

OD Interpretation of Mg-Vermiculite. Symbolism and X-ray Identification of its Polytypes

BY Z. WEISS

Coal Research Institute, 716 07 Ostrava-Radvanice, Czechoslovakia

AND S. ĎUROVIČ

Institute of Inorganic Chemistry, Slovak Academy of Sciences, 809 34 Bratislava, Czechoslovakia

(Received 10 May 1979; accepted 20 February 1980)

Abstract

In order to establish identification criteria for polytypes of Mg-vermiculite, all its 44 polytypes with maximum degree of order (MDO polytypes, identical with 'standard', 'simple' or 'regular' polytypes) were systematically derived and their respective diffraction patterns calculated. According to the diffractions $\pm 20l$ ($\pm 13l$), all polytypes of Mg-vermiculite can be categorized into four groups; diffractions $02l$ suffice, then, to give an unambiguous determination of any MDO polytype. The geometrical analysis leading to the derivation of MDO polytypes was based on the idealized model of the vermiculite structure which can be interpreted as an OD structure (four kinds of layers, category IV), which in turn makes it possible to apply consistently the apparatus of the OD theory. A practical example is also included.

1. Introduction

X-ray identification of sheet silicates is greatly obstructed by their polytypic character. Several polytypes (ordered or disordered) are often found in a single specimen, and routine methods using sets of standard diffraction patterns cannot in general be used for their identification. In such cases it is usual to carry out a crystallochemical analysis of a polytypic structure, predict the polytypes which are most likely to occur in natural or synthetic samples, calculate their diffraction patterns and compare the results with reality. Such an approach requires the knowledge of the structure of at least one polytype in sufficient detail and it has already been applied for kaolinites (Zvyagin, 1964; Bailey, 1969) and micas (Smith & Yoder, 1956). In attempting to treat in this way more complex structures, however, one encounters difficulties caused mainly by the low degree of abstraction so that the corresponding considerations become too complicated.

The aim of this paper is to work out identification criteria for polytypes of Mg-vermiculite. A consistent use of the theory of OD structures (Dornberger-Schiff, 1964, 1966, 1971) enabled us to work with a higher degree of abstraction (symmetry approach) and to introduce an analytical notation for individual polytypes, which considerably facilitated the entire work. Because all the vermiculites described hitherto in the literature (Gruner, 1934; Hendricks & Jefferson, 1938; Mathieson & Walker, 1954; Shirozu & Bailey, 1966) are two-layer polytypes, we present the final identification table for such polytypes only.

2. Idealized model of the structure of Mg-vermiculite and its OD interpretation

In order for a polytypic structure to be treated using the tools of the OD theory, it is necessary to show that it is actually an OD structure, *i.e.* that it can be considered as consisting of disjunct, two-dimensionally periodic parts (called OD layers) with the following properties:

- (a) OD layers are either all geometrically equivalent or they are relatively few in kind;
- (b) translation groups of all OD layers are either identical or have a common subgroup;
- (c) pairs of adjacent OD layers belonging to the same species remain geometrically equivalent in all polytypes.

The number of species of layer pairs (a constant number for the substance considered) is such that it is impossible to build a polytypic structure of the given substance with only a selection of these. An additional stipulation for the choice of OD layers is that it should explain all observed (or reasonably supposed to exist) stacking sequences in the substance considered.

In order to simplify further considerations, we shall deal with an idealized model of the structure of Mg-vermiculite (vermiculite, for short, in the follow-

ing).^{*} This structure can be qualified as an OD structure for the following choice of OD layers L_i (there are six OD layers per repeat unit, Fig. 1).

- L_{6n} OD layer (denoted Ic in the following) containing the plane of octahedrally coordinated interlayer Mg ions plus halves of the two adjacent planes of interlayer water molecules; layer symmetry $P(\bar{3})12/m$. Only one out of three octahedral positions per unit mesh is occupied by Mg ions – origins at these sites.
- $L_{6n\pm 1}$ OD layer (denoted H_2O) containing the plane of the remaining halves of interlayer water molecules; symmetry $H(6)mm$, origins at hexads.
- $L_{6n\pm 2}$ OD layer (denoted Tc) containing basal oxygen atoms, tetrahedral cations and halves of the apical oxygen atoms and OH ions at their level – all belonging to the tetrahedral sheet of the 2:1 layer; symmetry $P(6)mm$, origins at hexads.
- $L_{6n\pm 3}$ OD layer (denoted Oc) containing the plane of octahedrally coordinated cations plus halves of the two adjacent planes of apical oxygen atoms and OH ions; symmetry $H(\bar{3})12/m$, origins at $\bar{3}$.

* Although the structure model of Shirozu & Bailey (1966) exhibits deviations from idealized symmetry, the results of this paper remain practically uninfluenced by this fact.

PACKETS	BL	STRUCTURAL SCHEME	OD LAYERS	POLARITY OF OD LAYERS
P ₂	B ₅		L ₁₀	
	B ₄		L ₉	
P ₁	B ₃		L ₈	
	B ₂		L ₇	
P ₀	B ₁		L ₆	
	B ₀		L ₅	
P ₋₁	B ₁		L ₄ Tc	polar
	B ₀		L ₃ Oc	nonpolar
P ₋₁	B ₀		L ₂ Tc	polar
	B ₋₁		L ₁ H_2O	polar
			L ₀ Ic	nonpolar
			L ₋₁ H_2O	polar
			L ₋₂	
			L ₋₃	

Fig. 1. Schematic representation of vermiculite structure showing OD layers, their labelling, OD packets, building layers (BL's) and indicating the polarity of OD layers.

We have, thus, four kinds of OD layers (separated by planar boundary planes formally cutting across some oxygen atoms) and three species of layer pairs: (Ic ; H_2O), (H_2O ; Tc), (Tc ; Oc). Since Ic and Oc are non-polar, the structure belongs to category IV (Dornberger-Schiff, 1964). Evidently, all the above stipulations are fulfilled. The OD groupoid family symbol (Grell & Dornberger-Schiff, 1980) for vermiculites reads:

$$P(\bar{3})12/m \quad H(6)mm \quad P(6)mm \quad H(\bar{3})12/m \quad (1)$$

$$[\frac{1}{3}, 0] \quad [-\frac{1}{3}, -\frac{1}{3}] \quad [\frac{1}{3}, 0]$$

In the first line there are layer groups of all four kinds of OD layers in the sequence (L_{6n} ; ...; L_{6n+3}), in the second line the components of displacement vectors $v_{p-1,p}$ separating in the X_1X_2 projection the origins of L_{p-1} and L_p (see also below). A clay mineralogist will recognize that the triples (L_{6n+2} ; L_{6n+3} ; L_{6n+4}) and (L_{6n-1} ; L_{6n} ; L_{6n+1}) correspond to the 2:1 layer (talc part) and to the interlayer, respectively.

The symmetry of individual OD layers together with their relative position in any single polytype with unambiguously the number of geometrically equivalent positions $Z_{p(p-1)}$ of the OD layer L_p relative to L_{p-1}

$$Z_{p(p-1)} = N_{p-1}/F_{p-1,p}, \quad (2)$$

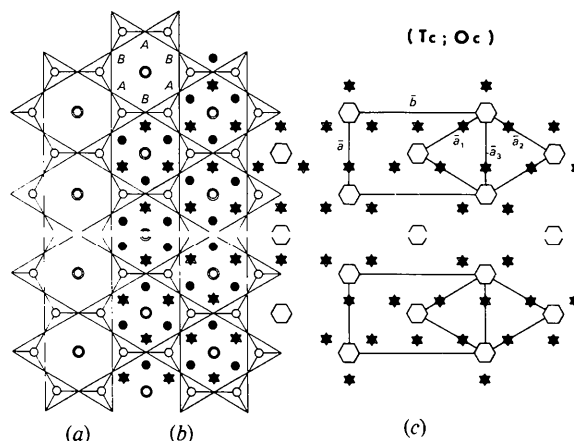


Fig. 2. Illustration of the NFZ relations for the pair of OD layers (Tc ; Oc). (a) Layer L_{6n+2} (Tc) with symmetry $P(6)mm$ and $N = 12$. (b) Possible positions for cations (labelled A and B) and corresponding positions of oxygen atoms closing their octahedral coordination (full circles). Top: first alternative, Oc in an e orientation; bottom: second alternative, Oc in a u orientation, for superposition of Oc onto Tc . (c) Schematic representation of the two OD layers. Hexagons represent L_{6n+2} , i.e. Tc (note that their orientation is the same as the orientation of hexagons drawn through the apical oxygen atoms), two superimposed triangles represent L_{6n+3} , i.e. Oc [note that the orientation of these two triangles correspond to the orientation of the lower (empty) and upper (full) basis of coordination octahedral. The pair (Tc ; Oc) has the symmetry $P(3)1m$; it follows that $F = 6$ and $Z = 2$. Both these equivalent alternatives for the investigated pair are shown (top and bottom part, respectively).

where N is the order of the subgroup of symmetry operations of L_{p-1} that do not turn the layer upside down, and F is the order of the layer group of the pair $(L_{p-1}; L_p)$. Thus, for example, for the pair $(Tc; Oc)$ we have the situation as shown in Fig. 2. The formula (2) is sometimes called the 'NFZ relation'.[†]

The implication of the NFZ relations is of considerable importance: $Z_{p(p-1)}$ depends only on the symmetry of L_{p-1} and on that of the pair $(L_{p-1}; L_p)$. Once these relations have been established (from a crystallochemical analysis of any single polytype), we can 'forget' about the concrete crystallochemical content and proceed further purely on the basis of symmetry. Then it also suffices to characterize the individual OD layers with symbolical figures showing their relevant symmetry and their relative positions, which puts all the considerations on a higher abstraction level and simplifies the entire work.

In a way similar to that used for $(Tc; Oc)$ in Fig. 2, the NFZ relations for the other five pairs of OD layers within one repeat unit were established (Fig. 3). The unusual values N_{p-1} for some layer groups [$H(6)mm$, 36; $H(\bar{3})12/m$, 18] are due to the H cell which is triple primitive if related to the common basic vectors \bar{a}_1, \bar{a}_2 .

A characteristic property of the idealized vermiculite structure is that any displacement vector $\bar{v}_{p,p-1}$ can assume only the values $\pm \bar{a}_i/3$ [$i = 1, 2, \bar{a}_3 = -(\bar{a}_1 + \bar{a}_2)$].

[†] For theoretical details see the original monograph of Dornberger-Schiff (1964); for an application of these procedures on kaolinite-type structures see Dornberger-Schiff & Đurovič (1975).

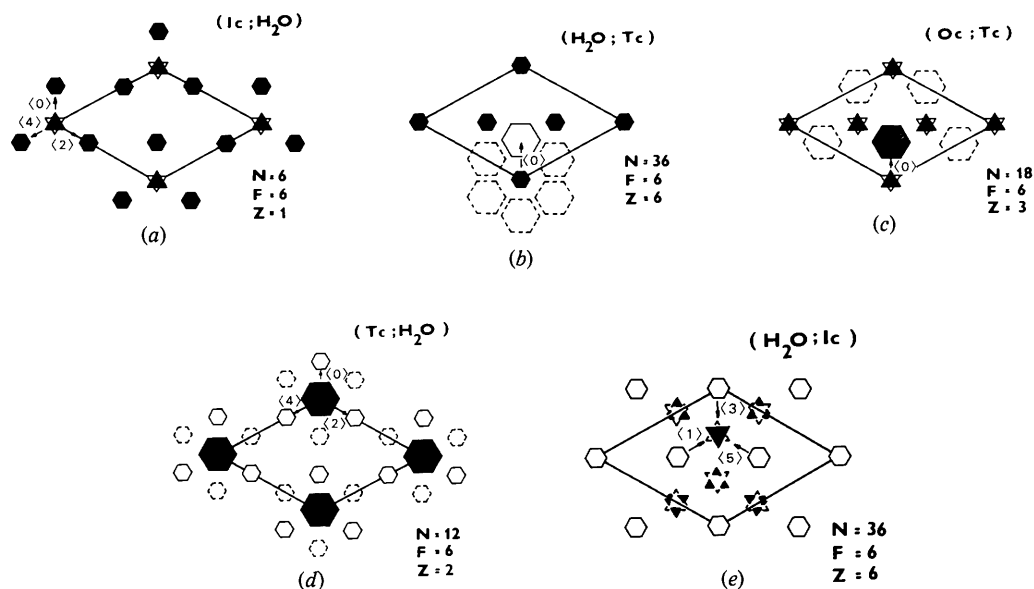


Fig. 3. The NFZ relations for pairs of OD layers within one repeat unit of an idealized vermiculite structure. One of the Z equivalent positions is emphasized, the others drawn in broken lines. Empty and full figures of the same size and shape represent an OD layer of the same kind but differing in the sense of the polarity. The pairs (a) $(L_{6n}; L_{6n+1})$, i.e. $(Ic; H_2O)$; (b) $(L_{6n+1}; L_{6n+2})$, i.e. $(H_2O; Tc)$; (c) $(L_{6n-3}; L_{6n-2})$, i.e. $(Oc; Tc)$; (d) $(L_{6n-2}; L_{6n-1})$, i.e. $(Tc; H_2O)$; (e) $(L_{6n-1}; L_{6n})$, i.e. $(H_2O; Ic)$.

It follows that any displacement vector \bar{v}_{pq} ($q - p \geq 1$) can only be one of the nine vectors shown in Fig. 4; they have been assigned conventional characters 0, 1, 2, 3, 4, 5,* (zero vector), + and -.

Layers $L_{6n\pm 1}$ and $L_{6n\pm 2}$ are hexagonal, layers $L_{6n\pm 3}$ and L_{6n} are trigonal. Their common subgroup is trigonal and then $L_{6n\pm 3}$ as well as L_{6n} can appear in two orientations denoted e and u , respectively, since the projection of any diagonal in an octahedron in an e (u) orientation onto its lower base consists of two equal even-(uneven-)numbered displacement vectors. These two orientations are related by a 180° rotation about the Z axis (cf. Figs. 2b and c). Geometrical properties of individual OD layers and of their pairs derived in this section are a prerequisite for our next consideration.

3. OD packets, polytype symbols and MDO polytypes

At present, the concept of MDO polytypes (Dornberger-Schiff, 1964, 1966) yields the most precise specification of the stacking of OD layers in 'standard', 'simple' or 'regular' polytypes. The original definition of MDO structures can be used with relative ease for a systematic derivation of all MDO polytypes, provided that the substance considered consists of equivalent OD layers. An application of the same approach to OD structures consisting of much more than one kind of OD layer, as in vermiculite, is much more complicated, because one has to keep record of all possible kinds of triples, quadruples, etc. of individual OD layers com-

patible with the NFZ relations and construct polytypes containing only an absolute minimum of these kinds. In such cases we can benefit from the use of the concept of OD packets (Đurovič, 1974) since any MDO polytype must contain only equivalent OD packets, and these bigger structural units are easier to handle than individual OD layers.

Our next job is thus to derive all kinds of vermiculite OD packets and to construct all possible periodic polytypes containing equivalent triples of OD packets. A more detailed theoretical analysis, which is of minor importance for this paper, shows that the vermiculite polytypes obtained in this way are in keeping with the definition of MDO structures.

OD packets and polytype symbols

From the definition of OD packets (Đurovič, 1974), it follows that a vermiculite packet consists of one-half of the 2:1 layer (talc half) and the adjacent half of the interlayer; the even-numbered and odd-numbered packets differ only in the sense of their polarity (Fig. 1). Any talc half ($L_{6n-3}/2$; L_{6n-2}) as well as any interlayer half (L_{6n-1} ; $L_{6n}/2$) has the symmetry $P(3)1m$ and it can appear in only two orientations, e and u , depending solely on the orientation of L_{6n-3} and L_{6n} , respectively (see above). Let the origin of the talc half be identical with that of L_{6n-2} , the origin of the interlayer half, with that of L_{6n} . The displacement vector separating these two origins in the projection onto the $X_1 X_2$ plane is then evidently the vector sum of two elementary displacements $\bar{v}_{6n-2,6n-1}$ and $\bar{v}_{6n-1,6n}$. If the interlayer half is in the e orientation, then the $\bar{v}_{6n-1,6n}$ can be only $\langle 0 \rangle$, $\langle 2 \rangle$ or $\langle 4 \rangle$ which, combined with $\bar{v}_{6n-2,6n-1}$ with an even character yields $\langle 1 \rangle$, $\langle 3 \rangle$, $\langle 5 \rangle$, otherwise $\langle * \rangle$,

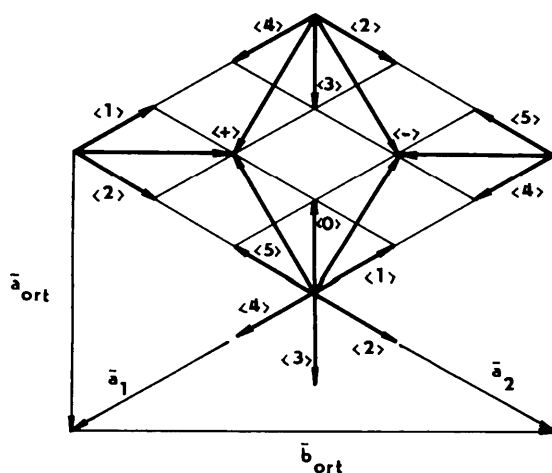


Fig. 4. Displacement vectors $\langle v \rangle$, their relation to the basic vectors \bar{a}_1 , \bar{a}_2 and their conventional characters: $\langle 0 \rangle = (-\frac{1}{3}, -\frac{1}{3})$; $\langle 1 \rangle = (-\frac{1}{3}, 0)$; $\langle 2 \rangle = (0, \frac{1}{3})$; $\langle 3 \rangle = (\frac{1}{3}, \frac{1}{3})$; $\langle 4 \rangle = (\frac{1}{3}, 0)$; $\langle 5 \rangle = (0, -\frac{1}{3})$; $\langle * \rangle = (0, 0)$; $\langle + \rangle = (-\frac{1}{3}, \frac{1}{3})$; $\langle - \rangle = (\frac{1}{3}, -\frac{1}{3})$.

$\langle + \rangle$, $\langle - \rangle$. For a u orientation of the interlayer half, the $\bar{v}_{6n-1,6n}$ can be only $\langle 1 \rangle$, $\langle 3 \rangle$ or $\langle 5 \rangle$ which, combined with $\bar{v}_{6n-2,6n-1}$ with an uneven character yields $\langle 1 \rangle$, $\langle 3 \rangle$, $\langle 5 \rangle$, otherwise again $\langle * \rangle$, $\langle + \rangle$, $\langle - \rangle$ (see Fig. 4). Any OD packet can now be described by *orientational characters* (e or u) of its two constituting parts, separated in the lower line by a character for the displacement of their origins (*displacement character*). Taking into account the above considerations we arrive at the following six non-equivalent (eight non-congruent) kinds of vermiculite OD packets (in order to emphasize the sense of the polarity, a dot (\cdot) is added, marking the position of the inversion centre within the talc part); see also Fig. 5;

even-numbered packets uneven-numbered packets

$e_* e.$	$\cdot e_* e$
$u_* e.$	$\cdot e_* u$
$e_+ e. (e_- e.)$	$\cdot e_+ e (e_- e)$
$u_+ e. (u_- e.)$	$\cdot e_+ u (e_- u)$
$e_3 e.$	$\cdot e_3 e$
$u_0 e.$	$\cdot e_0 u$

Enantiomorphs are in brackets. These six non-equivalent alternatives exhaust all possibilities permitted, since the packets $e_1 e.$ and $e_5 e.$ are geometrically equivalent to $e_3 e.$, and similarly $u_2 e.$ and $u_4 e.$ are geometrically equivalent to $u_0 e.$. The stacking sequence in any vermiculite polytype can now be described by the symbols for individual packets in the form of a zig-zag sequence

$$T_0 \quad T_1 \cdot T_2 \quad T_3 \quad T_4 \cdot T_5 \dots,$$

$$v_{01} \quad v_{12} \quad v_{23} \quad v_{34} \quad v_{45} \dots,$$

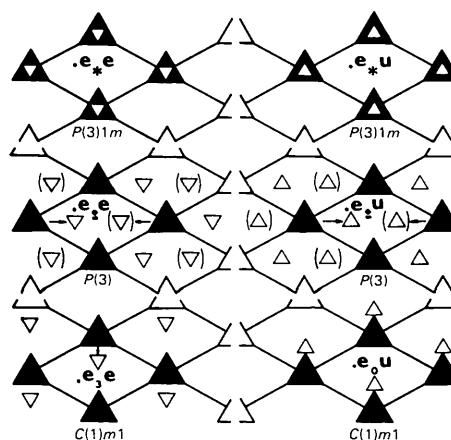


Fig. 5. Schematic representation of the six non-equivalent (eight non-congruent) OD packets in Mg-vermiculite by means of symbolical figures: big black equilateral triangles represent the talc half (origin at the hexad of L_{6n-2}), the small empty equilateral triangles represent half of the interlayer (origin at $\frac{1}{3}$ of L_{6n}).

where T_i are orientational characters (u or e): T_{3k} for the entire interlayer and $T_{3k\pm 1}$ for the 2:1 layer (as consisting of the two talc halves); $v_{j,j+1}$ are the corresponding displacement characters. It is evident that the dot (\cdot) and the orientational character T_{3k} at the packet boundaries need be given only once. Furthermore, it follows from the geometry of the 2:1 layer that the orientational characters T_{3k+1} and T_{3k+2} must be equal (both e or both u since this reflects the orientation of their common OD layer L_{6n+3}) and that the displacement vector separating the origins of the two adjacent talc halves must have a character of the opposite parity to $T_{3k\pm 1}$. Thus, for the symbol of any vermiculite polytype, the following *parity conditions* hold:

$$\begin{array}{ll} T_{3k+1} = T_{3k+2} & \text{both } e \text{ or both } u; \\ v_{3k+1,3k+2} & \text{even number if } T_{3k\pm 1} = u \text{ and } \textit{vice} \\ & \textit{versa}; \\ T_{3k} & e \text{ or } u \text{ (without limitations);} \\ v_{3k-1,3k} & \text{even number, } *, +, -, \text{ if } T_{3k} = u \\ v_{3k,3k+1} & \text{odd number, } *, +, -, \text{ if } T_{3k} = e \end{array}$$

These parity conditions are due to the circumstance that the packets can be stacked together only in such a way that the halves of octahedral OD layers L_{6n+3} and L_{6n} at their boundaries add up to form complete OD layers with cations in octahedral coordination. The parity conditions can thus also serve as a check whether or not the given polytype symbol is *a priori* wrong. The three building units to which the orientational characters T_i refer will be called 'building layers' (BL's) in the following (see also Fig. 1). We believe that a polytype symbol for vermiculites (and chlorites as well) based on BL's chosen in the way described above is more illustrative and less complicated than a symbol based either on individual OD layers (too many components) or on entire OD packets (there are six kinds of these with different symmetries, which would necessitate additional marks *etc.*). Besides, the symbols proposed are in keeping with the requirements on fully descriptive polytype symbolism accepted recently by the Joint Committee of IUCr and IMA (Bailey *et al.*, 1977; Dornberger-Schiff, ĀuroviĀ & Zvyagin, 1980).

MDO polytypes

All MDO polytypes of Mg-vermiculite can now be derived according to the following procedure (some details are explained in the Appendix):

(1) Take an OD packet of the given kind (one out of the six non-equivalent kinds shown in Fig. 5).

(2) Form all triples of equivalent packets of the kind ($P_0; P_1; P_2$) which are permitted by the parity conditions and for each one take note of all coincidence operations ${}_{01}[\rho]^+$. Similarly, take note of all coincidence operations ${}_{01}[\rho]$ and of all ${}_{12}[\rho]$. Keep only those packet triples for which exists at least one ${}_{01}[\rho]^+$ and one ${}_{12}[\rho]^+$.

(3) For any of the packet triples selected in (2), form all products ${}_{01}[\rho]^+ \cdot {}_{12}[\rho]^+ = {}_{02}[\tau]$ obtaining thus coincidence operations transforming P_0 into P_2 .

(4) Take these operations one by one and apply them on the triple ($P_0; P_1; P_2$), adding further packets P_4, P_5, \dots in proper positions and orientations until a packet translationally equivalent with P_0 is obtained. The coincidence operation applied becomes then a total symmetry operation of the polytype in which all packet triples are equivalent. These MDO polytypes were called ${}_{02}\tau$ MDO polytypes and only these have been considered in this paper.

(5) Determine other symmetry operations thus generated (the space group of the polytype), determine basic vectors and reorient the polytype into the conventional setting.

(6) Repeat this procedure for the remaining coincidence operations noted in (3).

(7) Repeat this procedure for all the remaining kinds of OD packets.

(8) Check the list of MDO polytypes thus derived and exclude redundant polytypes.

In this way all the MDO polytypes of Mg-vermiculite were derived. Their total number is 44: 12 one-layer (two-packet), 20 two-layer (four-packet) and 12 three-layer (six-packet) polytypes.*

As an example we can take the packet triplet

$$\begin{array}{cccc} u & e & e & u & e \\ 0 & 1 & 2 & 2 & \end{array} \quad (\text{symmetry of packets } Cm).$$

The procedure described in (2) reveals that this triplet should be kept in our list and that P_2 is related to P_0 by a three-fold screw operation around an axis perpendicular to the packet plane as well as by a glide operation across a plane parallel to X_1 and perpendicular to the packet plane. An application of the first operation leads to the sequence of packets

$$\begin{array}{cccccccc} u & e & e & u & e & e & u & e & e & e & e & e & e \\ 0 & 1 & 2 & 2 & 3 & 4 & 4 & 5 & 0 & 0 & \dots & \left| \begin{array}{cccccccc} u & e & e & u & e & e & u & e & e & e \end{array} \right| \end{array}$$

The second operation leads to the sequence

$$\begin{array}{cccccccc} u & e & e & u & e & e & u & e \\ 0 & 1 & 2 & 2 & 1 & 0 & 0 & \dots \end{array}$$

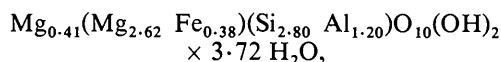
which after reorientation (rotation by 60°) gives the polytype symbol:

$$\left| \begin{array}{cccc} e & u & u & e & u & u \\ 5 & 0 & 1 & 1 & 0 & 5 \end{array} \right|.$$

* Lists of all the ${}_{02}\tau$ MDO polytypes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35142 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

4. Calculated diffraction patterns of vermiculite polytypes and their classification

Theoretical diffraction patterns of all MDO polytypes were calculated using a program *DIPO*, which utilizes the basic features of the program *DIFK* (Weiss & Krajiček, 1979) for modelling diffraction patterns of single crystals as well as of powders but differs from it in the algorithm for structure-factor calculation. Only the atomic positions within one OD packet in standard orientation (standard packet) need be given, the others are generated using the fully descriptive symbol for the particular polytype. In all cases the following crystallochemical formula (per one formula unit) was used,



neglecting the temperature and absorption factors. The atomic coordinates in the standard packet were derived from the idealized model. The 'height' of one packet and the lattice parameters a and b were set equal to 7.17, 5.28 and 9.24 Å, respectively, the monoclinic angle 97° follows from the unit-cell vectors used.

An analysis of the results thus obtained reveals that the MDO polytypes considered can be classified, according to the superposition-structure diffractions of type $\pm 20l$ and/or $\pm 13l$, into four groups which corresponds to the classification of MDO polytypes according to the packet type:

group A	packet types	.e u; .e u;
		* ±
group B	packet types	.e e; .e e;
		* ±
group C	packet type	.e u;
		0
group D	packet type	.e e
		3

From the properties of superposition structures it follows that this classification includes also periodic non-MDO as well as disordered polytypes containing the same types of OD packets. The intensities of diffractions $\pm 20l$, $\pm 13l$ are relatively high and their distribution in any of the *A*, *B*, *C*, *D* groups differs from those in other groups so drastically that it is possible to select one of them by a simple visual comparison. A visual representation of the calculated $|F|^2$ values for the superposition-structure diffractions $\pm 20l$ showing the classification into the groups *A*, *B*, *C*, *D* for four-packet polytypes (see *Introduction*) is given in Fig. 6. In Fig. 7, visual representations of $|F|^2$ for diffractions $02l$ are given. It turned out that it was possible to subdivide the polytypes mentioned above into five groups, denoted I, II, III, IV, V.

This brings us to an important conclusion that any four-packet MDO polytype of Mg-vermiculite can be

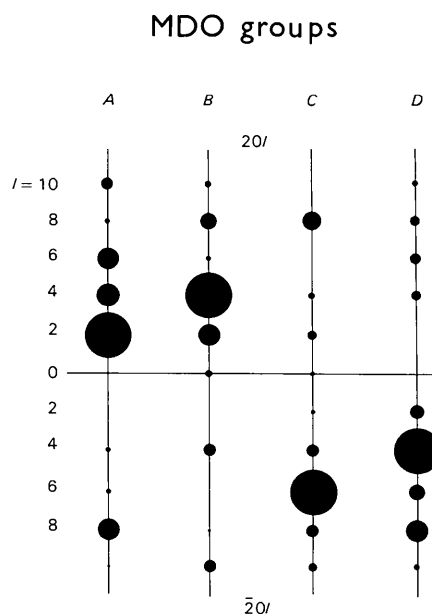


Fig. 6. Visual representation of calculated $|F|^2$ values (strongest $|F|^2$ value of each group is drawn as the biggest circle) for characteristic diffractions $\pm 20l$ in four-packet (two-layer) MDO polytypes of Mg-vermiculite and their classification into the groups *A*, *B*, *C* and *D*.

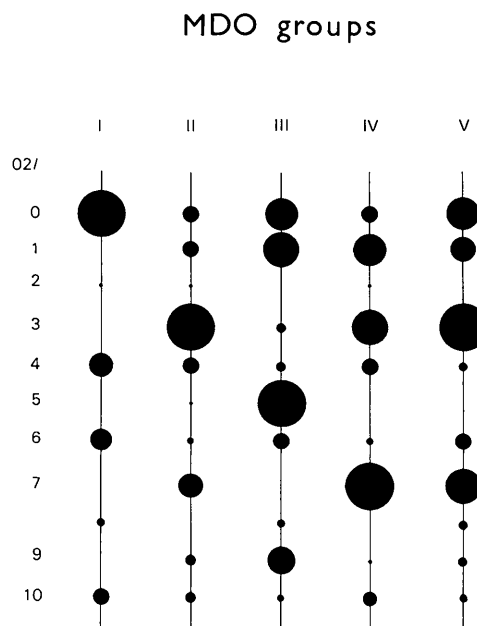


Fig. 7. Visual representation of calculated $|F|^2$ values (strongest $|F|^2$ value of each group is drawn as the biggest circle) for characteristic diffractions $02l$ in four-packet (two-layer) MDO polytypes of Mg-vermiculite and their classification into the groups I, II, III, IV and V.

unambiguously determined if the diffractions $\pm 20l$ ($\pm 13l$) and $02l$ are considered. Thus, for example, the MDO groups *A*/III and *C*/I correspond to the polytypes

$$\left| \begin{array}{cccc} u & e & e & u & e & e \\ - & 3 & + & + & 3 & - \end{array} \right| \quad \text{and} \quad \left| \begin{array}{cccc} e & u & u & e & u & u \\ 1 & 0 & 1 & 5 & 0 & 5 \end{array} \right| \quad \text{etc.}$$

These relations are summarized in Table 1. The calculated diffraction patterns correspond, of course, to structures with idealized symmetry and to the chemical composition as given above, but we believe that even so, at least a partial identification (classification into the groups *A* to *D* – their typical representatives, see Fig. 8) should be possible, if based on a powder diffraction pattern. An unambiguous determination of individual polytypes within these four groups merely on the basis of their powder diffraction patterns does not seem to be possible due to potential disorder, which does not affect diffractions $\pm 20l$ and $\pm 13l$, but which does affect diffractions $02l$. An identification on the basis of a single-crystal diffraction pattern is possible only if the diffractions $02l$ – which as a rule appear on diffuse streaks – are clearly developed.

The classification of polytypes into the groups mentioned above follows from the fact that any of the groups *A*, *B*, *C*, *D* has its characteristic superposition structure and thus also diffractions of the type hkl with $k = 3n$ from which, however, those with $h = 3n$ (e.g. $00l$, $06l$, $33l$) are useless as they are common for all groups. Similarly, the classification of the four-packet MDO polytypes into groups I to V is due to the fact that polytypes within any of these groups have a common projection onto the *YZ* plane and thus also the diffractions of the type $0kl$; among the latter those with $k = 6n$ (e.g. $00l$, $06l$) are useless. The diffractions $\pm 20l$ ($\pm 13l$) and $02l$, respectively, are the most prominent ones and thus most suitable for identification purposes. These facts can be deduced from a geometrical analysis of the structures considered and/or

their respective polytypes symbols. A detailed treatment of this question exceeds the scope of this paper.

Complete lists of calculated diffraction patterns for all MDO polytypes and for various experimental arrangements (powder diffractometer, Guinier camera, single-crystal patterns) are available from the first author on request.

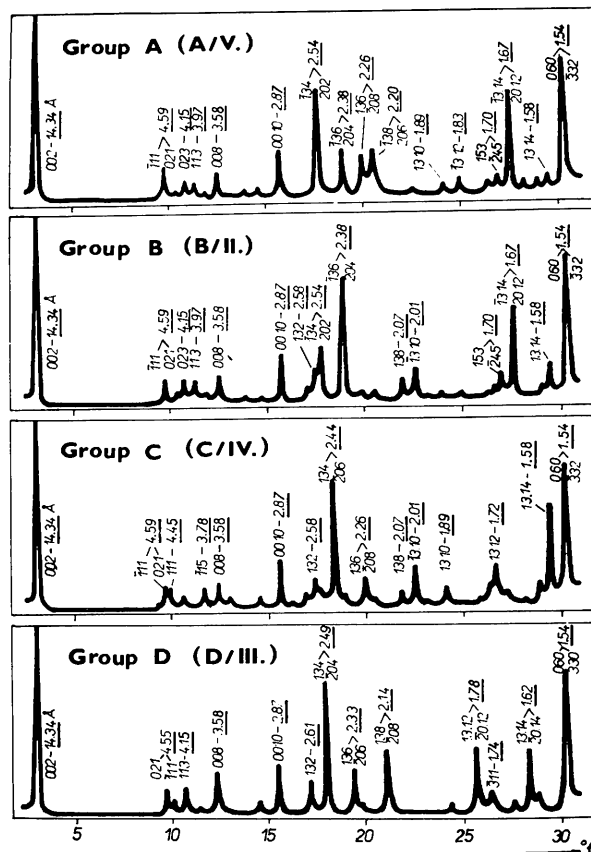


Fig. 8. Typical representatives of calculated powder diffraction patterns (experimental arrangement: Guinier camera) of MDO polytypes belonging to the groups *A*, *B*, *C*, *D*.

Table 1. Identification table for four-packet (two-layer) MDO polytypes of Mg-vermiculite

$\pm 20l$ \ / $02l$	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
I	$\left \begin{array}{cccc} u & e & e & u & e & e \\ - & 3 & - & + & 3 & + \end{array} \right $	$\left \begin{array}{cccc} e & e & e & e & e & e \\ - & 3 & - & + & 3 & + \end{array} \right $	$\left \begin{array}{cccc} e & u & u & e & u & u \\ 1 & 0 & 1 & 5 & 0 & 5 \end{array} \right $	$\left \begin{array}{cccc} e & e & e & e & e & e \\ 1 & 3 & 1 & 5 & 3 & 5 \end{array} \right $
II	$\left \begin{array}{cccc} u & e & e & u & e & e \\ * & 5 & * & * & 1 & * \end{array} \right $	$\left \begin{array}{cccc} e & e & e & e & e & e \\ * & 5 & * & * & 1 & * \end{array} \right $	$\left \begin{array}{cccc} e & u & u & e & u & u \\ 3 & 2 & 3 & 3 & 4 & 3 \end{array} \right $	$\left \begin{array}{cccc} e & e & e & e & e & e \\ 3 & 5 & 3 & 3 & 1 & 3 \end{array} \right $
III	$\left \begin{array}{cccc} u & e & e & u & e & e \\ - & 3 & + & + & 3 & - \end{array} \right $	$\left \begin{array}{cccc} e & e & e & e & e & e \\ - & 3 & + & + & 3 & - \end{array} \right $	$\left \begin{array}{cccc} e & u & u & e & u & u \\ 5 & 0 & 1 & 1 & 0 & 5 \end{array} \right $	$\left \begin{array}{cccc} e & e & e & e & e & e \\ 5 & 3 & 1 & 1 & 3 & 5 \end{array} \right $
IV	$\left \begin{array}{cccc} u & e & e & u & e & e \\ - & 5 & - & + & 1 & + \end{array} \right $	$\left \begin{array}{cccc} e & e & e & e & e & e \\ - & 5 & - & + & 1 & + \end{array} \right $	$\left \begin{array}{cccc} e & u & u & e & u & u \\ 5 & 2 & 5 & 1 & 4 & 1 \end{array} \right $	$\left \begin{array}{cccc} e & e & e & e & e & e \\ 1 & 5 & 1 & 5 & 1 & 5 \end{array} \right $
V	$\left \begin{array}{cccc} u & e & e & u & e & e \\ - & 1 & - & + & 5 & + \end{array} \right $	$\left \begin{array}{cccc} e & e & e & e & e & e \\ - & 1 & - & + & 5 & + \end{array} \right $	$\left \begin{array}{cccc} e & u & u & e & u & u \\ 1 & 2 & 1 & 5 & 4 & 5 \end{array} \right $	$\left \begin{array}{cccc} e & e & e & e & e & e \\ 5 & 5 & 5 & 1 & 1 & 1 \end{array} \right $

5. Example

For the determination of a four-packet MDO polytype, the single-crystal data published by Shirozu & Bailey (1966) for a Mg-vermiculite were used. The calculated $|F|^2$ values for diffractions $\pm 20l$ and $02l$ together with the corresponding observed values published by Shirozu & Bailey (1966) are presented in schematic form in Fig. 9. It is immediately apparent that they single out unambiguously the MDO group B/III and thus the MDO polytype with symbol

$$\left| \begin{array}{cccccc} e & e.e & e & e.e & e & e \\ + & 3 & - & - & 3 & + \end{array} \right|$$

whose stacking sequence is shown schematically in Fig.

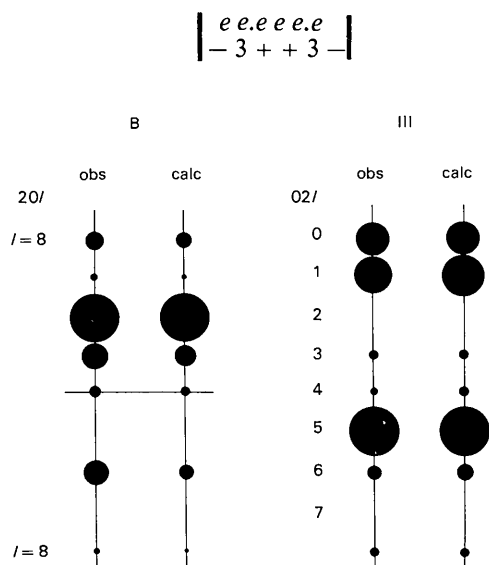


Fig. 9. Comparison of the characteristic $|F(\pm 20l)|^2$ and $|F(02l)|^2$ values calculated from the data of Shirozu & Bailey (1966) (obs) with the theoretical values calculated with the program *DIPO* for MDO group B/III (calc). Intensities are normalized to the strongest diffraction.

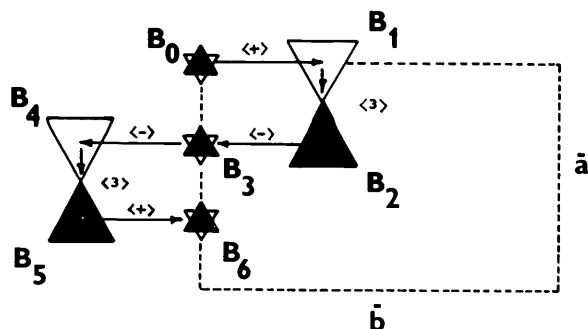


Fig. 10. Schematic representation of the stacking of BL's in the

MDO polytype B/III with symbol $\left| \begin{array}{cccccc} e & e.e & e & e.e & e & e \\ + & 3 & - & - & 3 & + \end{array} \right|$.

10. This is a further indication that deviations from the idealized symmetry in the specimens investigated play no significant role.

APPENDIX

Coincidence operations relevant for structures consisting of layer-like building units, can be categorized into two groups (Dornberger-Schiff, 1964):

ρ operations turning a layer upside down, *i.e.* reversing the sense of its polarity;

τ operations preserving the sense of polarity of a layer.

Pre-subscripts can be used if it is necessary to indicate the layers related by a coincidence operation, thus ${}_{12}[\rho]$ means that L_1 is converted into L_2 by a ρ operation. A superscript +, *e.g.* ${}_{01}[\rho]^+$ indicates that this operation has a reverse continuation, *i.e.* that this operation converts L_0 into L_1 and simultaneously L_1 into L_0 . Such an operation with reverse continuation is a layer-group operation for the layer pair $(L_0; L_1)$.

References

- BAILEY, S. W. (1969). *Clays Clay Miner.* **17**, 335–371.
- BAILEY, S. W., FRANK-KAMENETSKII, V. A., GOLDSZTAUB, S., KATO, A., PABST, A., SCHULZ, H., TAYLOR, H. F. W., FLEISCHER, M. & WILSON, A. J. C. (1977). *Acta Cryst.* **A33**, 681–684.
- DORNBERGER-SCHIFF, K. (1964). *Grundzüge einer Theorie der OD Strukturen aus Schichten, Abh. Dtsch. Akad. Wiss. Berlin Kl. Chem.* **3**.
- DORNBERGER-SCHIFF, K. (1966). *Lehrgang über OD Strukturen*. Berlin: Akademie Verlag.
- DORNBERGER-SCHIFF, K. (1971). *Krist. Tech.* **7**, 1035–1056.
- DORNBERGER-SCHIFF, K. & ĐUROVIČ, S. (1975). *Clays Clay Miner.* **23**, 219–246.
- DORNBERGER-SCHIFF, K., ĐUROVIČ, S. & ZVYAGIN, B. B. (1980). *Acta Cryst.* Submitted.
- ĐUROVIČ, S. (1974). *Acta Cryst.* **B30**, 76–78.
- GRELL, H. & DORNBERGER-SCHIFF, K. (1980). *Acta Cryst.* Submitted.
- GRUNER, J. W. (1934). *Am. Mineral.* **19**, 557–575.
- HENDRICKS, S. B. & JEFFERSON, M. E. (1938). *Am. Mineral.* **23**, 851–862.
- MATHIESON, A. McL. & WALKER, G. F. (1954). *Am. Mineral.* **39**, 231–255.
- SHIROZU, H. & BAILEY, S. W. (1966). *Am. Mineral.* **51**, 1124–1142.
- SMITH, J. V. & YODER, H. S. (1956). *Mineral. Mag.* **31**, 209–235.
- WEISS, Z. & KRAJÍČEK, J. (1979). *Modelling of X-ray Diffraction Patterns* (in Czech). Publication No. 4, Research Coal Inst., Ostrava, Czechoslovakia.
- ZVYAGIN, B. B. (1964). *Elektronografyia i Strukturnaya Kristallografyia Glinistykh Mineralov*. Moscow: Nauka.