

THE PYROSMALITE GROUP OF MINERALS III. DERIVATION OF POLYTYPES

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ABSTRACT

Possible ordered polytypic structures of the pyrosmalite group have been systematically studied in terms of the two kinds of unit layers, **P** and **M**, that characterize the pyrosmalite and mcGillite structures, respectively. The polytypes can be obtained (and classified) as follows: (i) by stacking **P** layers in parallel orientation, (ii) by stacking **M** layers in parallel orientation, (iii) by rotating either **P** or **M** unit-layers about the layer normal $n \times 60^\circ$ ($n = 1, 3, 5$), and (iv) by combining stacking sequences defined in (i), (ii) and (iii).

Keywords: pyrosmalite, mcGillite, polytypism.

SOMMAIRE

L'énumération des structures polytypiques ordonnées possibles du groupe de la pyrosmalite se fait en fonction des deux espèces de couches unitaires, **P** et **M**, qui caractérisent respectivement les types de structure de la pyrosmalite et de la mcGillite. On obtient quatre classes de polytypes par empilement: (1) de couches **P** de même orientation, (2) de couches **M** de même orientation, (3) de couches **P** ou **M** tournées l'une par rapport à l'autre de $n \times 60^\circ$ ($n = 1, 3, 5$) autour de leur commune normale, et (4) de séquences combinées de deux ou trois précédentes.

(Traduit par la Rédaction)

Mots-clés: pyrosmalite, mcGillite, polytypisme.

INTRODUCTION

The structures of the members of the pyrosmalite group, as summarized by Kato & Takéuchi (1983), are built up of brucite-type octahedral sheets alternating with $\text{Si}_{12}\text{O}_{30}$ tetrahedral sheets; a set of one octahedral sheet and a successive tetrahedral sheet may be regarded as a unit layer. The tetrahedral sheet is composed of six-membered rings of silicate tetrahedra in two different orientations. The apices of the tetrahedra in one orientation point away from the octahedral sheet, and those in the other orientation point toward the octahedral sheet to bond the octahedral cations. The tetrahedral ring in the former orientation has been called a *U* ring and that in the other

orientation a *D* ring (Ozawa *et al.* 1983). The *U* and *D* rings are linked together to form twelve-membered rings and four-membered rings to complete the continuity of the sheet.

In a series of papers on this mineral group (Kato & Takéuchi 1983, Ozawa *et al.* 1983), we have pointed out that there are, in fact, two alternate ways to locate the tetrahedral sheet on the octahedral sheet to form a unit-layer, thus yielding two types of unit-layers. One type, which we have denoted **P**, characterizes the pyrosmalite structure type (a 13.422, c 7.165 Å, $P\bar{3}m1$), and the other, which we denoted **M**, characterizes the mcGillite structure type (a 23.312, b 13.456, c 7.42 Å, β 105.17° $C2/m$). The unit cell of each structure type contains one unit-layer whose chemical composition may be expressed by the simplified formula $(\text{Mn,Fe})_{16}(\text{Si}_{12}\text{O}_{30})(\text{OH,Cl})_{20}$.

One of the striking features of the members of this mineral group is that their structures characteristically show stacking disorder; a variety of stacking sequences tend to occur in the same mineral species in addition to the major stacking sequence that defines it. This situation is such that it frequently gives rise to confusion in identifying mineral species of the group. It is, hence, of importance to study the polytypism underlying the variety of structures in this mineral group. The present paper presents the results of our study of the systematic derivation of polytypes.

DERIVATION OF POLYTYPES

Possible polytypic structures in the pyrosmalite group of minerals may be studied systematically in terms of the two kinds of unit-layers, **P** and **M**, defined by Ozawa *et al.* (1983). Suppose that a unit-layer of either kind is given. Then, in order to stack a second layer on top of the given first layer to form a structure, the following condition must be satisfied: the apical oxygen atoms of the *U* rings of the first layer should become the constituent members of the bottom oxygen sheet of the second layer (for further details, refer to Ozawa *et al.* 1983). The poly-

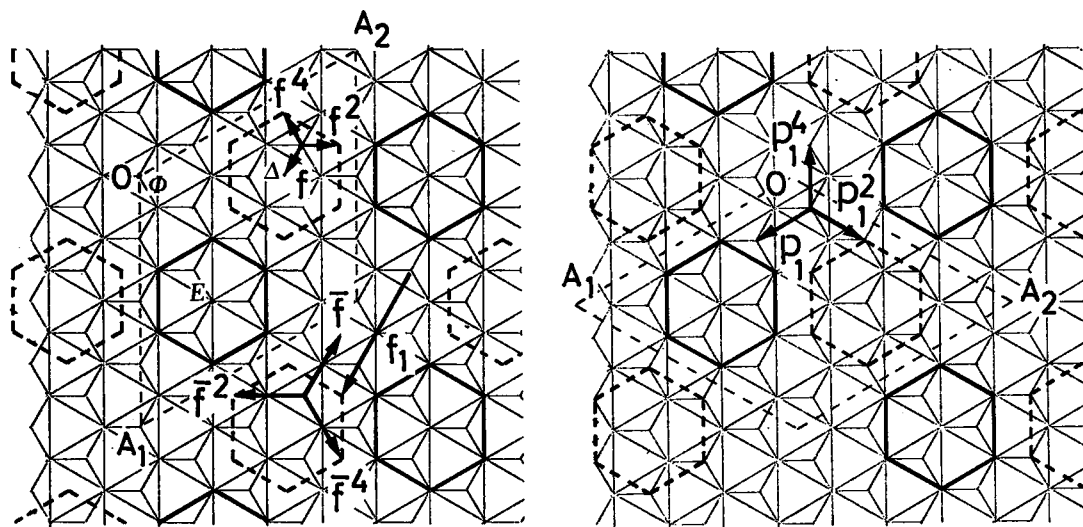


FIG. 1. Basic stacking vectors for the **M** unit-layer (i) and the **P** unit-layer (ii). The silicate sheets are schematically illustrated by the relative arrangement of the hexagonal rings of Si atoms; solid lines represent the *D* rings and dashed lines the *U* rings. Thin dashed lines show the unit cell. In (i) the rotation axes are indicated at Δ , *E* and Φ . For *D* ("down") and *U* ("up"), refer to Ozawa *et al.* (1983).

types can then be classified into the following four categories.

[i] *Polytypic series based on the M unit layer*

Among various possible triplets of basic vectors that satisfy the stacking condition, the simplest may be denoted by \mathbf{f} , \mathbf{f}^2 , \mathbf{f}^4 (Fig. 1); \mathbf{f}^2 is equivalent to \mathbf{f} by a rotation of 120° , and \mathbf{f}^4 by a rotation of -120° (or 240°) about an axis normal to the layer. The horizontal components of these vectors have the same absolute value $f = |f_h| = |(\mathbf{A}_1 + \mathbf{A}_2)| / 12$ (Table 1). Based on these stacking vectors, simple polytypes of the pyrosmalite group can be developed by analogy with those of the micas (Smith & Yoder 1956). One of the simplest cases is observed in mcGillite (Ozawa *et al.* 1983), which has the stacking sequence



Two other examples of simple stacking sequences and their symbols are:



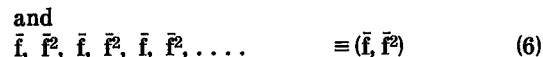
Sequence (2) gives a two-layer monoclinic structure and (3) gives a three-layer trigonal structure (Table 1). A marked feature of these polytypes is the rhombohedral substructure defined by the Mn atoms.

Let $\bar{\mathbf{f}}$ be a stacking vector similar to \mathbf{f} but with a horizontal component \bar{f}_h in the direction opposite to that of f_h . Then \bar{f}_h must have a value of $(\mathbf{A}_1 + \mathbf{A}_2)/6$ to satisfy the stacking condition (Fig. 1). We can likewise define $\bar{\mathbf{f}}^2$ and $\bar{\mathbf{f}}^4$. Based on $\bar{\mathbf{f}}$, we can derive polytypes that are similar to the above cases. For example,



gives a one-layer monoclinic structure ($\bar{\mathbf{f}}$), different from (\mathbf{f}).

Vectors like \mathbf{f} and $\bar{\mathbf{f}}$ may occur in the same stacking sequence. For example,



both give two-layer monoclinic structures, (6) having the same β angle as mcGillite (Table 1). It follows that sequence (6), like sequence (1) (mcGillite), simulates a twelve-year orthogonal structure with $c \approx 85 \text{ \AA}$ (Donnay *et al.* 1980). If \mathbf{f} and $\bar{\mathbf{f}}^2$ alternate, as in the sequence



the resulting polytype is triclinic (Table 1).

In general, stacking vectors may have horizontal components of either $f_h + n(\mathbf{A}_1 + \mathbf{A}_2)/4$

TABLE 1. STACKING SEQUENCES AND CELL DIMENSIONS OF CERTAIN POLYTYPIC VARIANTS IN THE PYROSMALITE GROUP OF MINERALS

No. in the text	Stacking symbol	Cell dimensions			Space group	
		a	b	c		
<i>Category i</i>						
1	(f)	A'	A	7.41 Å	$\beta=105.1^\circ$	C2/m
2	$(f, f^2) \equiv (f, f^4)$	A'	A	14.43	$\beta=97.7$	C2/c
3	(f, f^2, f^4)	A	-	21.45		P3 ₁
4	(\bar{f})	A'	A	8.13	$\beta=118.4$	C2/m
5	(f, \bar{f})	A'	A	14.43	$\beta=97.7$	C2/m
6	(\bar{f}, \bar{f}^2)	A'	A	14.81	$\beta=105.1$	C2/c
7	(f, \bar{f}^2)	A'	A	15.37	$\alpha=100.9, \beta=111.5$ $\gamma=90$	C1
8	$(3f_1)$	A	-	21.45		R3m
<i>Category ii</i>						
9	(p_0)	A	-	7.15		P3m1
10	(p_1)	A	A'	7.89	$\alpha=\gamma=90, \beta=115.1$	C1
11, 12	$(p_1, p_1^2) \equiv (p_1, p_1^4)$	A	A'	14.69	$\alpha=\gamma=90, \beta=103.2$	C1
13	(p_1, p_1^2, p_1^4)	A	-	21.45		P3 ₁
14	(p_1, \bar{p}_1)	A'	A	14.30	$\beta=90$	C2/c
<i>Category iii</i>						
15	$(s^1, \bar{s}^1, \bar{s}^1, \bar{s}^1)$	A	A'	14.30		Cmc2 ₁
16	(e^1, \bar{e}^1)	A	-	14.30		P6 ₃ mc
17	$(p_1, e, \bar{p}_1, \bar{e})$	A	A'	14.30	$\gamma=90$	C2 ₁
18	$(s^1, \phi^1, \bar{s}^1, \bar{\phi}^1)$	A	A'	14.30		Cmc2 ₁

The cell dimensions were calculated based on those of the two dimensional orthohexagonal cell, $A = 13.40 \text{ \AA}$, $A' = \sqrt{3} A = 23.21 \text{ \AA}$, of the unit layers and interlayer spacing of 7.15 Å.

or $\bar{f}_h + n(A_1 + \bar{A}_2)/4$ ($n = 0, 1, 2, 3$) (Fig. 1). The stacking vectors discussed above are special cases for $n = 0$. Consider the case of $n = 1$ in the first of the two general types of stacking vector and denote it f_1 ; its horizontal component is $(A_1 + \bar{A}_2)/12 + (A_1 + \bar{A}_2)/4 = (A_1 + \bar{A}_2)/3$. Thus,

$$f_1, f_1, f_1, f_1, f_1, f_1, \dots \equiv (3f_1) \quad (8)$$

gives a rhombohedral structure, which corresponds to the "3R structure" proposed by Frondel & Bauer (1953) for friedelite. Note that any unit-layer in a polytype in this category is congruent with another by a rotation of 120° followed by a translation of one of the above stacking vectors. Not all stacking vectors are shown above, but all can be generated from the ones given.

[ii] Polytypic series based on the P unit-layer

Stacking vectors p possible for the polytypes in this category may have the horizontal components $p_h = mA/4$ ($m = 0, 1, 2, 3$) (Fig. 1).

The simplest possible case of the polytypes can therefore be derived based on the stacking vector p_0 for which $m = 0$. The sequence of such a stacking vector

$$P_0, P_0, P_0, P_0, P_0, P_0, \dots \equiv (p_0) \quad (9)$$

yields a trigonal one-layer structure corresponding to that of pyrosmalite. Because of the trigonal symmetry of the unit-layer P, stacking vectors may occur (like f) in three directions. We denote these three vectors p_1, p_1^2, p_1^4 (only the case $m = 1$ will be considered). Examples of simple stacking sequences and their notations are:

$$P_1, P_1, P_1, P_1, P_1, P_1, \dots \equiv (p_1) \quad (10)$$

$$P_1, P_1^2, P_1, P_1^2, P_1, P_1^2, \dots \equiv (p_1, p_1^2) \quad (11)$$

$$P_1, P_1^4, P_1, P_1^4, P_1, P_1^4, \dots \equiv (p_1, p_1^4) \quad (12)$$

$$P_1, P_1^2, P_1^4, P_1, P_1^2, P_1^4, \dots \equiv (p_1, p_1^2, p_1^4) \quad (13)$$

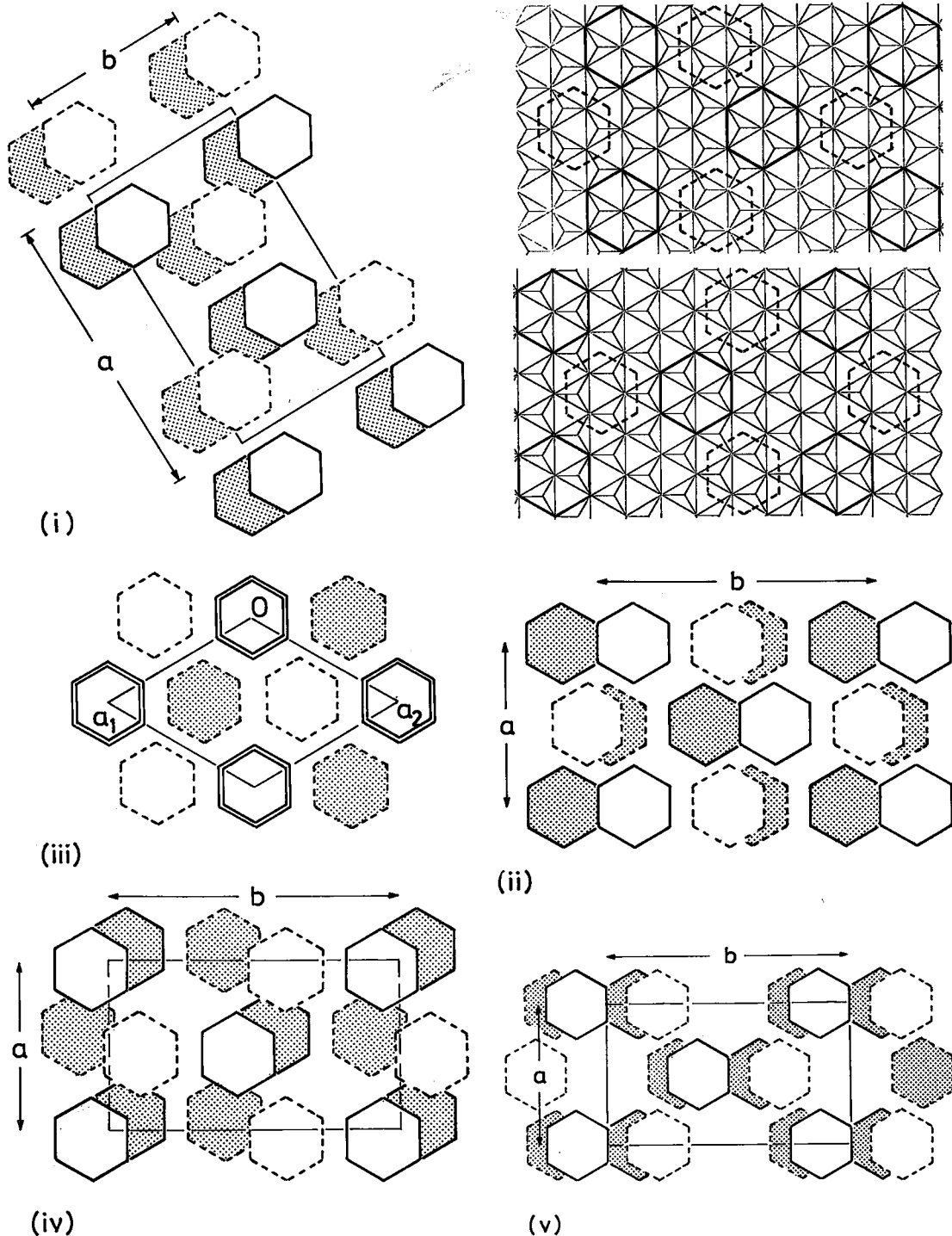


FIG. 2. Examples of two-layer structures, each one being represented by a relative arrangement of hexagons which indicate, as Figure 1, the six-membered rings of the silicate tetrahedra. The hexagons in the bottom layer are stippled. For cell dimensions and maximum symmetry, refer to Table 1. (i) (p_1, \bar{p}_1) ; (ii) $(s^2\bar{s}^3, \bar{s}^2s^3)$. Two successive unit layers are shown; (iii) (e^1, \bar{e}^1) ; (iv) $(p_1e, \bar{p}_1\bar{e})$, and (v) $(s^1\phi^1, \bar{s}^1\bar{\phi}^1)$.

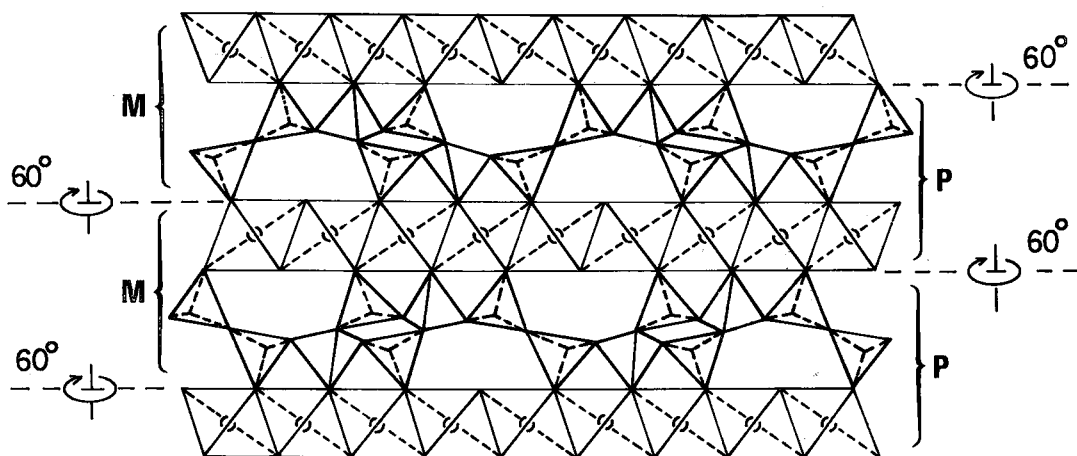


FIG. 3. A stacking of M unit-layers in which each layer is related to its adjacent ones by a rotation of 60° , showing that it is alternately expressed by a stack of P unit-layers.

Sequence (10) gives a one-layer triclinic structure, (11) and (12) give two-layer triclinic structures of the same type and (13) gives a three-layer trigonal structure (Table 1).

Let \bar{p}_1 be a stacking vector whose horizontal component is in the direction opposite to that of p_1 (we can likewise define \bar{p}_1^2 , and \bar{p}_1^4); clearly, we have $\bar{p}_1 = p_3$. The polytypic series that can then be derived are based on the stacking vectors, as are the \bar{f} series derived in section [i].

Stacking vectors like p_1 and \bar{p}_1 may occur in an ordered sequence to form a polytype. Thus, for example, the stacking sequence

$$\bar{p}_1, \bar{p}_1, p_1, \bar{p}_1, p_1, \bar{p}_1, \dots \equiv (\bar{p}_1, \bar{p}_1) \quad (14)$$

gives a two-layer monoclinic structure with $\beta = 90^\circ$ [Table 1, Fig. 2 (i)].

All other possible stacking vectors can be generated from p_m and \bar{p}_m . As p corresponds to the periodicity of the octahedral sheet, the polytypes in this category form a trigonal substructure of Mn atoms, with c corresponding to the interlayer distance and a to $A/4$. Any unit-layer in a polytype of this category is congruent with another by a rotation of 120° followed by a translation equal to one of the stacking vectors.

[iii] Polytypic series based on 60° rotations of unit-layers

Since the difference between the P and the M unit-layers lies only in the orientation of the silicate sheet with respect to the octahedral sheet, we can derive one from the other by rotating the silicate sheet by $(2n + 1) \times 60^\circ$, n being an integer. If we consider a pair of stacked

M unit-layers (Fig. 3) in which the top unit-layer is related to the bottom one by a rotation of 60° , the silicate sheet of the bottom unit-layer and the octahedral sheet of the top unit-layer constitute a P unit-layer. Thus, if M unit-layers are stacked together so that each layer is related to an adjacent one by a rotation of 60° , the resulting sequence is equivalent to a stacking of P unit-layers in which each layer is related to an adjacent one by a rotation of 60° . Similar results are obtained by stacking P layers instead of M layers. To derive polytypes in this category, we need consider only one of the two kinds of unit-layers, say M . As the unit-layer is trigonal, we must consider the rotations about the axes at three different locations: $1/3, 2/3, z$; $2/3, 1/3, z$ and $0, 0, z$. The rotation axes at these locations are denoted Δ , E , and Φ (Fig. 1).

(iii-a) Rotations of $n \times 60^\circ$ about Δ ; $n = 1, 3$ and 5

The three possible rotations, 60° , 180° and 300° , are denoted here δ^1 , δ^3 and δ^5 ($= \bar{\delta}^1$), respectively. To form a structure, each of these rotations must be followed by an interlayer shift with a horizontal component of either $f_h + n(A_1 + \bar{A}_2)/4$ or $\bar{f}_h + n(A_1 + \bar{A}_2)/4$, as in the case of polytypes of category (i). For simplicity, consider only the former case, with $n = 0$. The interlayer shift with this horizontal component may occur in three directions related by rotations of $\pm 120^\circ$ about an axis normal to the layers. Denoting the three shifts s^1 , s^3 and s^5 , respectively, the stacking operation may be represented by $s^1\delta^1$, a combined operation consisting of δ^1 followed by s^1 . For every operation

$s^1\delta^1$, there is operation $\bar{s}^1\bar{\delta}^1$ where the rotation $-\delta^1$ is followed by a shift \bar{s}^1 with a horizontal component in the direction opposite to that of s^1 .

The simplest possible stacking sequence of this category is thus

$$s^1\delta^1, \bar{s}^1\bar{\delta}^1, s^1\delta^1, \bar{s}^1\bar{\delta}^1, \dots \equiv (s^1\delta^1, \bar{s}^1\bar{\delta}^1) \quad (15)$$

Sequence (15) gives a two-layer orthorhombic structure. Another sequence, $(s^3\delta^3, \bar{s}^3\bar{\delta}^3)$, yields a structure that is identical to (15) [Fig. 2 (ii)], provided that the unit-layer has trigonal symmetry.

(iii-b) Rotation about E

The possible rotations of 60° , 180° and 300° about E (Fig. 1) will be denoted by ϵ^1 , ϵ^2 and ϵ^3 ($=\bar{\epsilon}^1$). Each rotation must be followed by an interlayer shift whose horizontal compo-

nent has a value of $nA/4$ ($n = 0, 1, 2, 3$). The accompanying interlayer shifts are similar to the horizontal components of the stacking vectors \mathbf{p} in category (ii). Thus, in the simplest case, the interlayer shift has no horizontal component. The stacking sequence of the simplest possible polytype is, therefore,

$$\epsilon^1, \bar{\epsilon}^1, \epsilon^1, \bar{\epsilon}^1, \epsilon^1, \bar{\epsilon}^1, \dots \equiv (\epsilon^1, \bar{\epsilon}^1) \quad (16)$$

As the threefold axes in the original unit-layer are preserved in the resulting structure, the polytype has a two-layer hexagonal structure [Fig. 2 (iii)], as derived by Takéuchi *et al.* (1969). An example of a stacking sequence that includes an interlayer shift \mathbf{p}_1 is shown in Figure 2 (iv); this is the sequence

$$\mathbf{p}_1\epsilon, \bar{\mathbf{p}}_1\bar{\epsilon}, \mathbf{p}_1\epsilon, \bar{\mathbf{p}}_1\bar{\epsilon}, \dots \equiv (\mathbf{p}_1\epsilon, \bar{\mathbf{p}}_1\bar{\epsilon}) \quad (17)$$

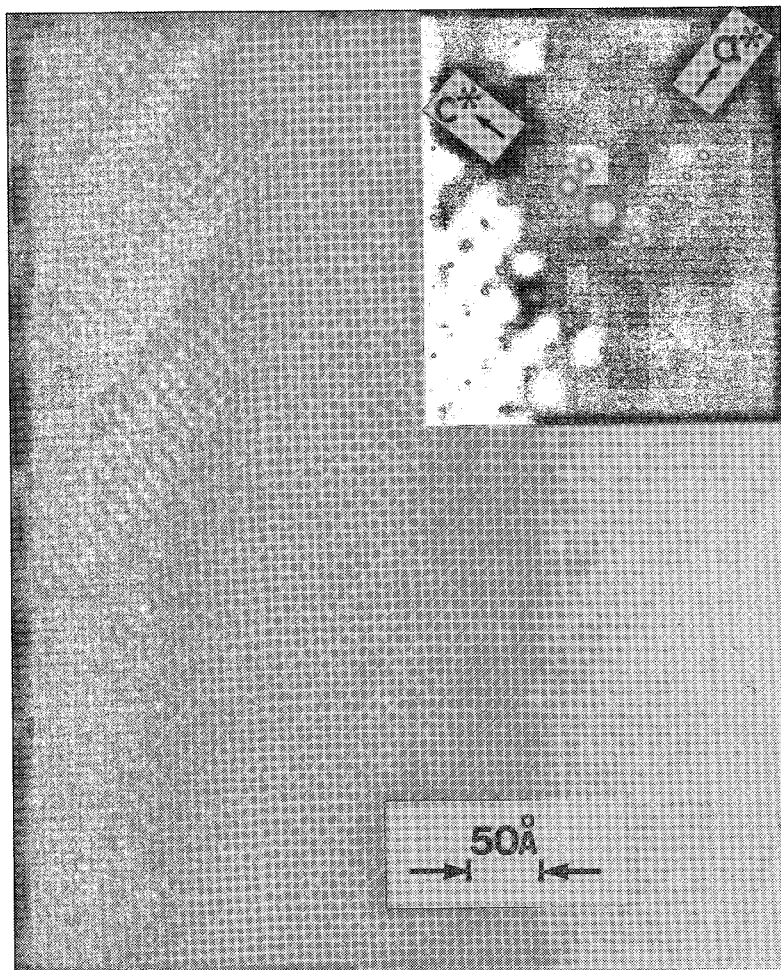


FIG. 4. Manganpyrosomalite: An example of an electron-diffraction pattern and corresponding micrograph, showing stacking disorder in the single-layer structure.

which gives a two-layer monoclinic polytype having orthogonal axes (Table 1).

(iii-c) *Rotation about Φ*

This case is similar to that of case *iii-a*. Let ϕ^1 , ϕ^3 and ϕ^5 ($=\bar{\phi}^1$) be the rotations about ϕ with angles of 60° , 180° and 300° , respectively. To satisfy the stacking condition, each rotation must be followed by an interlayer shift, which has a horizontal component like that in *iii-a*. Hence, by this analogy, one of the simplest possible stacking-sequences may be given as

$$s^1\phi^1, \bar{s}^1\bar{\phi}^1, s^1\phi^1, \bar{s}^1\bar{\phi}^1, \dots \equiv (s^1\phi^1, \bar{s}^1\bar{\phi}^1) \quad (18)$$

This is a two-layer orthorhombic structure [Fig. 2(v)] distinct from sequence (15).

[iv] *Mixed polytypic series*

In this category the stacking sequences are combinations of those defined in [i], [ii] and [iii].

DISCUSSION

Stacking mistakes (or twinning) are common, not only in friedelite and mcGillite (Ozawa *et al.* 1983), but in all members of the pyrosmalite group; such mistakes hinder structure refinement by X-ray methods. However, the fact that the structure of Fe-rich manganpyrosmalite has been well refined, whereas that of manganpyrosmalite has not (Kato & Takéuchi 1983), suggests that the frequency of the mistakes might be related to the Mn content, which

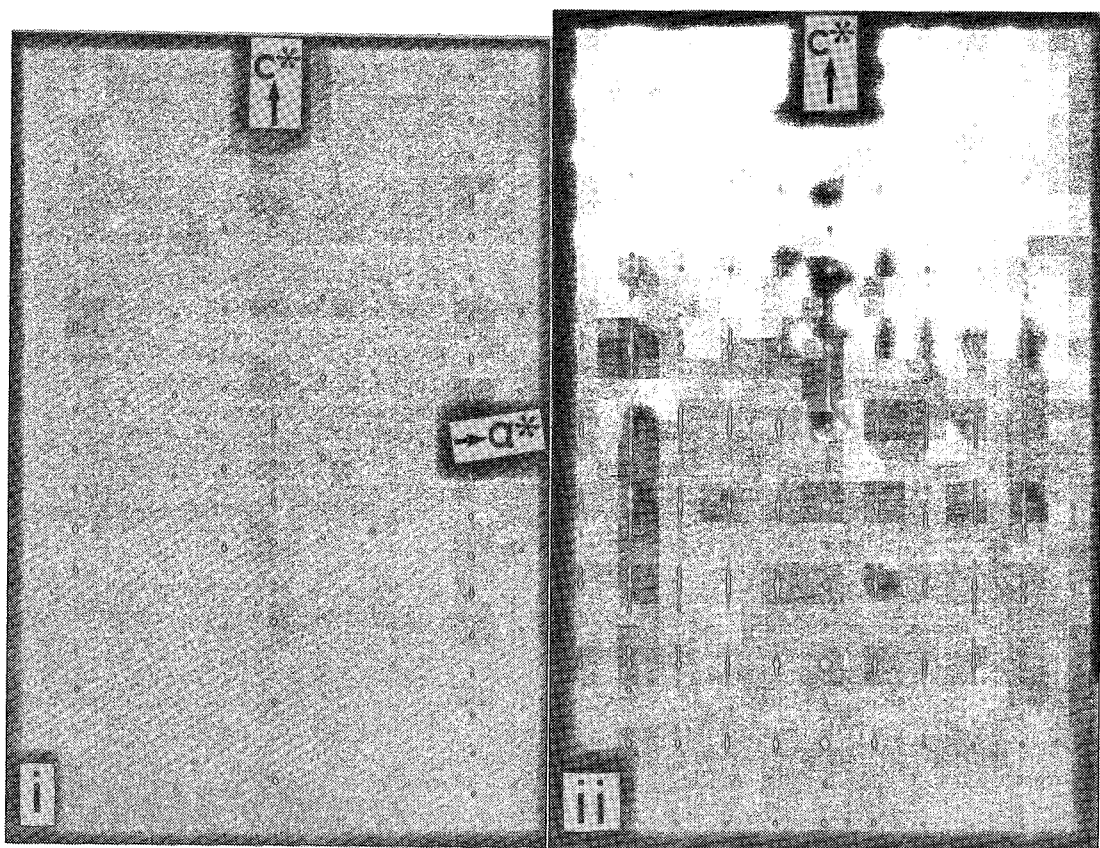
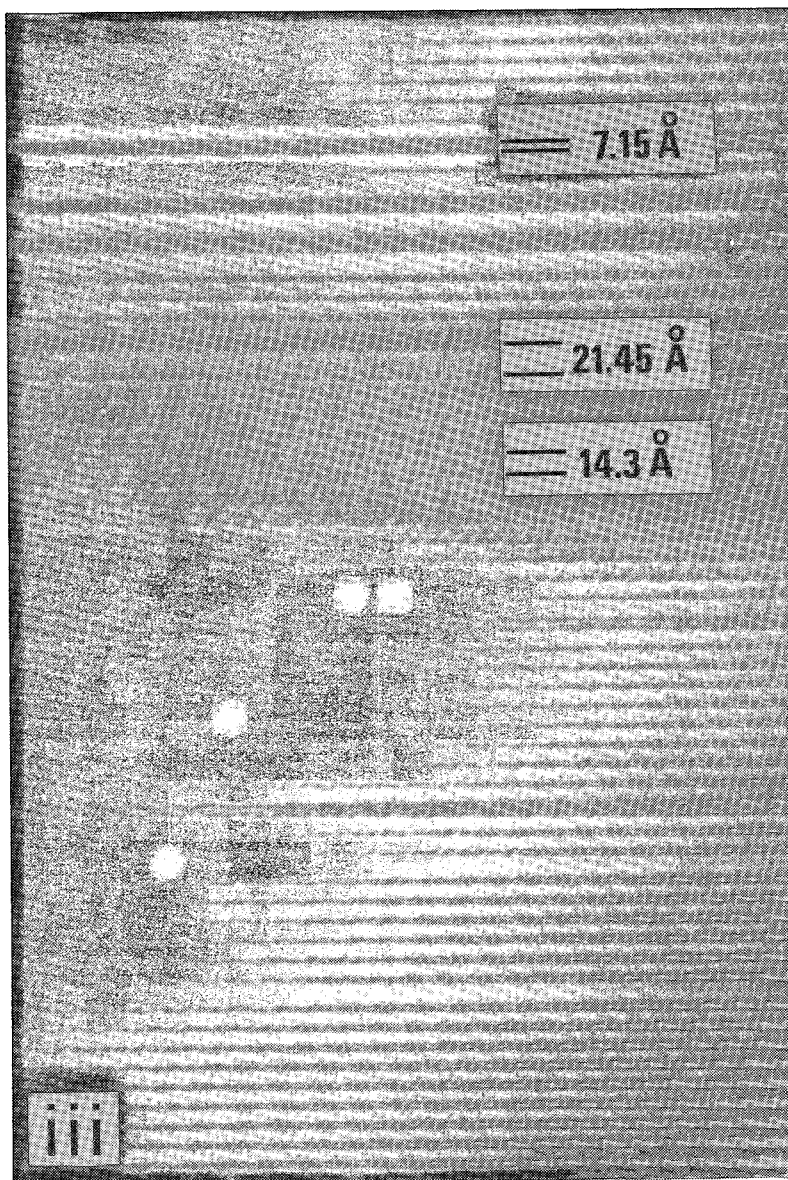


FIG. 5. Manganpyrosmalite: (i) An electron-diffraction pattern showing the existence of the stacking sequence of a two-layer monoclinic type (the acute angle β^* is $\sim 83^\circ$). (ii) A composite electron-diffraction pattern, with corresponding micrograph in (iii), which shows the existence of two-layer and three-layer stacking sequences in addition to the single-layer sequence characteristic of the pyrosmalite structure-type.



controls the lateral fit between tetrahedral and octahedral sheets. TEM imaging of manganpyrosmalite revealed the coexistence of various modes of stacking sequences other than the sequence (p_a) (Table 1), which is characteristic of the pyrosmalite type. The continuation of such a stacking sequence, however, scarcely extends over the thickness of more than several layers. Some examples of such stacking-sequences observed in manganpyrosmalite are given in Figures 4 and 5. Among them, note [Fig. 5(i)]

a diffraction pattern of a two-layer monoclinic type; as the angle β is $\sim 97^\circ$, the polytype probably corresponds to either No. 2 or No. 5 in category *i* (Table 1). Another diffraction pattern [Fig. 5(ii)] and corresponding image [Fig. 5(iii)] show the existence of a three-layer stacking sequence. In addition to these examples, we observed in manganpyrosmalite the existence of a stacking sequence corresponding to that of mcGillite, namely (f).

As the radius of Mn^{2+} is significantly larger

than that of Fe^{2+} , the misfit between the silicate hexagonal rings and the octahedral sheets increases with increasing Mn content (Takéuchi 1965), which would account for the difference in tilt of the tetrahedra with respect to the octahedral sheet. It would also control the distortion of the ring, which lowers its symmetry from hexagonal to ditrigonal and causes local strain in the crystal structure (the distribution of Mn over the cation sites in a crystal may not necessarily be homogeneous throughout the crystal structure). Stacking mistakes or the occurrence of various modes of stacking sequences in an "incipient" fashion (see Ozawa *et al.* 1983) would be instrumental in releasing such strain.

Among the two-layer polytypes in category *iii* (Table 1), the orthorhombic structure of polytype No. 15 best explains the features of electron-diffraction patterns and TEM images of schallerite which, like friedelite and mcGillite, is characterized by stacking disorder (details of the schallerite structure will be reported at a later date). Finally, it is certainly desirable to introduce a new series of polytype symbols instead of the stacking symbols as given in Table 1, so that they can be applicable to mineral names. In general, polytype symbols should be such that they not only are simple but also convey as much as possible of the information on the stacking sequences. The invention of such symbols for the pyrosmalite group is, however, beyond the scope of the present paper.

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