $i, k, m$ . By means of orientation characters mica polytypes are described as  $ikm \dots$  [33, 52]. Such notations depend on the choice of the unit cell in correspondence with the polytype symmetry. If instead of absolute orientations, relative rotations (orientation differences  $k - i, m - k$ , etc.) are used, the polytype symbols do not depend of the coordinate system automatically establishing the equivalence–nonequivalence of polytype structures described by different authors or deduced in a fixed coordinate system. It is especially convenient to use such symbols for inhomogeneous polytypes with long periods. Abbreviated notations like  $|0|_m|22|_n$  resemble the Zhdanov symbols but are using 6 numerical values: 0,  $\pm 1, \pm 2, 3$  [53].

If the 2:1-layers are noncentrosymmetric and the interlayer displacements of the tetrahedral sheets are different, the tetrahedral and octahedral sheets are acting as two kinds of structural units building the polytype diversity. The polytypes are described by displacement characters in the form  $ikOmpO \dots$  characters  $i$  and  $k, m$  and  $p$  being of the same parity [9]. 2:1-layers with  $i = k$  and  $i \neq k$  have substantially different structures which cannot be transformed one into another by any symmetry operations and are representing peculiar two-dimensional polymorphs forming two families of mica polytypes. Noncentrosymmetric layers were found in smectites [54] and construct the structure of a unique mica 510  $\dots$ , symmetry  $C2$  [55].

In the most complicated phyllosilicate structures of chlorites centrosymmetric 2:1-layers are designated by intralayer displacements  $ii$  while the alternating with them 0:1-layers are designated by orientations  $k$  with the indication of displacements separating the 0:1-layer and the adjacent T-sheets of the 2:1-layer. For instance, the di-trioctahedral one-packet Li-chlorite (cookeite) with the symmetry  $CT$  is described by the symbol  $\cdot 55 + ^3 + \dots$  [9] (the dots are bordering the symbols of 2:1-layers; with the orientation characters of the 2:1-layer the symbol would be  $\cdot ^5 \cdot + ^3 + \cdot$ ).

In the case of T,O-Frameworks [35] the polytype notations may include both displacements and the numbered positions of the layer origin positions in the projection on the unit cell basis  $ab$ . The number of translationally nonequivalent positions for astrophyllite, zussmanite, pyrosmalite and stilpnomelane is respectively 7, 13, 16 and 48, and they are not so clearly defined as in phyllosilicates. Depending on the  $\pm$  orientations of T,O-layers the subfamilies of astrophyllite, zussmanite and stilpnomelane are designated as OTO and OT $\bar{O}$ , and those of pyrosmalite—as TOT, T $\bar{O}T$ , TOT, and T $\bar{O}T$ . The pairs of adjacent layers of different subfamilies are not equivalent. The classes of the astrophyllite subfamilies have designations  $T_3T_3T_3, T_1T_2T_1$  and  $T_1T_2T_3$  indicating that the successive T-layers have equal orientations, are alternatively rotated by  $\pm 120^\circ$  or have successive rotations by  $120^\circ$ . The polytypes of each subfamily (class) differ by displacements (positions) of the T-layers. The theoretically vast polytype diversity is greatly decreased because of the features differing the real structures from ideal models.

These examples have shown that it is sometimes expedient to include the layer symbols (O-, T-) in the polytype notations. This is a part of a more general approach to the description of layer structures which is in fact, present in the works of Dornberger-Schiff and Grell [56, 57], although

these works had somewhat different objective aim. The authors have proposed to distinguish nonpolar and polar OD layers designating them by letters  $A$  and two mirrorly similar letters  $b$  and  $d$ . The 3 and 4 categories of layer structures are explicitly expressed by the distribution of these letters in the notations of the layer sequences. The structure is completely described after addition of symbols indicating operations relating layers and their combinations. There are  $\tau$ - and  $\rho$ -operations. The  $\tau$ -operations do not invert the top and bottom of the layers and preserve the layer sequence order, the  $\rho$ -operations invert the top and bottom and reverse the sequence order. As it was mentioned the number of symmetrically equivalent variants of the disposition of a layer relative to its neighbour is defined by the group symmetry order for single layers and layer pairs. Subjecting the layers to either symmetry operations which retain the equivalence of layer pairs different strictly periodic structures are constructed. The partial symmetry operations relating equivalent layer pairs become total operations converting the structure as a whole into itself. Such an approach which may be called symmetrical, is especially appropriate when the stacking rules and vicinity conditions for adjacent layers are not clear and cannot be easily explained and described.

Just this was the case of rare-earth borates [42]. In order to distinguish in greater detail the symmetry differences of the layers the latter were designated by letters  $H$  and  $V$  or  $A$ . If  $H$ -layers are unambiguously joined to the layers  $V$  or  $A$  forming combinations  $HVH$  or  $HAH$  the layers  $V(A)$  may be related by the  $\rho$ -operations of the intermediate  $H$ -layer in two ways: either by the symmetry centre  $\bar{1}$  forming combinations  $VHA$ ,  $AHV$ , or by rotation axis 2 forming combinations  $VHV$ ,  $AHA$ . That is the reason for the polytype diversity of these compounds. The letters  $H$  may be left out from the symbols so that solely letters  $V(A)$  would describe the structures. The structures are also described by the sequence of operations (2 and  $\bar{1}$ ). In analogy with the general principles one may use "orientation" characters for the inversion related forms: 1 e.g. for  $V$  and  $\bar{1}$  for  $A$ . Groups of successive equal symbols 1 or  $\bar{1}$  being replaced by the relevant numbers will form symbols analogous to those of Zhdanov. The two homogeneous and one inhomogeneous experimentally identified polytypes have the following symbols (in different variants) and characteristics: (1)  $VVV\dots, 22\dots, 1\dots$ , [10], repeat of one layer  $V$ , symmetry  $R32$  ( $C2$ —in the monoclinic aspect); (2)  $VA\dots, \bar{1}\bar{1}\dots, 1\bar{1}\dots$ , [11], repeat—two layers, symmetry  $C2/c$ ; (3)  $VVA\dots, 2\bar{1}\bar{1}\dots, 11\bar{1}\dots$ , [21], repeat—three layers, symmetry  $C2$ .

The principles of the symbolic description of layer polytype structures may be used for polytypes built of other structural units. For instance, considering the biopyribole structures as composed of 2:1-rods distributed into layers it is possible to form fully descriptive symbols taking in account constant values of  $n$  for one layer, two orientations of the rods  $n$  and  $\bar{n}$ , independence of the interrod displacements  $t_A$  and  $t_B$  caused by the tetrahedra rotations  $\psi_A$  and  $\psi_B$  at the opposite sides of octahedral ribbons [8]. In general it has looks like  $t_A n_i t_B \bar{n}_j \dots$ . In particular, the chesterite structure is described by the symbol  $t_A 2 t_B 3 t_A \bar{2} t_B \bar{3} \dots$  the values of  $t_A, t_B$  corresponding to the angles  $\psi_A \sim 4^\circ$  and  $\psi_B \sim 9.5^\circ$ . The displacement absolute value expressed in units of the period  $c = 1\sqrt{3}$  is  $t = \sqrt{3}\tau\psi/6$  ( $-1/6 \leq t \leq 1/6$ ). If the number  $n$  of the pyroxene chains composing the rods of one layer is not constant the structure notation represents a two-dimensional distribution of symbols.

In the case of pseudowollastonite-like structures the three-membered tetrahedral rings separated by the O-layer are related by the same displacements as those of the phyllosilicates, and the three homogeneous polytypes have symbols  $36\dots, 12\dots, 345612\dots$  and symmetries  $Ccmm, C2/c, P6, 22$ , respectively.

## 5. THE SCIENTIFIC SIGNIFICANCE OF CRYSTAL STRUCTURE POLYTYPISM

The analytical description of polytypes by means of symbolic notations presents an effective possibility of manipulating with such complicated crystallochemical objects as three-dimensional polytype structures. It becomes easy to model them in different coordinate systems and subject to different operations. Starting with structural data even for only one polytype it is possible, according to a definite procedure, to derive all the other polytypes which are theoretically possible in principle within the limits of certain restrictions [9, 16, 33]. Although there are two approaches

(namely those based on crystal chemistry or symmetry) in fact they are interconnected and combined borrowing the missing elements from one another. Both approaches allow theoretical deduction of polytype structures which are either known or unknown, which may be sought in the nature and synthesized experimentally. The valuable feature of polytype structures is that their diffractive properties may be expressed in a general analytical form by presenting the structural amplitudes  $F$  as sums of the layer amplitudes with phase factors depending on the layer origins [9, 33, 58, 59]. These  $F$ -values and their phase relations are in unequivocal correspondence with the space symmetry of the polytype structures and express the phase symmetry of the reciprocal lattices [60].

The calculated numerical values of  $F$  or  $|F|^2$  serve for the experimental identification of polytypes. Both existing and predicted polytypes are identified on the basis of the distinguishing features of geometry and intensities of the diffraction patterns deduced in advance. Such a possibility appears as a most perfect and effective form of the trial and error method in the study of crystal structures. The structural search is realized in this case not blindly but consciously among reliable variants and is applicable even in the cases of structurally imperfect objects giving poor diffraction patterns with a small number of reflexions that are however uniquely characteristic [61].

One of the most important distinguishing features of polytypism as a particular case of polymorphism is thus the possibility of an *a priori* structure-crystallographic comprehension based on the starting characteristics of each polytype family. The existence of general features is a prerequisite for the theory of polytypism possessing a predictions ability. Comparing the polytype structures one may distinguish the more or less probable ones according to some geometrical, energetic or other considerations and get an insight into their stability, formation conditions and physico-chemical limits of their existence. The requirement of constant composition may be moderated or discarded at all for this problem. On the contrary, it is possible to analyse the realization of different stackings of polytype structural units in dependence on compositional variations and/or distribution of isomorphous atoms over the structural positions.

Polytypism has thus several meanings. It is an important phenomenon in the world of crystal substances forming and transforming under definite physico-chemical conditions. It is a tool for comprehension of crystal structures not as isolated particular objects but as a community of interrelated members of a united system. Finally, it is an effective scientific cognition method permitting to operate with such complicated three-dimensional objects as polytype structures, to describe and to identify them. The polytypism data are important for the understanding of processes both natural and resulting from the human activity.

*Acknowledgement*—The author is indebted to the memory of A. V. Shubnikov, the meeting of whom in 1946 turned him to the crystallographic science and, in particular, brought him to write this article.

## REFERENCES

1. A. R. Verma and P. Krishna, *Polymorphism and Polytypism in Crystals*. Wiley, New York (1966).
2. *Polytype Structures* (Ed. P. Krishna). Pergamon Press, Oxford (1983).
3. L. Pauling, The structure of micas and related minerals, and the structure of chlorites. *Proc. natn. Acad. Sci. U.S.A.* **16**, 123–129 and 578–582 (1930).
4. W. L. Bragg and Y. West, The structure of certain silicates. *Proc. R. Soc. (London)* **114A**, 450–453 (1927).
5. N. V. Belov, *The Structure of Ionic Crystals and Metallic Phases (in Russian)*. U.S.S.R. Ac. Sc. Press, Moscow (1947).
6. W. L. Bragg and G. F. Claringbull, *Crystal Structures of Minerals*. Bell, London (1965).
7. J. B. Thompson, Biopyriboles and polysomatic series. *Am. Miner.* **63**, 239–249 (1978).
8. B. B. Zvyagin, Structural diversity and full symbolic description of chain-band silicates (in Russian). *Z. Kristallogr.* **31**, 1124–1129 (1986).
9. B. B. Zvyagin, Z. V. Vrublevskaia, A. P. Zhukhlistov, O. V. Sydorenko, S. V. Soboleva and A. F. Fedotov, *High-voltage Electron Diffraction in the Study of Layer Minerals (in Russian)*. Nauka-Press, Moscow (1979).
10. K. Dornberger-Schiff, S. Đurovič and B. B. Zvyagin, Proposal for general principles for the construction of fully descriptive polytype symbols. *Crystal Res. Technol.* **17**, 1449–1457 (1982).
11. V. A. Drits and B. A. Sakharov, *X-ray Analysis of Mixed-layer Minerals (in Russian)*. Nauka-Press, Moscow (1976).
12. H. T. Evans, Y. Allman and R. Allman, The crystal structure and crystal chemistry of valleriite. *Z. Kristallogr.* **127**, 73–93 (1968).
13. V. A. Drits, *Structure Analysis of Minerals by Means of Selected Area Diffraction and High-resolution Electron Microscopy (in Russian)*. Nauka-Press, Moscow (1981).
14. N. I. Organova, The crystal chemistry of modulated and incommensurate structures in minerals (in Russian). *Zap. vses. Miner. Obshch.* **115**, 288–300 (1986).

15. K. Dornberger-Schiff, *Grundzüge einer Theorie der OD-Strukturen*. Akademische, Berlin (1964).
16. K. Dornberger-Schiff and S. Đurovič, OD-interpretation of kaolinite-type structures. *Clays Clay Miner.* **23**, 219–246 (1975).
17. S. Đurovič and Z. Weiss, OD structures and polytypes. *Bull. mineral.* **109**, 15–29 (1986).
18. *Modulated Structures* (Eds J. M. Cowley et al.), American Institute of Physics, New York (1979).
19. P. P. Ewald und C. Hermann, *Strukturbericht I, 1913–1928*. Akademische, Leipzig (1931).
20. L. Pauling, *The Nature of Chemical Bond*. Cornell Univ. Press, Ithaca (1940).
21. N. V. Belov, The systematics of closest and close packings (in Russian). *Doklady Akad. Nauk S.S.S.R.* **13**, 171–175 (1939).
22. B. I. Nikolin, *Multilayer Structures and Polytypism in Metallic Alloys* (in Russian). Naukova Dumka Press, Kiev (1984).
23. H. Baumhauer, Über die verschiedene Modifikationen des Carborundums und die Erscheinung der Polytypie. *Z. Kristallogr.* **55**, 249–259 (1915).
24. C. Frondel and U. B. Marvin, Lonsdaleite a hexagonal polymorph of diamond. *Nature* **214**, 587–589 (1967).
25. Z. G. Pinsker, *Electron Diffraction*. Butterworths, London (1953).
26. B. C. Lippens, *Structure and Texture of Aluminas*. Delft (1961).
27. H. Saalfeld und O. Jarchow, Die Kristallstruktur von Norstrandites  $\text{Al}(\text{OH})_3$ . *N. Jb. Min. Abh.* **109**, 185–191 (1968).
28. *Hypergene Iron Oxides* (in Russian) (Ed. F. V. Chukhrov). Nauka-Press, Moscow (1975).
29. F. V. Chukhrov, B. B. Zvyagin, L. P. Ermilova, S. V. Soboleva and V. G. Chitrov, The polytypes of molybdenite and their place in ores (in Russian). *Geology Ore Deposits* **10**, 12–26 (1968).
30. J. C. J. M. Terhell, Polytypism in the III–VI layer compounds. **2**, 55–110 (1983).
31. F. G. Donika, S. I. Radautsan, G. A. Kyosse, S. A. Semiletov, T. V. Donika and I. G. Mustya, Crystal structure of two-packet polytype  $\text{ZnIn}_2\text{S}_4$  (II)a and refinement of the structure of three-packet polytype  $\text{ZnIn}_2\text{S}_4$  (III)a (in Russian). *Z. Kristallogr.* **16**, 235–236 (1971).
32. F. V. Chukhrov, B. B. Zvyagin, A. P. Zhukhlistov, N. I. Organova and L. P. Ermilova, Characterization of structural features of natural graphite (in Russian). *Izv. Akad. Nauk S.S.S.R. (ser. geol.)* **7**, 3–15 (1986).
33. B. B. Zvyagin, *Electron Diffraction Analysis of Clay Mineral Structures*. Plenum Press, New York (1967).
34. S. W. Bailey, Structures of layer silicates. In *Crystal Structures of Clay Minerals and their X-ray Identification* (Eds G. W. Brindley and G. Brown), pp. 2–123. Min. Soc., London (1980).
35. B. B. Zvyagin, Polytype features of some silicates with complicated tetrahedral radicals (in Russian). In *Crystallography and Crystal Chemistry, Collected Works In Memory of N. V. Belov*, pp. 274–278. Nauka-Press, Moscow (1986).
36. K. Dornberger-Schiff, V. A. Drits, S. Đurovič and B. B. Zvyagin, Special form of polytypism potentially presented by astrophyllite structures (in Russian). *Kristallografiya* **30**, 504–508 (1985).
37. D. A. Jefferson, Stacking disorder and polytypism in zussmanite. *Am. Miner.* **61**, 470–483 (1976).
38. A. A. Kashaev and V. A. Drits, The polytypism of pyrosmalite minerals (in Russian). *Kristallografiya* **15**, 52–56 (1970).
39. Y. Takeuchi, T. Ozawa and T. Takahata, The pyrosmalite group of minerals. III. Derivation of polytypes. *Can. Mineralogist.* **21**, 19–21 (1983).
40. E. S. Crawford, D. A. Jefferson and J. M. Thomas, Electron-microscope and diffraction studies of polytypism in stilpnomelane. *Acta Crystallogr.* **33A**, 546–553 (1977).
41. B. B. Zvyagin and K. Fichtner, Geometrical conditions for the formation of polytypes with a supercell in the basis plane. *Bull. mineral.* **109**, 45–47 (1986).
42. B. B. Zvyagin and E. L. Belokoneva, Special case of polytypism in the structures of R- borates (in Russian). *Kristallografiya* **29**, 291–297 (1984).
43. B. B. Zvyagin and T. Z. Lygina, Palygorskite polytypes and their symbolic description. *Abstr. 14th IMA Gen. Meeting*, Stanford, Calif. U.S.A., p. 284 (1986).
44. M. Mellini, G. Ferraris and R. Compagnoni, Carlosturanite: HRTEM evidence of a polysomatic series including serpentine. *Am. Miner.* **70**, 773–781 (1985).
45. D. A. Jefferson, The crystal structure of ganophyllite, a complex manganese aluminosilicate. I. Polytypism and structural variation. *Acta Crystallogr.* **A34**, 491–497 (1978).
46. R. A. Eggleton and S. Guggenheim, A re-examination of the structure of ganophyllite. *Min. Mag.* **50**, 307–315 (1986).
47. N. V. Belov, *Essays on the Structural Mineralogy* (in Russian). Nedra Press, Moscow (1976).
48. G. S. Zhdanov, Numerical symbol of spheres close packing and its application in the theory of sphere close packings (in Russian). *Doklady Akad. Nauk S.S.S.R.* **48**, 40–43 (1945).
49. B. B. Zvyagin, The use of symbolic structure notations for deduction of equivalence, symmetry and diffractive properties of the layer silicates. *Coll. Abstr. 2nd Eur. Crystallogr. Meet.*, Keszthely, Hungary, pp. 162–167 (1974).
50. Report of the International Mineralogical Association (IMA)—International Union of Crystallography (IUCr) Joint Committee on Nomenclature (Chairman S. W. Bailey). *Acta Crystallogr.* **A33**, 681–684 (1977).
51. Report of the International Union of Crystallography ad hoc Committee on the Nomenclature of Disordered, Modulated and Polytype Structures (Chairman A. Guinier). *Acta Crystallogr.* **A40**, 399–404 (1984).
52. A. Baronne, Some aspects of polytypism in crystals. *Prog. Crystal Growth Charact.* **1**, 151–211 (1978).
53. M. Ross, H. Takeda and D. R. Wones, Mica polytypes: description and identification. *Science* **151**, 191–193 (1966).
54. S. I. Tsipursky and V. A. Drits, The distribution of octahedral cations in the 2:1 layers of dioctahedral smectites studied by oblique-texture electron diffraction. *Clay Miner.* **19**, 177–193 (1984).
55. B. B. Zvyagin, V. T. Rabortnov, O. V. Sydorenko and D. D. Kotelnikov, The unique mica composed of non-centrosymmetric layers (in Russian). *Izv. Akad. Nauk S.S.S.R. (ser. geol.)* **5**, 121–124 (1985).
56. K. Dornberger-Schiff, Geometrical properties of MDO polytypes and procedures for their derivation. I. General concept and applications to polytype families consisting of OD layers all of the same kind. *Acta Crystallogr.* **A38**, 483–491 (1982).
57. K. Dornberger-Schiff and H. Grell, Geometrical properties of MDO polytypes and procedures for their derivation. II. OD families containing OD layers of  $M > 1$  kinds and their MDO polytypes. *Acta Crystallogr.* **A38**, 491–498 (1982).
58. R. Sadanaga and H. Takeda, Monoclinic diffraction patterns produced by certain triclinic crystals and diffraction enhancement of symmetry. *Acta Crystallogr.* **B24**, 144–149 (1968).
59. K. Dornberger-Schiff and M. Farkas-Jahnke, A direct method for the determination of polytype structures. *Acta Crystallogr.* **A26**, 24–34 (1970).

60. B. K. Vainshtein and B. B. Zvyagin, On the displaying of the crystal lattice symmetry in the reciprocal space (in Russian). *Kristallografiya* **8**, 147–157 (1963).
61. F. V. Chukhrov, B. B. Zvyagin, V. A. Drits, A. I. Gorshkov, L. P. Ermilova, E. A. Goilo and E. S. Rudnitskaya, The ferric analogue of pyrophyllite and related phases. *Proc. VI Int. Clay Conf.*, Oxford, pp. 55–64 (1978).