Derivation and Identification of Composite mica twins -Extension of The Minitnal Rhombus Approach

Massimo Nespolo

複合ウンモ双晶の推論及び同定
－最小菱形単位アプローチの拡張－

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Derivation and Identification of Composite mica twins
－Extension of The *Minimal Rhombus* Approach－

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Abstract

The identification of composite twins of $1M$ mica from the diffraction pattern is easily accomplished by analyzing the number and disposition of reflections along nine translationally independent reciprocal lattice rows parallel to c^*, which define a sort of asymmetric unit in reciprocal space, called *minimal rhombus*. Besides $1M$, other polytypes frequently occur in micas and they often form twins too. The extension of the minimal rhombus approach to the other polytypes is in principle hindered by the appearance of weak reflections violating the so-called *additional reflection conditions*. Because of these weak reflections, in principle reciprocal lattice rows which are translationally equivalent in $1M$ are no more such in other polytypes. However, these weak reflections can be recognized and distinguished from those characterizing the ideal structure ; by neglecting them, the minimal rhombus approach can be applied to all polytypes. A mathematical demonstration of the applicability of this method is here given.

Keywords : Diffraction pattern, Mica, Polytypes, Polytypism, Twinning, Twins

1. INTRODUCTION

Micas are important rock-forming minerals on Earth and their weathering products extensively occur in clay minerals. The relevance of mica polymorphism in metamorphic rocks is well known, and the possibility of employing mica polytypes as geothermo-barometer has been proposed [1].

Micas belong to layer silicates group and their polytypes are among the most representative examples of complex structures made up by a single basic structural unit : the *mica layer*. This consists of an octahedral sheet (O) sandwiched between two tetrahedral sheets (T) having the apices oriented towards the O sheet ; between two next layers, interlayer cations (I) take place (Fig. 1). The chemical formula of micas is expressed as (K^+, Na^+, Ca^{2+}, Ba^{2+},□)(M^{2+},$M^{3+}Li^+$,□)$_3$ (Si^{4+},Al^{3+},

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$Fe^{3+})_4O_{10}(OH)_2$. M^{2+} and M^{3+} represent di- and trivalent cations respectively, □ is a vacancy. The OH group can be substituted by F and, more rarely, by Cl or S. With respect to the co-ordination scheme, mica formula can be expressed as $IO_3T_4O_{10}(OH)_2$, where *I*, *O* and *T* stand for *interlayer*, *octahedral* and *tetrahedral* respectively. The coordination in the interlayer region is ideally hexagonal, but in the real structure it is trigonal antiprismatic or—more rarely—trigonal prismatic [2,3].

A pair of almost exactly orthohexagonal axes (*a*, *b*) in the plane of the layer can be chosen in all polytypes, which define a *C*-centred cell : the parameters along these two axes slightly change with the chemical composition, but they closely keep obedience to the orthohexagonal relation $b = a3^{1/2}$. The width of the layer along *c* direction is about 10 Å. In the *O* sheet three cation sites exist in the primitive cell (Fig. 1-2) : assuming ideal symmetry of the layer, namely $C12/m(1)$[1], one of the three sites ($M1$) contains the centre of symmetry, whereas the other two ($M2$) are related by the symmetry plane. Depending whether two or all of these three sites are occupied, micas are divided into the two groups of *dioctahedral* and *trioctahedral*. In dioctahedral micas, since one of the three octahedral sites is empty, the distortions from the ideal structure are marked [2,3,5].

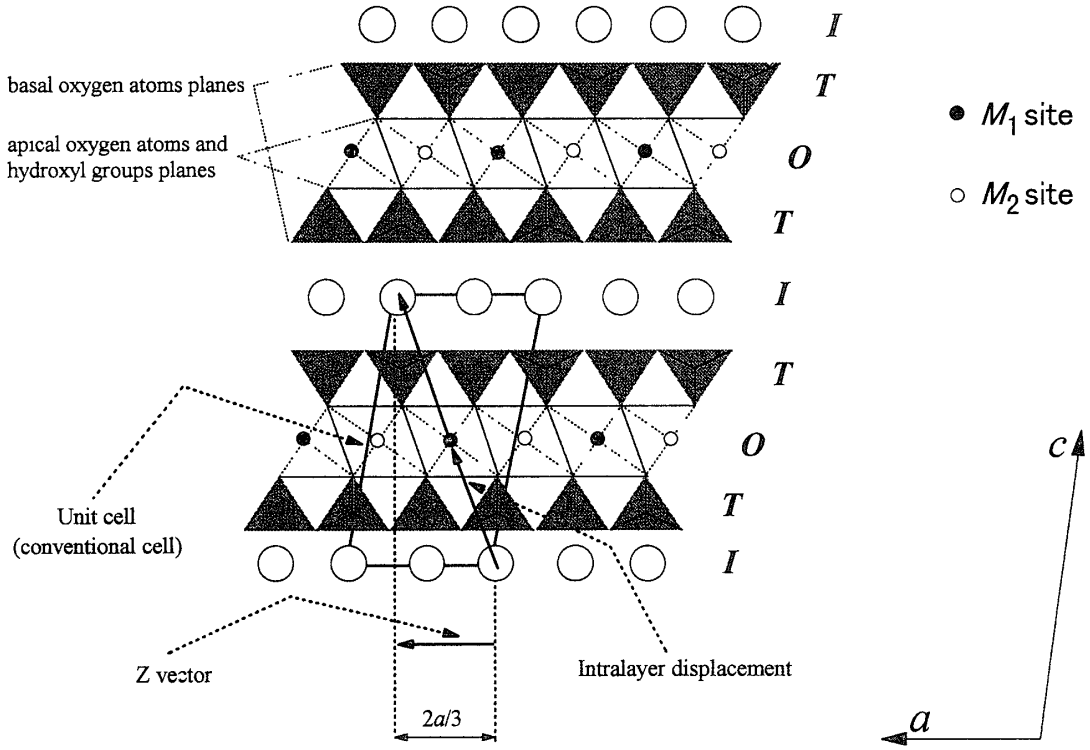

Fig 1. Projection along *b* axis of the mica structure, showing two layers with the same orientation(1*M* polytype). *I*, *O* and *T* represent interlayer region, octahedral sheet and tetrahedral sheet respectively. *M*1 and *M*2 cationic sites in the *O* sheet occupy crystallographically distinct positions (cf Fig 2) The scale along *c* is compressed because of drawing necessities (modified after [11])

[1]The layer group notation is that introduced by Dornberger-Schiff [4]. The round parenthesis indicates the direction of lacking periodicity.

Both O and T sheets have (ideal) trigonal symmetry and are staggered along the a axis by an integral submultiple of the translation periodicity (ideally $a/3$). The symmetry of the whole layer is thus reduced to monoclinic, but the symmetry of the atomic planes remains approximately trigonal [2,3]. As a consequence, micas extensively show pseudo-symmetries in both the direct and the reciprocal space. A pseudo-hexagonal lattice, in general multiple, is common to all mica polytypes [5], which also corresponds to the twin lattice, according to Friedel's [6,7] definition.

Layers are stacked by both translation and rotations : the translation is in the direction defined by the layer stagger (c axis), while the rotations are in the plane of the layer and correspond to $n \cdot 60°$, where $n = 0$-5 [8]. Polytypes differ in the periodicity along c axis and in the stacking sequence, whose description and identification is fairly complex [9]. Besides, because of their marked pseudo-symmetries, micas frequently undergo twinning, and the relative rotations of individuals in mica twins and of layers in mica polytypes are almost identical [10]. Polytypes and twins are thus two aspects arising from the same basic structural features, and the recognition of twinning by diffraction methods is particularly difficult [11].

The period of the single-layer polytype coincides with the layer width along c axis (about 10 Å) and is labelled c_1. In reciprocal space it corresponds to a period along c^* axis of about 0.1 $Å^{-1}$, which is labelled c^*_1 [12]. In an N-layer polytype, along reciprocal lattice rows parallel to c^* in the c^*_1 repeat there are as many nodes as the number of layers in the polytype. The corresponding

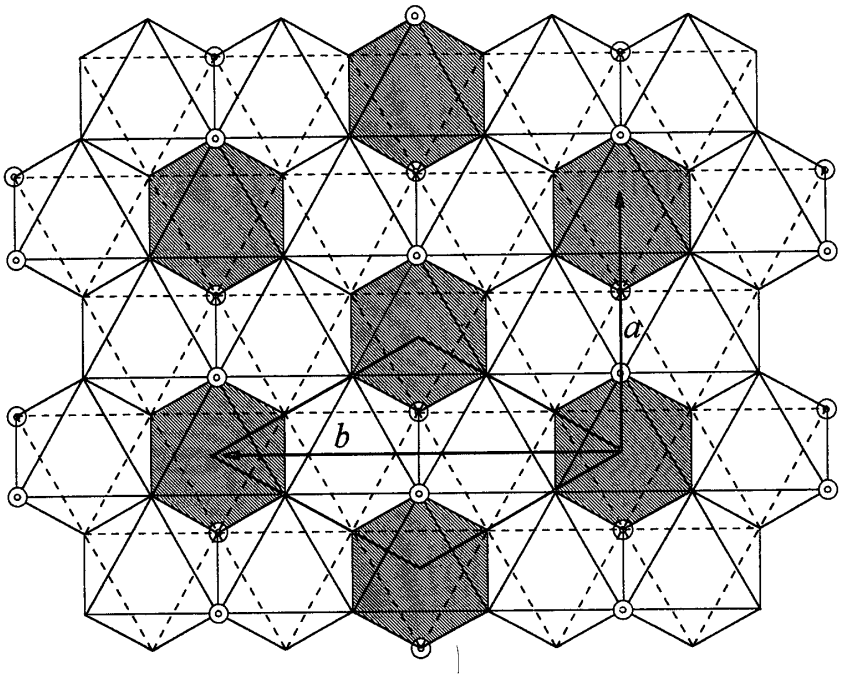

Fig 2. Projection of the O sheet onto the (001) plane. a and b are the (pseudo) - orthohexagonal axes($b \approx a3^{1/2}$). Shaded and unshaded octahedra represent $M1$ and $M2$ sites respectively. Double circles are OH groups. In the ideal layer symmetry $C12/m(1)$, the two-fold axis is along b and the mirror plane normal to b, so that $M1$ site contains the centre of symmetry. The rhombus-shaped mesh is the primitive mesh with pseudo-hexagonal symmetry, it contains one $M1$ site and two $M2$ sites (modified after [11]).

reflections can be partly absent from the diffraction pattern due to particular positions occupied by the atoms in the unit cell. These absences correspond partly to space-group extinctions and partly to non-characteristic orbits of space groups [13] and are expressed through the *reflection conditions* [14]. In the real structure there are several distortions from the ideal geometry [15,16], whose effect is especially relevant in case of dioctahedral micas [9]. As a consequence, some of the reflections expected to be absent actually appear, with low intensity. In trioctahedral micas the distortions are relatively limited, and the reflections violating the reflection conditions are either really absent or very weak. For this reason they have been called *dioctahedral reflections* [17].

$1M$ is the simplest polytype. Its periodicity corresponds to a single layer, and thus the diffraction pattern shows only one reflection in the c^*_1 ($0.1\,\text{Å}^{-1}$) repeat along each reciprocal lattice row parallel to c^*. Weak reflections never appear between two reflections separated by c^*_1 and this makes relatively easy the interpretation of the diffraction patterns of $1M$ twins, which is accomplished by analyzing the number and disposition of reflections along nine translationally independent reciprocal lattice rows [18]. In this paper it will be shown that the same approach can be used to deal with the other polytypes as well, with the condition of neglecting the weak reflections that would be absent for an ideal geometry of the mica layer.

2. TWINNING

Twins are oriented crystal associations of two or more crystals of the same compound. The operation relating two crystals in a twin is a point group operation called *twin operation* : it cannot belong to the point group of the crystal, otherwise it would produce a parallel growth. The lattice common to the individuals is called *twin lattice* and the symmetry element of the twin lattice that relates a pair of twinned crystals is called *twin element*. The twin element expresses the geometrical law relating a pair of twinned crystals, which is called *twin law* [6,7]. When more than two crystals are twinned according to two or more different twin laws the term *composite twin* is used [18].

3. SYMBOLIC DESCRIPTION OF MICA POLYTYPES

The descriptive symbolism of polytypes developed by Ramsdell [19] is used also for micas. Ramsdell's symbols are written as NS_n, where N is the number of layers, S is the symbol of the syngony (crystal system) according to the IUCr *Ad-Hoc* committee recommendations [20], and n a sequence number, usually (but not always) indicating the order in which polytypes have been discovered. Due to the exponential increase of the number of possible polytypes with the number of layers in the repeat unit [21,22] Ramsdell notation has to to be accompanied by some more informative symbolism, from which the basic properties, first of all symmetry, can be obtained.

Zvyagin [23] introduced a numerical vectorial description (Z symbols, hereafter) giving the stacking of half-layers, as defined by the interlayer cations and the origin of the O sheet. Z symbols are oriented symbols linked to a space-fixed, orthohexagonal reference with (a, b) axes in (001) plane [23-26]. It has a and b axes ($a < b$) directed North and West respectively (up and right in the plane of the page ; see Fig. 3). This reference has been labelled C_1 [12,27] ; for non-orthogonal N-layer polytypes, the period along c axis of this setting corresponds to $3N$ layers (Fig. 4). The vector connecting the origin of the octahedral sheet with the nearest interlayer site and vice versa, always looking at the sequence of layers in the same direction, is called *intralayer displacement* : its

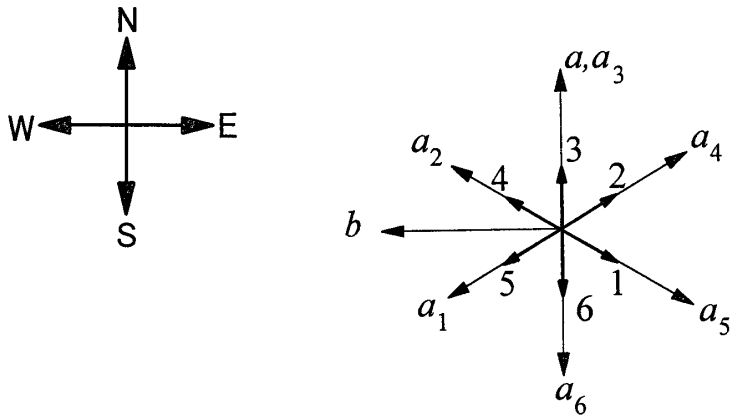

Fig 3. Axes of the space-fixed reference (C_1 setting) and of the structure-related references in the six possible orientations, and corresponding Z symbols. The two a and b axes in the plane of the layer, directed N and W, define the C_1 setting, having c axis (ideally) perpendicular to the layer. The six axes a_1-a_6 indicate the six possible directions of the structure related references, and thus the six possible orientations of the layer (b_1-b_6 axes, not shown in the figure, are normal to the corresponding a axes in the plane of the layer, forming right-handed references). The direction of the intralayer displacement is indicated by Z symbol i (i=1-6) when the a_i axis is parallel to the space fixed a axis (modified after [26]).

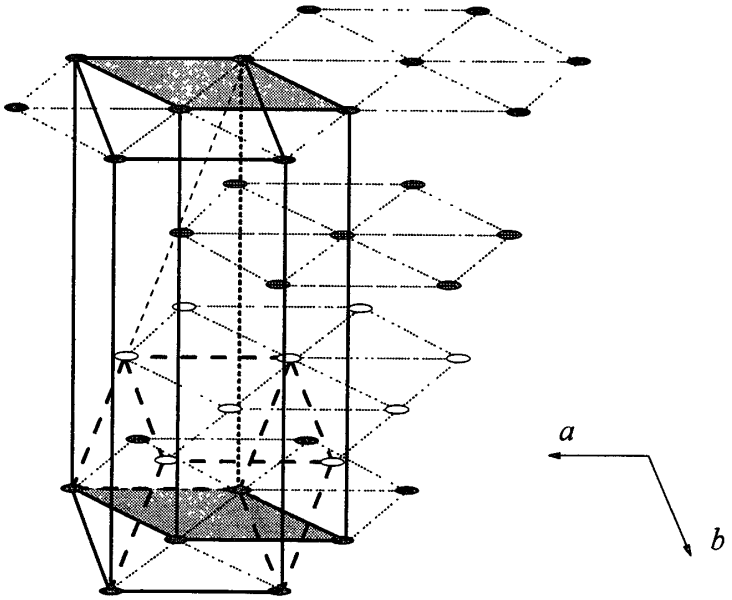

Fig 4. Unit cells of mica lattice. The layers are represented by lattice planes with symmetry ideally hexagonal. Each layer is staggered along a axis by-$a/3$: an ideally orthogonal cell is thus obtained by stacking three layers. The conventional cell (ideally monoclinic) is shown by dashed lines. The (pseudo)-orthohexagonal cell is shown by solid lines and has the two axes in the plane of the layer (a, b) in common with the conventional cell. The dashed meshes correspond to the primitive mesh shown in Fig. 2 and locate a pseudo-hexagonal cell, which commonly is used only for trigonal or hexagonal polytypes (modified after [12]).

projection on the (001) plane has length $|a|/3$ (Fig. 1). There are six possible orientations for each half layer, indicated by the six structure-related a_i axes (i = 1-6). The projection of the intralayer displacement is indicated by the Z symbol i (i = 1-6) when the a_1 axis is parallel to the space-fixed axis a (Fig. 3)[5,23-26]. The (a, b) components (s_x, s_y) of that projection, expressed by including the C centring condition when necessary, are given in Table 1. For the large majority of micas discovered to date the two half layers have the same intralayer displacements, so that the stacking vector for each layer (*Z vectors*) is obtained taking twice the components of the corresponding interlayer displacement, namely ($2s_x$, $2s_y$) (Table 1). Since $\pm 2/3$ is translationally equivalent to $\mp 1/3$, in practice the (a, b) components of the Z vectors are the same as those of the intralayer displacements, but with the signs exchanged [26].

Table 1. Z symbols and (a, b) components of the corresponding intralayer vectors in the C_1 setting. s_X and s_Y are expressed as multiples of 1/3 (after [5])

Z symbol	(s_X, s_Y)
3	(1, 0)
4	(-1, -1)
5	(1, -1)
6	(-1, 0)
1	(1, 1)
2	(-1, 1)

4. METRIC RELATIONS IN C^1 SETTING AND THE DEFINITION OF THE *MINIMAL RHOMBUS*

The cell of the twin lattice is a (pseudo)-orthohexagonal cell which, for non-orthogonal polytypes, contains three repeat units (Fig. 4)[12]. Among the axial settings of micas recently introduced and classified [12,27], the most suitable one to describe the twin lattice is C_1 setting. For an N-layer polytype, the period along c axis (c_N) is approximately Nc_1. In reciprocal space $a^* > b^*$; the period along c^* axis in C_1 setting is $c^*_{3N} = c^*_3/N = c^*_1/3N \approx 0.1/3N$ Å^{-1}. In this setting, the l index of a reciprocal lattice node of an N-layer non-orthogonal polytype may take one of the three values: 0, 1 or 2 (mod 3) in the c^*_N repeat. The orientation of c axis classifies non-orthogonal mica polytypes into two *Classes*, for which the following relations hold [12,27]:

$$\textit{Class } a \text{ polytypes}: \quad l \pmod 3 = h \pmod 3 \qquad (1a)$$

$$\textit{Class } b \text{ polytypes}: \quad l \pmod 3 = k \pmod 3. \qquad (1b)$$

In the twin lattice, reciprocal lattice rows from different crystals related by $n60^\circ$ overlap, but nodes on these rows have in general different l indices, as shown by Eq. (1a) and (1b).

For 1M polytype, in the twin reciprocal lattice 1, 2 or 3 reflections in the c^*_1 (0.1 Å^{-1}) repeat may appear (Fig. 5)[18]. Taking into account the geometry of the diffraction pattern (number and

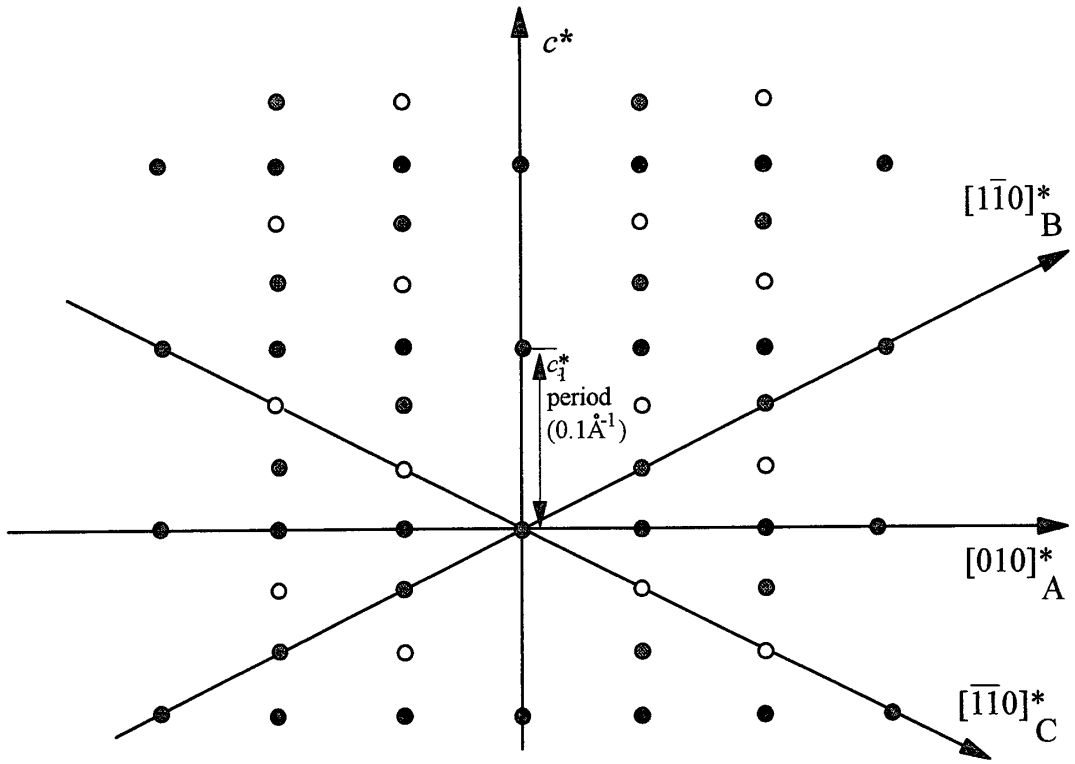

Fig 5. A reciprocal lattice plane from a 1*M* twin formed by three individual rotated by 120° and 240°. Black, grey and white circles represent reciprocal lattice nodes belonging to individuals A, B and C respectively. The height of the nodes is given by Eq. (1*a*). The three reciprocal lattice planes $(0kl)_A$, $(h\bar{h}l)_B$ and $(hhl)_C$, located by the common c^* axis and by the directions $[010]^*_A$, $[1\bar{1}0]^*_B$ and $[\bar{1}\bar{1}0]^*_C$ respectively, overlap. The resulting reciprocal lattice planes shows thus six nodes and it might be mistaken for the reciprocal plane of an untwinned 6-layer polytype.

disposition of the reflections) and disregarding the intensities, reciprocal lattice rows parallel to c^* and related by $(3p, 3q)$ translations along (a^*, b^*) axes (p and q are coprime integers of the same parity) - both of the single-crystal and the twin lattice - are translationally equivalent. It follows that there are only nine translationally independent rows. These rows define two units of rhombic shape in reciprocal space : the *tessellation rhombus*, which represents a unit by which the whole reciprocal space can be tessellated, and the *minimal rhombus*, which represents a sort of asymmetric unit containing the complete information on the geometry of the reciprocal space [18]. The six possible equivalent orientations of the two rhombi define a *star-polygon* (Fig. 6). By comparing the minimal rhombus obtained from the diffraction pattern with the theoretically calculated minimal rhombi, the relative orientation of crystals in the twin can be obtained.

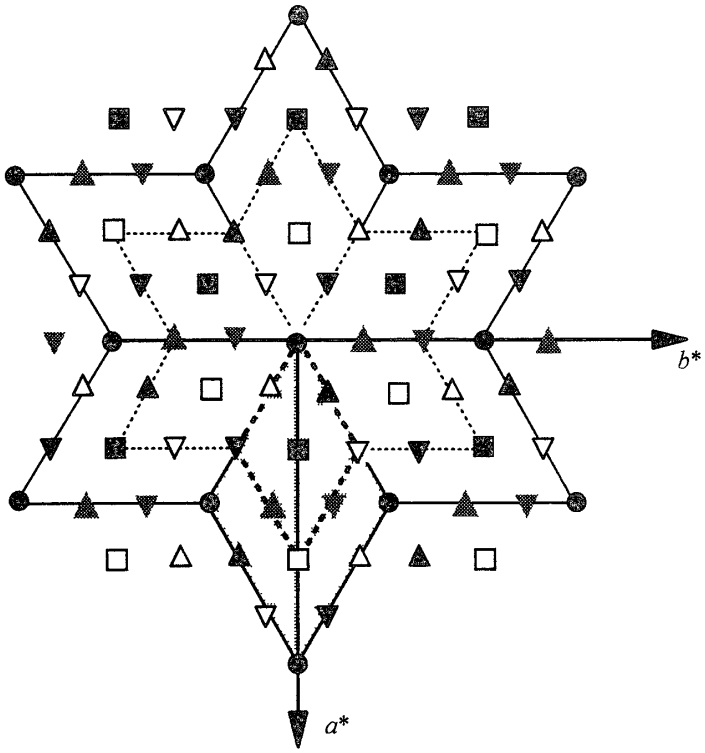

Fig 6. The transfationally independent portions of the reciprocal lattice space of mica twins The smallest unit (shaded region limited by dashed lines) is the *minimal rhombus*, a sort of asymmetric unit containing the whole information about the geometry of the reciprocal space A larger unit (shaded region limited by solid lines) is the *tessellation rhombus*, a unit by which the whole reciprocal space can be *tessellated, i.e.* reproduced by translations Six orientations of the minimal and of the tessellation rhombus are possible around the origin, which differ for the disposition of the reciprocal lattice rows. These six orientations have to be considered when comparing the calculated rhombi with those measured from the diffraction pattern. Circles, squares and triangles represent lattice rows . translationally equivalent rows are shown by the same symbol. For a detailed classification of the reciprocal lattice rows see [18] (modified after [18]).

5. MICA STRUCTURE FACTOR IN TERMS OF ZVYAGIN'S FUNCTIONS

The general expression of the structure factor of mica polytypes is given by Zvyagin's functions [5], calculated in the C_1 setting. As shown by Nespolo and Kogure [28], Zvyagin's functions can be expressed as:

$$F(hkl) = \sum_{m=0}^{N-1} F_m(hkl) = \sum_{m=0}^{N-1} \Phi_m(hkl) \exp 2\pi i \left[hu_x(m) + ku_y(m) + lu_z(m) \right]$$
$$= \sum_{m=0}^{N-1} \Phi_3(h_m k_m l) \exp 2\pi i \left[hu_x(m) + ku_y(m) + lu_z(m) \right] \quad (2)$$

where :
F_m is the contribution to the structure factor from the m^{th} layer ;
$[u_x(m) / u_y(m) / u_z(m)]$ are the x, y, z components of the stacking vector leading from the origin of the 1st layer to the origin of the m^{th} one ;

$$\Phi_m(hkl) = \sum_{j=1}^{n} f_j \exp 2\pi i \left[h x_{im}(N, j, 0) + k y_{im}(N, j, 0) + l z(N, j, 0) \right] \tag{3}$$

in which :
$[x_{im}(N, j, 0) / y_{im}(N, j, 0) / z(N, j, 0)]$ are the fractional atomic coordinates of the j^{th} atom inside the first layer ($m = 0$) of a N-layer polytype ;
$i_m(m = 0, N-1 ; i_m = 1,2,...6)$ is the orientation of the *m-th* layer.
z coordinate is not affected by the layer orientation. This function is equivalently expressed as

$$\Phi_3(h_m k_m l) = \sum_{j=1}^{n} f_j \exp 2\pi i \left[h_m x_3(N, j, 0) + k_m y_3(N, j, 0) + l z(N, j, 0) \right] \tag{4}$$

in which the fractional atomic coordinates are expressed for orientation Z = 3 of the first layer, while are the Miller indices to be rotationally transformed [28].

The origin is taken at the centre of symmetry located in $M1$ site (Fig. 1) and only the real part of Φ_3 needs to be taken into account : it is hereafter labelled A_3. z_{OH} is the z coordinate of both hydroxyl atoms and apical oxygen atoms, which are on the same atomic plane ; z_{OB} is the z coordinate of the basal oxygen atoms (Fig. 1). Assuming ideal geometry of the layer, the A_3 function can be written as [28] :

$$\begin{aligned} A_3(hkl) = {} & f_{M_1} + 2 f_{M_2} \cos 2\pi k/3 + f_I \cos 2\pi (h/3 + l/2N) \\ & + 2 f_O (1 + 2 \cos 2\pi k/3) \cos 2\pi (h/3 + l z_{OH}/N) \\ & + 4 f_T \cos 2\pi (h/3 + l z_T/N) \cos 2\pi k/3 \\ & + 2 f_O \left[\cos 2\pi (-h/6 + l z_{O_B}/N) + 2 \cos 2\pi (h/12 + l z_{O_B}/N) \cos 2\pi k/4 \right] \end{aligned} \tag{5}$$

Peculiarities of the cation composition are in the atomic scattering factor. $4f_T$ is a short notation that depends upon the actual occupation of T sites ; f_I represents the atomic scattering factor of the interlayer cations.

Eq. (5) can be simplified in the term regarding the basal oxygen atoms contribution. Since $h/12 = -h/6 + h/4$ and remembering that $2\cos(A)\cos(B) = \cos(A-B)+\cos(A+B)$ and $2\sin(A)\cos(B) = \sin(A-B)+\sin(A+B)$, the second term can be written as :

$$\begin{aligned}\cos 2\pi\left(\frac{h}{12}+\frac{lz_{O_B}}{N}\right)\cos 2\pi\left(\frac{k}{4}\right)&=\cos 2\pi\left(-\frac{h}{6}+\frac{lz_{O_B}}{N}\right)\cos 2\pi\left(\frac{h}{4}\right)\cos 2\pi\left(\frac{k}{4}\right)\\&\quad-\sin 2\pi\left(-\frac{h}{6}+\frac{lz_{O_B}}{N}\right)\sin 2\pi\left(\frac{h}{4}\right)\cos 2\pi\left(\frac{k}{4}\right)\\&=\frac{1}{2}\cos 2\pi\left(-\frac{h}{6}+\frac{lz_{O_B}}{N}\right)\left[\cos 2\pi\left(\frac{h-k}{4}\right)+\cos 2\pi\left(\frac{h+k}{4}\right)\right]\\&\quad-\frac{1}{2}\sin 2\pi\left(-\frac{h}{6}+\frac{lz_{O_B}}{N}\right)\left[\sin 2\pi\left(\frac{h-k}{4}\right)+\sin 2\pi\left(\frac{h+k}{4}\right)\right]\end{aligned}\tag{6}$$

However, because of the C-centring reflection condition $h + k = 0(\mathrm{mod}\ 2)$, which implies also $h-k = 0(\mathrm{mod}\ 2)$, it follows that $2\pi(h\pm k)/4 = K\pi$ (K integer) and $\cos[2\pi(h\pm k)/4] = \pm 1$, $\sin[2\pi(h\pm k)/4] = 0$. The sine terms thus disappear; the remaining cosine terms lead to a contribution that can be 0 or $\pm$ the one in parenthesis. The term $\cos 2\pi(h/4)\cos 2\pi(k/4)$ is 1 when $(h + k) = 0(\mathrm{mod}\ 4)$ and -1 when $(h + k) = 2(\mathrm{mod}\ 4)$. Eq. (6) becomes:

$$\cos 2\pi\left(\frac{h}{12}+\frac{lz_{O_B}}{N}\right)\cos 2\pi\left(\frac{k}{4}\right)=\cos 2\pi\left(-\frac{h}{6}+\frac{lz_{O_B}}{N}\right)\left[\frac{1+(-1)^h}{2}\cdot(-1)^{\frac{h+k}{2}}\right]\tag{7}$$

The expression in square brackets simply assumes the values 0 or ± 1 according to h and k values. A_3 function can thus be simplified into:

$$\begin{aligned}A_3(h_mk_ml)=&f_{M_1}+2f_{M_2}\cos 2\pi k_m/3+f_I\cos 2\pi(h_m/3+l/2N)\\&+2f_O(1+2\cos 2\pi k_m/3)\cos 2\pi(h_m/3+lz_{OH}/N)\\&+4f_T\cos 2\pi(h_m/3+lz_T/N)\cos 2\pi k_m/3\\&+2f_O\cos 2\pi(-h_m/6+lz_{O_B}/N)\left\{1+\left[1+(-1)^{h_m}\right]\cdot(-1)^{\frac{h_m+k_m}{2}}\right\}\end{aligned}\tag{5'}$$

6. PERIODIC REPETITION OF THE SYSTEMATIC ABSENCES

The expression of the structure factor for mica polytypes (Eq. 2) can be re-written putting in evidence the atomic contributions. Neglecting the term relative to the origin shift when the origin of the structure does not coincide with the origin of the first layer (external to the summations), it assumes the form:

$$\begin{cases}F(hkl)=\sum_{j=1}^{n}f_j\Omega_j\\\Omega_j=\sum_{m=0}^{N-1}\exp 2\pi i\left[h_mx_3(N,j,0)+k_my_3(N,j,0)+lz(N,j,0)\right]\exp 2\pi i\left[hu_x(m)+kh_y(m)+lu_z(m)\right]\end{cases}\tag{2'}$$

A systematic absence appears when the resulting waves diffracted by each layer destructively interfere leading to an (ideally) zero contribution. However, the wave diffracted by each layer in

turn receives a contribution from each atomic site. The final destructive interference can result in two ways :

1. the contribution from each atomic site [that is at least formally separable, as in Eq. (2')] *does not* lead to cancellation (site by site) but only the final, resulting wave is "extinguished". This means that the contribution from one site is canceled by those from the other sites ;
2. the contribution from each atomic site (summed up over all the layers) is (ideally) zero. The final wave is zero because is the sum of zero contributions.

The first case would hardly lead to *systematic* absences, since different atoms possess different atomic scattering factors, which vary with the scattering angle in a different way. Since the absence should be systematic, regular and repeated, the second route is the reliable one.

Starting from the simplified expression of Zvyagin's A_3 function (Eq. 5'), let us consider how does it transforms by incrementing h and k by integral multiples of three. For the sake of clearness, $3p$ will be the values added to h and $3q$ the one added to k ($3p_m$ to h_m, $3q_m$ to k_m, m being Z symbol).

6.1 Layer with orientation Z = 3.

Contributions from all sites different from basal oxygen atoms have h and k divided by 3 and thus they remain unchanged by adding $3p_3$ and $3q_3$. The situation for basal oxygen sites requires a short analysis.

From the C-centring condition the following parity rules derive : $h_3+k_3 = 0(\mathrm{mod}\ 2)$; $p_3+q_3 = 0(\mathrm{mod}\ 2)$; $(h_3+p_3)(\mathrm{mod}\ 2)= (-1)^{p_3}h_3(\mathrm{mod}\ 2)$; $(k_3+q_3)(\mathrm{mod}\ 2)= (-1)^{q_3}k_3(\mathrm{mod}\ 2)$. Furthermore, $(-1)^{3p_3} = (-1)^{p_3}$ and $(-1)^{3q_3} = (-1)^{q_3}$.

The addition of $3p_3$ in the last term of Eq. (5') leads to :

$$\begin{aligned}\cos 2\pi\left(-\frac{h_3+3p_3}{6}+lz_{O_B}\right)&=\cos 2\pi\left(-\frac{h_3}{6}+lz_{O_B}\right)\cos(-p_3\pi)-\sin 2\pi\left(-\frac{h_3}{6}+lz_{O_B}\right)\sin(-p_3\pi)\\&=(-1)^{p_3}\cos 2\pi\left(-\frac{h_3}{6}+lz_{O_B}\right)\end{aligned} \tag{8}$$

so that the multiplication factor becomes :

$$(-1)^{p_3}\left\{1+\left[1+(-1)^{h_3+p_3}\right](-1)^{\frac{h_3+k_3+p_3+q_3}{2}}\right\} \tag{9}$$

The ratio of the contribution from this site and the original one is thus :

$$\frac{(-1)^{p_3}\left\{1+\left[1+(-1)^{h_3+p_3}\right](-1)^{\frac{h_3+k_3+p_3+q_3}{2}}\right\}}{1+\left[1+(-1)^{h_3}\right](-1)^{\frac{h_3+k_3}{2}}} \tag{10}$$

The denominator can assume the values ± 1 and $+3$, while the numerator ± 1 and ± 3. As a result, moving from reciprocal lattice node (h_3, k_3, l) to (h_3+3p_3, k_3+3q_3, l) the contribution of the basal oxygen term is just multiplied by ± 1, ± 3 or $\pm 1/3$. In terms of Eq. (2') this means that:

$$\begin{aligned} &\Omega_{j\neq O_B}(h_3+3p_3\,,\,k_3+3q_3\,,\,l)=\Omega_{j\neq O_B}(h_3\,,\,k_3\,,\,l)\\ &\Omega_{O_B}(h_3+3p_3\,,\,k_3+3q_3\,,\,l)=\omega\cdot\Omega_{O_B}(h_3\,,\,k_3\,,\,l)\\ &\omega=\pm 1\,,\,\pm 3\,,\,\pm 1/3 \end{aligned} \tag{11}$$

If $\Omega_{O_B}(h_3, k_3, l)=0$ also $\Omega_{O_B}(h_3+3p_3, k_3+3q_3, l)=0$. Therefore, within the ideal geometrical model, every systematic absence is repeated regularly along a^* and b^* by intervals of integral (mod 3) values.

6.2 Layers with orientation Z ≠ 3.

The six functions A_1-A_6, expressed in terms of the atomic coordinates in each layer, can be substituted by the A_3 function, expressed in terms of the atomic coordinates in the layer with orientation 3, but with the Miller indices rotationally transformed (Eqs. 3-4). Following Arnold [29], covariant components are written as row matrices. The general transformation rule applying to Miller indices when passing from this layer to another one is:

$$\begin{cases} h_m=h_3(\mathbf{U}_{3\to m})_{11}+k_3(\mathbf{U}_{3\to m})_{21}\\ k_m=h_3(\mathbf{U}_{3\to m})_{12}+k_3(\mathbf{U}_{3\to m})_{22} \end{cases} \tag{12}$$

whereas l does not change. Adding $3p_3$ to h_3 and $3q_3$ to k_3 the transformation rule is exactly the same:

$$\begin{cases} p_m=p_3(\mathbf{U}_{3\to m})_{11}+q_3(\mathbf{U}_{3\to m})_{21}\\ q_m=p_3(\mathbf{U}_{3\to m})_{12}+q_3(\mathbf{U}_{3\to m})_{22} \end{cases} \tag{12'}$$

The rotation matrix elements, shown in Table 2 (after [30]), assume only the values ± 1, $\pm 1/2$ [elements **U**(11), **U**(21) and **U**(22) of the rotation matrices] and ± 1, $\pm 3/2$ [element **U**(12)]. Disregarding the values $+1$ (layer in orientation Z = 3) and -1 (layer in orientation Z = 6), which lead to the situation described in the previous paragraph, the result in the rotated layers can be easily calculated by means of the correspondences:

$$\begin{aligned} &h_3+3p_3\leftrightarrow h_m+3p_m=\pm\frac{h_3\pm k_3}{2}\pm\frac{3}{2}(p_3\pm q_3)\\ &k_3+3q_3\leftrightarrow k_m+3q_m=\pm\frac{3h_3\pm k_3}{2}\pm\frac{3}{2}(3p_3\pm q_3) \end{aligned} \tag{13}$$

Table 2. Rotation matrices $U_{3\to m}$ representing n60° counterclockwise rotations around the direction normal to the layer (after [30]). Matrices are given for a row-matrix representation of the covariant components, following the crystallographic standard [29]. i_m is the orientation in C_1 setting, expressed through the corresponding Z symbol of the m-th layer.

i_m	$3\wedge 1_m$	$U_{3\to m}$	i_m	$3\wedge i_m$	$U_{3\to m}$
1	240°	$\bar{1}/2\ \ 3/2\ \ 0$ $\bar{1}/2\ \ \bar{1}/2\ \ 0$ $0\ \ 0\ \ 1$	4	60°	$1/2\ \ \bar{3}/2\ \ 0$ $1/2\ \ 1/2\ \ 0$ $0\ \ 0\ \ 1$
2	300°	$1/2\ \ 3/2\ \ 0$ $\bar{1}/2\ \ 3/2\ \ 0$ $0\ \ 0\ \ 1$	5	120°	$\bar{1}/2\ \ \bar{3}/2\ \ 0$ $1/2\ \ \bar{1}/2\ \ 0$ $0\ \ 0\ \ 1$
3	0°	$1\ \ 0\ \ 0$ $0\ \ 1\ \ 0$ $0\ \ 0\ \ 1$	6	180°	$\bar{1}\ \ 0\ \ 0$ $0\ \ \bar{1}\ \ 0$ $0\ \ 0\ \ 1$

6.2.1 Sites different from the basal oxygen.

The characteristic contribution depends upon $h_m/3$ and/or $k_m/3$, so that:

$$\cos 2\pi\left(\frac{h_m \pm \frac{3}{2}(p_3 \pm q_3)}{3}\right) = \cos 2\pi\left(\frac{h_m}{3}\right)\cos \pi(p_3 \pm q_3) \mp \sin 2\pi\left(\frac{h_m}{3}\right)\sin \pi(p_3 \pm q_3) \qquad (14)$$
$$= \cos 2\pi\left(\frac{h_m}{3}\right)$$

with the same result for k. Also for layers in orientation different from Z = 3, the contribution from these sites does not change adding an integral multiple of three to h and k.

6.2.2 Basal oxygen sites

$$\cos 2\pi\left(-\frac{h_m \pm \frac{3}{2}(p_3 \pm q_3)}{6} + \frac{lz}{N}\right) = \cos 2\pi\left(-\frac{h_m}{6} + \frac{lz}{N}\right)\cos 2\pi\left(\pm\frac{p_3 \pm q_3}{4}\right) \qquad (15)$$
$$\mp \sin 2\pi\left(-\frac{h_m}{6} + \frac{lz}{N}\right)\sin 2\pi\left(\pm\frac{p_3 \pm q_3}{4}\right)$$

Since $p_3 + q_3 = 0 (\mathrm{mod}\ 2)$, the related term is always $\pm K\pi$, with K integer. Once more the sine term is zero, while the cosine term is ± 1. The coefficient (+1 or −1) depends upon which of the six possible layers is involved and, in terms of the original (not rotated) values h_3, k_3, p_3 and q_3, it obeys the correspondence rule:

$$\cos\left(\pm\frac{p_3+q_3}{2}\pi\right)=(-1)^{p_3+q_3} \qquad \cos\left(\pm\frac{p_3-q_3}{2}\pi\right)=(-1)^{p_3-q_3} \tag{16}$$

while the contribution from the added p_3 and q_3 obeys the rule:

$$\begin{aligned}(-1)^{\pm\frac{3}{2}(p_3+q_3)}&=(-1)^{\pm\frac{3}{2}(3p_3-q_3)}=(-1)^{p_3+q_3}\\(-1)^{\pm\frac{3}{2}(p_3-q_3)}&=(-1)^{\pm\frac{3}{2}(3p_3+q_3)}=(-1)^{p_3-q_3}\end{aligned} \tag{17}$$

Finally, although the actual value of the multiplication coefficient can be a quite complex function of h_m, k_m, p_3 and q_3, the possible values are the same as in the layer with orientation Z = 3, namely ±1, ±3, ±1/3.

The structure factor (Eq. 2) is made up just by as many A_3 functions as the number of layers, each expressed in terms of the rotationally transformed Miller indices, multiplied by an exponential term where the atomic coordinates do not appear. In that exponential term the origin shift of each layer appears, which takes always the values 0 or ±1/3 for both h and k [5]. By adding and integral multiple of 3 to h or k also the contribution from this exponential term does not change. Therefore, the systematic absences along reciprocal lattice rows parallel to c^* are repeated along a^* and b^* according to $3p$ and $3q$, p and q being coprime integers of the same parity.

Thinking now to the effect of distortions from the ideal geometry, the "absent" reflections actually appear, but with a weak intensity. This intensity is a function of f_j and Ω_j and in general will not follow the periodicity found in the hypothesis of $\Omega_j = 0$. However, with the limited aim of distinguishing "permitted" reflections (Ω_j larger than a certain threshold) from "weak" (ideally absent) reflections (Ω_j smaller than a certain threshold), the above results are straightforwardly applicable. From Eq. (11), since the highest possible value of ω is 3, the repetition law is still valid and can be expressed as:

$$F(h_m, k_m, l) \leq F_{min} \Rightarrow F(h_m+3p_m, k_m+3q_m, l) \leq 3F_{min} \tag{18}$$

where $F_{min} = 0$ if the structural distortions are neglected.

7. CONCLUSIONS

The identification of the individual orientation in the twin of the simplest mica polytype, *i.e.* $1M$, is accomplished in the easiest and most general way by considering a sort of asymmetric unit in reciprocal space. This unit is called *minimal rhombus* and gives the number and disposition of the reflections along nine translationally independent reciprocal lattice rows. The comparison of the theoretically derived minimal rhombus with the one obtained from the measured diffraction pattern identifies the orientation of crystals in the twin. The application of this method to longer period polytypes is in principle hindered by the appearance of weak reflections violating the reflection conditions calculated for ideal geometry of the unit layer. However, these reflections have weak intensities, especially in trioctahedral micas. In the diffraction pattern two kinds of reflections can

thus be classified : "permitted" (strong reflections) and "forbidden" (weak reflections). Each of these two kinds of reflections has the same translational periodicity, as expressed through ($3p$, $3q$) translations along (a^*, b^*) axes of the C_1 setting, which is also the periodicity valid for the reciprocal lattice rows of $1M$ polytype. This aspect allows the direct extension of the *minimal rhombus* approach to the derivation and identification of composite twins of polytypes others than $1M$ (to be published elsewhere).

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References.

[1] Sassi, F.P., Guidotti, C.V., Rieder, M. and De Pieri, R. (1994). On the occurrence of metamorphic $2M_1$ phengites : some thoughts on polytypism and crystallization conditions of $3T$ phengites. *Eur. J. Mineral.* **6**, 151-160.

[2] Sadanaga, R. and Takeda, H. (1969). Description of Mica Polytypes by New Unit Layers. *J. Mineral. Soc. Japan*, **9**, 177-184 (in Japanese).

[3] Takeda, H. and Sadanaga, R. (1969). New Unit Layers for Micas. *Mineral. J.*, **5**, 434-449.

[4] Dornberger-Schiff, K. (1959). On the nomenclature of the 80 plane groups in three dimensions. *Acta Crystallogr.*, **12**, 173.

[5] Zvyagin, B.B. (1967). *Electron diffraction analysis of clay mineral structures*. New York : Plenum Press, XIV+364 pp.

[6] Friedel, G. (1904). Étude sur les groupements cristallins. Extrait du *Bullettin de la Société de l'Industrie minérale*, Quatrieme serie, Tomes III e IV. Saint-Étienne, Societé de l'Imprimerie Thèolier J. Thomas et C., 485 pp.

[7] Friedel, G. (1926). *Leçons de Cristallographie*, Berger-Levrault, Nancy, Paris, Strasbourg, XIX+602 pp.

[8] Ross, M. Takeda, H. and Wones, D.R. (1966). Mica Polytypes : Systematic Description and Identification, *Science*, **151**, 191-193.

[9] Takeda, H. and Ross, M. (1995). Mica Polytypism : Identification and Origin. *Am. Mineral.*, **80**, 715-724.

[10] Sadanaga, R. and Takéuchi, Y. (1961). Polysynthetic twinning of micas. *Z. Kristallogr.*, **116**, S. 406-429.

[11] Nespolo, M. (1998). *Discovery of a complex mica polytype belonging to non-basic structural series, and its formation mechanism.* Doctoral dissertation, University of Tokyo, 257 pp.

[12] Nespolo, M., Takeda, H. and Ferraris, G. (1997). Crystallography of Mica Polytypes. *In* Merlino, S. (Ed.) *Modular aspects of minerals / EMU Notes in Mineralogy*, vol. 1. Budapest : Eötvös University press, 81-118.

[13] Engel, P., Matsumoto, T., Steinamann, G. and Wondratschek, H. (1984). *The non-characteristic orbits of the space groups. Z. Kristallogr.*, Supplement Issue No. 1.

[14] Hahn, Th. and Vos, A. (1996). Reflection conditions. *In* Hahn, Th. (Ed.) : *International Tables for Crystallography*, Vol. A, Section 2.13. Dordrecht / Boston / London : Kluwer Academic Publishers.

[15] Takéuchi, Y. (1965). Structures of brittle micas. *Proc. 13th Natl. Conf. Madison, Wisconsin, 1964*, *Clays and clay minerals*. Pergamon Press, 1-25.
[16] Griffen, D. T. (1992).Silicate Crystal Chemistry, Oxford University Press, 432p.
[17] Rieder, M. (1968). Zinnwaldite : Octahedral Ordering in Lithium-Iron Micas. *Science*, **160**, 1338-1340.
[18] Nespolo, M., Takeda, H., Ferraris, G. and Kogure, T. (1997b). Composite Twins of 1*M* Mica : Derivation and Identification. *Mineral. J.*, **19**, 173-186.
[19] Ramsdell, L.S. (1947). Studies on Silicon Carbide. *Am. Mineral.*, **32**, 64-82.
[20] Guinier, A., Bokij, G.B., Boll-Dornberger, K., Cowley, J.M., Ďurovič, S., Jagodzinski, H., Khrisna, P., DeWolff, P.M., Zvyagin, B.B., Cox, D.E., Goodman, P., Hahn, Th., Kuchitsu, K. and Abrahams, S.C. (1984). Nomenclature of Polytype Structures. Report of the International Union of crystallography *Ad-Hoc* Committee on the Nomenclature of Disordered, Modulated and Polytype Structures *Acta Crystallogr.* **A40**, 399-404.
[21] Mogami, K., Nomura, K., Miyamoto, M., Takeda, H. and Sadanaga, R. (1978). On the Number of Distinct Polytypes of Mica and SiC with a Prime Layer-Number. *Can. Mineral.*, **16**, 427-435.
[22] McLarnan, T.J. (1981). The number of polytypes in sheet silicates. *Z. Kristallogr.* **155**, 247-268.
[23] Zvyagin, B.B. (1962). A theory of polymorphism of micas. *Sov. Phys. Crystallogr.*, **6**, 571-580.
[24] Zvyagin, B.B., Vrublevskaya, Z.V., Zhukhlistov, A.P., Sidorenko, O.V. Soboleva, S.V. and Fedotov, A. F. (1979). High-voltage electron diffraction in the study of layered minerals. Moscow : Nauka Press, 224 pp. (in Russian)
[25] Zvyagin, B.B. (1985). Polytypism in contemporary crystallography, *Sov. Phys. Crystallogr.* **32**, 394-399.
[26] Zhukhlistov, A.P., Zvyagin, B.B. and Pavlishin, V.I. (1990). Polytypic 4M modification of Ti-biotite with nonuniform alternation of layers, and its appearance in electron-diffraction patterns from textures. *Sov. Phys. Crystallogr.*, **35**, 232-236.
[27] Nespolo, M., Takeda, H. and Ferraris, G. (1998). Representation of the axial settings of mica polytypes. *Acta Crystallogr., A***54**, 348-356.
[28] Nespolo, M. and Kogure, T. (1998). On the indexing of 3*T* mica polytype. *Z. Kristallogr.*, **213**, 4-12.
[29] Arnold, H. (1996). Transformations in crystallography. *In* Hahn, Th. (Ed.) : *International Tables for Crystallography* Vol. A, Section 5. Dordrecht / Boston / London : Kluwer Academic Publishers.
[30] Takeda, H. (1967). Determination of the Layer Stacking Sequence of a New Complex Mica Polytype : A4-layer Lithium Fluorophlogophite. *Acta Crystallogr.*, **22**, 845-853.

要　　旨

ウンモは主な造岩鉱物の一つであり，一つの単位層が積み重なることによって様々な種類（ポリタイプ）が形成される。X線或いは電子線の回折図形に表れる反射の強度分布の周期性を利用すると積層順序を決定することが出来る。しかし，双晶がある場合には上記の決定法は応用が難くなる。従って，実験で得られた回折図形を解釈する際に先ずは双晶の存在を確かめる必要がある。「最小菱形単位」という逆格子の非対称単位を利用することによって最も単純なポリタイプ（1*M*）の双晶の有無および双晶則を同定することが出来る。他のポリタイプにおいて，陽イオン置換などによる構造の変形によって弱い反射が回折図形に現れるので同様の方法を応用出来なくなる。ただし，その弱い反射を無視すれば全てのポリタイプにおいて上記の同定法が利用可能なことを本論文で数学的証明する。