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Article in *European Journal of Mineralogy* · November 2001

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Effects of the stacking faults on the calculated electron density of mica polytypes – The Đurovič effect

MASSIMO NESPOLO^{1,*} and GIOVANNI FERRARIS²

¹Japan Science and Technology Corporation, National Institute of Research in Inorganic Materials,
1-1 Namiki, Tsukuba-shi, Ibaraki 305-0044, Japan

²University of Torino, Department of Mineralogical and Petrologic Sciences,
Via Valperga Caluso 35, 10125 Torino, Italy

Abstract: The occurrence of residues in the Fourier map of OD structures (polytypes in which pairs of building modules are geometrically equivalent) in the positions of the 'virtual atoms' of the corresponding family structure derives from the presence of stacking faults inside an otherwise ordered (periodic) matrix. These residues are commonly spurious peaks deriving from the refinement of the structure with a single scale factor for both the family and the non-family reflections, which may be instead on a different scale because of the different peak shape and background characterizing the two types of reflections, resulting in broadening and streaking of the non-family reflections. The 'virtual atoms' occur in the same positions of the atoms corresponding to the stacking faults, but the spurious peaks are in a quantitative relation with them only if the stacking faults diffract coherently. The case of mica polytypes is illustrated also with the aid of examples taken from the literature.

Key-words: OD structures, micas, polytypes, structure refinement, disordered structures, stacking faults.

Introduction

The difference electron density of the first described *2O* polytype and of a coexisting *1M* polytype of phlogopite (Ferraris *et al.*, 2001) is characterised by the occurrence of large residues in positions corresponding to shifts $\pm b/3$ from the positions of T cations, basal oxygen atoms and interlayer cations along the directions [010], [310] and $[3\bar{1}0]$. Similar electron residues were reported before for plutonic *1M* biotites (Brigatti & Davoli, 1990) and for cronstedtite-*3T* (Smrcok *et al.*, 1994) and cronstedtite-*1T* (Hybler *et al.*, 2000). The latter authors have shown that in the two cronstedtite polytypes the residues disappear by allowing two different scale factors for family and

non-family reflections. In this paper a general treatment of the effect of the scale factor on the calculated electron density of disordered polytypes and, in particular, of the appearance of electron residues at $\pm b/3$ positions in the mica polytypes is presented.

Polytypes as OD structures

Compounds built by stacking two-dimensionally periodic layers, or which can be described in terms of layer stacking, represent a relevant fraction of inorganic compounds, both in the mineral realm and among compounds with technological importance (see, *e.g.*, Verma & Krishna, 1966;

*E-mail: massimo.nespolo@nims.go.jp

Merlino, 1997a). If the position of a layer is uniquely defined by the position of the adjacent layers and by the so-called *vicinity condition* (VC), which states the geometrical equivalence of layer pairs, the resulting structure is termed *fully ordered*. If, on the other hand, more than one position is possible that obeys the VC, the resulting structure is an *OD structure*. OD stands for "Order-Disorder" and indicates that the stacking of layers may produce both periodic ("ordered") and non-periodic ("disordered") structures; it has no relation with the atomic order-disorder phenomena. *VC structures* may thus be either fully ordered structures or OD structures (Dornberger-Schiff, 1956, 1964, 1966, 1979; see also Đurovic, 1999). All OD structures are polytypic; the reverse is not necessarily true (see the arguments in Zvyagin, 1993 and Makovicky, 1997).

The OD interpretation assumes that any polytype of a given substance may be considered as consisting of disjoint parts periodic in two dimensions, called *OD layers*, whose pairs remain geometrically equivalent in any polytype of the same family. The OD layers do not necessarily coincide with the layers commonly chosen on the basis of the chemical identity and/or cleavage properties (e.g. Dornberger-Schiff *et al.*, 1982 for the case of micas). Besides, the choice of the OD layers in general is not unique (Grell, 1984). Pairs of OD layers are related by symmetry operation that, in general, are valid in a subspace of the crystal space only (*local symmetry operations*, opposed to *global symmetry operations*, valid in the entire crystal space), and as such do not appear in the space-group type of the compound. The set of all the local and global symmetry operations constitutes a *space groupoid* (Dornberger-Schiff, 1964; Fichtner, 1965, 1977, 1980).

All OD structures, even of different substances, built according to the same symmetry principle, belong to an *OD groupoid family*: this is an abstract family, whose members are the groupoids describing the symmetry of the substances sharing the same symmetry principle. Then, the OD structures of the same substance built on the same structural principle belong to one and the same *family*: the members of a family are individual, real structures (Đurovic & Weiss, 1986). If two or more identical copies of the same polytype are translated by a *superposition vector* (i.e. a vector corresponding to a submultiple of a translation period) and superposed, a fictitious structure is obtained, which is termed *superposition structure*. An *n-fold* superposition structure is obtained from a translation supergroup of order *n*.

Among the infinitely many possible superposition structures of a family, that in which all the possible positions of all OD layers are simultaneously realized is termed *family structure* and is common to all polytypes of the same family (Dornberger-Schiff, 1964; Đurovic, 1994). The superposition vectors of the family structure create additional 'virtual atoms' which may present physically unrealistic interatomic distances: they appear in the family structure, which is a purely mathematical construction, as a consequence of the group-theoretical process of completing the local symmetry operations of a space groupoid into global symmetry operations of a space group (Fichtner, 1977, 1980).

The weighted reciprocal lattice of an O structure can be decomposed into a sublattice (the family weighted sublattice, which is the Fourier transform of the family structure) and one or more cosets. The reflections building the family sublattice are termed family reflections and are ideally identical in position and intensity for all polytypes, both ordered (periodic) and disordered (non-periodic), belonging to the same family. The intensity of the family reflections actually more or less deviates from the ideal value following the structural distortions that modify the real layers with respect to the layer archetypes in terms of which the phenomenon of polytypism has to be defined and described. This deviation can be neglected in the first stage of polytype identification, also because the relative intensities, rather than the absolute values, are required. The family reflections reveal the symmetry of the family structure, i.e. the symmetry principles governing the stacking mode in each polytype. The non-family reflections are instead characteristic of each polytype and reveal the individual stacking sequence. For ordered polytypes the non-family reflections are sharp, and from the intensity distribution the stacking sequence can be directly obtained provided that the structure of the ideal building layer is known (e.g., Tokonami & Hosoya, 1965; Dornberger-Schiff & Farkas-Jahnke, 1970; Takeda, 1967; Nespolo *et al.*, 1999). The stacking sequence is then expressed in terms of the relation $\sigma_{ij}: L_i \rightarrow L_j$, where σ_{ij} is the local symmetry operation transforming the layer L_i into the layer L_j . However, with the increase of the degree of stacking disorder the non-family rows become streaked, eventually forming a continuous line in case of completely disordered polytypes (Đurovic & Weiss, 1986); in the latter case, only the symmetry principle of the stacking mode, as revealed by the family reflections, can be identified.

The Đurovič effect

As said above, in case of an (almost) ordered polytype, if the stacking sequence and the atomic positions inside the building layer are known, a model of the structure can be obtained from the relation $\sigma_{ij}: L_i \rightarrow L_j$. The actual atomic positions inside each layer in general slightly deviate from those obtained by applying the above relation, depending on the actual stacking of the layers in the investigated crystal (*desymmetrization of OD structures*: Đurovič, 1979), but the structural model obtained in this way is sufficiently close to the final solution (e.g. Merlino, 1997b).

In case of a partially disordered polytype, *i.e.* containing some stacking faults (layers with orientation/displacement different from those expected for the fully-ordered matrix *but* still obeying the VC), some of the atomic positions do not match the coordinates of the unfaulted matrix ('displaced atoms'). The presence of stacking faults affects only the non-family reflections which may appear broadened and with streaks; consequently, the precision with which the intensity is measured may vary with the family or non-family character of the reflections. A common effect is that the family and the non-family reflections in routine measurements are no longer on the same scale at least for the following reasons: (i) the measure of the integrated intensities is affected by the form of the peak (spot) and (ii) the evaluation of the background is different for the two groups of reflections because of the streaks accompanying the non-family reflections. Finally, the stacking faults produce spurious peaks in the Fourier map which derive from having constrained both the family reflections and the non-family reflections on the same scale. The appearance of spurious peaks in the Fourier map of partially disordered OD structures as a consequence of constraining family and non-family reflections on the same scale is here termed *Đurovič effect*, after Prof. S. Đurovič (Slovak Academy of Sciences, Bratislava), who, as senior author, first pointed out its existence (Smrcok *et al.*, 1994; Hybler *et al.*, 2000).

The Đurovič effect has a simple explanation in terms of the OD theory. By calculating the Fourier transform of the weighted sublattice built on family reflections only, the family structure is obtained: it consists of the electron density of the polytype, plus additional peaks at \mathbf{t} (where \mathbf{t} represents the superposition vectors of the family structure), which correspond to the 'virtual atoms' occurring in the family structure (Smrcok *et al.*, 1994). If the polytype is ordered, these additional

peaks disappear when the contribution of the non-family reflections is included. If the polytype is instead disordered, the different scale on which the intensity of the non-family reflections is commonly measured makes the contribution from these reflections no longer sufficient to completely remove the additional peaks. Since the layers corresponding to the stacking faults obey the VC, the positions of the 'displaced atoms' coincide with the positions of the 'virtual atoms'. The additional peaks occurring in the Fourier map of a partially disordered OD structure may thus bear two different meanings, corresponding to the two extreme cases which can be conceived: 1) the stacking faults are concentrated in sufficiently large number and diffract coherently; 2) the stacking faults are dispersed in the bulk of the matrix and/or do not diffract coherently. In the first case the 'displaced atoms' are imaged in the Fourier map. In the second case, which is the most common one according to High Resolution Transmission Electron Microscope (HRTEM) observations (see, e.g., Baronnet, 1997), the main influence of the stacking faults is on the intensity of the non-family reflections, which are no longer on the same scale of the family reflections. The 'displaced atoms', should rarely appear in the Fourier map, and the additional peaks are thus essentially spurious peaks deriving from the refinement of the structure with reflections constrained to the same scale. The introduction of a separate scale factor for the non-family reflections may compensate the effect of the different peak shape and background on the intensity measurement of the non-family reflections, and remove the spurious peaks. In case of disordered regions coherently diffracting, the additional peaks are real images of the 'displaced atoms' and cannot be removed by introducing a separate scale factor, which concerns only the diffracted intensities and not the diffracted amplitudes with their phases. In practice, a contribution from both effects can be expected and a clear distinction may require a HRTEM investigation, but in principle the two cases are clearly distinct.

Polytypism in micas

Mica polytypes are built by stacking a unit layer (commonly indicated as "M layer", but also known as *TOT* or 2:1 layer) rotated about c^* by $n \times 60^\circ$ ($0 \leq n \leq 5$). These rotations are nothing else than a *description* of the stacking mode in micas: they are not *generating* operations from either the geometrical or the crystal-growth viewpoint. The

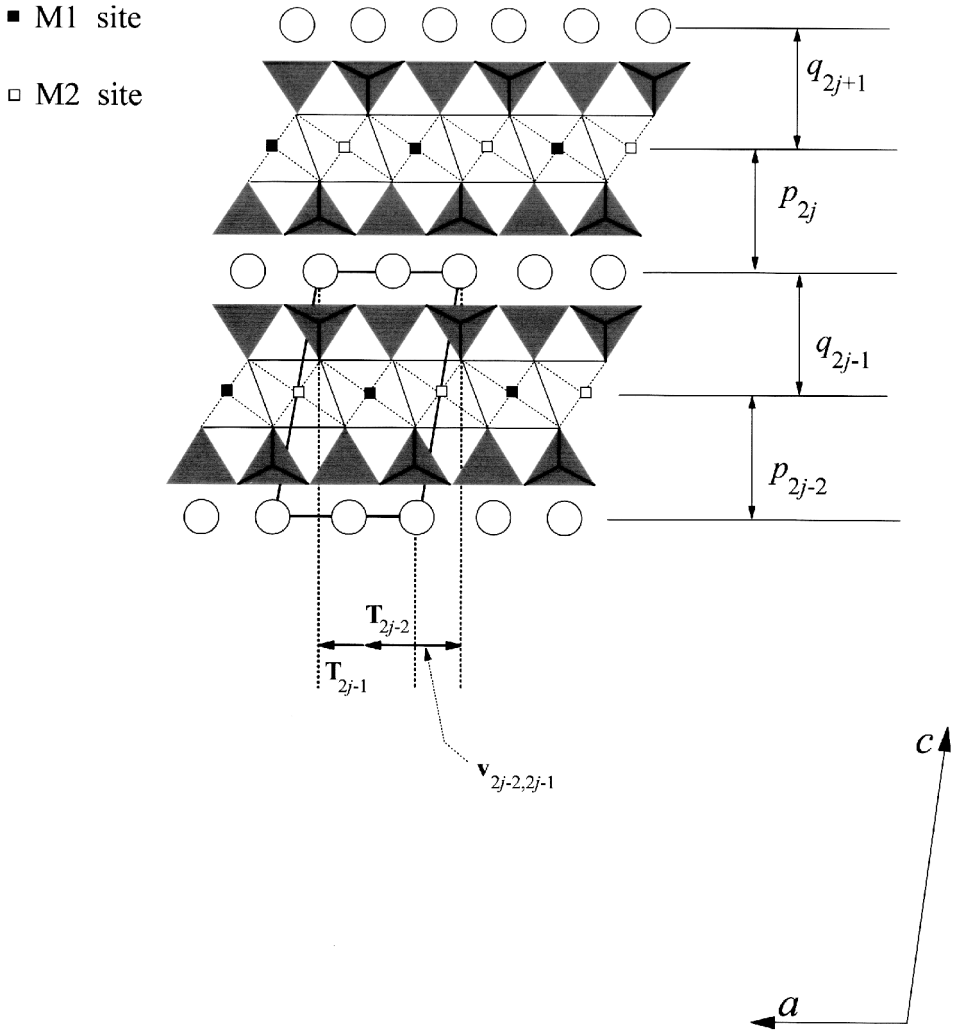


Fig. 1. Schematic representation of a slab $b/4$ thick, showing two layers of the $1M$ polytype. The M layer and the OD packets are shown.

generating operations are best shown by dividing the M layer into a pair of OD packets. An OD packet corresponds to half an M layer plus half the plane of the interlayer cations, and constitutes the smallest continuous part, periodic in two dimensions, representing fully the chemical composition of a polytype (Đurovic, 1974; Dornberger-Schiff *et al.*, 1982). OD packets are polar and are indicated with the letters p (packet pointing $+c$) and q (packet pointing $-c$) (Fig. 1) From the structural viewpoint, the M layer is described in terms of an octahedral (O) sheet sandwiched between a pair of tetrahedral (T) sheets with opposite polarity,

stacked along c and staggered by $|a|/3$ (ideally) in the (001) projection. Two translationally independent cation sites are present in each T sheet, and three in the O sheet. Of the latter, one ($M1$) has two OH groups in *trans*, whereas the other two sites ($M2$ and $M3$) have two OH groups in *cis*. On the basis of the occupation of the three octahedral sites, micas are classified into three families: *homo-octahedral* (all the three M sites are occupied by one and the same cation), *meso-octahedral* (one M site is differently occupied from the other two), and *hetero-octahedral* (all the three M sites are differently occupied). In these three families

the idealised λ -symmetry (symmetry of the layer) of the *O* sheet is $H(3)1m$, $P(\bar{3})1m$, and $P312$ respectively (Dornberger-Schiff *et al.*, 1982; the layer-group notation is given according to Dornberger-Schiff, 1959). The *indicative symbols* (Ramsdell, 1947) commonly used for polytypes, in case of micas are rigorously correct only for the homo-octahedral family, whereas they are nothing else than an approximation in the two other families, and should be accompanied by *descriptive symbols*, reported below. Another common, but less detailed classification, is that in tri- and dioctahedral micas, depending on whether the number of octahedral cations in the *O* sheet *per formula unit* is formally 3 or 2 (Rieder *et al.*, 1998).

In the meso- and hetero-octahedral families, the symmetry of a mica polytype can be lowered to a subgroup of the ideal homo-octahedral space-group type because of cation ordering (Bailey, 1984). Besides, in most cases the space-group type of a polytype does not require a λ -symmetry as high as that of the homo-octahedral layer [$C12/m(1)$ for the entire M layer, $C1m(1)$ for the OD packet], which can be desymmetrized to one of the layer subgroups. The ideal λ -symmetry of the *T* sheet is $P(6)mm$ (Pauling model: Pauling, 1930), but in most cases the ditrigonal rotation of the tetrahedra about c^* (measured by the angle 2α between the prolongation of one edge of a basis of a tetrahedron and the corresponding edge of the basis of the tetrahedron sharing one oxygen atom with it: Weiss *et al.*, 1992) reduces the λ -symmetry to $P(3)1m$ (Trigonal model; Belov, 1949; Radoslovich, 1961). Within the Trigonal model, each family of mica polytypes is subdivided into three groups: *subfamily A polytypes* only [$2n \times 60^\circ$ rotations], *subfamily B polytypes* [only $(2n+1) \times 60^\circ$ rotations], and *mixed-rotation polytypes* [both $2n \times 60^\circ$ and $(2n+1) \times 60^\circ$ rotations] (Backhaus & Đurović, 1984; Đurović *et al.*, 1984; Nespolo, 1999).

The stacking sequence of a mica polytype can be obtained from the intensity distribution along reciprocal lattice rows parallel to c^* . These rows are usefully classified into three kinds, labelled S ($h = 3n, k = 3n$), D ($h \neq 3n, k = 3n$) and X ($k \neq 3n$) (Nespolo *et al.*, 2000). The S rows are family reflections of the Pauling model and are thus common to all polytypes of the same family. The D rows are family reflections of the Trigonal model and are thus common to all polytypes of the same family and of the same subfamily (either A or B); they are instead non-family reflections for mixed-rotation polytypes, and are thus characteristic of each mixed-rotation polytype. Finally, the X rows

are non-family reflections for all polytypes and thus are characteristic of each polytype. The intensity distribution along D rows reveals the symmetry principle (practically, the parity of n in the $n \times 60^\circ$ rotations), whereas that along X rows permits to identify the stacking sequence (Đurović *et al.*, 1984; Nespolo *et al.*, 1999).

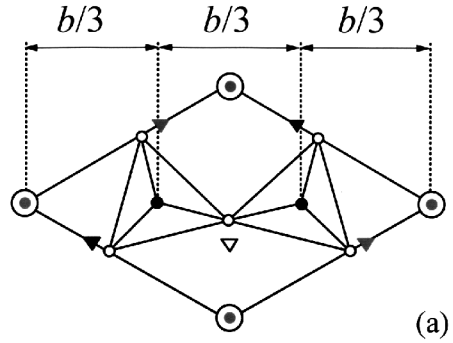
The Đurović effect in micas

The family structure of micas in the Trigonal model is three-fold and the superposition vectors are $\pm b/3$; its symmetry for subfamily A is $H_R\bar{3}1m$ (where the subscript *R* indicates that the smallest cell is rhombohedral), and for subfamily B is $H6_3/mcm$ (Đurović, 1994). To any of the atoms in the layer, two additional ‘virtual atoms’ are generated in the family structure, with coordinates $(x, y \pm 1/3)$ (Fig. 2). By calculating the Fourier transform of the weighted sublattice built on S and D rows only, the family structure is obtained: it consists of the electron density of the polytype, plus additional peaks at $\pm b/3$, which correspond to the ‘virtual atoms’ occurring in the family structure. If the polytype is ordered, these additional peaks disappear when the contribution of the X rows (non-family reflections) is included and the structure of the specific polytype is obtained. If the polytype contains a significant amount of stacking faults, the intensities along the X rows can be affected by scale error, as discussed above, and the additional peaks of the family structure are not completely removed.

Stacking faults and the Đurović effect

The stacking faults in micas may correspond to entire M layers rotated by $\pm 120^\circ$ with respect to the orientation expected in the unfaulted matrix, or to $\pm b/3$ slips in the octahedral sheet (“crystallographic slips”: Takéuchi & Haga, 1971), which modify the orientation of one of the packets of the M layer. These slips have been directly observed (*e.g.* Bell & Wilson, 1977) or simulated (Noe & Veblen, 1999) in TEM images of biotite. The simplest way to show the effect of the stacking faults is to exploit the information contained in the symbols describing the stacking sequence of mica polytypes. The most general symbols were introduced by the OD school (Dornberger-Schiff *et al.*, 1982; Backhaus & Đurović, 1984; Đurović *et al.*, 1984). These symbols consist of a sequence of characters referring to one period, placed between vertical bars; two lines of characters are used:

- ⊙ $1/2(K)+OH$
- $T + O_{apical}$
- O_{basal}
- ▼ ▼ ▼ $1/2(M1, M2, M3)$



- $1/2(K)+OH+2(T, O_{apical})$
- $1/2(M1+M2+M3)$
- O_{basal}

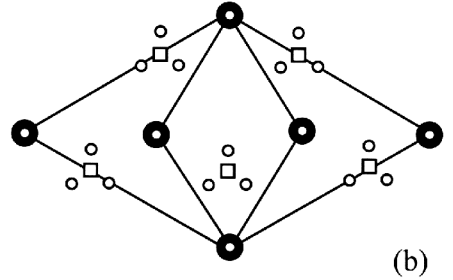


Fig. 2. Derivation of the family structure by means of the superposition vectors $\pm b/3$. (a) A hetero-octahedral mica packet projected onto the (001) plane. (b) The family structure obtained by applying the superposition vectors $+b/3$ and $\pm b/3$ to each of the atoms in the packet shown in (a). The hP cell in (a) corresponds to the hH cell in (b); the hP cell of the family structure is also shown in (b).

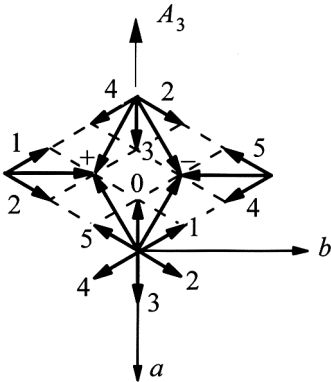


Fig. 3. The nine possible displacements in the structure of polytypes of phyllosilicates, shown by the OD symbols and corresponding vectors within the primitive hexagonal unit cell (modified after Āurovic, 1999). The sum of any two vectors is indicated, and the result of the summation of any number of vectors should be taken modulo primitive hexagonal cell. The individual vectors are designated by their conventional numerical characters $\langle 0 \rangle \sim \langle 5 \rangle$ and $\pm b/3$ displacements $\langle + \rangle$ and $\langle - \rangle$, whereas the zero displacement $\langle * \rangle$ is not indicated.

indicates the *orientation* of each packet with reference to a space-fixed axial setting, and the second line the packet-to-packet *displacements*. A dot “.” separates the two packets of the same M layer:

$$\begin{vmatrix} T_0 & \cdot & T_1 & T_2 & \cdot & T_3 & \dots \\ v_{0,1} & & * & & v_{2,3} & * & \dots \end{vmatrix}$$

where $T_j = 0 \sim 5$, $v_{2j,2j+1} = T_{2j} + T_{2j+1}$ (v , T are the vectors corresponding to v and T characters, and the vector sum has to be taken *modulo* primitive hexagonal cell). $\langle * \rangle$ indicates null vector (no displacement). If the interlayer cations are not present (as in the case of other phyllosilicates) the inter-layer displacement can correspond to the nine vectors $\langle * \rangle$, $\langle 0 \rangle \sim \langle 5 \rangle$, $\langle + \rangle$ and $\langle - \rangle$ (where $\langle + \rangle$ and $\langle - \rangle$ represent $+b/3$ and $-b/3$ respectively) (Fig. 3). The parity of the orientational characters is necessarily opposite to that of the displacement characters. In the hetero-octahedral family the chirality of the packets has to be taken into account: right- and left-handed packets are indicated by a prime (\prime) or double prime ($\prime\prime$), respectively, *substituting* the dot (\grave{D} urovic *et al.*, 1984). In the homo-octahedral

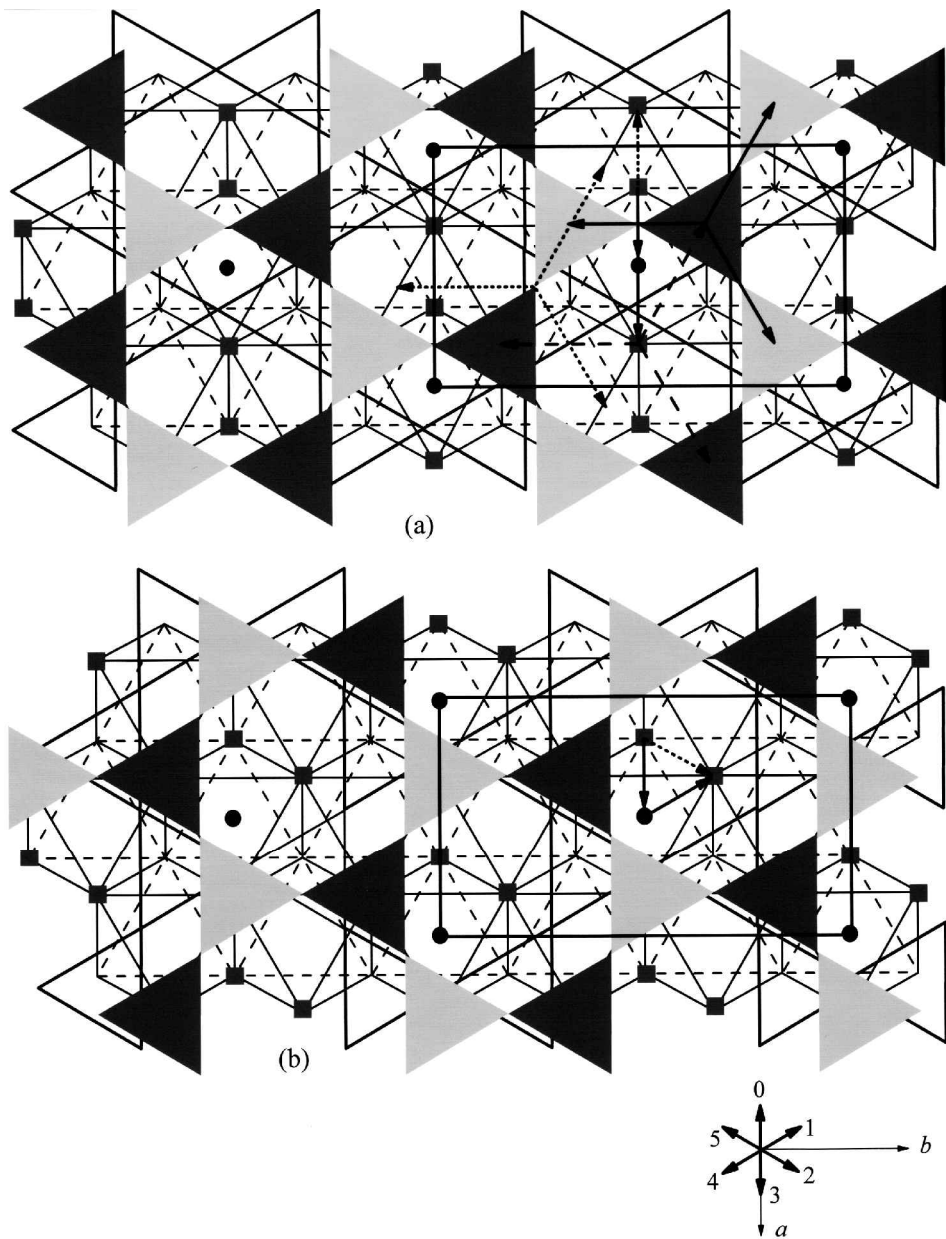


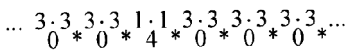
Fig. 4. The (001) projection of an M layer before (a) and after (b) a $-1/3[010]$ slip of the upper (q) OD packet. To improve the readability, the figure is drawn in the Pauling model (null ditrigonal rotation of the tetrahedra), and the lower *T* sheet (unaffected by the slip) is indicated by a single type of line. The two translationally independent tetrahedra in the upper *T* sheet are instead shown by two different tones of grey. Close circles indicate the origin of the *O* sheet, according to Đurovic *et al.* (1984) (site with different occupation in the meso-octahedral family; site with lowest electron density in the hetero-octahedral family). Grey square indicate the OH// positions [overlapped in the (001) projection]. Thick arrows represent orientational (solid) and displacement (dotted) vectors. The orthohexagonal mesh in the (001) plane is also shown. (a): The directions of the slips $-1/3[010]$, $1/6[310]$ and $-1/6[3\bar{1}0]$ are indicated for the tetrahedra (solid arrows), OH groups and *I* cations (dashed arrows) and basal oxygen atoms (dotted arrows) (the slips in the opposite directions are not shown). The figure is drawn for the ${}_{0}^{3,3}$ M1 layer. (b) The result of a $-1/3[010]$ slip of the upper (q) OD packet. The ${}_{0}^{3,3}$ M1 layer is transformed into the ${}_{2}^{0,1}$ M2 layer. Inset in the right-bottom: space-fixed reference axes and direction defining the OD vectors.

family there are only two distinguishable orientations of the packets, *e* and *u*, corresponding to even- or odd (*uneven*)- numbered characters, respectively (Dornberger-Schiff *et al.*, 1982).

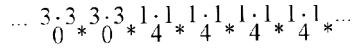
We can easily analyse the effect of a stacking fault with the help of Fig. 3. For simplicity, but without lack of generality, let us consider a meso-octahedral 1*M* polytype, for which the OD symbol is $\left[\begin{smallmatrix} 3 \\ 0 \end{smallmatrix} \begin{smallmatrix} 3 \\ * \end{smallmatrix} \right]$. A 120° or 240° counterclockwise rotation about the normal to (001) passing through the position of an *I* cation below the layer transforms the symbol into $\left[\begin{smallmatrix} 1 \\ 4 \end{smallmatrix} \begin{smallmatrix} 1 \\ * \end{smallmatrix} \right]$ and $\left[\begin{smallmatrix} 5 \\ 2 \end{smallmatrix} \begin{smallmatrix} 5 \\ * \end{smallmatrix} \right]$ respectively. A *b*/*3* or - *b*/*3* slip along [010] of the upper packet (*q*) of a layer moves only one plane of apical oxygen atoms, and the *T* sheet bonded to it, with respect to the other plane kept fixed, and leaves unmoved the octahedral cations, resulting in the modified sequence $\begin{smallmatrix} 3 \\ 4 \end{smallmatrix} \begin{smallmatrix} 5 \\ - \end{smallmatrix}$ or $\begin{smallmatrix} 3 \\ 2 \end{smallmatrix} \begin{smallmatrix} 1 \\ + \end{smallmatrix}$ respectively (a slip of the lower packet, *p*, or a rotation about the normal to (001) passing through the position of an *I* cation *above* the layer, gives an analogous result). The effects of the rotation/slip in *q* are (Fig. 4): 1) exchanging the position of the upper OH group with that of one of the nearest apical oxygen atoms; 2) exchanging one of the translationally independent tetrahedron with the other one, and bringing the second tetrahedron where the centre of the ‘hexagon’ of tetrahedra was originally located; 3) moving all the basal oxygen atoms in a previously empty position; 4) moving all the interlayer cations above the position previously occupied by one of the translationally independent tetrahedron; 5) only in case of a slip: exchanging the occupation of the octahedral sites, with the transformation of an M1 layer (the two orientation vectors of each packet parallel: $\begin{smallmatrix} 3 \\ 0 \end{smallmatrix} \begin{smallmatrix} 3 \\ * \end{smallmatrix}$) into an M2 layer (the two orientation vectors of each packet rotated by ± 120°: $\begin{smallmatrix} 3 \\ 4 \end{smallmatrix} \begin{smallmatrix} 5 \\ * \end{smallmatrix}$ or $\begin{smallmatrix} 3 \\ 2 \end{smallmatrix} \begin{smallmatrix} 1 \\ * \end{smallmatrix}$) (Nespolo, 2001).

The slip may occur isolated, without any compensation in the adjacent layer: in this case the adjacent coordination site for the interlayer cation is destroyed (displacement vector ⟨+⟩ or ⟨−⟩ instead of ⟨*⟩). When instead the slip is recovered by another, opposite slip in the adjacent layer, the coordination of the interlayer cation is restored. For a single stacking fault the following cases can be conceived (only one of the two enantiomorphous possibilities is indicated):

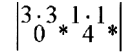
(1a) rotation of the entire M layer without inheritance:



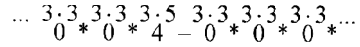
(1b) rotation of the entire M layer with total inheritance (*e.g.*, in case of a growing crystal, when only the rotated layer appears in the growth spiral):



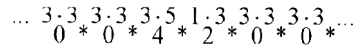
(1c) rotation of the entire M layer with partial inheritance (*e.g.*, in case of a growing crystal, when both un-rotated and rotated layers appear in the growth spiral of a growing crystal):



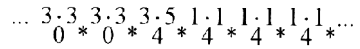
(2) un-recovered *l*/*3* slip of the packet *q* in a pre-formed matrix:



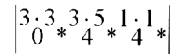
(3a) recovered *l*/*3* slip of the packet *q* without inheritance (*e.g.* recovered slip in a matrix undergoing physical deformation):



(3b) recovered *l*/*3* slip of the packet *q* with total inheritance:



(3c) recovered *l*/*3* slip of the packet *q* with partial inheritance:



The result is a planar defect in cases (1a), (2) and (3a); a twin in cases (1b) and (3b); a different polytype in cases (1c) and (3c) (only the simplest polytype obtained in this way is shown: the resulting stacking sequence depends on the number of layers in the growth spiral; for details see Nespolo, 2001). If the stacking fault is not unique but is repeated several times, isolated stacking faults [(1a), (2), (3a)], microtwins [(1b), (3b)] or a mixture of polytypes [(1c), (3c)] arise. Cases (b) and (c) correspond to the so-called ‘OD intergrowth’ (Đurovic, 1997), *i.e.* domains in which different polytypes appear in one, coherently scattering crystal block: only in these cases, and provided that the size of the OD intergrowth is large enough, the additional peaks in the Fourier map may have a quantitative relation with the ‘displaced atoms’. In all the other cases the stacking faults are in general too dispersed and cannot diffract coherently, also because they belong to different domains of the mosaic structure; they simply affect the intensities of the non-family reflections and the additional peaks correspond to the Đurovic effect. The case (2) is in principle distinguishable because it implies incomplete occupa-

tion of the interlayer region (talc-like layers), due to the destruction of the coordination polyhedra (displacement vector $\langle + \rangle$ or $\langle - \rangle$ instead of $\langle * \rangle$).

The distinction between M1 layer (3_0^3) and the M2 layer (3_2^1 or 3_4^5) becomes meaningless in the homo-octahedral family, since the three orientations with the same parity of symbols are equivalent, and a $\pm b/3$ slip produces a result indistinguishable from a $\pm 120^\circ$ rotation of the layer ($u_0^u \rightarrow u_2^u$ or $u_0^u \rightarrow u_4^u$).

Not only the $\pm b/3$ slips at the *O* sheet in trioctahedral micas are well known, but also their formation and recovery during the growth of the crystal is considered a key mechanism in the genesis of long-period polytypes (Nespolo, 2001). Unrecovered slips represent instead a situation energetically less stable; they may hardly occur at concentration sufficiently high to give an image in the Fourier map. A high concentration of planar defects in trioctahedral micas is considered the first stage of decomposition (Kogure & Nespolo, 2001).

Examples

The occurrence of $\pm b/3$ residues in the Fourier map of micas was reported by Brigatti & Davoli (1990) for plutonic *1M* biotites and by Ferraris *et al.* (2001) for pegmatitic *1M* and *2O* coexisting phlogopites from the Khibiny massif, Kola peninsula, Russia. Brigatti & Davoli (1990) explained the residues as due to "small domains containing microtwins on one of the following axes: $[310]$, $[3\bar{1}0]$, $[110]$ and $[1\bar{1}0]$ ". Actually, only the first two twin laws may explain the $\pm b/3$ peaks, the latter two corresponding instead to $\pm a/3$ shifts or $(2n+1) \times 60^\circ$ rotations (Takéuchi & Haga, 1971; Nespolo, 2001). The possibility that the residues corresponded to spurious peaks deriving from the Đurovic effect was not investigated, since the Đurovic effect itself was not recognized yet. The interpretation given there may thus need to be reconsidered. Ferraris *et al.* (2001), on the other hand, refined the structures of the coexisting phlogopite-*1M* and phlogopite-*2O* with separate scale factors for the family and non-family reflections, obtaining the disappearance of the spurious peaks and demonstrating that they were due to the Đurovic effect, rather than to coherently diffracting regions within the matrix. A similar treatment was also adopted with success by Smrcok *et al.* (1994) and Hybler *et al.* (2000) in refining the crystal structure of *3T* and *1T* cronstedtite respectively.

Conclusions

The examples illustrated above suggest that the Đurovic effect may occur rather frequently in polytypic structures (not only phyllosilicates) and prompts for trying a refinement with separate scale factors whenever residues occur in the Fourier map of OD structures corresponding to the position of the 'virtual atoms' of the corresponding family structure. Presumably, the effect has been almost neglected so far not only because it was not yet clearly described with a dedicated paper; actually (and unfortunately), disordered structures are often abandoned because of the difficulties met in solving or refining their structures.

Slips and stacking faults are rarer in di- than in tri-octahedral micas, because of the larger structural distortions and the higher structural control, connected mainly with the empty octahedral site (see, *e.g.*, Bell & Wilson, 1981). Concretely, the lower frequency in the dioctahedral micas can be rationalized keeping into account that in these compounds: (i) a $\pm b/3$ slip would exchange an occupied with an empty octahedral site; (ii) the roughness (Δz) of the *T* sheets is larger because of the larger difference in size between the empty and the occupied octahedral sites, which can create less favourable interlayer coordination for odd values of *n* in the $n \times 60^\circ$ rotation.

Acknowledgement: The authors wish to express their gratitude to (i) Prof. Slavomil Đurovic (Slovak Academy of Sciences, Bratislava) for profitable discussions and for drawing our attention on the effect of the stacking disorder onto the intensity distribution along X rows, which we have now termed "Đurovic effect", and (ii) to Prof. Stefano Merlino (Pisa University) who has been a very constructive referee. This research was financially supported by the Italian MURST ('Layer silicates: crystal chemical, structural and petrologic aspects' project) and CNR ('Igneous and metamorphic micas' project) grants.

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Received 12 January 2001

Modified version received 5 March 2001

Accepted 10 April 2001