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DISTRIBUTION OF MICA POLYTYPES AMONG SPACE GROUPS

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ABSTRACT

All the possible space groups for mica polytypes have been deduced by making use of the characteristics of the mica unit layer and stacking mode. Studies on algebraic properties of the vector-stacking symbol of Ross, Takeda, and Wones lead to a simple algorithm to deduce the space group from this symbol. A method of enumerating all possible stacking sequences of mica polytype by computer is developed, and the space groups of the derived symbols are obtained for polytypes with up to 6 layers.

Statistics on the observed polytypes show that space groups $C2$, $C\bar{1}$, $C1$ are frequent among the complex ones. Considering that these sequences are based on the $1M$ and $3T$ forms, one can conclude that the growth mechanism may bias the distribution of polytypes among space groups.

INTRODUCTION

The $1M$, $2M_1$, $2M_2$, and $3T$ forms designated by Smith and Yoder (1956) have long been the only mica polymorphs whose stacking sequences have been known. Recently, with the aid of the periodic intensity-distribution function (Takeda, 1967), there have been elucidated the stacking sequences of more than ten complex mica polytypes, whose cell dimension along the stacking direction range from 40 Å to more than 200 Å (Ross, Takeda, and Wones, 1966).

To describe the stacking sequences of these complex mica polytypes, Ross, Takeda, and Wones have proposed a "vector stacking symbol," which is different from one proposed previously by Zvyagin (1960) for mica polytypes. They have also established the principles for the systematic generation of all the possible layer-stacking sequences of mica polytypes.

The present method of enumerating mica polytypes is based in part on the same principles, but utilizes some algebraic properties of the Ross-Takeda-Wones symbol. When it is carried out by a computer, this method of enumeration is more direct and faster than the old one.

The same algebraic properties of the symbol are also used to derive the space groups of the sequences generated. Because of the restrictions on the symmetry and cell dimensions of the unit layer, and on the amount of layer stagger, only a limited number of space groups are possible for mica polytypes. All are derived in this paper, and the distribution of mica polytypes of up to 6 layers among these space groups, has been

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displayed. This probability distribution enables us to draw some conclusions regarding the most frequent space groups among mica polytypes, which may throw light on the problem of the probability distribution of space group in general.

Possible Space Groups in Mica Polytypes

In this derivation, we will adopt the conventional assumptions of the cell dimensions and the symmetry of the mica unit layer, which have been used in earlier studies of mica polytypes. They may be restated as:

(1) The symmetry of the mica unit layer is $1C12/m$.
(2) The cell dimensions of the unit layer are characterized by the relation $b=\sqrt{3}\cdot a$, and the layer stagger, $(1/3)a$ with respect to orthogonal axes.

It follows that the resulting polytypes may have C-centered lattices. For some space groups, in particular those of trigonal or hexagonal symmetry in which the axis perpendicular to layers is an unique axis characterized by a screw axis, a primitive lattice (P) should be used instead of the C lattice.

Among the space groups with C or P lattices, possible structures have been screened by trial with the aid of the following restrictions:

(1) Because of the layer stagger upon stacking, no rotation axis such as 2-, 3-, or 6-fold axis can exist perpendicular to the layers; only the screw axes 2_1, 3_1, 3_2, 6_1, or 6_5 are allowed.

(2) A mirror plane may only be perpendicular to the b axis (of the unit layer) or parallel to the layer.

(3) No glide plane can exist parallel to the layer, because a glide component of half the distance between lattice points can not be built up to include the stagger component $(1/3)a$.

(4) For an orthorhombic space group having a mirror perpendicular to the b axis, there must also be a mirror perpendicular to the c axis.

Conditions (1) and (2) come from the restriction that the layer stagger upon stacking prohibits the repetition of the same unit on the same level. Thus, screw axes 6_2, 6_3, 6_4, are not allowed. Condition (1) also eliminates the existence of rhombohedral lattices in mica polytypes, since 3 or $\bar{3}$ axes are not allowable.

It should be noted that space groups such as Cm, $P3_1$, $P3_2$, $P6_1$, $P6_5$, $P3_121$ or $P3_221$ appear only for those polytypes with higher layer numbers due to lower symmetry. Using these four conditions as a filter, the possible space groups (listed in Table 1) can be selected. The stackings that have a polar axis perpendicular to the layers belong to $C1$, $P2_1$, Cm, Cc, $P3_1$, $P3_2$, $P6_1$, and $P6_5$.

TABLE 1. POSSIBLE SPACE GROUPS WHICH ARE EXPECTED IN MICA POLYTYPES. SYMBOLS ARE IN ORIENTED HERMANN-MAUGIN SYMBOLS. THE x AND y AXES ARE PARALLEL TO THE PLANE OF THE LAYERS

	Acentric	Centric
Triclinic	$C1$ $(=P1)$	$C\bar{1}$ $(=P\bar{1})$
Monoclinic (first setting)	$P2_1$ $(=C112_1)$,	$P2_1/m$ $(=C112_1/m)$,
(second setting)	$C2$, Cm, Cc.	$C2/m$, $C2/c$.
Orthorhombic	$C222_1$,	
	$Cc2m=C2cm$, $C2mm$.	$Ccmm$
Trigonal	$P3_1$, $P3_2$,	
	$P3_112$, $P3_212$, $P3_121$, $P3_221$.	
Hexagonal	$P6_1$, $P6_5$,	
	$P6_122$, $P6_522$.	

ALGEBRAIC PROPERTIES OF THE MICA-POLYTYPE SYMBOL

The vector-stacking symbol proposed by Ross, Takeda, and Wones (1966) expresses the stacking sequence of an N-layer mica by a series of N numbers, the jth number a_j of the series referring to the relative angle of rotation between the jth and $(j+1)^{\text{th}}$ mica layer. The number a_j can have the values 0, ±1, ±2, or 3, which refer, respectively, to rotations of 0°, $\pm60°$, $\pm120°$, and 180° between adjacent layers. It expresses the rotation in units of 60°, positive when counterclockwise. Apart from the geometrical and structural implications of the symbol, we treat the symbol as a string of numbers, to which mathematical operations are to be applied, so that the enumeration of the possible stacking sequences and deduction of its space group can be done by a suitable algorithm.

Representing a string of N numbers by

$$M = a_1a_2 \cdots a_j \cdots a_{N-1}a_N,$$

where a_j is the jth element of the sequence, we can define three operations, by which the symbol M may be *transformed into* those shown below,

$$M' = a_Na_{N-1} \cdots a_{j'} \cdots a_2a_1,$$
$$\overline{M} = \bar{a}_1\bar{a}_2 \cdots \bar{a}_j \cdots \bar{a}_{N-1}\bar{a}_N,$$
$$\overline{M}' = \bar{a}_N\bar{a}_{N-1} \cdots \bar{a}_{j'} \cdots \bar{a}_2\bar{a}_1,$$

and

$$M^i = a_{i+1}a_{i+2} \cdots a_{j+i} \cdots a_Na_1a_2 \cdots a_i,$$

where

$$j' = N - (j - 1).$$

In the above definition, there is no priority between the operation $\overline{M}$ and M'. Thus, $\overline{M}' = (\overline{M})'$.

For convenience, we shall call M' the transpose of M, $\overline{M}$ the supplement of M, and M^i a cyclic permutation of i elements. Among the M^i operations, the following will be of crystallographic interest. If a symbol of an even layer polytype, has an internal repetition as below,

$$M = a_1 a_2 \cdots a_j \cdots a_{N/2} a_1 a_2 \cdots a_j \cdots a_{N/2},$$

for which the equality $M = M^{N/2}$ holds, its structure may have higher symmetry. There are two similar subperiods, for which the equality $M = M^{N/3}$ or $M = M^{N/6}$ holds. Also it should be mentioned that no cyclic permutations other than the $N/2$, $N/3$, and $N/6$ cycles are possible, because of the condition

$$\sum_{j=1}^{N} a_j = 0 \mod 6.$$

By successive applications of these operations, the symbol may be brought into self-coincidence n times, n depending upon the mode of arrangement of the elements in the symbol. This multiplicity n of the symbol, which is related to some algebraic properties of the symbol, is used as an efficient clue for deducing the space group from the symbol.

Enumeration of the Vector-stacking Symbols

To establish the mathematical principles for enumerating the possible stacking sequences of a mica polytype, the three operations, namely, *transposition*, taking the *supplement*, and *cyclic permutation*, must be interpreted in crystal-structure terms.

By definition each element represents a relative interlayer-rotation, and after the N rotations for an N layer mica, the next layer, *i.e.*, the $(N+1)^{\text{th}}$ layer must be in the same orientation as the 1st layer, thus the N numbers $a_1 a_2 \cdots a_N$ must obey the relation,

$$\sum_{j=1}^{N} a_j = 0 \mod 6.$$

Therefore, this relation ensures the periodicity of the stacking.

Next, the cyclic permutation of the N numbers corresponds to successive shifts of the origin at which the first layer begins. The choice of the first layer in the succession of stacked layers is essentially arbitrary. Therefore *cyclic permutation* is a permissible operation for the mica-polytype symbol. That is, the actual structure is invariant with respect to it.

The *transposition* also does not change the structural body, because the unit layer has a center of symmetry in its mid-point. To *transpose* means to stack the layers in the reverse order. However, taking the *supplement* does change the structure. It reverses the hand of the structure, giving an enantiomorph. But since we excluded enantiomorphs from our derivation, the operation is considered to be a permissible one.

The method of enumerating all possible stacking sequences of mica polytypes using the vector-stacking symbols, has been briefly described in the paper by Ross, Takeda, and Wones (1966). A computer program was also written using these principles by Takeda, who enumerated polytypes with up to 9 layers. The method described below differs from the former one in some points. Both methods utilize a ternary or senary number (numbers using base 3 or 6) to represent a stacking sequence. This representation is a simple case of the well known coding problem; for example, for SiC, the base is 2 and for DNA, 4. However, the new method expresses a sequence by the smallest such number, and thus the principle of the enumeration lies in that a number expressing a sequence will be rejected if it becomes smaller when any of the three operations is applied.

The details of the present method will be found in the Fortran IV (HARP) listings of the new program (Takeda, unpublished, 1968). Itemized explanations of each step in the flow diagram of the program follow:

(1) Generate ternary or senary number M.

(2) Convert the number into a Ross-Takeda-Wones symbol and eliminate it if it does not obey the relation $\sum_{j=1}^{N} a_j = 0 \bmod 6$.

(3) Make M'.

(4) Apply cyclic permutations M^i for $i=1$ to N. For each i, test and reject it if M is larger than M^i or $(M')^i$ or both; if $M^i = M$, proceed to the next i.

(5) Make $\overline{M}$ and $(\overline{M'})$.

(6) Apply cyclic permutations $(\overline{M})^i$ and $((\overline{M'}))^i$ for $i=1$ to N and test and reject it in the same way as in step (4).

(7) Discard the sequence having a subrepeat that represents a sequence of lower layer numbers. This test is carried out only if $M = M^i$. Say $M = M^{N/n}$ (n is an integer smaller than N), then $a_j = a_{j+N/n}$ and $\sum_{j=1}^{N/n} a_j = 0 \bmod 6$.

Only a symbol that has passed these seven tests, is eligible to represent a possible sequence of mica polytype. When a number fails to pass any of the tests, control returns to step (1), and repeats the same steps for the next integer.

A similar method can also be applied to generate all possible mica polytypes using the symbol proposed by Takeda and Sadanaga (1969). The details of this method will be described elsewhere.

Derivation of Space Group

Some triclinic mica polytypes show monoclinic diffraction patterns and therefore we have to know the space group of each stacking sequences in order not to overlook such cases. It is difficult to find all the symmetry elements in the drawing of the structure of a complex mica polytype, especially for polytypes with very high layer numbers. A quick and direct method of deriving the space groups from the stacking symbol is also needed for finding the statistical distribution of mica polytypes among the space groups, since the number of possible polytypes increases rapidly with the layer number.

The space group of a polytype with a certain stacking sequence may be deduced, if the orientation and the position of each layer is known, together with the axial setting of a given polytype. However, as was mentioned before, the Ross-Takeda-Wones symbol is orientation-free and therefore it is necessary to convert this symbol to another, so that the geometrical picture of the stacked layer is evident for the deduction of the space group.

Nevertheless, given a Ross-Takeda-Wones symbol, one may be able to find a direct method for deducing the space group of a polytype, by making use of the algebraic properties of the symbol. Such a method has been developed by the present author, but the method was tested only with the aid of a geometrical construction and further study may be required, in order to be sure of the general method.

Our aim is to correlate the algebraic properties of any R-T-W symbol and its multiplicity n with the possible space groups for mica polytypes. First, we investigate how an algebraic operation applied to the symbol transforms a geometrical object consisting of stacked layers. Then, the space group may be derived by the combination of such operations.

An interpretation of the equality, $M = M'$, is as follows. As was stated above, operation M' implies stacking the layers in the reverse way. Therefore, $M = M'$ simply means that the reversed sequence is identical to the original sequence and accordingly indicates the existence of a 2-fold axis perpendicular to the stacking direction. As the operation $\overline{M}$ implies a change of hand of stacking, the equality $M = \overline{M}$ requires a mirror reflection which leaves the sequence invariant.

The operation $M^{N/n}$ implies that the stacked layers are shifted by a period N/n along the direction of stacking, and therefore $M = M^{N/n}$ implies the existence of a screw axis, for example, 2_1, 3_1, and 6_1 for $n = 2$, 3, and 6, respectively. A similar geometrical approach will also lead us to correlate inversion and glide reflection with the operations. For this purpose, we shall examine the combination of the above three operations.

The combination M' with $M^{N/n}$ does not make any geometrical sense.

$M=(\overline{M})^{N/2}$ implies a glide plane with glide component along the stacking direction, because the operation changes its hand after a shift of $N/2$. The last case, $M=\overline{M}'$ is connected with a center of symmetry. By drawing stacking vectors which satisfy the operation, starting in the middle of the sequence and working both upwards and downwards, we find that the upper half is the reversed sequence of the lower half, with a change of hand.

From the combination of these fundamental operations, we will be able to differentiate mica polytypes into space groups. For this purpose, we use symbols M, M', $\overline{M}$, *etc.*, to mean that the stacking-sequence symbol is brought into self-coincidence by these operation. A simple key (Table 2) differentiates symbols into space groups. A hierarchy number is used so that whenever an operation of higher number is found, the space group must be found under it.

It is also to be noted that the operation $M^{N/3}$ implies $M^{2N/3}(n=3)$. Likewise $M^{N/6}$ implies $M^{2N/6}, \cdots M^{5N/6}$ $(n=6)$. $M^{N/3}$ and M' indicate that, in addition to the operation $M^{N/3}$, operations $(M^{i})'$, $(M^{N/3+i})'$, and $(M^{2N/3+i})'$ $(n=6)$ are possible. Likewise, $M^{N/6}$ and M' represent a group of operations in addition to $M^{N/6}$: $(M^{1})'$, $(M^{N/6+1})'$, $\cdots$ $(M^{5N/6+1})'$ $\cdots$ $(n=12)$.

TABLE 2. DIFFERENTIATION OF POLYTYPE SYMBOLS INTO SPACE GROUPS ACCORDING TO THE HIERARCHY NUMBER

Hierarchy	Operation	Subdivision	Operation	Space Groups
(1)	M		....	$C1$
	$\overline{\mathrm{M}}'$		....	$C\bar{1}$
	M′		....	$C2$
(2)	$\mathrm{M}^{N/2}$	(a)	M	$P2_1$
		(b)	$\overline{\mathrm{M}}'$	$P2_1/m$
		(c)	M′	$C222_1$
	$\mathrm{M}^{N/3}$	(a)	M	$P3_{1,2}$
		(b)	M′	$P3_{1,2}12$, $P3_{1,2}21$
	$\mathrm{M}^{N/6}$	(a)	M	$P6_{1,2}$
		(b)	M′	$P6_{1,2}22$
(3)	$\overline{\mathrm{M}}^{N/2}$	(a)	$\overline{\mathrm{M}}'$, M'........	$C2/c$
		(b)	$\overline{\mathrm{M}}'$, M′, $(\mathrm{M}')^{N/2}$.....	$Cc2m=C2cm$
(4)	$\overline{\mathrm{M}}$	(a)	M	Cm
		(b)	$\overline{\mathrm{M}}'$, M′........	$C2/m$, $C2mm$
		(c)	$\overline{\mathrm{M}}'$, M′, $\mathrm{M}^{N/2}$, $\overline{\mathrm{M}}^{N/2}$.....	$Ccmm$

We list, below, the space groups and, for each one, the corresponding operations of the symbol. In the list of operations, it is understood that the symbol is rearranged so that the operation is applicable directly to the written symbol. Note also that we have to consider the symbol as a ring rather than a string, even though it is written in string form. For some sequences, the symbol, as written in the present string form, will be brought into self-coincidence only after an additional M^1 operation (one shift of symbol) has been applied. Some stacking sequences, given as examples below, are illustrated by Smith-Yoder diagrams (Figures 1, 2, 3).

Triclinic Space Groups.

$C1(=P1)$: The symbol is not brought into self-coincidence by any operation, other than M(identity), $n=1$.

$C\bar{1}(=P\bar{1})$: M and $\overline{M}'$ (which implies $a_j=\bar{a}_{N-j+1}$), no other symmetry, $n=2$.

Monoclinic Space Groups. The cell must be monoclinic or metrically orthorhombic.

$P2_1(=C112_1)$: M and $M^{N/2}$, no other operation. Example: 012012.

$P2_1/m(=c112_1/m)$: M, $M^{N/2}$, and $\overline{M}'$. Example: $13\bar{1}13\bar{1}$.

$C2$: M and M', $n=2$.

Cc : M and $(\overline{M})^{N/2}$, $n=2$.

Cm : M and $\overline{M}$. This implies a_j must be either 0 or 3. No other symmetry present. $n=2$. Example: 0030333.

$C2/c$: M, M', $\overline{M}'$, and $(\overline{M})^{N/2}$. Each operation takes place at a different position; for example one operation is applicable after the other followed by permutation $M^{N/4}$.

$C2/m$: M, M', $\overline{M}$ and $\overline{M}'$ are required with condition $a_j=0$ or 3.

Orthorhombic Space Groups. The cell must be orthogonal.

$C222_1$: M, $M^{N/2}$ and M', no other operation is permissible, $n=2$. $\sum_{j=1}^{N/2} a_j=3 \bmod 6$.

$Cc2m$: M, $\overline{M}^{N/2}$, and after M^i operation $\overline{M}'$, M', or $(M')^{N/2}$. The symbol may have form $a_1 \cdots 2 \cdots a_{(N/2)-1}3 \cdots \bar{2} \cdots a_{n-1}3$, where 2 and $\bar{2}$ are at $N/4$ and $3N/4$, respectively. For the symbol having no element at such positions, the general form will be

$$a_1 \cdots 11 \cdots a_{(N/2)-1}3 \cdots \overline{11} \cdots a_{N-1}3$$

or

$$a_1 \cdots 22 \cdots a_{(N/2)-1}3 \cdots \overline{22} \cdots a_{N-1}3.$$

$C2cm$: The same as above, but the symbol may have form $a_1 \cdots 1 \cdots a_{(N/2)-1}3 \cdots \bar{1} \cdots a_{N-1}3$.

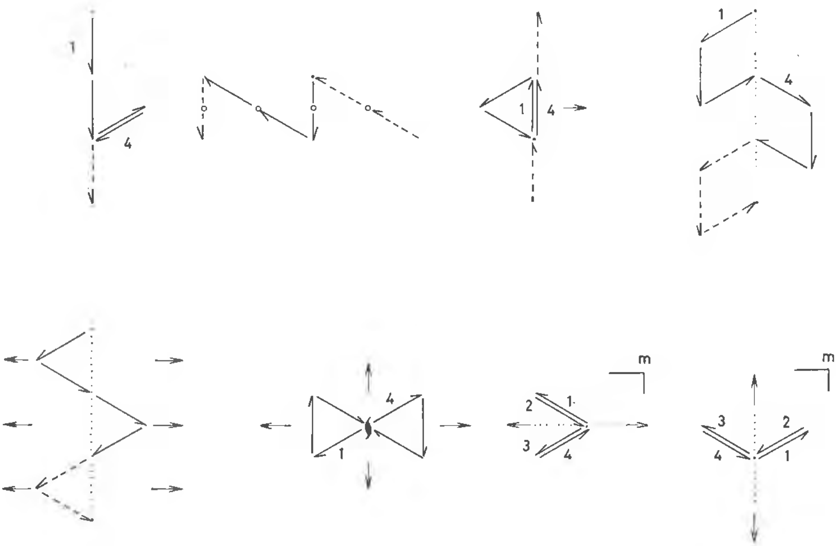

FIG. 1. Examples of stacking sequences for space groups with no mirror perpendicular to the *b* axis drawn by Smith-Yoder diagrams projected along c^*. The symbols of symmetry elements are the same as those of *International Tables for X-ray Crystallography* Vol. 1. (The Kynoch Press, Birmingham, England, 1965.) Some of the stacking symbols are not in accordance with the convention given in the text. (Left to right) $C1$ 0231, $C\bar{1}$ $\bar{2}$02, $C2$ 2220, Cc $12\bar{1}\bar{1}\bar{2}1$, $C2/c$ $20\bar{2}0$, $C222_1$ $\bar{2}\bar{2}1\bar{2}\bar{2}1$, $Cc2m$ $3\bar{2}32$, $C2cm$ $3\bar{1}31$.

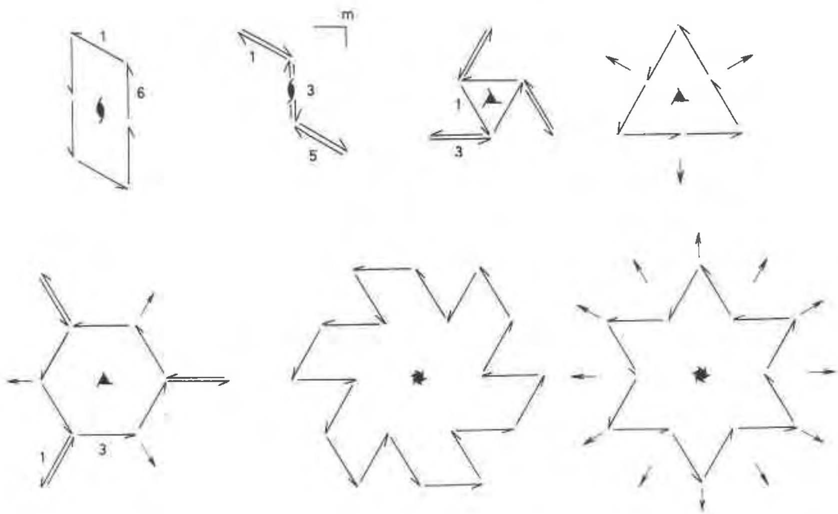

FIG. 2. Examples of space groups with the unique axes as the *c* axis, drawn by Smith-Yoder diagrams projected along this axis. (Left to right) $P2_1(C112_1)$ 201201, $P2_1/m(C112_1/m)$ $3\bar{1}13\bar{1}1$, $P3_1$ $(\bar{2}31)_3$, $P3_112$ $(02)_3$, $P3_121$ $(3\bar{1}1\bar{1})_3$, $P6_1$ $(12\bar{2})_6$, $P6_122$ $(2\bar{1})_6$.

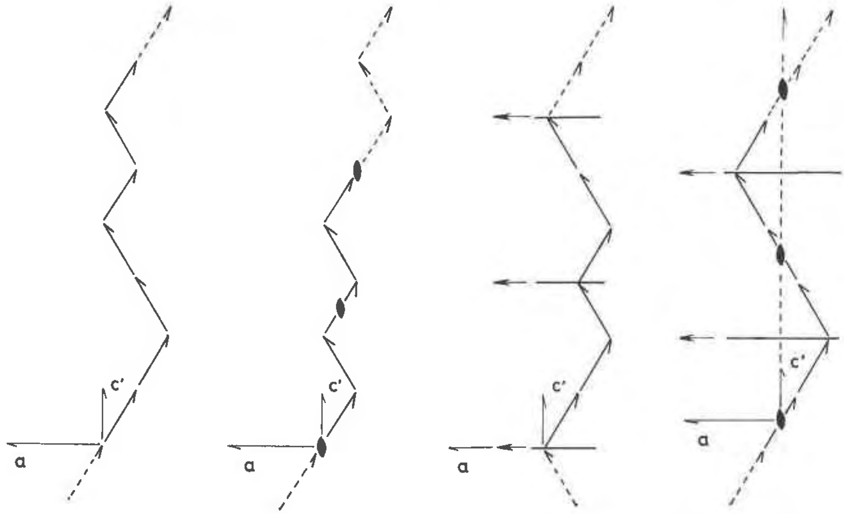

FIG. 3. Examples of space groups with mirror perpendicular to the b axis, drawn by Smith-Yoder diagrams projected along this axis. (Left to right) Cm 0303330, $C2/m$ 33330, $C2mm$ 033303, $Ccmm$ 030030.

$C2mm$: M, $\overline{M}$, M', and $\overline{M}'$, $n=4$. $a_j=0$ or 3 only. The general form is given as $3a_2a_3 \cdots a_{N/2}3a_{N/2} \cdots a_3a_2$.

$Ccmm$: M, $\overline{M}$, $M^{N/2}$, $\overline{M}^{N/2}$, M', $(M')^{N/2}$, $(\overline{M})'$, and $((\overline{M})')^{N/2}$, $n=8$. $a_j=0$ or 3 only. General form: $0a_2a_3 \cdots 3 \cdots a_{N/2}0a_{N/2} \cdots 3 \cdots a_3a_2$, where 3 is at $N/4$ and $3N/4$.

Trigonal Space Groups. Primitive hexagonal lattice derived from metrically orthorhombic C lattice.

$$\sum_{j=1}^{N/3} a_j = 2 \bmod 6 \quad \text{or} \quad 4 \bmod 6.$$

$P3_1$ or $P3_2$: M, $M^{N/3}$, and $M^{2N/3}$, $n=3$, no other operation. Example:

$$1\bar{2}31\bar{2}31\bar{2}3.$$

$P3_1 12$ or $P3_2 12$: M, $M^{N/3}$, M', $n=6$, but $a_i=2$ or $\bar{2}$. Example: 020202.

$P3_1 21$ or $P3_2 21$: The same as above, but $a_i=1$, $\bar{1}$ or 3. Example:

$$\bar{1}3\bar{1}\bar{1}13\bar{1}11\bar{3}11.$$

Hexagonal Space Groups. Primitive lattice derived from metrically orthorhombic C lattice,

$$\sum_{j=1}^{N/6} a_j = 1 \mod 6 \quad \text{or} \quad 5 \mod 6.$$

$P6_1$ or $P6_5$: M and $M^{N/6}$, $n=6$, no other operation. Example:

$$12\bar{2}12\bar{2}12\bar{2}12\bar{2}12\bar{2}12\bar{2}.$$

$P6_122$ or $P6_522$: M, $M^{N/6}$ and M', $n=12$. Example: $2\bar{1}2\bar{1}2\bar{1}2\bar{1}2\bar{1}2\bar{1}$.

A method of deriving the space group from another kind of polytype symbol may also be found. Since Takeda and Sadanaga's symbol gives the position of the individual layer in the given coordinate system, it will be easy to find space group directly. Conversion of other symbols into this will give another check on the space group derived.

Distribution of Mica Polytypes Among the Space Groups

The enumeration of possible mica polytypes has been carried out with a program written in Fortran IV (HARP) on HITAC5020E. The number of possible mica polytypes having any combination of 0°, ±60°, ±120° and 180° layer rotation (senary case) has been obtained for up to 6 layers, and the number of those having 0° and ±120° rotations only (ternary case), for up to 9 layers (Ross, Takeda, and Wones, 1966). By our new program, the 572 possible polytypes (ternary) for 10 layers have been enumerated, and 1776 and 9212 polytypes (senary) for 7 and 8 layers, respectively.

The space groups of these polytypes were deduced completely up to 4 layers by Ross, Takeda, and Wones (1966), who used graphical methods. The same space groups have been obtained by our new method, and the method has been applied to derive all possible space groups of the polytypes of 5 and 6 layers. Part of them are listed in Table 3 under the layer numbers and space groups. Their distribution among the 23 possible space groups is listed in Table 4. The numbers found in natural and synthetic micas are given in Table 5.

It may be interesting to note that the orthorhombic space groups appear for polytypes with layer number $N=0 \mod 2$; the trigonal space groups for $N=0 \mod 3$; and the hexagonal space groups for $N=0 \mod 6$. Some acentric space groups, for example, Cc, Cm, $P3_1$, $P3_2$, $P6_1$, and $P6_5$ may appear for polytypes with very high layer numbers.

Discussion

From Table 4 and 5 we may conclude the following: For polytypes with high layer numbers, some space groups of low symmetry occur with high frequency, and also tend to occur frequently in nature. However, one can-

TABLE 3. ALL POSSIBLE STACKING SEQUENCES FOR A GIVEN LAYER NUMBER N CLASSIFIED UNDER SPACE GROUPS (ROSS, TAKEDA, AND WONES, 1966)

$N=1$		$N=4$		
$C2/m$	0 (1M)	$C1$	$011\bar{2}$	0213
			0123	$13\bar{2}\bar{2}$
			0132	$1\bar{1}\bar{2}2$
$N=2$		$C\bar{1}$	$01\bar{1}0$	$133\bar{1}$
$C2/c$	$2\bar{2}$ ($2M_1$)		$02\bar{2}0$	$233\bar{2}$
	$1\bar{1}$ ($2M_2$)		$1\bar{2}2\bar{1}$	
$Ccmm$	33 (2O)	$C2$	$01\bar{2}1$	1221
			0222	$1\bar{2}3\bar{2}$
			1131	
$N=3$		$C2/c$	$010\bar{1}$	$2\bar{2}\bar{2}2$
$C1$	123		$020\bar{2}$	$12\bar{1}\bar{2}$
			$1\bar{1}\bar{1}1$	
$C\bar{1}$	$02\bar{2}$ ($3Tc_1$)			
	$01\bar{1}$	$C2/m$	0033	
$C2$	$11\bar{2}$	$C222_1$	1212	
$C2/m$	033	$Cc2m$	$23\bar{2}3$	
		$C2cm$	$13\bar{1}3$	
$P3_112$	222 (3T)			
		$Ccmm$	0303	

not say that the lower the symmetry, the more frequent the occurrence. The reason for this may be that there are two or three series of mica polytypes which occur very frequently in nature and their space groups are $C\bar{1}$, $C2$, or $C1$.

In silicon carbides the polytypes $4H$, $6H$, and $15R$ have been considered to be the basic forms from which the complex polytypes can be derived. The similarity between silicon-carbide polytype and complex mica polytypes has been discussed (Takeda, 1967). In the mica case, complex polytypes are derived from the $1M$, $3T$, or $2M_1$ forms (no good example of the $2M_1$ series has yet been observed). These phenomena may be attributed to the spiral growth mechanism of polytypes proposed by Frank (1951) and Mitchell (1957).

The six simplest mica polymorphs proposed by Smith and Yoder (1956), namely, $1M$, $2M_1$, $2M_2$, $2O$, $3T$, and $6H$ have given the impression that these six forms might also occur frequently in nature. However, up to the present time two of them $2O(Ccmm)$, and $6H(P6_122)$ have not

TABLE 4. DISTRIBUTION OF MICA POLYTYPES WITH N LAYERS ($N=1$ TO 6) AMONG 23 POSSIBLE SPACE GROUPS

(Space groups, Cm, $P3_1$, $P3_2$, $P3_121$, $P3_221$, $P6_1$, and $P6_5$ are not listed below, because they appear for N greater than 6).

N / Space Groups	1	2	3	4	5	6
$C1$ ($P1$)			1	6	48	259
$C\bar{1}$ ($P\bar{1}$)			2	5	16	53
$C2$			1	5	16	52
$C2/c$		2		5		12
$Cc2m=C2cm$				2		10
Cc						4
$C2/m$	1		1	1	3	3
$P3_112$, $P3_212$			1			2
$Ccmm$		1		1		1
$C222_1$				1		1
$P2_1/m$						2
$P2_1$						1
$C2mm$						1
$P6_122$, $P6_522$						1
Total	1	3	6	26	83	402

yet been found. We might consider that the absence of these two forms with very high symmetry could be due partly to chance, as was pointed out by Mackay (1967) for the absence of some space groups, even if the basal oxygen net work approaches ideal hexagonality.

Apart from the simple structures such as silicon carbide, this kind of structural control must also be taken into account for such complex structures as micas. The predominance of those polytypes which have 0° or ±120° interlayer rotations, is definitely due to the ditrigonal nature of the basal oxygens. Thus, $1M$, $2M_1$, and $3T$ have the highest frequency among micas. The problem on this subject, that is, structural control of mica polytypism, is an important field in mica crystal chemistry and has been discussed by many workers.

The reasons why the $3T$ form is found relatively frequently in spite of its high symmetry, have to be investigated thermodynamically and crystal-chemically as is being done for SiC by other workers. One reason may be the structural control mentioned in the above paragraph and discussed by Güven and Burnham (1967). $3T$ is one of the basic forms of the series which occur frequently. The stacking sequence, expressed by the Takeda-Sadanaga layer-position symbol (Takeda and Sadanaga,

TABLE 5. DISTRIBUTION OF MICA POLYTYPE CRYSTALS AMONG SPACE GROUPS

Space Groups	No. of Crystals	Stacking Sequence[a]	
$C2/m$	94	1M (0)	(1)
$C2/c$	66 {56	$2M_1$ $(2\bar{2})$	
	{10	$2M_2$ $(1\bar{1})$	
$P3_112$	6	3T (222)	
$C\bar{1}$	5	$3Tc_1$ $(02\bar{2})$	(2)
		$8Tc_1$ $((0)_62\bar{2})$	(2)
		$14Tc_1$ $((0)_{12}2\bar{2})$	(2)
		$23Tc_1$ $((0)_{21}2\bar{2})$	(2)
		$8Tc_2$ $((2\bar{2})_3\bar{2}2)$	(3)
$C1$	3	$4Tc_5$ (0132)	(4)
		$8Tc_{12}$ $(0002\bar{2}\bar{2}02)$	(2)
		$10Tc_3$ $((2)_5\bar{2}2200)$	(2)
$C2$	3	$4M_2$ (2220)	(2)
		$8M_8$ $((222)_22\bar{2})$	(2)
		$11M_1$ $((222)_32\bar{2})$	(2)

[a] References: (1) Statistics reported by Takeda and Mackay (1969); (2) Ross, Takeda, and Wones (1966); (3) Smith and Yoder (1956), and Takeda (1969); (4) Takeda (1967).

1969), is seen to be one of the simplest sequences with a periodic displacement of the layers.

The statistics of the distribution of the crystallized compounds over space groups have been given by Nowacki and his co-workers (Donnay and Nowacki, 1954; Nowacki, Matsumoto, and Edenharter, 1967; Nowacki, 1967). They reveal that the zig-zag arrangement of the organic molecules probably accounts for the predominance of space group such as $P2_12_12_1$ and $P2_1/c$, and that the closest packing of spheres or its modifications, give a high frequency to some space groups.

Now, from our statistics we must conclude that principles other than those considered above must account for the abundance of certain space groups. The case of the mica polytypes and other polytypes such as SiC, ZnS, or CdI_2, are certainly examples where the frequency distribution is governed by the principles other than the above, though the total number of these compounds may not be large enough to affect the distribution of *all* compounds taken together among the space groups. In general, when structures are made up of simple units of one kind with regular stacking principles, the resultant space groups will be greatly restricted in number.

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References

Donnay, J. D. H. and W. Nowacki (1954) Crystal data. classification of substances by space groups and their identification from cell dimensions. *Geol. Soc. Amer., Mem.* **60.**

Frank, F. C. (1951) The growth of carborundum; dislocations and polytypism. *Phil. Mag.* **42,** 1014–1021.

Güven, N. and C. W. Burnham (1967) The crystal structure of 3T muscovite. *Z. Kristallogr.* **125,** 163–183.

Mackay, A. L. (1967) The statistics of the distribution of crystal substances among the space groups. *Acta Crystallogr.* **22,** 329–330.

Mitchell, R. S. (1957) A correlation between theoretical screw dislocations and the known polytypes of silicon carbide. *Z. Kristallogr.* **109,** 1–28.

Nowacki, W. (1967) Crystal data, systematic tables, *2nd ed., Amer. Crystallogr. Assoc. Monogr.* **6.**

———, T. Matsumoto, and A. Edenharter (1967) Classification of crystalline substances by crystal systems, crystal classes, Bravais lattices and space groups. *Acta Crystallogr.* **22,** 935–940.

Ross, M., H. Takeda, and D. R. Wones (1966) Mica polytypes: systematic description and identification. *Science* **151,** 191–193.

Smith, J. V., and H. S. Yoder, Jr. (1956) Experimental and theoretical studies of the mica polymorphs. *Mineral. Mag.* **31,** 209–235.

Takeda, H. (1967) Review of complex mica polytypes. *J. Mineral. Soc. Jap.* **8,** Spec. Issue No. 1, 39–41.

——— (1967) Determination of the layer stacking sequence of new complex mica polytype: a 4-layer lithium fluorphlogopite. *Acta Crystallogr.* **22,** 845–853.

——— (1969) Existence of complex mica polytype series based on $2M_1$ sequence (abstr). *Autumn Meet. Mineral. Soc. Jap.*

——— and A. L. Mackay (1969) Mica-polytype symbols and its space groups. *J. Mineral. Soc. Jap.* **9,** 357.

———, and R. Sadanaga (1969) New unit layers for micas. *Mineral. J.* **5,** 434–449.

Zvyagin, B. B., (1960) Theory of mica polymorphism. *Kristallografiya* **6,** 714. [*Transl. Sov. Phys. Crystallogr.* **6,** 571].

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