Atti Soc. tosc. Sci. nat., Mem., Serie A, 111 (2006)
pagg. 31-44, figg. 11

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OD CHARACTER AND POLYTYPIC FORMS OF TSCHERNICHITE AND ITS SYNTHETIC COUNTERPART ZEOLITE BETA

Abstract - Tschernichite is a very rare zeolite structurally related to the synthetic zeolite beta, a useful catalyst for several reactions. Both the natural phase and its synthetic counterpart present structural disorder evidenced by the presence of a set of diffuse reflections. The OD character of these zeolites is presented and discussed in order to give indication of the common symmetry properties of the whole family and to derive and describe the most simple polytypes. Two MDO (Maximum Degree of Order) structures exist in this OD family and correspond to the main polytypes: MDO_1, tetragonal, with space group $P4_122$ and cell parameters $a = b \approx 12.5$, $c \approx 26.4$ Å (referred to as Tschernichite 4*Q*); MDO_2, monoclinic, with space group $C2/c$ and cell parameters $a \approx b \approx 12.5\text{x}\sqrt{2}$, $c \approx 14.4$ Å, $\beta \approx 114°$ (referred to as Tschernichite 2*M*). The common diffraction features of the whole family (corresponding to the «family structure», with space group $P4_2/mmc$ and cell parameters $a = b \approx 4.2$, $c \approx 13.2$ Å), as well as the diffraction peculiarities of the MDO structures, are derived and discussed on the basis of the OD character of the compound.

Key words - OD theory, polytypism, X-ray diffraction features, beta-type zeolite, tschernichite.

Riassunto - *Carattere OD e forme politipiche della tschernichite e del corrispondente composto sintetico zeolite beta.* La tschernichite è una rarissima zeolite naturale strutturalmente correlata alla zeolite beta sintetica, catalizzatore utilissimo in molte reazioni. Sia la fase naturale sia il corrispondente composto sintetico mostrano disordine strutturale, chiaramente evidenziato dalla presenza di un insieme di riflessi caratterizzati da diffusione in una specifica direzione. Il carattere OD di queste zeoliti è presentato e discusso allo scopo di dare indicazioni sulle proprietà di simmetria comuni all'intera famiglia di strutture OD e di derivare e descrivere i politipi più semplici. Esistono, in tale famiglia, due strutture MDO (Maximum Degree of Order), corrispondenti ai due principali politipi: MDO_1, tetragonale, con gruppo spaziale $P4_122$ e parametri di cella $a = b \approx 12{,}5$, $c \approx 26{,}4$ Å (denominato Tschernichite 4*Q*); MDO_2, monoclino, con gruppo spaziale $C2/c$ e parametri di cella $a \approx b \approx 12{,}5\text{x}\sqrt{2}$, $c \approx 14{,}4$ Å, $\beta \approx 114°$ (denominato Tschernichite 2*M*). Gli aspetti «diffrattometrici» comuni all'intera famiglia (caratteristici della «struttura di famiglia», con gruppo spaziale $P4_2/mmc$ e parametri di cella $a = b \approx 4{,}2$, $c \approx 13{,}2$ Å), nonché le peculiarità dei diffrattogrammi delle due strutture MDO, sono ricavati e discussi sulla base del carattere OD del composto.

Parole chiave - Teoria OD, politipismo, aspetti diffrattometrici, zeolite beta, tschernichite.

INTRODUCTION

Zeolite beta, first described in 1967 by Wadlinger *et al.* (1967), is a large-pore high-silica zeolite with a three-dimensional channel system. Due to its peculiar pore structure and high acidity, zeolite beta is a very important catalyst for a wide spectrum of reactions, where its activity and selectivity play a relevant role.

The framework structure of this zeolite was solved independently by Newsam *et al.* (1988) and Higgins *et al.* (1988) through a clever combination of various techniques, from model building to DLS refinement, high resolution electron microscopy imaging, electron diffraction, X-ray powder diffraction and X-ray powder pattern simulation. The authors established the lattice geometry of zeolite beta by X-ray and electron diffraction data, pointing – through observation of *hk*0 diffraction pattern – to a net with $a = b \approx 12.5$ Å. They discussed the peculiar diffraction pattern of the compound, characterized by a set of sharp reflections at $h = 3n$ and $k = 3n$, and a set of diffuse maxima for $h \neq 3n$ or $k \neq 3n$, frequently superimposed to continuous streaks parallel to **c***, pointing to a structure disordered in the direction normal to (001) with disorder characterized by ±**a**/3 and ±**b**/3 displacements in the (001) plane. Both Newsam *et al.* (1988) and Higgins *et al.* (1988) agreed that the structure of zeolite beta could be described as a disordered sequence of different polytypes with frequent planar faults. More precisely according to Newsam *et al.* (1988) it may be described in terms of only two polytypes: polytype A, tetragonal with space group symmetry $P4_122$ (or $P4_322$) and cell parameters $a = b \approx 12.5$ Å and $c \approx 26.4$ Å, and polytype B, monoclinic with space group symmetry $C2/c$ and cell parameters $a \approx b \approx 12.5\text{x}\sqrt{2}$ Å, $c \approx 14.4$ Å and $\beta \approx 114°$. According to Higgins *et al.* (1988) a third polytype is present besides those just indicated: polytype C, monoclinic with space group symmetry $P2$ (actually $P2/c$) and cell parameters $a \approx b \approx 12.5$ Å, $c \approx 27.7$ Å and $\beta \approx 107°$.

The occurrence of the natural counterpart of synthetic zeolite beta at Goble, Oregon, USA, was described by Smith *et al.* (1991), who named tschernichite the new natural species. The occurrence of the structure-type of zeolite beta in a natural phase is extremely important, as it implies, as correctly suggested by Smith *et al.* (1991), that an organic template may not be necessary

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for the synthesis and that, as suggested by the Si:Al ratio of tschernichite, crystals of zeolite beta with relatively low Si:Al ratio may be prepared.

In the report by Smith *et al.* (1991) it was observed that «the tschernichite patterns match best with computed X-ray pattern for an approximately equal amount of the A and B arrangements in a random sequence», where A and B refer to the polytypic forms described by Newsam *et al.* (1988) and Higgins *et al.* (1988). A more detailed study of the mineral by Boggs *et al.* (1993) pointed to the presence in the Goble Creek basalt of tschernichite crystals of two distinct types, namely as large single or twinned crystals and as small drusy crystals building up radiating hemispherical groups. The chemical analyses performed for both crystal types revealed a higher silica content in the small crystals than in the large ones, «probably as a result of differing condition during their formation» (Boggs *et al.*, 1993).

Later, tschernichite crystals displaying the two morphological types were found by Galli *et al.* (1995) in fractures of basalts from Mt. Adamson (Northern Victoria Land, Antarctica). As pointed out by these authors, the powder pattern reported by Boggs *et al.* (1993) for the specimen from Goble shows significant differences, mainly in the low θ range, with respect to that reported for Mt. Adamson tschernichite; these differences in the powder patterns were attributed to a different ratio of the two A and B polymorphs and/or the presence of other beta-type polytypes.

A structural study through single-crystal X-ray diffraction was carried out on crystals of both morphological types from Mt. Adamson by Alberti *et al.* (2002). Their study revealed the great prevalence of polytype B (monoclinic) in the large crystals and polytype A (tetragonal) in the small crystals and indicated that only a small amount (if any) of the tetragonal polytype was present in dominantly monoclinic crystals and *vice versa*. The structural refinements were carried out on data collected with automatic four-circle Nonius KappaCCD diffractometer (MoKα radiation) and converged to R = 0.132 [2322 unique reflections with Fo>5σ(Fo)] for polytype B [$C2/c$, a = 17.983(3), b = 17.966(2), c = 14.625(2) Å, β = 114.31(1)°] and R = 0.106 [1434 unique reflections with Fo>5σ(Fo)] for polytype A [$P4_122$, a = 12.634(1), c = 26.608(3) Å].

Newsam *et al.* (1988) described, besides the A and B polytypes, another possible phase for zeolite beta, built up by stacking succeeding layers without displacements in the (001) plane and named it polymorph C [it is proper to stress that it is distinct from the polytype C described by Higgins *et al.* (1988)]. It is tetragonal with cell parameters $a \approx 12.5$, $c \approx 13.3$ Å and space group $P4_2/mmc$ and its framework is characterized by linear 12-membered-ring channels running along **c**, as well as by the presence of double 4-rings of tetrahedra. This structure-type, coded BEC by the *Structure Commission of International Zeolite Association*, has been first found by Conradsson *et al.* (2000) in FOS-5, a new porous material, with chemical composition $[(CH_3)_3N]_6[Ge_{32}O_{64}](H_2O)_{4.5}$, obtained as small needle-shaped crystals from an aqueous solution containing germanium dioxide and hydrofluoric acid. Actually FOS-5 is tetragonal, with space group symmetry $I4_1/amd$ and a = 22.990, c = 27.271 Å, but the germanate framework topology is the same of BEC. Subsequently the preparation of the pure C structure-type with composition $Si_{1-x}Ge_xO_2$ or of distinct single-crystal pillars of the C structure-type overgrown on ordinary zeolite beta has been realized by Corma *et al.* (2001) and Liu *et al.* (2001) respectively, from high Ge/Si and/or fluoride containing media. Whereas Corma *et al.* (2001) determined the structure of the single-phase $Si_{1-x}Ge_xO_2$ compound by Rietveld refinement of powder X-ray diffraction data, Liu *et al.* (2001) revealed the structural arrangement of the «overgrown pillars» with a new procedure combining HRTEM imaging with the use of a Patterson map, derived from SAED patterns, to enhance the sharpness of the peak positions (Ohsuna *et al.*, 2002).

It is interesting to recall that Newsam *et al.* (1988) clearly stated that «neither electron diffraction micrographs, nor powder X-ray diffraction data provide any evidence for the occurrence of the structure C stacking arrangement in any of the zeolite beta samples studied» by them. Also in the subsequent preparations of phases characterized by BEC structure-type, that topology does not actually mix with those corresponding to the ordinary zeolite beta, as also in the preparation by Liu *et al.* (2001) the «overgrown pillars» present a peculiar morphology and are neatly distinguished from the matrix of zeolite beta.

The neat distinction between the BEC structure-type on one side and the various polytypic forms of zeolite beta and tschernichite on the other side can be most clearly appreciated on the basis of the OD approach. The OD character of zeolite beta has been first indicated by Marler *et al.* (1993) who prepared relatively large single crystals and collected the full set of sharp reflections, corresponding to the average structure (family structure in OD terminology), with $a = b$ = 4.121, c = 13.01 Å, space group $P4_2/mmc$, and refined that sub-structure to conventional R = 0.054. The OD character has been subsequently shortly discussed by Böhme (1993) and by Reinecke *et al.* (1999).

A more detailed presentation of the OD character of zeolite beta, and its natural counterpart tschernichite, will be presented in the following, with indication of the correct symmetry properties of the whole family and derivation of the two [not three, as maintained by Böhme (1993)] MDO structures, namely those sequences of OD layers realizing the Maximum Degree of Order.

It will appear that the OD approach favours a deep understanding of the complex structural aspects in the whole family, consents an easy interpretation of the peculiar diffraction patterns and explains the frequent occurrence of few polytypes (generally the A and B forms). Moreover it will permit to construct more complex polytypes with easy derivation of their metrics and symmetries. As a matter of fact the OD approach was instrumental in the interpretation of the diffraction data collected from the specimens of tschernichite from Mt. Adamson and, more generally, in the whole structural study of tschernichite (Alberti *et al.*, 2002).

OD CHARACTER OF TSCHERNICHITE

The peculiar diffraction features as well as the polytypic character of zeolite beta and tschernichite clearly indicate they are OD structures (Dornberger-Schiff, 1956, 1964, 1966; Ďurovič, 1997; Merlino, 1997; Ferraris *et al.*, 2004) consisting of equivalent layers. In those structures neighbouring layers can be arranged in two or more geometrically, and therefore energetically, equivalent ways; distinct ways – two ways in the present case – of stacking neighbouring layers allow the existence of a series of both disordered and ordered sequences (polytypes), all of them constituting a family of OD structures. In all the members of the family pairs of adjacent layers are geometrically equivalent. A very interesting, peculiar character of the present family is that also triples of adjacent layers are geometrically equivalent. The various disordered and ordered structures display diffraction patterns with common features (*family reflections*: reflections which present the same position and intensities in all the structures of the family, namely reflections with h,k = 3n in the present case, with reference to the **a** and **b** vectors of the single layer) and can be distinguished for the position and intensities of the other reflections. The family reflections are always sharp and define the unit cell of the family structure ($a = b = 4.2$, $c = 13.2$ Å, space group $P4_2/mmc$), whereas the other reflections can be more or less diffuse, sometimes appearing as continuous streaks along **c***, if the two stacking ways follow each other in a random sequence. In case of single ordered sequences (polytypes), also reflections corresponding to h or k different from 3n will be sharp and will correspond to the particular structure with its specific periodicities and space group symmetry.

The symmetry properties common to all the members of an OD family are described by the *OD groupoid family* symbol, which reports the partial symmetry operations (POs) which transform each layer into itself (λ operations), or into an adjacent one (σ operations). The symbol allows to obtain the symmetry properties of each particular ordered sequence, the general features of the diffraction pattern and to correctly derive the MDO (Maximum Degree of Order) structures, namely those polytypes in which not only pairs (and triples, in this particular family) of layers, but also quadruples … n-tuples of layers are geometrically equivalent. MDO polytypes are the simplest among all the possible ordered sequences and usually correspond to the most frequently occurring polytypes in the family.

On the basis of the reliable structural arrangements obtained by Higgins *et al.* (1988) and Newsam *et al.* (1988) for zeolite beta, the structure of tschernichite can be described in terms of structural layers (Fig. 1: rows of up-pointing tetrahedra run along **b** and rows of down-pointing tetrahedra run along **a**; the two kind of

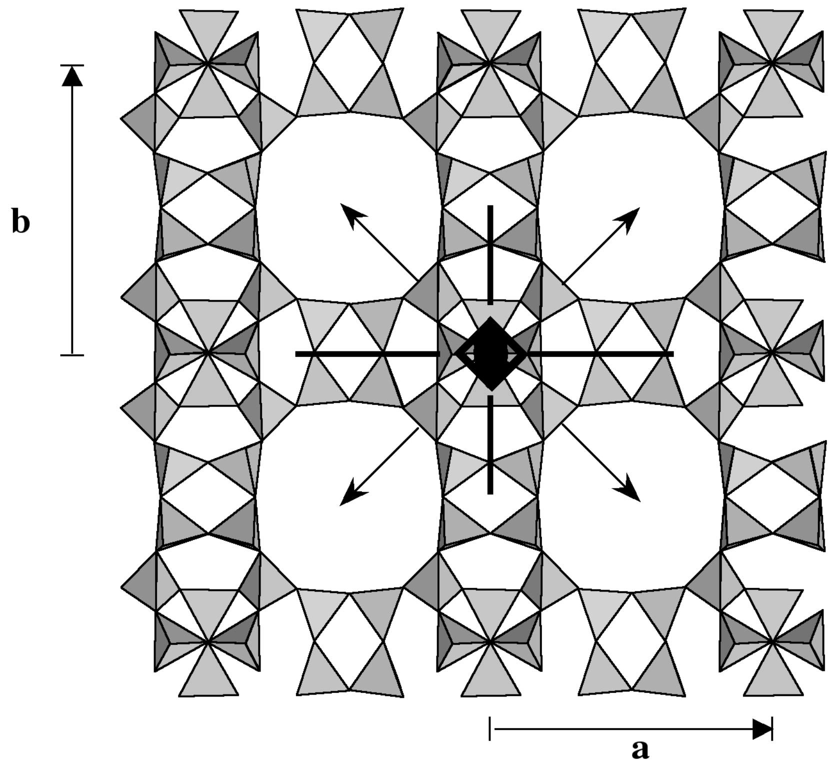

Fig. 1 - Schematic drawing of the single layer in zeolite beta and tschernichite, with indication of the λ operations.

rows are connected through additional tetrahedra), with basic vectors **a**, **b** (translation vectors of the layer, with $a = b = 12.5$ Å) and $\mathbf{c_o}$ ($c_o = 6.6$ Å) and layer group symmetry $P\,\bar{4}m2$ (λ POs), or more precisely:

$$P\ m\ m\ (\bar{4})\ 2\ 2 \qquad \text{(a)}$$

(The layer groups, or two-sided planar groups, are the groups of symmetry operations of a structure built up with three-dimensional objects, but with two-dimensional lattice. The eighty layer groups were derived more than seventy years ago by Alexander & Hermann [1929], Weber [1929], Heesch [1930] and introduced in the crystallographic literature by Holser [1958a,b] and afterwards by Dornberger-Schiff [1956] in her presentation of OD theory.)

In the case of square lattices (as well as in the case of trigonal/hexagonal lattices) more than three positions are necessary to indicate the operators related to the various directions. With the square lattice the operators corresponding to the direction **a**, **b**, **c**, **a**+**b**, **a**-**b** have to be specified; the parentheses in the symbol (a) indicate that the direction **c** is that of missing periodicity.

OD theory derives the various possible sets of σ-operations compatible with each layer group and presents a complete list of possible OD groupoid families. In the case of the layer group (a) there are two possible OD groupoid families. The correct one for the present OD family, as well as the translational components of its σ-operations, may be derived considering that the λ- and σ-operations must be in keeping with the operations of the family structure (as it will be explained in the following) and its symbol is here reported

$$\begin{matrix} P & m & m & (\bar{4}) & 2 & 2 \\ \{ & 2 & 2_{2/3} & (4_4/n_{0,2/3}) & n_{-1/3,2} & n_{1/3,2}\ \} \end{matrix} \qquad \text{(b)}$$

or, more simply:

$$\begin{matrix} P & m & m & (\bar{4}) & 2 & 2 \\ \{ & 2 & 2_{2/3} & (4_4/b_{2/3}) & n_{-1/3,2} & n_{1/3,2}\ \} \end{matrix} \qquad \text{(c)}$$

The notations used for σ-POs are analogous to the international notations for space group operations; for example $2_{2/3}$ in the second position in (c) indicates a twofold screw axis parallel to **b** with translational component **b**/3; 4_4 in the third position in (c) indicates a fourfold screw axis parallel to $\mathbf{c_o}$ with translational component $\mathbf{c_o}$; $n_{1/3,2}$ in the last position in (c) indicates a *n* glide normal to **a**-**b**, with translational component (**a**+**b**)/6+$\mathbf{c_o}$.

As it was previously mentioned, the family structure has space group $P4_2/mmc$, with $a = b = 4.2$, $c = 13.2$ Å. Namely its *a* and *b* parameters are one third of the corresponding parameters of the single layer, whereas its *c* parameter is twice the corresponding c_o parameter of the single layer. The symmetry operations of the space group of the family structure may be derived by considering both λ and σ operations in the symbol (b), modifying the translational components of any screw and glide in agreement with the passing from the parameters of the single layer to the parameters of the family structure, namely multiplying by three the translational components referring to **a** and **b** and dividing by two those referring to $\mathbf{c_o}$.

The symbols (b) and (c) mean that the whole family of structures is characterized by layers as those represented in Figure 1, layers which follow each to the other through the σ-operations listed in the second row of (b) and (c) and represented in Figure 2.

Note that all the σ-operations listed in (b) or (c) bring the second layer in one position relatively to the first layer. The other geometrically equivalent position of the second layer may be obtained by the action of a set of σ-operations related to the previous ones through the λ-operations of the layer. Let us look at the operator $b_{2/3}$ (normal to **c** in Fig. 2); due to the symmetry plane normal to **b** in the layer, both translations by **b**/3 or by -**b**/3 (after the mirror operation) may be applied; the two operators are denoted $b_{2/3}$ and $b_{-2/3}$ respectively and both give rise to geometrically equivalent pairs of layers. The new layer now presents the ribbon of up-pointing tetrahedra running along **a** and the corresponding σ-operators are now denoted $a_{2/3}$ and $a_{-2/3}$. Infinite possible sequences may exist, corresponding to the infinite sequences of alternating operators $b_{\pm 2/3}$ and $a_{\pm 2/3}$.

Derivation and symmetry of the two MDO polytypes

Among the infinite possible sequences of layers, two of them correspond to the MDO structures. A useful concept in deriving the MDO structures is the concept of generating operation. Each MDO structure is characterized by a generating operation, namely that operation which, by its continuous application, gives rise to the structure; the use of one operation guarantees for the homogeneity of the stacking sequence. One such operation is that indicated 4_4 in Figure 2. By applying it [rotating by 90° counter-clockwise and by translating the whole vector $\mathbf{c_0}$ ($c_0 = 6.6$ Å, the width of the layer)] the new layer is in such position that it is possible to re-apply the operation 4_4, etc. Through a constant application of the operation 4_4 we build up the MDO_1 structure: the 4_4 partial operation becomes a total 4_1 operation in a tetragonal structure with $a = 12.5$ Å and $c = 4c_0 = 4 \times 6.6$ Å; one diagonal λ-operation 2 in each layer becomes total operation (at $z = 1/8, 3/8$ …), whereas the σ-operations 2 become total twofold rotations at $z = 1/4, 3/4$ …; the resulting space group is $P4_122$. MDO_1 corresponds to the structure-type A of Higgins *et al.* (1988) and Newsam *et al.* (1988).

A second generating operation is the glide reflection of type $n_{1/3,2}$ [reflection in a plane normal to **a**-**b** and translation of $\mathbf{c}_0$+(**a**+**b**)/6]. The application of that operation brings the layer in such position that the same operation may be applied once more. A repeated application of this operation gives rise to the MDO_2 structure. To obtain the symmetry and metrics of it, we may first observe that the double application of the operation $n_{1/3,2}$ corresponds to a pure translation of (**a**+**b**)/3+2$\mathbf{c_0}$. Assuming the reference frame with **a’** = -(**a**+**b**); **b’** =

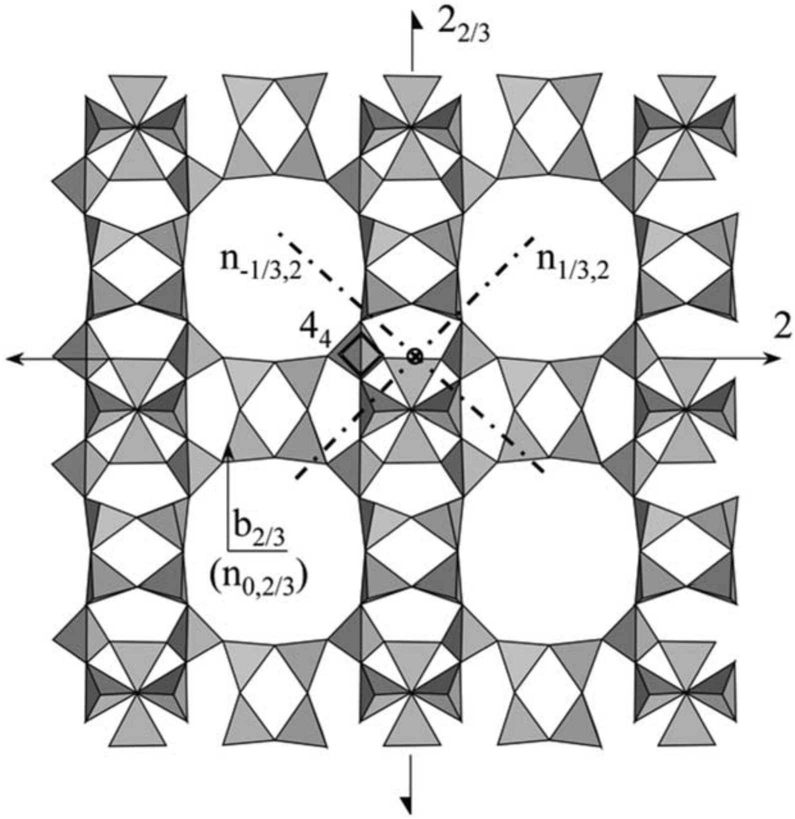

Fig. 2 - Schematic drawing of the single layer in zeolite beta and tschernichite, with indication of the σ operations.

a-**b**; **c'** = 2$\mathbf{c_0}$+(**a**+**b**)/3, we observe that **a'**,**b'** plane is centered (*C* centering); the glide reflection $n_{1/3,2}$ (partial symmetry operation) becomes a total glide operation *c* in a cell with the **c**' vector just indicated (Fig. 3); moreover the twofold axis parallel to (**a**-**b**) of the single layer is total symmetry element valid for the whole structure, which therefore has space group *C*2/*c* (*a*' = 17.7, *b*' = 17.7, *c*' = 14.5 Å, β = 114°) and corresponds to the structure B of Higgins *et al.* (1988) and Newsam *et al.* (1988).

The operational element 4_4 may act also in another position, related to the first one through the mirror plane normal to **a** in the single layer. In this case the constant application of the clockwise rotation by 90°, followed by the translation $\mathbf{c_0}$, gives rise to the structure MDO_1', with space group symmetry $P4_322$, enantiomorphous of MDO_1.

Moreover four distinct operational elements of type $n_{1/3,2}$ may be active, related each to the other by the mirror planes of the single layer: they give rise to four twin-related MDO_2 structures.

In conclusion there will be the following MDO structures:

– MDO_1 $P4_122$ $P4_322$ (enantiomorphous structures)
– MDO_2 *C*2/*c* (four possible twin-related orientations of the same structure)

In the Appendix we shall discuss the diffractional features of zeolite beta and tschernichite on the basis of their OD character and shall compare the results obtained for both MDO polytypes with selected diffraction patterns.

EXAMPLE OF POSSIBLE POLYTYPES AND NOMENCLATURE

Obviously, besides the two MDO structures, an infinite number of other polytypes may be sketched, corresponding, as suggested above, to the infinite sequences of alternating operational elements $b_{\pm 2/3}$ and $a_{\pm 2/3}$. They may be conveniently denoted by a sequence of symbols in which ±a/3 and ±b/3 regularly alternate. The six simplest sequences (up to six layers in the repeat unit) are given in the following, with indication of the repeating sequence, the name of the polytype of the natural phase, tschernichite, according to the indications of the IMA-IUCr Joint Committee on nomenclature (Bailey *et al.*, 1977), as well as the unit cell parameters and space group symmetry. The cell parameters of the various polytypes have been derived assuming the following values for the parameters of the single layer: *a* = *b* = 12.5, c_o = 6.6 Å.

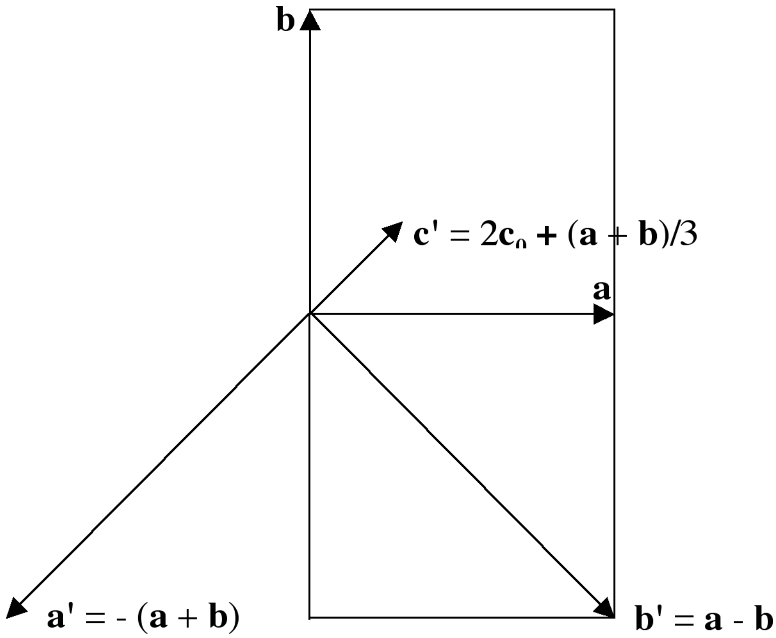

Fig. 3 - Reference frame assumed for the MDO_2 polytype.

– *2 layers in the repeat unit*:
  [b/3; a/3] … (Fig. 4) - MDO_2 - Tschernichite 2*M*; polytype B of Higgins *et al.* (1988) and Newsam *et al.* (1988); *C*2/*c*, *a* ≈ *b* ≈ 12.5 x √2 = 17.7 Å, *c* ≈ 14.5 Å, β ≈ 114°.
– *4 layers in the repeat unit*:
  [b/3; a/3; -b/3; -a/3] … (Fig. 5) - MDO_1; Tschernichite 4*Q*; polytype A of Higgins *et al.* (1988) and Newsam *et al.* (1988); $P4_122$, *a* = *b* ≈ 12.5, *c* ≈ 26.4 Å.
  [b/3; a/3; -b/3; a/3] … (Fig. 6) - Tschernichite 4*M*; polytype C of Higgins *et al.* (1988); *P*2/*c*, *a* ≈ 12.5, *b* ≈ 12.5, *c* ≈ 27.7 Å, β ≈ 107.5°.
– *6 layers in the repeat unit*:
  [b/3; a/3; -b/3; -a/3; -b/3; a/3] … (Fig. 7) - Tschernichite 6M_1; *C*2/*c*, *a* ≈ 17.7, *b* ≈ 17.7, *c* ≈ 40.1 Å, β ≈ 98.6°.
  [b/3; a/3; -b/3; -a/3; b/3; a/3] … (Fig. 8) - Tschernichite 6M_2; *C*2, *a* ≈ 17.7, *b* ≈ 17.7, *c* ≈ 40.1 Å, β ≈ 98.6°.
  [b/3; a/3; b/3; a/3; b/3; -a/3] … (Fig. 9) - Tschernichite 6*A*; $P\bar{1}$; *a* ≈ 12.5, *b* ≈ 12.5, *c* ≈ 41.7 Å, α ≈ 107.5°, β ≈ 95.9°, γ ≈ 90°.

CONCLUSION

The preceding OD discussion plainly explains the frequent – sometimes exclusive – occurrence in specimens of tschernichite and zeolite beta of the A and B polytypes, just those polytypes corresponding to the two MDO structures of this family, namely the structures presenting a full homogeneity in the stacking sequence.

Moreover the OD approach may be very helpful to reliably and easily interpret the complex diffraction patterns of zeolite beta and tschernichite. Each diffraction pattern presents a set of sharp reflections common to all polytypes (for *h* and *k* equal to 3n, relatively to the *a* and *b* parameters of the single layer), a set which offers a convenient reference frame; by carefully looking at the reflections with *h* or *k* different from 3n, it is possible to obtain information about the degree of disorder (a random sequence of layers gives rise to continuous streaks along **c***), about the presence of ordered domains (more or less diffuse maxima at proper positions in the reciprocal space), their relative volume, as well as about the presence of twin-related orientations of domains.

The OD discussion also clearly indicates that the polymorph C firstly described by Newsam *et al.* (1988) does not belong to the OD family of zeolite beta and tschernichite. In that structure-type the layers stack in a unique and distinct way; actually it does not generally occur in samples of zeolite beta and tschernichite; also in the case of the preparation by Liu *et al.* (2001) the single-crystal pillars of the C polymorph appear neatly distinguished from the matrix of zeolite beta polytypes.

ACKNOWLEDGMENTS

The work was supported by MIUR (Ministero dell'Istruzione, dell'Università e della Ricerca) and University of Pisa through grants to the national project «Minerals to materials: crystal chemistry, microstructures, modularity, modulations».

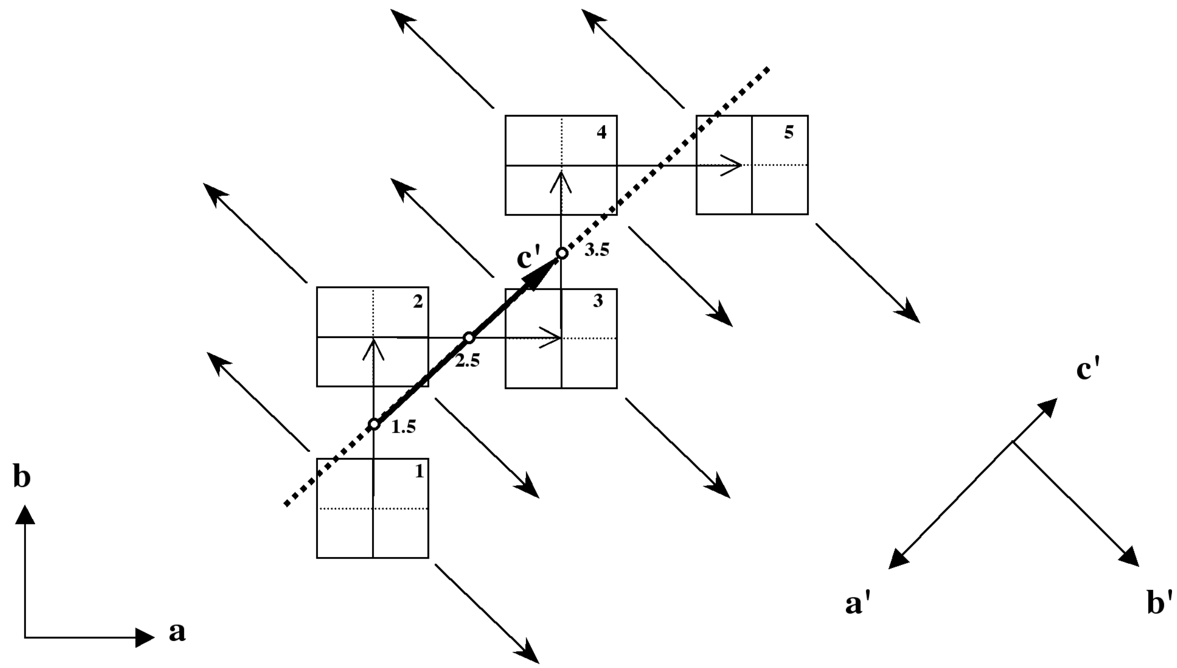

Fig. 4 - Schematic reconstruction of Tschernichite 2*M*. The single layers are represented by a square in which the dotted line corresponds to the ribbon of down-pointing tetrahedra and the continuous line corresponds to the ribbon of up-pointing tetrahedra. The stacking sequence is shown by layer numbers, with light arrows indicating the path of the stackings. The bold arrow indicates the **c**' vector of the polytype. The symmetry operations of the polytype are also indicated. The numbers (1.5, 2.5, 3.5) placed near to the symbols of the symmetry centers indicate that they are located at intermediate levels between neighboring layers. The orientation of the starting layer is presented on the left side of the drawing, whereas the orientation of the resulting structure is given on the right side of the drawing.

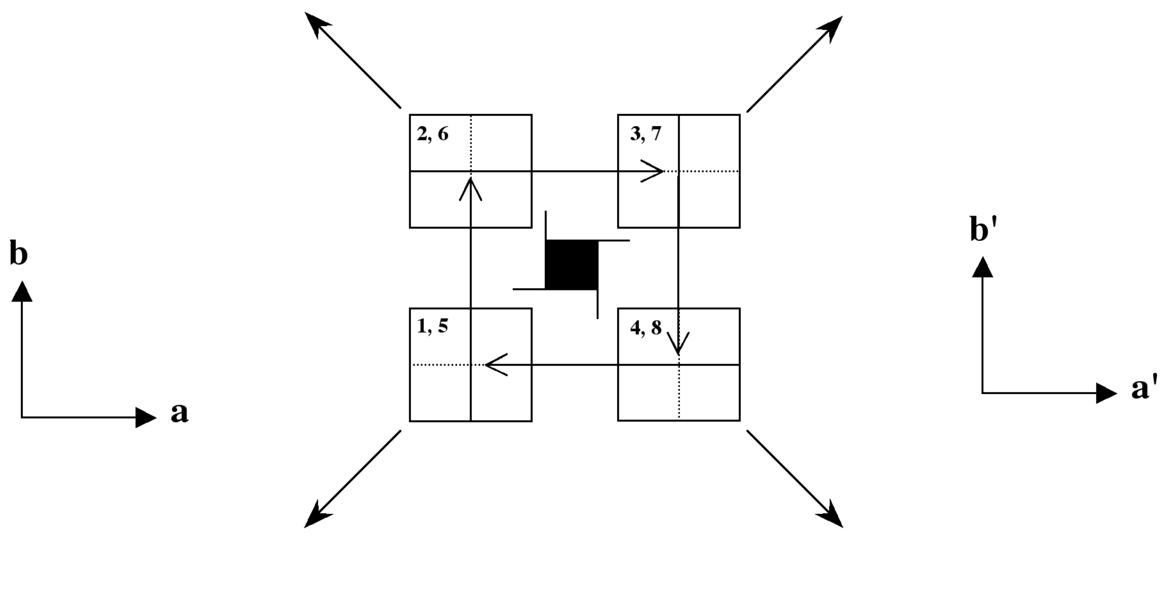

Fig. 5 - Schematic reconstruction of Tschernichite 4*Q* (see caption of Fig. 4 for the symbols).

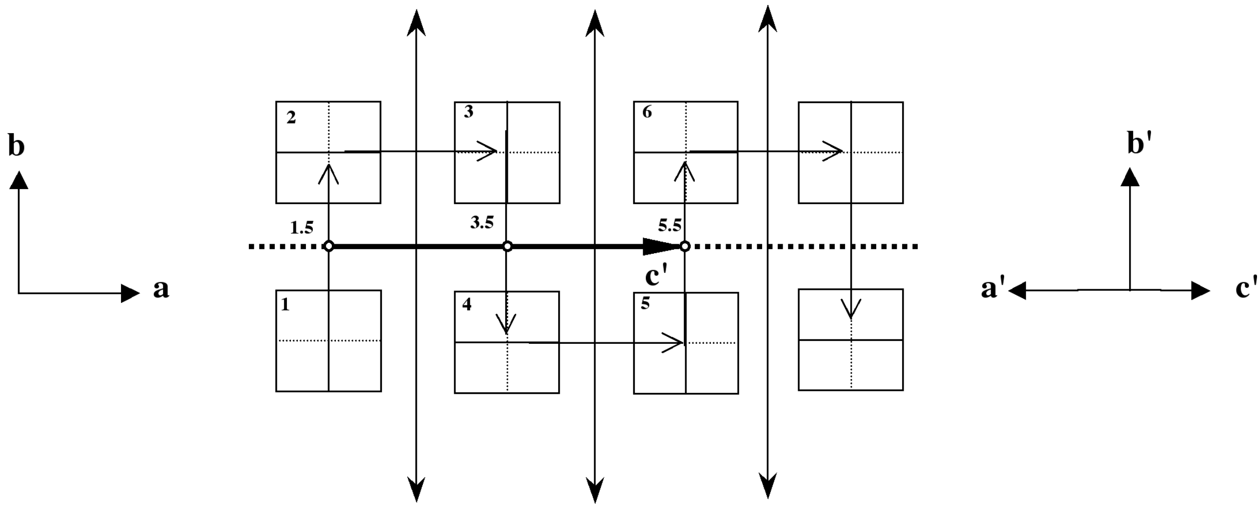

Fig. 6 - Schematic reconstruction of Tschernichite 4*M* (see caption of Fig. 4 for the symbols).

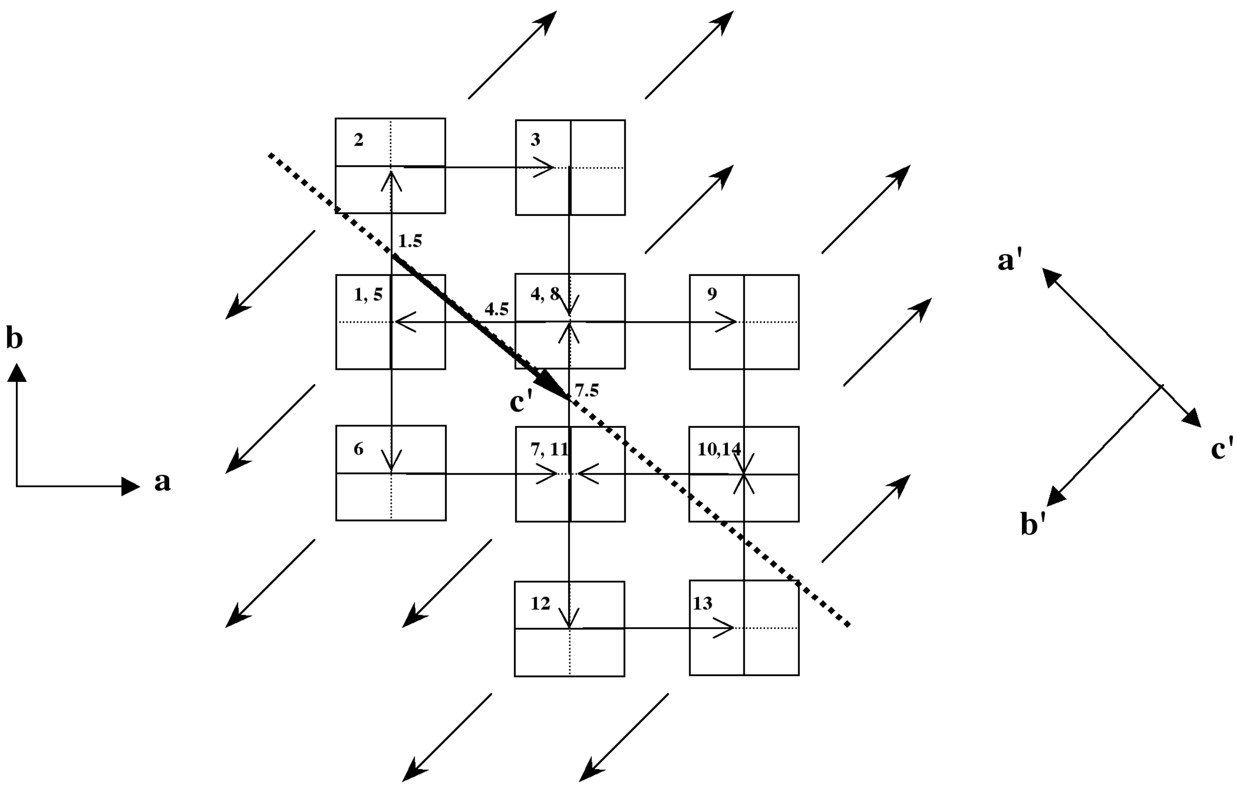

Fig. 7 - Schematic reconstruction of Tschernichite 6M_1 (see caption of Fig. 4 for the symbols).

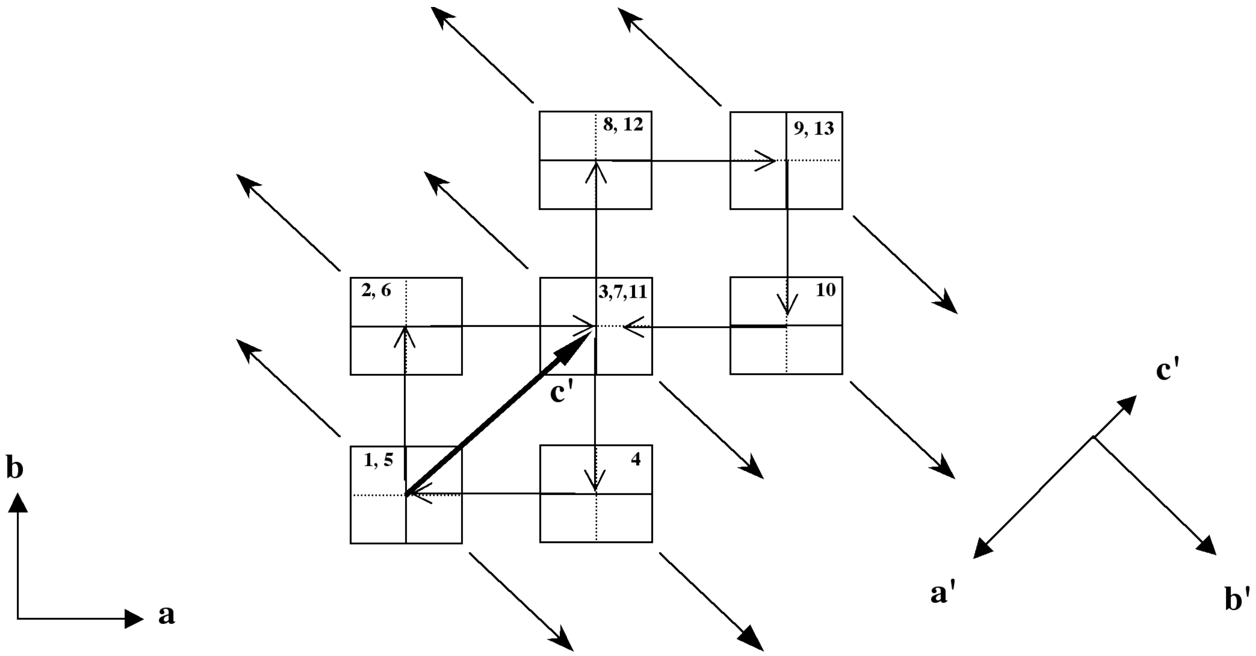

Fig. 8 - Schematic reconstruction of Tschernichite $6M_2$ (see caption of Fig. 4 for the symbols).

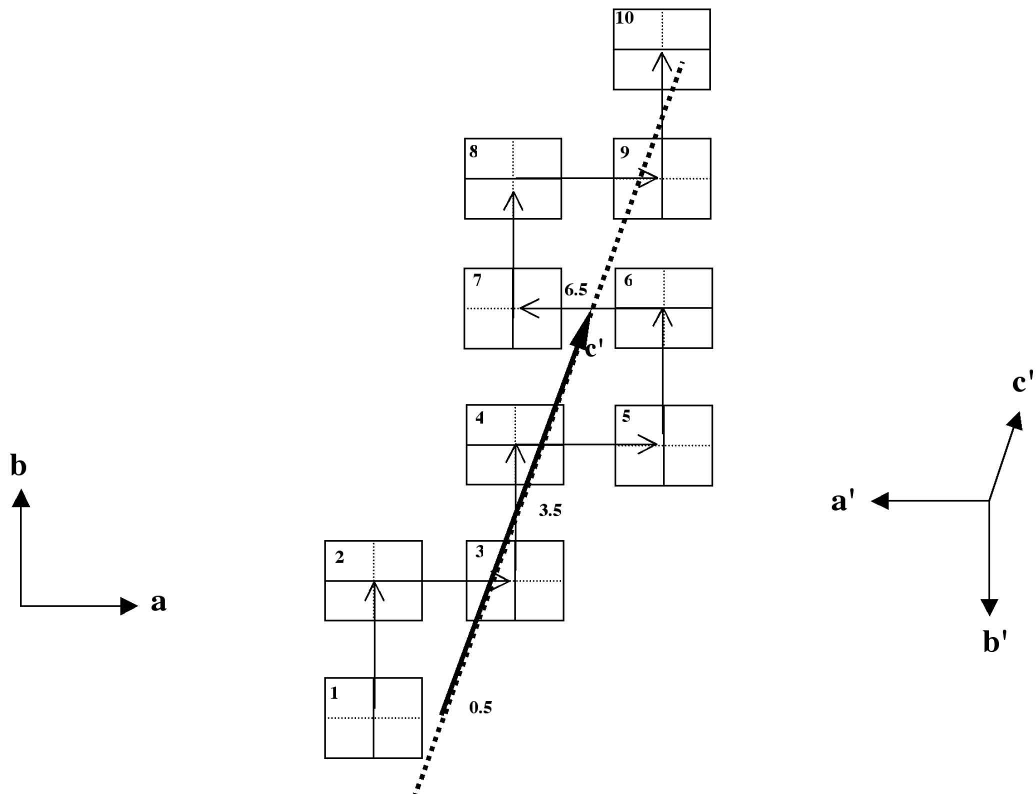

Fig. 9 - Schematic reconstruction of Tschernichite 6*A* (see caption of Fig. 4 for the symbols).

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APPENDIX
DISCUSSION OF THE DIFFRACTION PATTERNS ON THE BASIS OF THE OD CHARACTER OF TSCHERNICHITE

It seems useful to discuss the diffractional features common to all polytypes, and also to the disordered sequences, in the whole OD family of tschernichite, as well as the characteristic features of individual polytypes. In particular it is useful to describe the diffractions which characterize the two most important polytypes, namely MDO_1 (Tschernichite 4Q) and MDO_2 (Tschernichite 2M).

The Fourier transform of the whole structure may be obtained summing the contributions of the single layers

$$F(\mathbf{r}^*) = \Sigma_q F_q(\mathbf{r}^*)$$

The Fourier transform can be different from zero only in points $hk\lambda$ (indices are referred to the parameters of the single layer with $a = b = 12.5$, $c_o = 6.6$ Å) of the reciprocal space, if the layers are periodic with translation vectors **a**, **b**. The succession of the layers may be periodic or aperiodic; therefore the Fourier transform may be different from zero for discrete values of λ or for any value of λ. Consequently we shall obtain either diffraction patterns with only sharp spots, or diffraction patterns with diffuse «streaks»; moreover, as a disordered structure may contain ordered domains, we may also observe relatively sharp maxima placed on the diffuse «streaks».

As previously described, starting from the layer L_o [we shall indicate $\phi_o(hk\lambda)$ its contribution], the subsequent layer is related by a reflection in the plane of the layer and translation by $\pm\mathbf{b}/3$; the atomic coordinates x, y, z in L_o are transformed to coordinates $x, y\pm1/3, -z+1$ in L_1. The following notation is used:

$[L_1] = [-L_o] \pm\mathbf{b}/3 + \mathbf{c_o}$; its contribution is $\phi_1(hk\lambda) = \phi_o(hk\bar{\lambda}) \exp[2\pi i(\pm k/3+\lambda)]$

The next layer L_2 is related to L_1 through a reflection in the plane of the layer and translation by $\pm\mathbf{a}/3$; etc. By using the notation just introduced:

$[L_2] = [-L_1] \pm\mathbf{a}/3 + \mathbf{c_o} = [L_o] \pm\mathbf{a}/3 \pm\mathbf{b}/3 + 2\mathbf{c_o}$
$[L_3] = [L_1] \pm\mathbf{a}/3 \pm\mathbf{b}/3 + 2\mathbf{c_o}$

It can be observed that all the even layers $[L_{2q}]$ and all the odd layers $[L_{2q+1}]$ are translationally equivalent to the layers $[L_o]$ and $[L_1]$ respectively, namely

$[L_{2q}] = [L_o] + m_{2q}\,\mathbf{a}/3 + n_{2q}\,\mathbf{b}/3 + 2q\,\mathbf{c_o}$;
$[L_{2q+1}] = [L_1] + m_{2q+1}\,\mathbf{a}/3 + n_{2q+1}\,\mathbf{b}/3 + 2q\,\mathbf{c_o}$,

where $m_{2q} = \Sigma\,\alpha_j$ for the even layers; $n_{2q} = \Sigma\,\beta_j$ for the even layers
$m_{2q+1} = \Sigma\,\alpha_j$ for the odd layers; $n_{2q+1} = \Sigma\,\beta_j$ for the odd layers, with $\alpha_j = \pm1$ and $\beta_j = \pm1$

The Fourier transform of the whole structure may be expressed as:

$F(hk\lambda) = \phi_o(hk\lambda)\,S_o(hk\lambda) + \{\phi_o(hk\bar{\lambda}) \exp[2\pi i(\pm k/3+\lambda)]\}\,S_1(hk\lambda)$ (A1)
$S_o(hk\lambda) = \Sigma_q \exp[2\pi i(hm_{2q}/3 + kn_{2q}/3 + 2q\lambda)]$ (A2)
$S_1(hk\lambda) = \Sigma_q \exp[2\pi i(hm_{2q+1}/3 + kn_{2q+1}/3 + 2q\lambda)]$ (A3)

As m_{2q}, m_{2q+1}, n_{2q} and n_{2q+1} are integer numbers, obtained by summing +1 and -1 contributions in variable sequences, for $h,k = 3n$ the expressions (A2) and (A3) become:

$S_o(hk\lambda) = S_1(hk\lambda) = \Sigma_q \exp[2\pi i(2q\lambda)]$ (A4)

This expression is independent on the parameters m_{2q}, m_{2q+1}, n_{2q} and n_{2q+1}, namely is independent on the disorder. With a large number of layers the expression (A4) vanishes except for values of $\lambda = l/2$, with l integer (namely for $\lambda = \ldots$ -1, -0.5, 0, 0.5, 1, 1.5, 2 …). These values define a **c** repeat in direct space which is $2\mathbf{c_o}$. Moreover the rule $h,k = 3n$ points to **a** and **b** vectors which are one third of the corresponding vectors of the single layer, just defining the basic vectors of the family structure. In fact the reflections we are discussing about are not affected by disorder, they are always sharp and have the same values for any possible sequence of the layers (*family reflections*).

The diffraction patterns of the various polytypes (diffraction patterns which differ only in reflections with h or $k = 3n\pm1$) will be obtained from the expressions (A1), (A2) and (A3), on the basis of the actual sequence of layers.

For the polytype MDO_1 (Tschernichite 4Q) the sequence of layers is denoted as [b/3; a/3; -b/3; -a/3] and is represented in Figure 10 *a*. The sequence of even layers L_{2q} is such that the layers L_{4q+2} (L_2, L_6, L_{10} …) are translated by $\mathbf{a}/3 + \mathbf{b}/3$ with respect to L_o, whereas the layers L_{4q} (L_4, L_8 …) are not translated at all with respect to L_o. The sequence of odd layers is such that the layers L_3, L_7, L_{11} … are translated by $\mathbf{a}/3 - \mathbf{b}/3$ with respect to L_1, whereas the layers L_5, L_9 … are not translated at all with respect to L_1. Therefore:

$$S_o(hk\lambda) = \Sigma_q \{\exp[2\pi i(h/3 + k/3 + (4q+2)\lambda)] + \exp[2\pi i(4q\lambda)]\} \quad (A5)$$
$$S_1(hk\lambda) = \Sigma_q \{\exp[2\pi i(h/3 - k/3 + (4q+2)\lambda)] + \exp[2\pi i(4q\lambda)]\} \quad (A6)$$

Let us consider the expressions (A5) and (A6) in the case h or k = 3n±1 (the case h,k = 3n has been already considered in a general way, as it corresponds to that of the family reflections). Both expressions (A5) and (A6) vanish for a large number of layers, except in cases $\lambda = l/4$, with l integer. These values define a **c** repeat in direct space which is four times the $\mathbf{c_o}$ vector of the single layer, just corresponding to the repeat period $\mathbf{c_Q}$ of the 4Q polytype. If the l indices are referred to $\mathbf{c_Q}$ the expressions (A5) and (A6) take the forms:

$$S_o(hkl) = \Sigma_q \{\exp[2\pi i(h/3 + k/3 + (q+1/2)l)] + \exp[2\pi iql)]\} \quad (A5')$$
$$S_1(hkl) = \Sigma_q \{\exp[2\pi i(h/3 - k/3 + (q+1/2)l)] + \exp[2\pi iql)]\} \quad (A6')$$

These expressions may be used to calculate the approximate relative intensities of reflections in the various diffraction patterns of the 4Q polytype. For example let us consider the hhl pattern: according to (A6') $S_1(hhl) = 0$; as regards (A5') all the terms of the sum are equal and the square of their module is 3 for $h \neq$ 3n and l = 2n+1, whereas it is 1 for $h \neq$ 3n and l = 2n. We may add that for h = 3n (family reflexions) the square of the module of each term in (A5') is 0 for l = 2n+1 and 4 for l = 2n. Similar characteristic features, shown in Figure 10b and 10c, are displayed by the $h0l$ pattern. The non-family reflections ($h \neq$ 3n) are strong for l = 2n+1 and very weak (or not visible) for l = 2n. The expressions (A5') and (A6') for the $h0l$ reflections of MDO_1 polytype are:

$$S_o(h0l) = S_1(h0l) = \Sigma_q \{\exp[2\pi i(h/3 + (q+1/2)l)] + \exp[2\pi iql]\} \quad (A7)$$

All the terms of the sum (A7) are equal and the square of the module is 3 for $h \neq$ 3n and l = 2n+1, whereas it is 1 for $h \neq$ 3n and l = 2n, which is in keeping with the observed diffraction pattern [for h = 3n, namely for the family reflections, the square of the module of each term in (A7) is 0 for l = 2n+1 and 4 for l = 2n].
For the polytype MDO2 (Tschernichite 2M) the sequence of layers has been denoted as [b/3; a/3] and is represented in Figure 11a. The L_{2q} and L_{2q+1} layers are translationally equivalent to L_o and L_1 respectively, according to the same translation vector:

$$\mathbf{T}_{2q} = 2q\,(\mathbf{a}/3 + \mathbf{b}/3) + 2q\,\mathbf{c_o}$$

For this sequence the expressions (A2) and (A3) become:

$$S_o(hk\lambda) = S_1(hk\lambda) = \Sigma_q \exp\{2\pi i\,[(2q(h + k)/3 + 2q\lambda]\} \quad (A8)$$

We shall consider only the cases in which h or $k \neq$ 3n (non-family reflections).
For a large number of layers the expression (A8) vanishes except that for:
– values $\lambda = l/2 + 1/6$, with l integer, when $h + k$ = 3n+1;
– values $\lambda = l/2 + 2/6$, with l integer, when $h + k$ = 3n+2;
– values $\lambda = l/2$, with l integer, when $h + k$ = 3n.
The $h0l$ pattern of this polytype is shown in Figure 11b and c.

(ms. pres. il 31 maggio 2006; ult. bozze il 1° febbraio 2007)

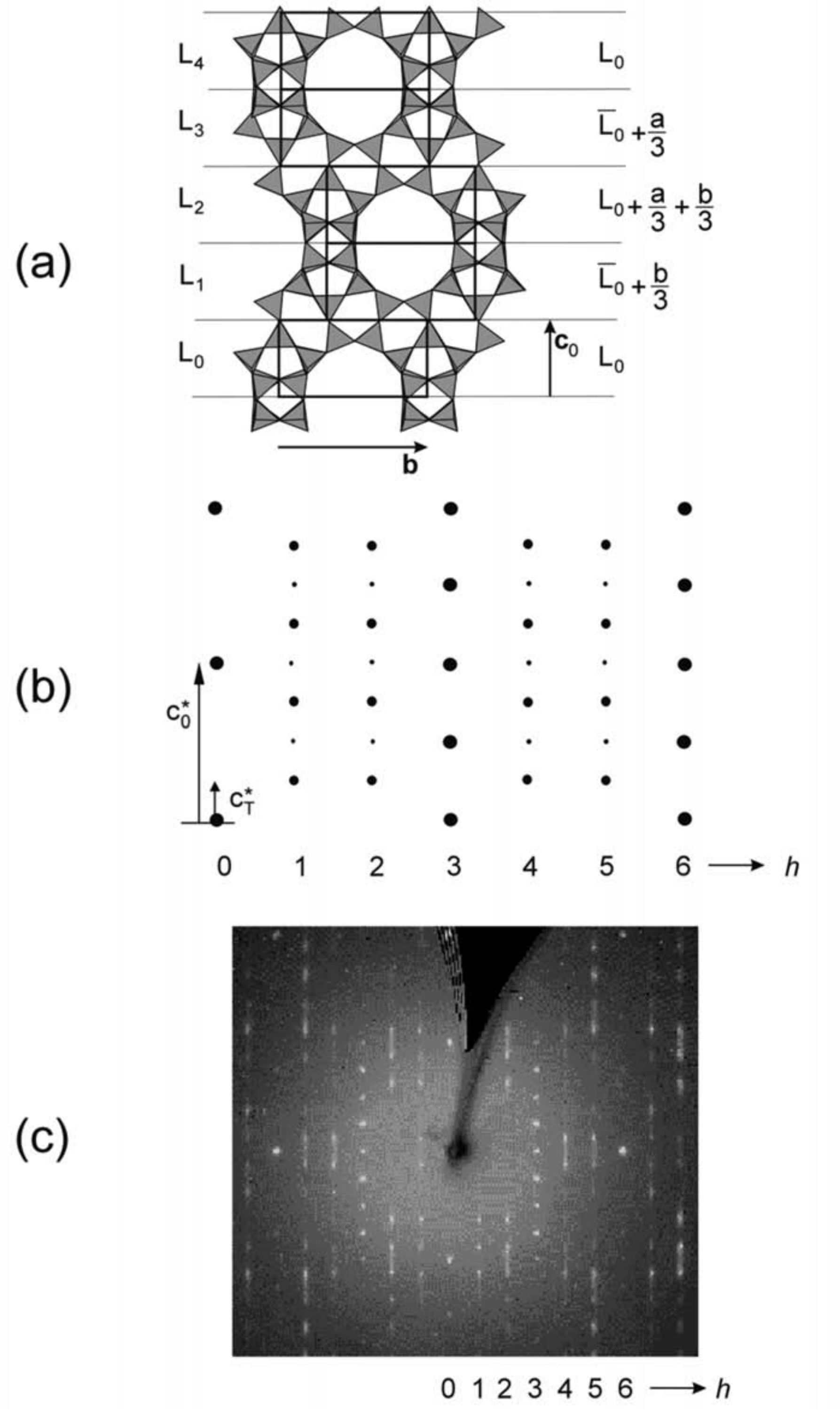

Fig. 10 - a) Layer sequence in the MDO_1 polytype as seen along **a** (the **b** and $\mathbf{c_0}$ axes of the starting layer are indicated). b) Detail of the theoretical diffraction pattern *h*0*l* of the pure MDO_1polytype. Detail of the diffraction pattern *h*0*l* of the dominant tetragonal polytype (small crystal after Alberti *et al.*, 2002) of tschernichite.

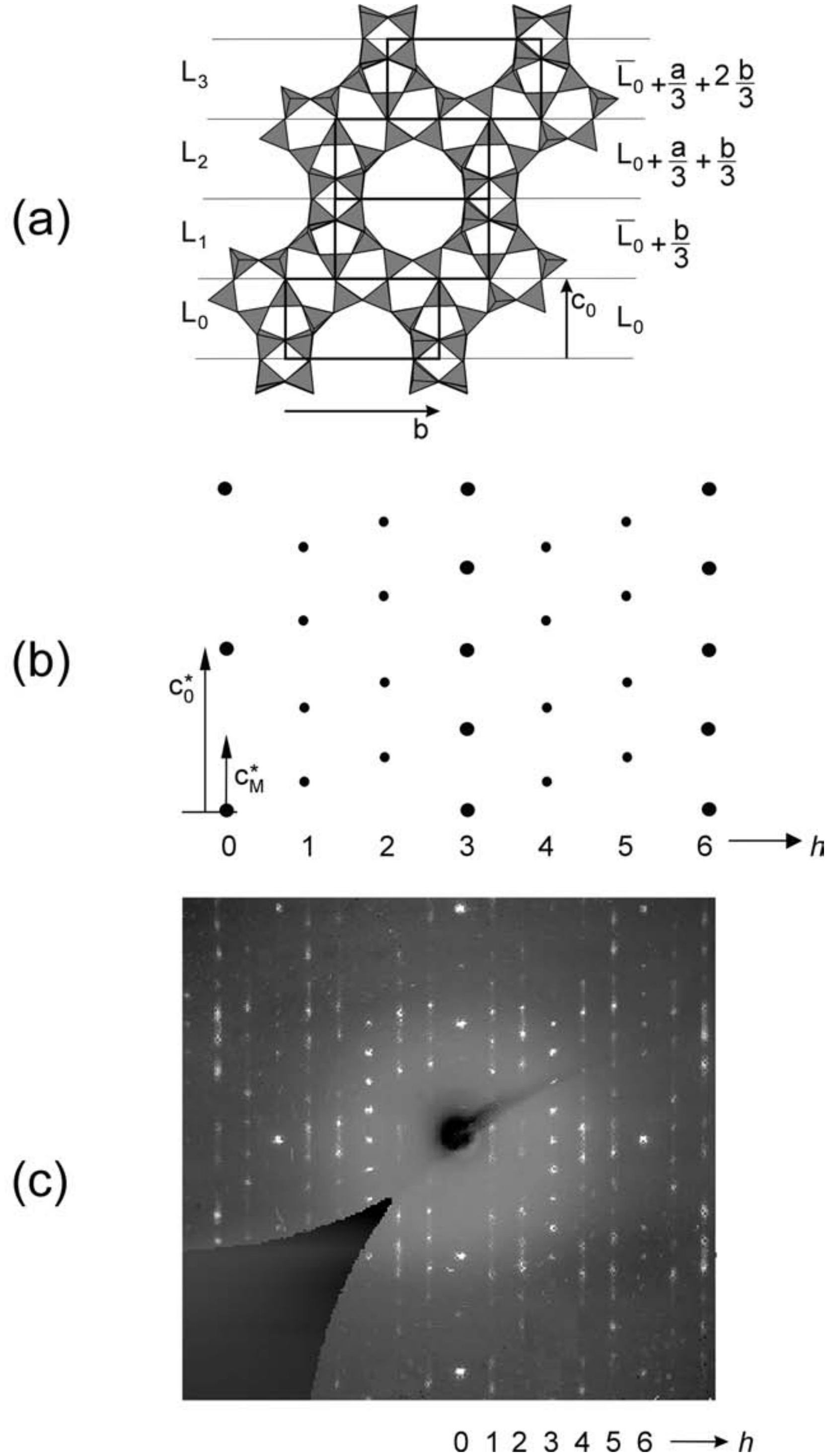

Fig. 11 - a) Layer sequence in the MDO_2 polytype as seen along [-1 1 0], with reference to the a', b', c' frame of Figs. 3 and 4. The **b** and $\mathbf{c_0}$ axes of the starting layer are indicated. b) Detail of the theoretical diffraction pattern *h*0*l* (indices referred to the «tetragonal» cell of the single layer) of the pure MDO_2 polytype; it corresponds to the *hhl* diffraction pattern in the reference frame of the polytype MDO_2. c) Detail of the diffraction pattern *h*0*l* (indices referred to the «tetragonal» cell of the single layer) of the dominant monoclinic polytype (large crystal after Alberti *et al.*, 2002) of tschernichite.