

Some Complex Structures Built up of Modules Obtained from the $R\text{-Nb}_2\text{O}_5$ Structure through Chemical Twinning*

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Twinning of a parent structure of the type $R\text{-Nb}_{205}$ on the unit-cell level is used to derive various structural elements or modules. They combine to form structures with a pseudo-hexagonal symmetry and constitute the structural basis of many compounds with seven- or seven- and six-coordinated metal atoms, such as $\text{Nb}_3\text{O}_7\text{F}$ (high-pressure modification), UVO_5 , α - and β - U_3O_8 , $\text{CaUMo}_4\text{O}_{16}$, β - KYb_2F_7 and U_2MoO_8 . A natural consequence of these relationships is the possibility of intergrowths between parent and derived (daughter) structures and between the daughters themselves.

$T\text{-Nb}_2\text{O}_5$ (with some interstitial metal atoms) is shown to be an ordered intergrowth of the $\text{Nb}_3\text{O}_7\text{F}$ (hp) and UVO_5 types. Interstitial metal atoms and the occurrence of UVO_5 -type structure elements in, e.g., $L\text{-Ta}_2\text{O}_5$ may diminish the need for distortion planes as a structural ingredient in this phase and in similar ones. The use of modules for the derivation of homologous series is demonstrated.

The concept of chemical twinning on the unit-cell level is useful in the classification and understanding of many compounds.^{1–9} In a recent paper¹⁰ we discussed the structure of some transition-metal oxides, e.g. UVO_5 , α - U_3O_8 and β - U_3O_8 , from the point of view of chemical twinning. It was shown that when deriving these types of structures we could use ReO_3 with anti-phase boundaries as a parent structure on which the twin planes operate. These planes may all have the same orientation, giving rise to one class of compounds, or there may be two sets perpendicular to each other, giving rise to another class of compounds built up of so-called fourlings. In this paper we will discuss the conditions wherein one set of twin planes operates on a different type of parent structure, namely $R\text{-Nb}_2\text{O}_5$.¹¹ This structure (Fig. 1), which is of an idealized V_2O_5 type,^{12,13} can also be interpreted as derived by crystallographic shear from the ReO_3 type.¹⁴ With $R\text{-Nb}_2\text{O}_5$ as a parent structure we are able to describe and classify not only the above-mentioned oxides but also several other related compounds. In the following we will apply this technique to compounds whose structures have been determined with a high degree of precision, involving in most cases three-dimensional single-crystal X-ray structure analysis.

$R\text{-Nb}_2\text{O}_5$ as a parent structure

Fig. 2(a) shows a pair of coherent twin individuals of an idealized $R\text{-Nb}_2\text{O}_5$ structure. Referring to that structure we find that the twin plane is $(0\bar{1}1)$. In that plane there is a new

type of interstice not found in the parent structure. Fig. 2(a) thus shows metal atoms coordinated by anions that form a pentagonal bipyramid. Note that a small displacement of the $\text{M-O-M-O}\dots$ string has occurred from the position in the parent structure to the one at the centre of the bipyramid. The repeat distance a' along $[011]$ is half a face diagonal of the unit cell shown in Fig. 1. If we assume

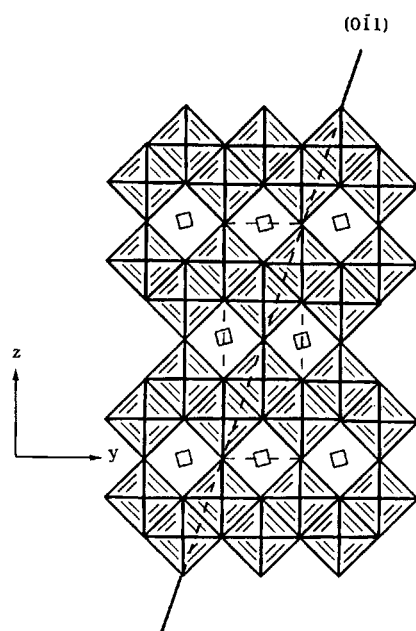


Fig. 1. The idealized crystal structure of $R\text{-Nb}_2\text{O}_5$. The plane $(0\bar{1}1)$ is indicated. The small squares (\square) indicate non-occupied sites.

* Dedicated to Professor Reginald Gruhn, University of Giessen, on his 60th birthday.

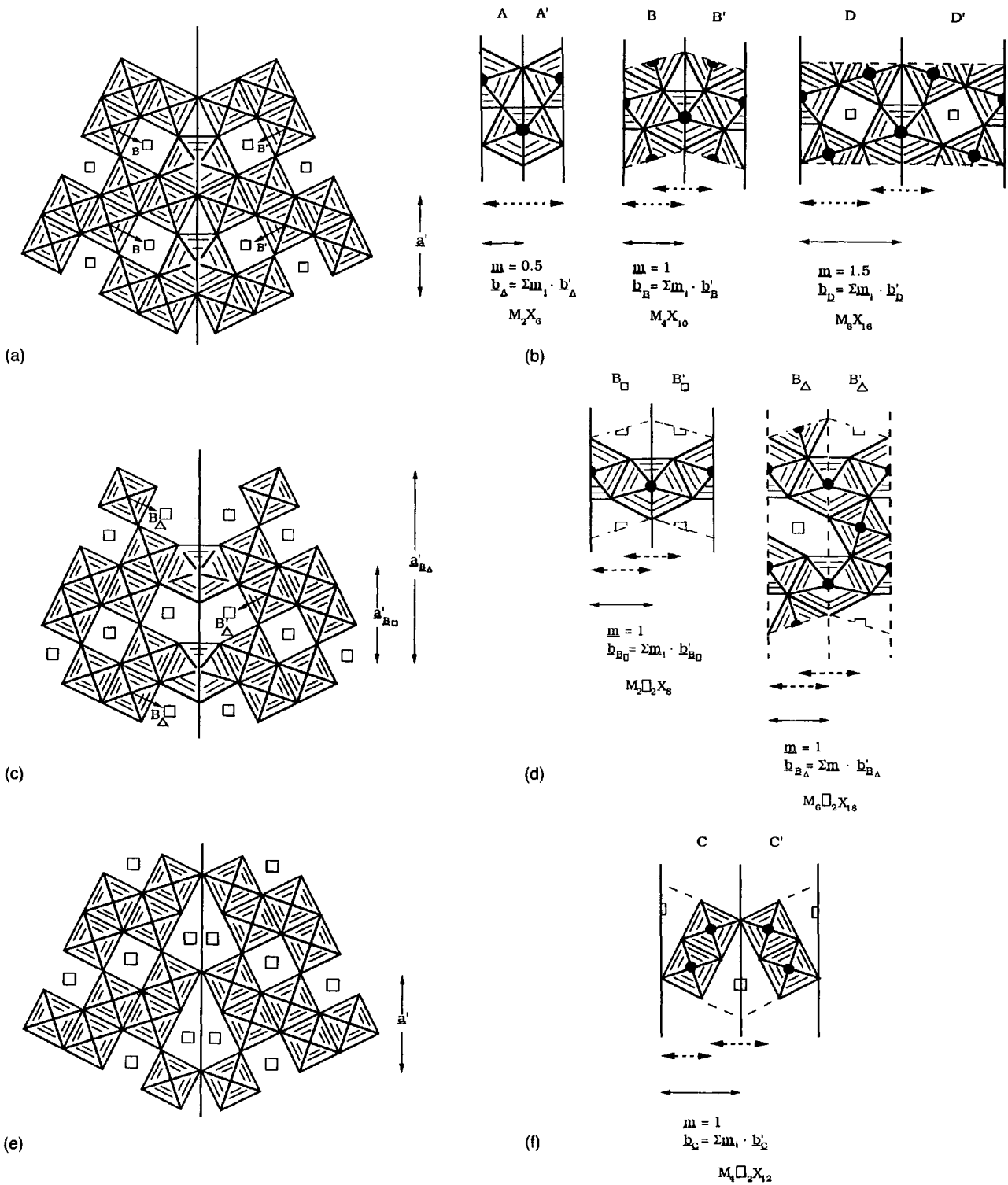


Fig. 2. (a) A pair of coherent individuals of the $R\text{-Nb}_2\text{O}_5$ structure with a mirror plane. A variant arrangement is also shown where an $\text{M-O-M-O}\dots$ string perpendicular to the plane of the paper has occupied the sites indicated B and B' (shown with arrows). a' is the repeat distance along $[011]$. (b) The introduction of further mirror planes in the $R\text{-Nb}_2\text{O}_5$ structure gives rise to the modules A , B and D and their mirror images A' , B' and D' . The B and B' modules are obtained from the variant arrangement in (a). The width of a module is shown by a double arrow, and the associated multiplicity m is given below. Dashed double arrows indicate M-M distances projected on the perpendicular to the twin plane. The subcell repeat distance b' is an average of these projected distances. b is the repeat distance (perpendicular to the twin plane) of two modules. The unit-cell content corresponding to two modules is also given. (c) Another pair of coherent twin individuals and a variant arrangement indicated by B_Δ and B'_Δ . (d) modules B_\square and B'_\square with mirror planes, and modules B_Δ and B'_Δ with glides obtained from (c). (e) A third pair of coherent twin individuals of idealized $R\text{-Nb}_2\text{O}_5$. (f) Modules C and C' obtained from (e).

regular octahedra with a space diagonal c' we find $a' = c' (1/2) \sqrt{10}$. c' is also the repeat distance perpendicular to the plane of the paper.

By introducing further twin planes parallel to the one in Fig. 2(a) we obtain the structural elements depicted in Fig. 2(b). Small displacements of $M\text{-O-M-O}\dots$ strings have occurred so that the strings are exactly in the twin planes. The structures may be thought of as built up of modules denoted A , B and D and of their counterpart twins A' , B' and D' . The repeat distances of these structures are a' and c' in the twin plane, but they differ in the perpendicular direction; they are denoted b_A , b_B and b_D , respectively. The stoichiometries of the modules are also given in Fig. 2(b). Note that in obtaining the structure BB' we have had to modify the parent structure by displacing an $M\text{-O-M-O}\dots$ string to a vacant site (denoted \square) as indicated in Fig. 2(a).

Our discussion of modules is essentially in accordance with that of Andersson and Hyde.^{1,2} These authors look upon the region between the twin planes as having an infinite extension in two directions parallel to the twin

planes and with a finite distance between them. This distance is characterized by the number of rows of atoms parallel to the twin plane and along the close-packed planes. The region is variously termed a close-packed part, twin block, twin band or twin lamella.

Two varieties of the B module are obtained from the coherent twins illustrated in Fig. 2(c). They give rise to the structures $B_{\square}B_{\square}'$ and $B_{\Delta}B_{\Delta}'$ shown in Fig. 2(d). In the case of B_{Δ} the parent structure is modified as shown in Fig. 2(c), which causes the B_{Δ} module to be related to B_{Δ}' through a glide translation along $[011]$. Finally, the $R\text{-Nb}_2\text{O}_5$ twins in Fig. 2(e) give rise to a structure composed of modules C and C' shown in Fig. 2(f).

Two important features should be noted regarding the modules described above. First, they are all completely compatible in the sense that they can be combined with each other, in any sequence along a direction perpendicular to the twin plane, to form a structure. An interesting consequence of this fact is that a parent structure may form an intergrowth with a derived (daughter) structure and that the daughter structures in turn may form intergrowths with

Table 1. Structures built up of one type of module.

Multipli- city, m	Compound space group; Z	Observed lattice constants	Sequence of modules Subcell dimensions observed	Remarks
–	$R\text{-Nb}_2\text{O}_5$ $A 2/m; 2$	$a = 3.983 \text{ \AA}$, $b = 3.826 \text{ \AA}$, $c = 12.79 \text{ \AA}$, $\beta = 90.75^\circ$	– –	Fig. 1. Ref. 11.
1	MeX_3 –	–	$AA'A\dots$ –	Fig. 3a shows a hypothetical structure.
2	UVO_5 $Pbma; 4$	$a = 12.31 \text{ \AA}$, $b = 7.19 \text{ \AA}$, $c = 4.115 \text{ \AA}$	$BB'B\dots$ $a' = 6.16 \text{ \AA}$ ($a/2$), $b' = 3.60 \text{ \AA}$ (b), $c' = 4.115 \text{ \AA}$ (c), $a'/b' = 1.71$	Fig. 3b shows a substructure, Ref. 16.
2	CaCrF_5 $C2/c; 4$	$a = 9.005 \text{ \AA}$, $b = 6.472 \text{ \AA}$ $c = 7.533 \text{ \AA}$, $\beta = 115.85^\circ$	$BB'B\dots$ $a' = 6.472 \text{ \AA}$ (b), $b' = 3.767 \text{ \AA}$ (c), $2c' = a \sin \beta \rightarrow c' = 4.047 \text{ \AA}$, $a'/b' = 1.718$	Fig. 3c, Ref. 17. CaMnF_5 is isostructural. Ref. 18.
2	PaCl_5 $C2/c; 4$	$a = 7.97 \text{ \AA}$, $b = 11.35 \text{ \AA}$, $c = 8.36 \text{ \AA}$, $\beta = 106.4^\circ$	– $c \sin \beta = mb' \rightarrow b' = 4.01 \text{ \AA}$	Ref. 22. Fig. 4a shows a related, hypothetical structure of MX_4 .
3	$\text{CaUMo}_4\text{O}_{16}$ $P2/n; 2$	$a = 11.447 \text{ \AA}$, $b = 6.715 \text{ \AA}$, $c = 8.236 \text{ \AA}$, $\beta = 90.44^\circ$	$DD'D\dots$ $a' = 6.715 \text{ \AA}$ (b), $b' = 3.816 \text{ \AA}$ (a), $c' = 4.118 \text{ \AA}$ ($c/2$), $a'/b' = 1.743$	Fig. 3d, Ref. 19 and 20.
3	iriginite $\text{UMo}_2\text{O}_9 \cdot 3\text{H}_2\text{O}$, $Pca2_1; 4$	$a = 12.77 \text{ \AA}$, $b = 6.175 \text{ \AA}$, $c = 11.53 \text{ \AA}$	– $a' = 6.175 \text{ \AA}$ (b), $b' = 3.843 \text{ \AA}$ (c), $a'/b' = 1.747$	Synthetic. Ref. 21.
3	$\text{NH}_4\text{MnFeF}_6$ $Pb2n; 8$	$a = 7.844 \text{ \AA}$, $b = 12.819 \text{ \AA}$, $c = 10.582 \text{ \AA}$	$CC'C\dots$ $a' = 6.410 \text{ \AA}$ ($b/2$), $b' = 3.527 \text{ \AA}$ (c), $c' = 3.922 \text{ \AA}$ ($a/2$), $a'/b' = 1.817$	Ref. 25. cf. BaNb_2O_6 .
3	BaNb_2O_6 $Pbmm; 2$	$a = 6.030 \text{ \AA}$, $b = 10.461 \text{ \AA}$, $c = 3.946 \text{ \AA}$	$CC'C\dots$ $a' = 6.030 \text{ \AA}$ (a), $b' = 3.487 \text{ \AA}$ (b), $c' = 3.946 \text{ \AA}$ (c), $a'/b' = 1.729$	High-temperature modification. Fig. 4c, Ref. 24.

Table 2. Structures built up of two or more types of modules.

Multiplicity, m	Compound space group; Z	Observed lattice constants	Sequence of modules Subcell dimensions observed	Remarks
1.5	Nb ₃ O ₇ F(hp) <i>Cmmm</i> ; 2	$a = 6.475 \text{ \AA}$, $b = 10.496 \text{ \AA}$, $c = 3.922 \text{ \AA}$	$A'BA'...$ $a' \approx 6.174 \text{ \AA}$, $b' \approx 3.676 \text{ \AA}$, $c' = 3.922 \text{ \AA}$ (c), $a'/b' = 1.680$	High-pressure modification. For a' and b' see text. Fig. 5a, Ref. 27.
1.5	Ta ₃ O ₇ F <i>Cmmm</i> ; 2	$a = 6.478 \text{ \AA}$, $b = 10.496 \text{ \AA}$, $c = 3.907 \text{ \AA}$	$A'BA'...$ $a' \approx 6.167 \text{ \AA}$, $b' \approx 3.675 \text{ \AA}$, $c' = 3.907 \text{ \AA}$ (c), $a'/b' = 1.678$	Low-temperature modification. For a' and b' see text. Fig. 5a and Ref. 28.
1.5	β -U ₃ O ₈ <i>Cmcm</i> ; 4	$a = 7.069 \text{ \AA}$, $b = 11.445 \text{ \AA}$, $c = 8.301 \text{ \AA}$	$A'BA'...$ $a' \approx 6.726 \text{ \AA}$, $b' \approx 4.010 \text{ \AA}$, $c' = 4.150 \text{ \AA}$ ($c/2$), $a'/b' = 1.678$	For a' and b' see text. Fig. 5c, Ref. 27 and 30.
1.5	β -KYb ₂ F. <i>P2</i> ; 1	$a = 6.528 \text{ \AA}$, $b = 4.217 \text{ \AA}$, $c = 6.435 \text{ \AA}$, $\beta = 115.94^\circ$	$B_{\square}A'B_{\square}...$ $a' = 6.528 \text{ \AA}$ (a), $b' = 3.858 \text{ \AA}$, $c = 4.217 \text{ \AA}$ (b), $a'/b' = 1.692$	$c \sin \beta = mb'$, Fig. 5b, Ref. 29.
2	LaTa ₃ O ₉ <i>Pnma</i> ; 4	$a = 6.595 \text{ \AA}$, $b = 7.664 \text{ \AA}$, $c = 12.48 \text{ \AA}$	$B_{\Delta}B'B_{\Delta}...$ $a' = 6.240 \text{ \AA}$ ($c/2$), $b' = 3.300 \text{ \AA}$ (a), $c' = 2 \times 3.832 \text{ \AA}$ ($b/2$), $a'/b' = 1.891$	Fig. 4b, Ref. 23.
3	α -U ₃ O ₈ <i>C2mm</i> ; 2	$a = 6.716 \text{ \AA}$, $b = 11.960 \text{ \AA}$, $c = 4.1469 \text{ \AA}$	$AA'BB'A...$ $a' = 6.716 \text{ \AA}$ (a), $b' = 3.987 \text{ \AA}$ (b), $c' = 4.1469 \text{ \AA}$ (c), $a'/b' = 1.685$	Fig. 6a, Ref. 31.
4	CsYb ₃ F ₁₀ <i>Pc</i> ; 2	$a = 4.2893 \text{ \AA}$, $b = 6.7437 \text{ \AA}$, $c = 16.196 \text{ \AA}$, $\beta = 90^\circ$	$AB_{\square}'AA'B_{\square}'A'A...$ $a' = 6.7437 \text{ \AA}$ (b), $b' = 4.049 \text{ \AA}$ (c), $c' = 4.2893 \text{ \AA}$ (a), $a'/b' = 1.666$	Fig. 6b, Ref. 33.
5	U ₅ O ₁₂ Cl <i>Pbmm</i> ; 2	$a = 7.111 \text{ \AA}$, $b = 19.628 \text{ \AA}$, $c = 4.130 \text{ \AA}$	$AB'BA'BB'A...$ $a' = 7.111 \text{ \AA}$ (a), $b' = 3.925 \text{ \AA}$ (b), $c' = 4.130 \text{ \AA}$ (c), $a'/b' = 1.812$	Fig. 6c, Ref. 33.
6	U ₂ MoO ₈ <i>P2₁2₁2₁</i> ; 4	$a = 6.734 \text{ \AA}$, $b = 23.24 \text{ \AA}$, $c = 4.115 \text{ \AA}$	$A'DA'BD'BA'...$ $a' = 6.734 \text{ \AA}$ (a), $b' = 3.873 \text{ \AA}$ (b), $c' = 4.115 \text{ \AA}$ (c), $a'/b' = 1.738$	Fig. 6d, Ref. 34.
7	Zr ₇ O ₉ F ₁₀ <i>Pbam</i> ; 2	$a = 6.443 \text{ \AA}$, $b = 26.851 \text{ \AA}$, $c = 4.071 \text{ \AA}$	$AB'AA'BA'BA'AB'A...$ $a' = 6.443 \text{ \AA}$ (a), $b' = 3.836 \text{ \AA}$ (b), $c' = 4.071 \text{ \AA}$ (c), $a'/b' = 1.680$	Fig. 6e, Ref. 35.
8	<i>T</i> -Nb ₂ O ₅ <i>Pbam</i> ; 8.4	$a = 6.175 \text{ \AA}$, $b = 29.175 \text{ \AA}$, $c = 3.930 \text{ \AA}$	$AB'AB'BA'BA'BB'A...$ $a' = 6.175 \text{ \AA}$ (a), $b' = 3.647 \text{ \AA}$ (b), $c' = 3.930 \text{ \AA}$ (c), $a'/b' = 1.693$	42 oxygen atoms per unit cell. Fig. 6f, Ref. 36.
8	Ta ₁₅ Al _{1/3} W _{2/3} O ₄₀ <i>P2</i> ; 1	$a = 6.182 \text{ \AA}$, $b = 29.200 \text{ \AA}$, $c = 3.876 \text{ \AA}$, $\alpha = 90^\circ$	$a' = 6.182 \text{ \AA}$ (a), $b' = 3.650 \text{ \AA}$ (b), $c' = 3.876 \text{ \AA}$ (c), $a'/b' = 1.694$	40 oxygen atoms per unit cell, Ref. 38.

each other (see below). Secondly, a structure built up of modules related to each other by mirror planes will display its metal-atom arrangement as having pseudo-hexagonal symmetry [cf. the AA' and BB' structures of Fig. 2(b)]. Consequently the structure will exhibit a subcell with the orthohexagonal cell dimensions a' , b' and c' , with a' and c' having the same meaning as before. The value of b' is obtained from the M–M distances whose direction more or less coincides with that of the perpendicular to the twin plane; it is in general an average of the projections of the M–M distances onto that perpendicular. Note that the ideal

value of the ratio a'/b' is $\sqrt{3}$; in general there are deviations, as can be seen in Tables 1 and 2). Thus BB' and DD' of Fig. 2(b) have $b_B = 2b'_B$ and $b_D = 3b'_D$, with multiplicities 2 and 3, respectively. In fact it is found that the multiplicity m associated with a module (with repeat distances a' and c') is half the number of sites that are suitable as hosts for larger metal atoms. This is to be interpreted such that sites of the three- and four-sided cavities of DD' do not count in this respect, but those of CC' and B_{\square} do. Thus the multiplicities attributed to the modules A , B , C and D are $1/2$, 1 , $3/2$ and $3/2$, respectively.

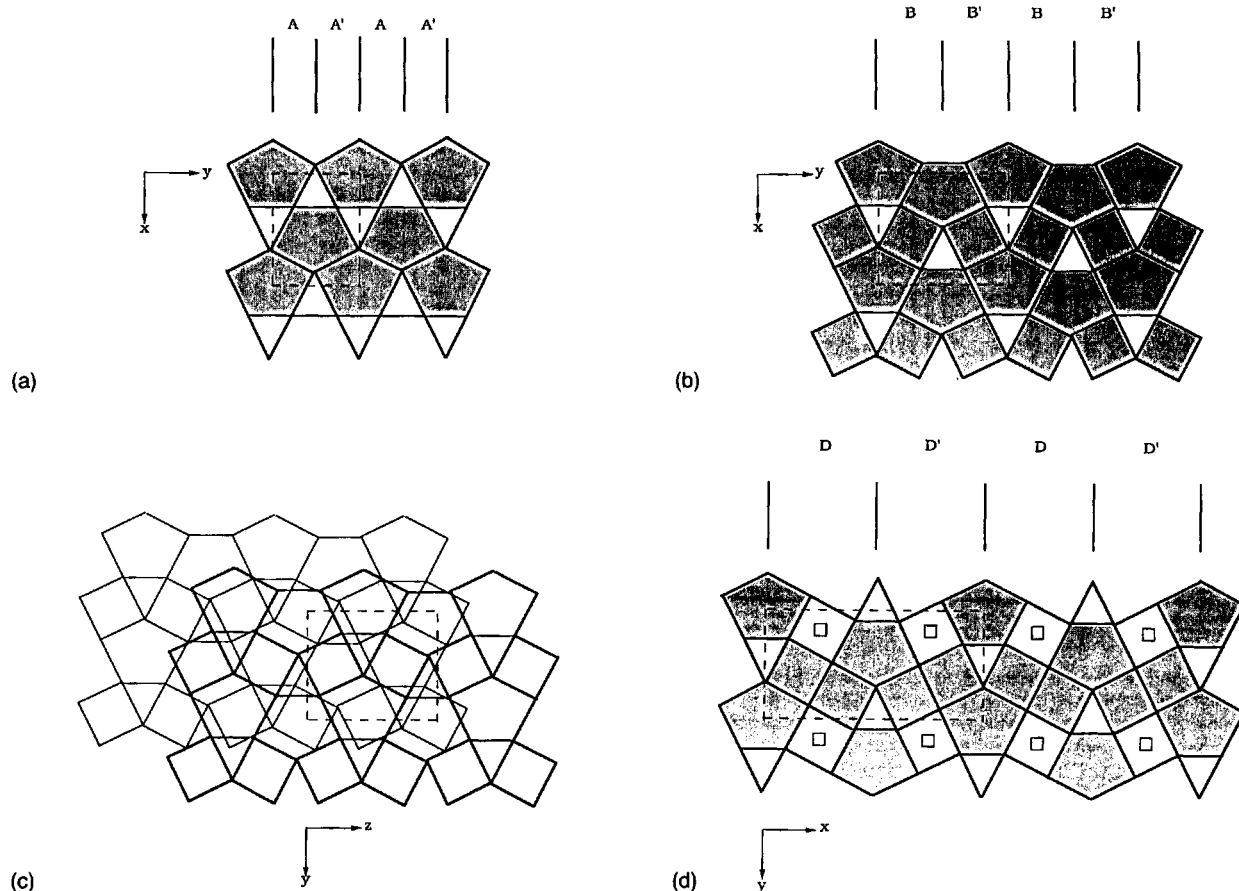


Fig. 3. (a) The idealized crystal structure of a hypothetical compound of MX_3 composition built up of the modules A and A' . The pentagons indicate pentagonal bipyramids. (b) The modules B and B' constitute the idealized crystal structure of UVO_5 . The squares indicate octahedra. (c) The idealized crystal structure of CaCrF_5 . (d) The idealized crystal structure of $\text{CaUMo}_4\text{O}_{16}$ built of D and D' modules. Note the empty sites (marked with \square) in the structure.

Structures built up of one type of module

In this section we will describe structures built up entirely of one type of module. Fig. 3(a) shows a hypothetical structure of MX_3 stoichiometry built up of A modules. A highly distorted version of this structure is part of $H\text{-Ta}_2\text{O}_5$.¹⁵ In Fig. 3(b) the idealized structure of UVO_5 is shown as built up of B modules. The real structure¹⁶ has $a = 2a'$ (Table 1).

The structures of CaCrF_5 ¹⁷ and CaMnF_5 ¹⁸ are built up of layers of the UVO_5 type. These are superposed on each other so that octahedra are on top of bipyramids and vice versa, as indicated in Fig. 3(c). These structures have monoclinic symmetry (Table 1).

The recently determined crystal structure of $\text{CaUMo}_4\text{O}_{16}$ ^{19,20} is shown in idealized form in Fig. 3(d). It is a member of a new family of isotopic oxides where Mg, Mn, Cd, Hg, Sr and Pb may be substituted for Ca. It is built up of D modules consisting of pentagonal bipyramids with calcium and uranium and of octahedra with molybdenum, as indicated in Fig. 3(d). As calcium and uranium alter-

nately occupy the bipyramids along the c -axis, this axis is doubled; cf. Table 1.

Synthetic iriginite, $\text{UO}_3 \cdot 2\text{MoO}_3 \cdot 3\text{H}_2\text{O}$,²¹ has a layer structure built up of pentagonal bipyramids and octahedra coordinating the uranium and molybdenum atoms, respectively. In the layers the polyhedra are arranged exactly as in $\text{CaUMo}_4\text{O}_{16}$. The layers are held together by van der Waals bonds and by hydrogen bonds from the water molecules.

Fig. 4(a) shows a hypothetical structure built of B_{\square} modules and with multiplicity $m = 2$. The formula is derived from $\text{MX}_{6/2}\text{X}_{1/1}$, i.e. MX_4 . Features of this structure are found in PaCl_5 ,²² which contains PaCl_7 units sharing pentagonal edges to form infinite chains in the b' direction. The stoichiometry is derived from the structural formula $\text{PaCl}_{4/2}\text{Cl}_{3/1}$. Thus there is no connection between the chains in the c' -direction. Another version of the B module is shown in Fig. 4(b), which gives the idealized structure of LaTa_3O_9 .²³ Note the glide plane between the modules. Lanthanum atoms reside in the tunnels. Fig. 4(c), finally, shows C modules forming the structure of BaNb_2O_6 .²⁴ Barium atoms reside in the tunnels. A similar structure is

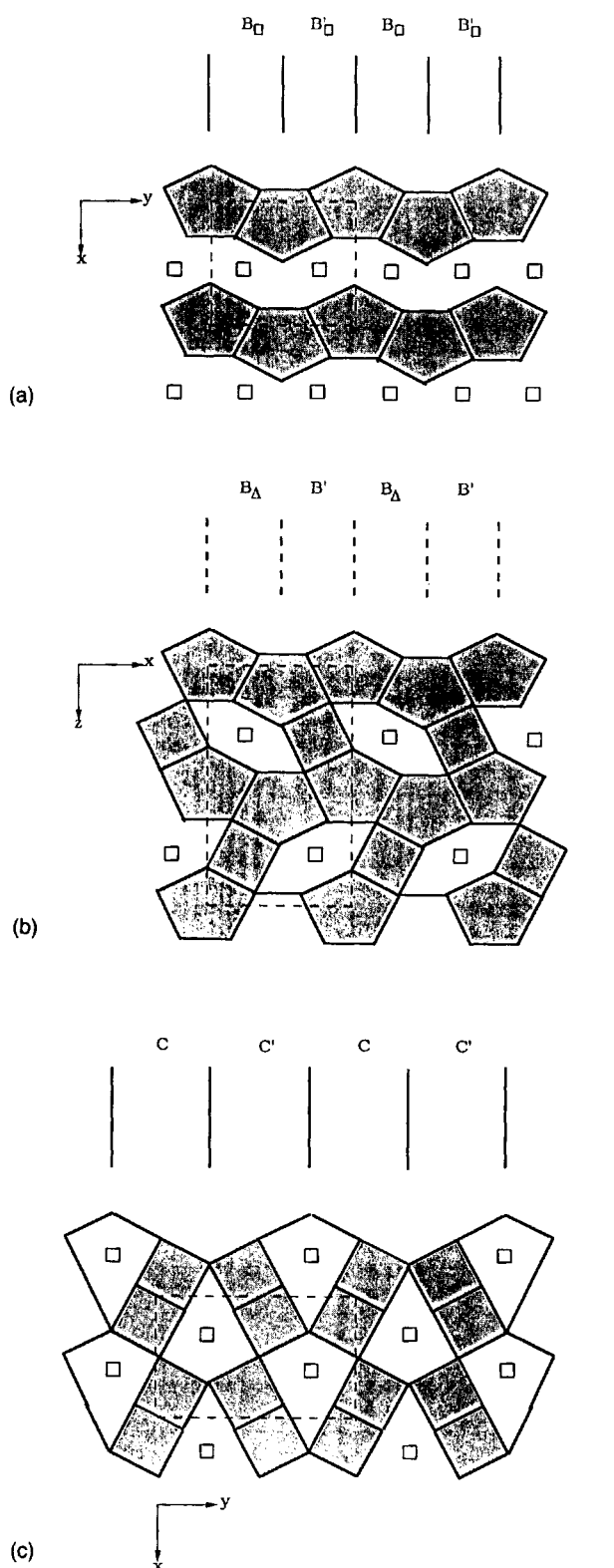


Fig. 4. (a) The idealized crystal structure of a hypothetical compound of MX_4 composition built up of B_{\square} and B_{\square}' modules and related to $PaCl_5$. (b) The idealized crystal structure of $LaTa_3O_9$ built up of B_{Δ} and B' modules. The lanthanum atoms reside in the tunnels (marked with \square). (c) The idealized crystal structure of $BaNb_2O_6$ built up of C and C' modules. The barium atoms reside in the tunnels (marked with \square).

adopted by NH_4MnFeF_6 .²⁵ Owing to cationic ordering of Mn and Fe there are structural differences, however; cf. Table 1.

Structures built up of two or more types of modules

This section deals with structures built up of different modules. The simplest, and in this context most important, structure is that of the high-pressure modification

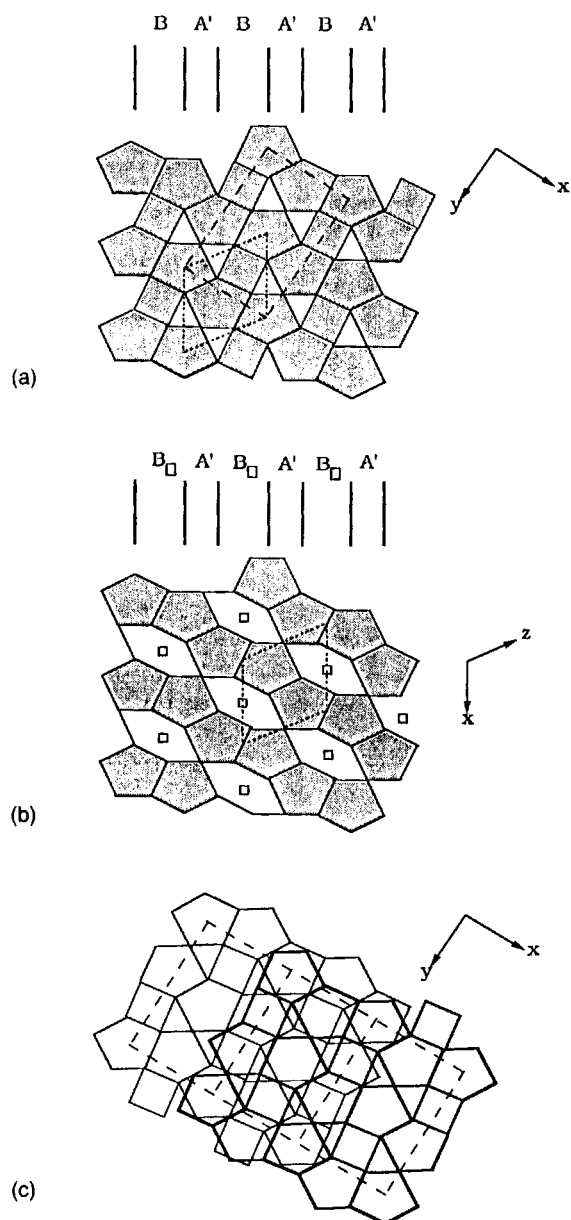


Fig. 5. (a) The $Nb_3O_7F(hp)$ structure as built up of A' and B modules. A primitive monoclinic unit cell is outlined (dotted), and a C -centred pseudo-orthorhombic cell (dashed) corresponding to the true orthorhombic one is also shown. (b) The β - KYb_2F_7 structure as built up of A' and B_{\square} modules. Potassium atoms reside in the tunnels (marked with \square). (c) The β - U_3O_8 structure as built up of two layers of $Nb_3O_7F(hp)$ type which are superposed on each as indicated in the figure.

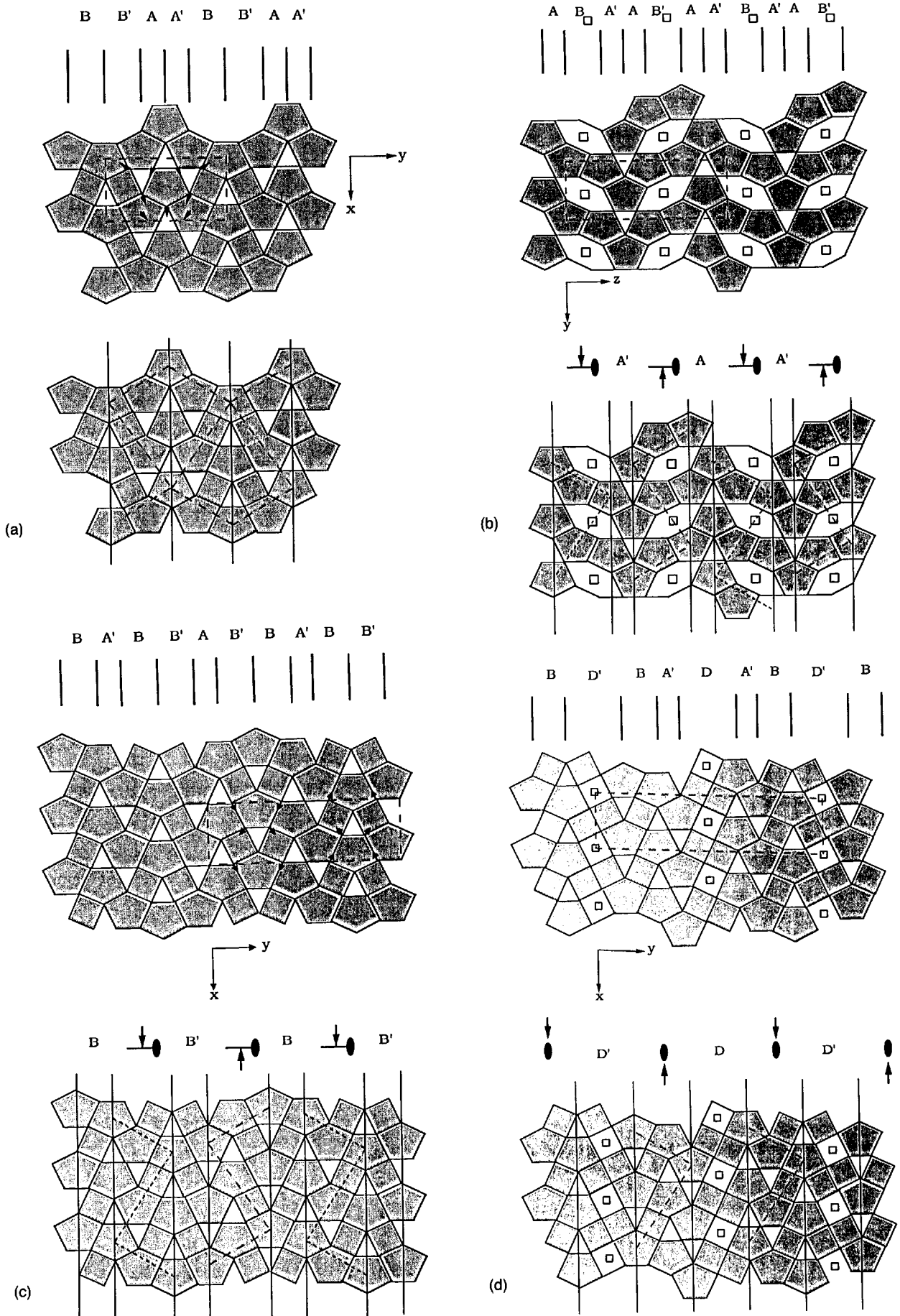


Fig. 6. (a)-(d). For caption see next page.

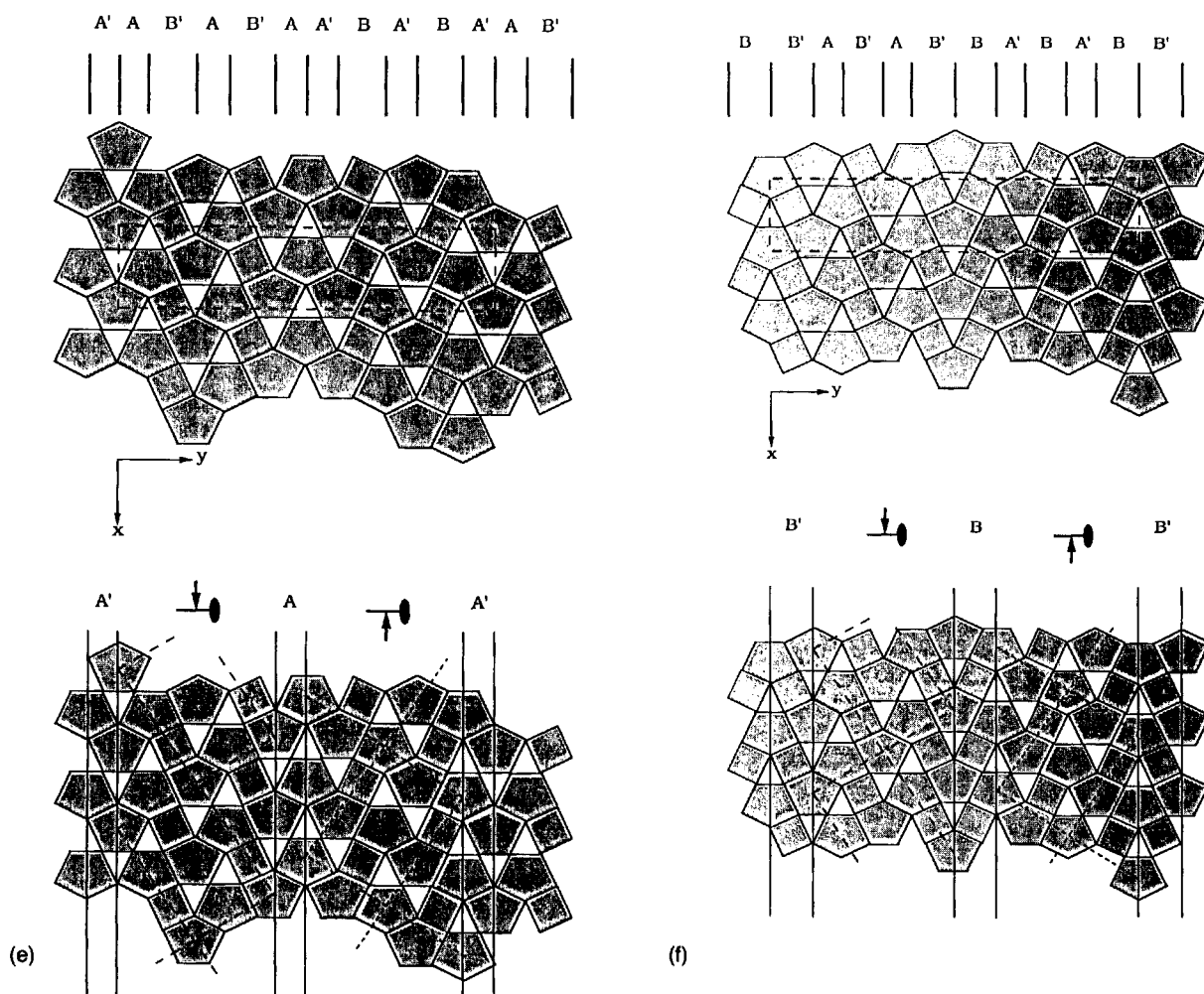


Fig. 6. (a) The idealized crystal structure of α - U_3O_8 is shown at the top and as twinned blocks of $Nb_3O_7F(hp)$ below. The real structure is obtained by a change in the atomic positions as indicated by arrows in the top figure. (b) The idealized crystal structure of $CsYb_3F_{10}$ is shown at the top. It may alternatively be described as an ordered intergrowth of a hypothetical MX_3 structure [Fig. 3(a)] and blocks of a modified type of $Nb_3O_7F(hp)$ as shown below. The relationship between the blocks is also indicated. (c) The idealized crystal structure of $U_5O_{12}Cl$ is shown above and as an ordered intergrowth of $Nb_3O_7F(hp)$ and UVO_5 below. The relation between the Nb_3O_7F blocks is also shown. The real structure is obtained by a change in the atomic positions as indicated by arrows in the top figure. (d) The idealized monoclinic crystal structure of U_2MoO_8 is shown above and as an ordered intergrowth of $Nb_3O_7F(hp)$ and $CaUMo_4O_{16}$ below. The relation between the Nb_3O_7F blocks is also shown. Note the empty sites (marked with \square) in the structure. The real structure has orthorhombic symmetry. (e) The idealized crystal structure of $Zr_7O_{19}F_{10}$ is shown above and as an ordered intergrowth of $Nb_3O_7F(hp)$ and the hypothetical MX_3 structure [Fig. 3(a)] below. (f) The idealized crystal structure of $T-Nb_2O_5$ is shown above and as an ordered intergrowth of $Nb_3O_7F(hp)$ and UVO_5 below.

$Nb_3O_7F(hp)$. It was prepared and characterized in 1970,²⁶ and its crystal structure was determined in 1971 by Jahnberg.²⁷ A low-temperature modification of Ta_3O_7F is isotypical.²⁸ The structure of $Nb_3O_7(hp)$ is fundamental because it forms part of larger and more complicated structures, as will be demonstrated in the following. The idealized structure of $Nb_3O_7(hp)$ is shown in Fig. 5(a) as a sequence of $A'B'A'B\dots$ modules. Note that the twin planes in the figure are not part of any of the mirror plane sets of $Cmmm$, the space-group of $Nb_3O_7F(hp)$. A primitive monoclinic unit cell is outlined (dotted) and a C -centred pseudo-orthorhombic one (dashed), corresponding to the true orthor-

hombic one in the real structure, is also given. Approximately values of the subcell dimensions a' and b' may be obtained from the real structure: $a' = (1/2)(a^2 + b^2)^{1/2}$ and $b'm(a^2 + b^2)^{1/2} = ab$ with $m = 3/2$. Here $b'm$ is the projection of a or b on the perpendicular to the twin planes. Actual values are given in Table 2.

The structure of β - KYb_2F_7 ²⁹ is built in exactly the same way as $Nb_3O_7F(hp)$, but B_{\square} substitutes for B as shown in Fig. 5(b) [cf. the primitive unit cells of Figs. 5(a) and (b)]. Potassium atoms reside in the tunnels. In β - U_3O_8 ³⁰ there are two layers of $Nb_3O_7F(hp)$ structure superposed on each other in such a way that half of the pentagonal bipyramids

in one layer are above octahedra in the other. The other half of the bipyramids are above bipyramids in the other layer,²⁷ cf. Fig. 5(c). This arrangement causes a doubling of the c -axis in $\beta\text{-U}_3\text{O}_8$.

In idealized $\alpha\text{-U}_3\text{O}_8$, Fig. 6(a), the sequence of modules is different from the one in $\text{Nb}_3\text{O}_7\text{F}(\text{hp})$. In fact, the $\alpha\text{-U}_3\text{O}_8$ structure can be regarded as blocks of $\text{Nb}_3\text{O}_7\text{F}(\text{hp})$ twinned on the unit-cell level, as shown in Fig. 6(a) (bottom), where the blocks are built of modules of types A and B . Only minute changes in the atomic positions [indicated by the arrows in Fig. 6(a) (top)] are required to convert the idealized structure into the real one, which is entirely built up of pentagonal bipyramids.³¹

$\text{CsYb}_3\text{F}_{10}$ ³² is built of modules of types A and B_{\square} as shown in Fig. 6(b). This structure may alternatively be looked upon as being built up of blocks of two types. One is a modified form of $\text{Nb}_3\text{O}_7\text{F}(\text{hp})$ where the $M\text{-X-M-X}\dots$ strings at the centre of the octahedra have been removed. In the resulting tunnels the cesium atoms are located. The other block is simply an A module. The blocks on both sides of an A module are related to each other by a two-fold axis perpendicular to the twin planes, as indicated in Fig. 6(b) below. The stoichiometry and multiplicity of the basic structure is determined by the kind and number of modules present: $4A + 2B_{\square}$ give $4\text{MX}_3 + 2\text{MX}_4$ or $2\text{M}_3\text{X}_{10}$, with $m = 4$; [$4 \times (1/2) + 2 \times 1$].

The idealized structure of $\text{U}_5\text{O}_{12}\text{Cl}^{33}$ is shown in Fig. 6(c). The stoichiometry is obtained from two A and four B modules: $2\text{MX}_3 + 4\text{M}_2\text{X}_5$ or $2\text{M}_5\text{X}_{13}$, with $m = 5$; [$2 \times (1/2) + 4 \times 1$]. The figure also shows the structure built of two types of blocks; one is of $\text{Nb}_3\text{O}_7\text{F}(\text{hp})$ type and the other is a B module. The relation between the blocks on both sides of the B module is also indicated. The real structure is composed entirely of pentagonal bipyramids. We can easily achieve this arrangement by small changes (shown by arrows in the figure) in the anion positions of the idealized structure, cf. $\alpha\text{-U}_3\text{O}_8$ above. A hypothetical oxide M_5O_{13} has been described as having a primary anion net created by an intergrowth of nets of $\beta\text{-U}_3\text{O}_8$ and UVO_5 .⁶

The next structure contains three types of modules as shown in Fig. 6(d). The stoichiometry is derived from $2A + 2B + 2D$: $2\text{MX}_3 + 2\text{M}_2\text{X}_5 + 2\text{M}_3\text{X}_8$ or $4\text{M}_3\text{X}_8$ with $m = 6$; [$2 \times 1/2 + 2 \times 1 + 2 \times 3/2$]. It is the idealized structure of U_2MoO_8 .³⁴ Alternatively it may be described as built up of blocks of $\text{Nb}_3\text{O}_7\text{F}(\text{hp})$ type and D module type, as shown below in the same figure. The blocks on both sides of the D module are related to each other by a twofold axis perpendicular to the plane of the paper. The idealized structure shows monoclinic symmetry, while that of the real one is orthorhombic. The sequence of modules is $D'BA'DA'BD'\dots$. A structure with the same stoichiometry and multiplicity is given by the sequence $D'BA'DB'AD'\dots$. O'Keeffe and Hyde derived the primary oxygen net of U_2MoO_8 by rotations of a group of pentagons in $\beta\text{-U}_3\text{O}_8$ in a specified manner. They describe U_2MoO_8 as containing strips of $\alpha\text{-U}_3\text{O}_8$ separated by composition/twin lines.⁶

The idealized structures of the last two compounds are quite similar. One is $\text{Zr}_7\text{O}_9\text{F}_{10}$,³⁵ shown in Fig. 6(e), and the other is $T\text{-Nb}_2\text{O}_5$,³⁶ shown in Fig. 6(f). Both are built of A and B modules from which their main stoichiometry and multiplicity can be derived, cf. Table 2. (There is an extra complexity in the real structure of $T\text{-Nb}_2\text{O}_5$ in the fact that additional metal atoms have entered into some of the three-sided tunnels.) The structures can also be described as composed of blocks of $\text{Nb}_3\text{O}_7\text{F}(\text{hp})$ type and A modules ($\text{Zr}_7\text{O}_9\text{F}_{10}$) or B modules ($T\text{-Nb}_2\text{O}_5$), cf. below in Figs. 6(e) and 6(f). O'Keeffe and Hyde describe $\text{Zr}_7\text{O}_9\text{F}_{10}$ as composed of twinned $\beta\text{-U}_3\text{O}_8$ intergrown with $\alpha\text{-U}_3\text{O}_8$.⁶

Some further relevant structures

In their structural studies of the system $\text{Ta}_2\text{O}_5\text{-WO}_3$ Stephenson and Roth^{37,38} used the following model. Straight chains of regular pentagons are arranged so that one chain combines with other identical chains by corner sharing, thereby creating sites between them which are rectangular in projection. In this way a three-dimensional structure with pentagonal bipyramids and octahedra is obtained, having the composition M_3O_8 .

The O/M ratio is reduced if the chains are folded. The minimum number of linearly arranged pentagons is four, according to these authors, leading to a unit cell with the composition $\text{M}_{10}\text{O}_{26}$ and with $\text{O/M} = 2.60$ and $m = 5$. In Figs. 7(a) and 7(b) we illustrate using A and B modules the chain arrangement with shaded pentagons. The composition along a chain is also given.

Evidently structures with O/M ratios of 2.67 to 2.60 can be described in the way these authors have suggested. As the O/M ratios of the actual compounds in the $\text{Ta}_2\text{O}_5\text{-WO}_3$ system are all less than 2.60, the authors proposed that oxygen atoms were missing in so-called distortion planes introduced parallel to (010) and having a regular distance between them. From each distortion plane one oxygen atom per unit cell is missing. The multiplicities observed of the structures in this system are 8, 11, 13 and 19.

In connection with the structure determination of $\text{Zr}_7\text{O}_9\text{F}_{10}$ ($m = 7$) Holmberg³⁵ derived the expression of a homologous series based on an idealized $\alpha\text{-UO}_3$ structure.³⁹ Unit cells of this structure type were merged, and a specified number of oxygen atoms were removed in an ordered way.

In her dissertation²⁷ Jahnberg discussed the twinning problem in $\text{Nb}_3\text{O}_7\text{F}(\text{hp})$ and derived two possible models. One is the same as that found at the folding of a chain as described above by Roth and Stephenson (an BB' arrangement in our terminology). The other model corresponds to an AA' arrangement of modules. She further observed that the structures in the $\text{Ta}_2\text{O}_5\text{-WO}_3$ system could be described as "twinning at the atomic level". She also noticed a similarity in that system with that of $\text{Ta}_2\text{O}_5\text{-TaO}_2\text{F}$, the latter with unit cells showing multiplicities of 8, 13 and 19 as observed from single-crystal data.

Joubert and Gaudreau reported on the system $\text{ZrO}_2\text{-}$

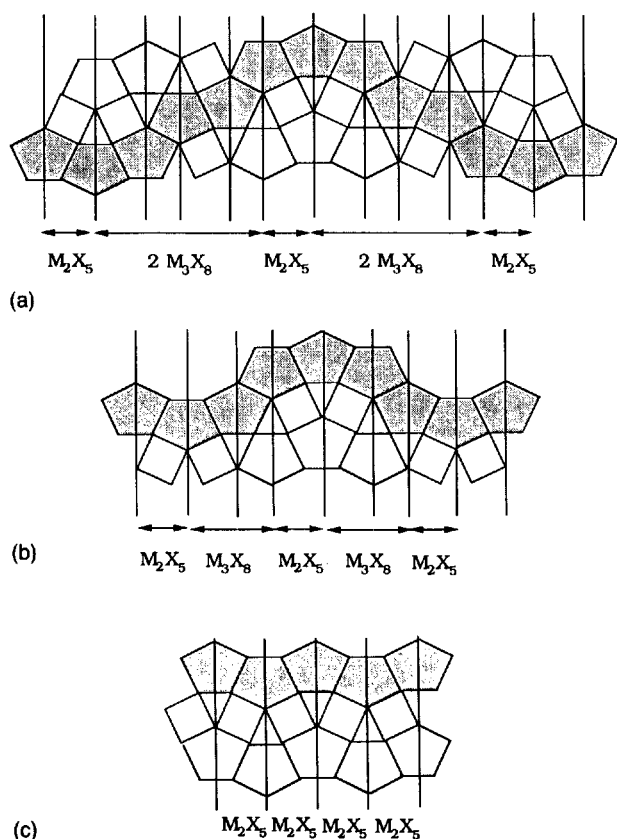


Fig. 7. Chains of pentagons built up the idealized structures of (a) $T\text{-Nb}_2\text{O}_5$, (b) $\text{U}_5\text{O}_{12}\text{Cl}$ and (c) UVO_5 . Modules of A and B type are also shown, as well as the composition along a chain.

ZrF_4 .⁴⁰ Using X-ray and electron diffraction techniques they found in the composition range $\text{ZrX}_{2.75}\text{--ZrX}_{2.67}$ compounds with multiplicities 4, 7 (cf. $\text{Zr}_7\text{O}_9\text{F}_{10}$) and 10. No detailed structure determination was reported, however.

Papiernik *et al.*⁴ reported on the $\text{ZrO}_2\text{--UF}_4$ system. In the same composition range ($\text{MX}_{2.75}\text{--MX}_{2.67}$) they observed phases with multiplicities 17, 23 and 29 registered with X-ray and electron diffraction techniques. They also derived formulas of homologous series based on the number n of pentagons in a straight chain. One series (type I) gives compositions M_3X_{8-x} , $0 \leq x \leq 0.2$, while the other series (type II) represents M_3X_{8+x} , $0 \leq x \leq 0.25$. They also state that $n \geq 4$.

Concerning the phases in the $\text{ZrO}_2\text{--ZrF}_4$ system, of composition $\text{Zr}_3\text{X}_{8+x}$, $0 \leq x < 1$, Papiernik *et al.*⁸ stated that the only simple phases in this system were those with multiplicities 3, 7, 10 and 13, i.e. they contain two straight, equally long chains of pentagonal bipyramids. (The phase with $m = 4$ reported earlier⁴⁰ was actually a mixture of $\text{Zr}_7\text{O}_9\text{F}_{10}$ and hexagonal $\text{Zr}_3\text{O}_2\text{F}_8$.)

The other phases observed in this system ($m = 17, 23$ and 29) are very likely more or less ordered intergrowths of phases with $m = 7$ and 10 , $m = 10$ and 13 and $m = 13$ and 16 , i.e. they contain $(2 + 2)$ straight chains (of different lengths) of pentagonal bipyramids per unit cell. No detailed

structure determinations of these complicated structures were made.

Discussion

In what follows we will use the concept of modules discussed above to point briefly at the possibilities of intergrowths between various structures. We will then use it to illustrate the derivation of homologous series and continue by pondering the question of distortion planes. Finally we will comment on the low-temperature polymorphs of Ta_2O_5 .

As mentioned earlier, a parent structure such as $R\text{-Nb}_2\text{O}_5$ is able to form an intergrowth with a daughter structure. In Fig. 8 is shown as an example a possible intergrowth with $\text{Nb}_3\text{O}_7(\text{hp})$. The daughter structures themselves may form intergrowths with each other, and ample examples have already been given and illustrated in Fig. 6. Thus the structure of $\text{CsYb}_3\text{F}_{10}$ is an ordered intergrowth of $\beta\text{-KYb}_2\text{F}_7$ and the hypothetical structure MX_3 (module A), Fig. 6(b), $\text{U}_5\text{O}_{12}\text{Cl}$ (like $T\text{-Nb}_2\text{O}_5$) is an ordered intergrowth of $\text{Nb}_3\text{O}_7(\text{hp})$ and UVO_5 , Figs. 6(c) [and 6(f)], while U_2MoO_8 is formed by $\text{Nb}_3\text{O}_7(\text{hp})$ and $\text{CaUMo}_4\text{O}_{16}$, Fig. 6(d).

It is easy to derive a formula for a homologous series using modules. Suppose a structure is built up of n B modules and $(n - 2)$ A modules, the modules alternating with each other. This is equivalent to a structure with straight chains of n pentagons and folded according to Roth and Stephenson,³⁷ i.e. a B module is the beginning and the end of a chain. The structural formula of a module is given with superscripts on the metal atom to show the coordination, i.e. an A module is given as $\text{M}^{[7]}\text{X}_3$ and a B module as $\text{M}^{[7]}\text{M}^{[6]}\text{X}_5$. The formula obtained is

$$n \text{M}^{[7]}\text{M}^{[6]}\text{X}_5 + (n - 2) \text{M}^{[7]}\text{X}_3 = \text{M}^{[7]}_{2n-2} \text{M}^{[6]}_n \text{X}_{8n-6}$$

with $n = 2, 4, 6, \dots$ (type I according to Papiernik *et al.*⁴). The minimum value of n is 2, which gives the formula M_4X_{10} , cf. the structure of UVO_5 . The limiting structure for large values of n is M_3X_8 , cf. $\text{Nb}_3\text{O}_7(\text{hp})$. As the modules A and B contribute multiplicities $m = 1$ and $m = 1/2$, respectively, the resulting multiplicity of a member of the series is given by $m = n \times 1 + (n - 2) \times 1/2$ or $m = 3n/2 - 1$.

Another series is obtained if we consider a structure built of $(n - 2)$ B modules and nA modules. This is equivalent to a structure built of straight chains of n pentagons and folded according to Jahnberg,²⁷ i.e. an A module starts and ends a chain:

$$(n - 2) \text{M}^{[7]}\text{M}^{[6]}\text{X}_5 + n \text{M}^{[7]}\text{X}_3 = \text{M}^{[7]}_{2n-2} \text{M}^{[6]}_{n-2} \text{X}_{8n-10}$$

with $n = 2, 4, 6, \dots$ (type II according to Ref. 4). The minimum value of n is again 2, which represents the hypothetical structure of MX_3 , see Fig. 3(a). The limiting structure for large n is M_3X_8 , i.e. the same as in type I. The multiplicity of a member in the series is $3n/2 - 2$. Thus the

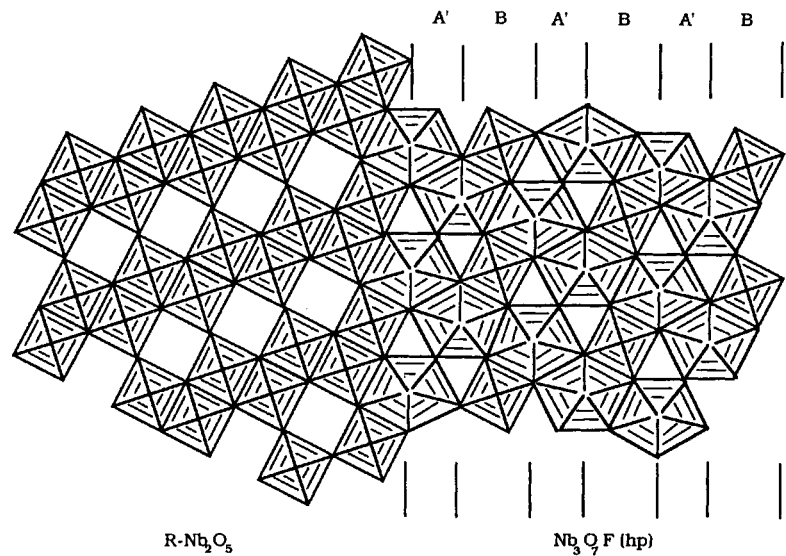


Fig. 8. A possible intergrowth between a parent structure ($R\text{-Nb}_2\text{O}_5$) and a daughter [$\text{Nb}_3\text{O}_7\text{F}(\text{hp})$] structure.

two homologous series represent ideal structures with compositions that cover the whole range from $\text{MX}_{2.5}$ to $\text{MX}_{3.0}$. The formulae obtained above are the same as those derived in Ref. 4 by Papiernik *et al.*, except that these authors claim that n has a minimum value of 4.

One may notice that neither of these series with A and B modules will give the multiplicity of 6 for integral n . One may further notice that the only real structure so far known of that multiplicity is U_2MoO_8 (Table 2) which, however, besides the A and B modules also contains a D module.

Aléonard *et al.*⁷ substitute a monovalent cation L for $\text{M}^{[6]}\text{X}$ in the series of types I and II and obtain $L_n\text{M}^{[7]}_{2n-2}\text{X}_{7n-6}$ and $L_{n-2}\text{M}^{[7]}_{2n-2}\text{X}_{7n-8}$, respectively. For large values of n the latter formula gives $\text{LM}^{[7]}_2\text{X}_7$, corresponding to the structure of $\beta\text{-KYb}_2\text{F}_7$ [Fig. 5(b)]. Similarly $n = 4$ corresponds to $\text{CsYb}_3\text{F}_{10}$ [Fig. 6(b)]. If we exchange half the number of $\text{M}^{[6]}\text{X}$ in $\text{M}^{[7]}_{2n-2}\text{M}^{[6]}_n\text{X}_{8n-6}$ (type I) for L we obtain $L_{n/2}\text{M}^{[7]}_{2n-2}\text{M}^{[6]}_{n/2}\text{X}_{7.5n-6}$, which for $n = 2$ gives the structural formula of LaTa_3O_9 [Fig. 4(b)]. Other combinations of modules will give rise to further series.

It was pointed out in Ref. 36 that the minimum length of a chain can be two pentagons. In this way there will be no contact at all between identical chains which, however, are held together by octahedra as shown in Fig. 7(c). Such a structure has an M_2X_5 composition and is illustrated by the modules BB' , cf. the structure of UVO_5 . As it is perfectly compatible with chains of pentagons, we may include more or less of this structural element into a structure of straight chains of pentagonal bipyramids. It is then possible to represent any composition between $\text{MX}_{2.67}$ and $\text{MX}_{2.50}$, thus reducing the need for distortion planes (cf. the structures in the $\text{Ta}_2\text{O}_5\text{-WO}_3$ system above).

Another means of making the concept of distortion planes superfluous is illustrated by the structures of $T\text{-Nb}_2\text{O}_5$ ³⁶ and $\text{Ta}_{15}\text{Al}_{1/3}\text{W}_{2/3}\text{O}_{40}$ ³⁸ (Table 2). They have the same multiplicity ($m = 8$) and almost the same cell dimensions. There are 42 oxygen atoms and 16.8 metal atoms in

$T\text{-Nb}_2\text{O}_5$. 0.8 Nb, i.e. 4.8% of all metal atoms are found with nine-coordination in the three-sided tunnels of the structure. The structure of $\text{Ta}_{15}\text{Al}_{1/3}\text{W}_{2/3}\text{O}_{40}$, on the other hand, has an ideal content of 42 oxygens, but two of them are removed from distortion planes so as to match the supposed metal content. From a structural point of view, however, it seems easier to grasp the idea of metal atoms entering a structure interstitially than to contemplate the occurrence of ordered planes with vacant oxygen positions.³⁶ One would therefore anticipate the latter structure as having fully occupied oxygen positions and containing some additional metal atoms in interstitial positions.

Roth and Waring⁴¹ discuss two low-temperature polymorphs of Ta_2O_5 . One is that described by Stephenson and Roth,³⁸ obtained by quenching a specimen held at 1350°C for two weeks. The multiplicity of this one is 11. The other polymorph was observed in as-received materials from various sources. It has a multiplicity of 14 and is stable below 1000°C .

As regards the first polymorph we may assume an ideal $\text{Ta}_{22}\text{O}_{58}$ structure, i.e. the one suggested by Stephenson and Roth.³⁸ In our notation the structure is composed of six A and eight B modules. A high-temperature treatment may, however, favour a state with some metal atoms in an interstitial position, i.e. in the three-sided tunnels of the structure, cf. $T\text{-Nb}_2\text{O}_5$, thus giving an overall composition of $\text{Ta}_{23.2}\text{O}_{58}$, i.e. with 5.2% of the metal atoms forced away from their "normal" positions. Note that the crystals used in the structure determination in the $\text{Ta}_2\text{O}_5\text{-WO}_3$ system were all prepared at high temperatures and then quenched. Reported density measurements are not very helpful when one wishes to establish a probable unit-cell content of Ta_2O_5 , as they exhibit a wide range of values.⁴² (This may be due to different heat treatments of the Ta_2O_5 specimens.) If, however, one assumes the presence of interstitial metal atoms in Ta_2O_5 , then distortion planes would become unnecessary.

As regards the polymorph treated at temperatures below 1000°C, it would have a smaller proportion of interstitial metal atoms, and a probable structure would contain more of the *B* modules. Four *A* modules and 12 *B* modules, for instance, give a multiplicity of 14 and a composition of Ta₂₈O₇₂, which means that an additional 0.8 tantalum atom (i.e. 2.8% of all the metal atoms) has entered interstitial positions.

Conclusion

We have shown that twinning on the unit-cell level plays an important role when we want to describe structures with seven- and six-coordinated metal atoms. The introduction of modules derived from *R*-Nb₂O₅ facilitates the description of such structures. Thus modules of types *A* and *B* serve to derive closely related phases of types I and II,⁴ while the *D* module is used to describe CaUMo₄O₁₆ and U₂MoO₈.

The model of twinning of the *R*-Nb₂O₅ structure also explains the pseudo-hexagonal character of these phases. In these cases one has often assumed the presence of a subcell of the α-UO₃ type. As the nature of this structure is not known in detail,⁴³⁻⁴⁵ it appears more satisfying to refer to *R*-Nb₂O₅. The model also illustrates the high degree of adaptability of the structures concerned to changes in composition. It clearly shows the possibility of disorder when the crystals grow. Finally, the capacity of forming intergrowths of this type of related structures is a natural and permanent quality of this model as evidenced in several examples above.

A forthcoming paper will deal with further instances of the use of modules of this and similar kinds.

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