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Moser's C-Line, the Apparent Multiplicity m' and Modules in Descriptions of L-Ta_2O_5 and Related Structures

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Several L-Ta_2O_5 related phases, often classified as type I and type II structures, are described as composed of elements of α- and β-U_3O_8 type. Published powder patterns are reindexed in a four-index notation using a modulation vector $\mathbf{q} = q\mathbf{b}^*$. From the so-called C-line a relation between the apparent multiplicity m' and q is obtained: $m' = 1/|2-3q|$. A modified (AB) module, based on the α-U_3O_8 structure, is given and used in modeling the structures. It is shown that the proportion of metal atom sites with octahedral surrounding, f_{oct}, is linearly related to q. © 2001 Academic Press

Key Words: **α-U_3O_8; β-U_3O_8; C-line; L-Ta_2O_5; modules; modulated structures; apparent multiplicity.**

INTRODUCTION

In his studies of L-Ta_2O_5 by X-ray powder diffraction techniques, Moser in 1965 used the so-called C-line, a reflection occurring between 2Θ-values of about 25° and 27° for Cu$K\alpha_1$ radiation, to characterize the various Ta_2O_5 phases observed (1). This reflection was among those that changed position markedly, depending on the kind of thermal treatment that the investigated sample had undergone.

Later, several investigators also used this reflection to characterize their samples (2–8), especially in the system $(1-x)Ta_2O_5 \cdot xWO_3$ $(0 \le x \le 0.267)$. This system was considered by Papiernik *et al.* (9, 10) to belong to a type I homologous series, $M^{[7]}_{2n-2}M^{[6]}_{n}X_{8n-6}$, with M_3X_8 as limiting structure, while phases in the ZrO_2–UF_4 and ZrO_2–ZrF_4 were described as a type II homologous series, $M^{[7]}_{2n-2}M^{[6]}_{n-2}X_{8n-10}$, also with M_3X_8 as a limit. Several X-ray powder patterns of type II phases were given and indexed by these authors. They also defined the concept of apparent and real multiplicities, m' and m. Marinder in 1990 showed how several type I and type II phases could be described by use of so-called A and B modules (11).

Thompson *et al.* in 1991 studied part of the system ZrO_2–ZrF_4, namely the compound $ZrO_{2-x}F_{2x}$, with $0.698 \le x \le 0.714$. Instead of describing it as a series of line phases, with intermediary compositions resulting from intergrowth of the line phases on the unit cell level, they preferred to describe $ZrO_{2-x}F_{2x}$ as an incommensurately modulated structure with the composition-dependent primary modulation wave vector $\mathbf{q} = x\mathbf{b}^*$ (12).

In 1992 Schmid *et al.* showed how the system $(1-x)Ta_2O_5 \cdot xWO_3$ could be treated as a solid-solution phase by using a four-index notation in their X-ray powder diffraction and electron microscopy diffraction studies (7). Thus it was found that

$$\mathbf{d}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}, \qquad [1]$$

where $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ are the reciprocal lattice vectors of an underlying orthorhombic parent structure and $\mathbf{q} = q\mathbf{b}^*$ is a modulation vector, could be used for indexing any given reflection. They noted that Moser's C-line was an $1, 1, 0, -3$ reflection in this four-index notation. They also noted (like the authors of (3) and (8)) that the C-line was on the origin side of the very strong reflection $1, 1, 0, 0$ (see Fig. 1).

In this paper we will consider the connection between the apparent multiplicity m' as defined by Papiernik *et al.* (9, 10) and the magnitude of $\mathbf{q}/\mathbf{b}^*$ as given by Schmid *et al.* (7) and by Thompson *et al.* and Withers *et al.* (12) for phases of types I and II, as mentioned above. We have indexed published powder diffraction data in four-index notation, found the q values by a least-squares refinement procedure, and then calculated the m' values. A modified (AB) module based on the α-U_3O_8 structure is given, which has been used in modeling phases of structure types I and II, which are here described by formulas slightly different from to those in (9). Finally, we show how the proportion of metal sites with octahedral character is related to q for structures of types I and II.

THE m' FORMULA

Figure 1 schematically shows an [001] subcell zone-axis diffraction pattern of an L-Ta_2O_5-related structure of type I with reciprocal-lattice vectors from one of the parent structures discussed by Lehovec (13). Note the position of

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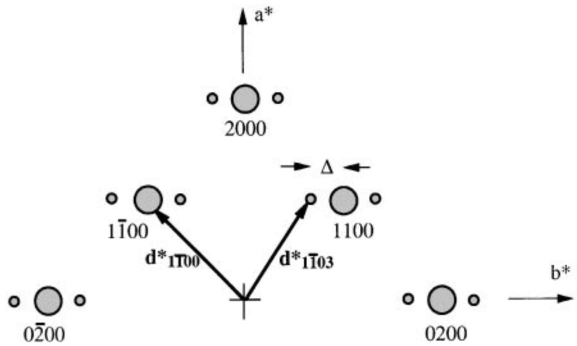

FIG. 1. A schematic diagram of part of an [001] subcell zone-axis diffraction pattern of an L-Ta_2O_5-related structure. A four-index notation (h, k, l, m) is used for indexing the reflections. Δ is the distance along $\mathbf{b}^*$ between the the C line $1, -1, 0, 3$ and the strong $1, 1, 0, 0$ reflection.

the C-line $1, -1, 0, 3$ or $1, 1, 0, -3$ at a lower diffraction angle than the strong reflection $1, 1, 0, 0$ or $1, -1, 0, 0$. The reciprocal distance Δ shown in the figure as the distance between the $1, -1, 0, 3$ and the $1, 1, 0, 0$ reflections along the $\mathbf{b}^*$ direction is given by

$$\Delta = |(1, 1, 0, 0) - (1, -1, 0, 3)| = |(0, 2, 0, -3)| = (2 - 3q)b^*,$$

and the apparent multiplicity as defined by Papiernik *et al.* (9,10) is then given by

$$m' = b^*/\Delta \qquad [2]$$

or

$$m' = 1/|2 - 3q|. \qquad [3]$$

For $q > 2/3$ (type II structures) it can be shown that the position of the $1, -1, 0, 3$ reflection is beyond $1, 1, 0, 0$, cf. densitometer traces from XRD Guinier exposures in Ref (12). Thus the absolute value has to be used in Eq. [3]. For $q = 2/3$ it is found that the position of the $1, -1, 0, 3$ reflection coincides with that of $1, 1, 0, 0$, giving $\Delta = 0$. In this case Δ is taken as the distance between the reciprocal vectors $(1, 1, 0, 0,)$ and $(1, 1, 0, -1)$:

$$\Delta = |(1, 1, 0, 0) - (1, 1, 0, -1)| = |(0, 0, 0, 1)| = qb^*$$

or

$$m' = 1/q$$

or

$$m' = 1.5.$$

Note first, that the C-line $1, 1, 0, -3$ occurs between d values of about 3.30 and 3.60 Å in structures of type I. Sometimes it is too weak to be observed, as in the T-Nb_2O_5 pattern (14). Second, the weak reflection $1, 1, 0, -1$ and the very weak reflection $0, 2, 0, -2$ are observed in patterns of both type I and type II structures. The first weak reflection, $1, 1, 0, -1$ occurs at about $d = 5.10$ and 5.85 Å in type I structures and is identical to the second weak reflection, at about $d = 5.70$ and 5.95 Å, in type II structures. The 0,2,0, -2 reflection is the second weak one, at about $d = 4.70$ and 5.00 Å, in type I structure patterns, whereas it occurs at about $d = 6.25$ and 6.80 Å as the first weak reflection in those of type II structures.

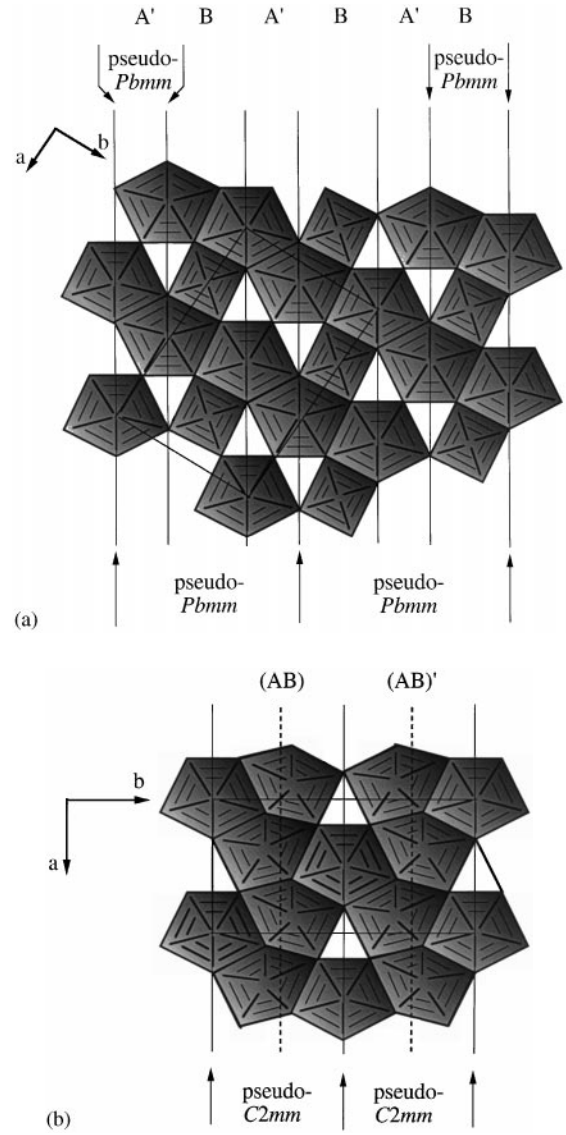

FIG. 2. (a) The structure of the β-U_3O_8 subcell is shown as built up of A and B modules. Note that B and the sequence BAB form structures of pseudo-*Pbmm* symmetry, with compositions $M_{3n-1}X_{8n-3}$, $n = 1$ and 2, respectively. A and the sequence ABA form structures of the same symmetry, with compositions $M_{3n-2}X_{8n-5}$, $n = 1$ and 2, respectively. (b) The crystal structure of α-U_3O_8 shown as being built up of (AB) modules of pseudo-*C2mm* symmetry.

TABLE 1
Apparent Multiplicity Values m' for Some Type I and II Structures, Calculated from q Values Derived from Published X-Ray Powder Diffraction Data

Compounds modules	Ref.	X/M	q	$m' = 1/\|2-3q\|$	m	f_{oct}	Remarks
$CuO \cdot 5Ta_2O_5$ $4(AB)+6A+10B$	(22)	2.364	0.6317(6)	9.5(2)	19	0.263	Type I, $m = 8 + 11$, see Table 2a: $n = 2$ and 3. The model is monoclinic and C-centered as is also found from systematic absences in the powder pattern.
T-Nb_2O_5 (*Pbam*) $2(AB)+2A+4B$	(14, 16)	2.500	0.6249(5)	7.99(8)	8	0.250	Type I, see Table 2a: $n = 2$, c.f. Fig. 3a. The real structure is reported with interstitial niobium atoms. As regards f_{oct}, see text.
L-Ta_2O_5 (*pm*) $2(AB)+4A+6B$	(4, 20)	2.500	0.6366(5)	11.1(2)	11	0.273	Type I, see Table 2a: $n = 3$. The model is orthorhombic.
$Ta_{30}W_2O_{81}$ (*Pbam*) $2(AB)+2A+4B$	(4, 20)	2.531	0.6251(4)	8.03(7)	8	0.250*	Type I, see Table 2a: $n = 2$. $Ta_{74}W_6O_{203}$ is isotypic. The structure has oxygen vacancies.
$Ta_{22}W_4O_{67}$(*C*112/*m*) $4(AB)+2A+6B$	(4, 20)	2.577	0.6156(3)	6.52(4)	13	0.231*	Type I, $m = 5 + 8$, see Table 2a: $n = 1$ and 2. The model is monoclinic and *C*-centered, as is the real structure which contains oxygen vacancies as well.
$U_5O_{12}Cl$ (*Pbmm*) $2(AB)+2B$	(21)	2.600	0.6000	5	5	0.200	Type I, see Table 2a: $n = 1$ No standard deviations, as no powder data available. In the real structure all U-atoms are seven-coordinated, i.e., $f_{oct} = 0$.
Nb_3O_7F(hp) (*Cmmm*) $2A+2B$	(23, 24)	2.667	0.667(2)	1.500(4)	3	0.333*	Type I and II, see Table 2a and b: $n = \infty$. The compound represents the subcell of β-U_3O_8 type.
$Zr_{19}U_{10}O_{38}F_{40}$ $4(AB)+18A+14B$	(9)	2.690	0.691(1)	13.7(4)	29	0.241	Type II, $m = 13 + 16$, see Table 2b: $n = 4$ and 5. The model has monoclinic symmetry. It is *C*-centered as is also found from systematic absences in the powder pattern.
$Zr_{15}U_8O_{30}F_{32}$ $4(AB)+14A+10B$	(9)	2.696	0.694(2)	12.1(5)	23	0.217	Type II, $m = 10 + 13$, see Table 2b: $n = 3$ and 4. The model has monoclinic symmetry. It is *C*-centred as found from systematic absences in the powder pattern.
$Zr_{10}O_{13}F_{14}$ $2(AB)+6A+4B$	(10)	2.700	0.699(1)	10.3(2)	10	0.200	Type II, see Table 2b: $n = 3$.
$Zr_{17}O_{22}F_{24}$ $4(AB)+10A+6B$	(10)	2.706	0.706(1)	8.5(2)	17	0.176	Type II, $m = 7 + 10$, see Table 2b: $n = 2$ and 3. The model has monoclinic symmetry. It is *C*-centered as is also found from systematic absences in the powder pattern.
$Zr_{11}U_6O_{22}F_{24}$ $4(AB)+10A+6B$	(9)	2.706	0.706(1)	8.5(2)	17	0.176	As above.
$Zr_7O_9F_{10}$ (*Pbam*) $2(AB)+4A+2B$	(17)	2.714	0.714(1)	7.02(7)	7	0.143*	Type II, see Table 2b: $n = 2$ c.f. Fig. 3b.
$Zr_7O_9F_{10}$ $2(AB)+4A+2B$	(10)	2.714	0.714(2)	7.0(2)	7	0.143	As above.

Note. Real multiplicities m are also given, as well as the ratio $f_{oct} = \Sigma M^{[6]}/(\Sigma M^{[6]} + \Sigma M^{[7]})$ in the unit cell according to the model (observed f_{oct} values are marked with an asterisk). $A = M^{[7]}X_3$, $B = M^{[7]}M^{[6]}X_5$, and $(AB) = M_3^{[7]}X_8$.

THE T-Nb_2O_5 AND $Zr_7O_9F_{10}$ STRUCTURES

Structures of types I and II have been described as being built up by modules in various combinations (11). The subcell of β-U_3O_8 is given by a sequence like $ABA\ldots$, where A has MX_3 composition with a seven-coordinated metal atom, $M^{[7]}$, whereas B has M_2X_5 composition with one seven-coordinated and one six-coordinated metal atom, $M^{[7]}$ and $M^{[6]}$ (see Fig. 2a). The α-U_3O_8 structure is described by the sequence $AA'BB'A\ldots$ (A and A' are related

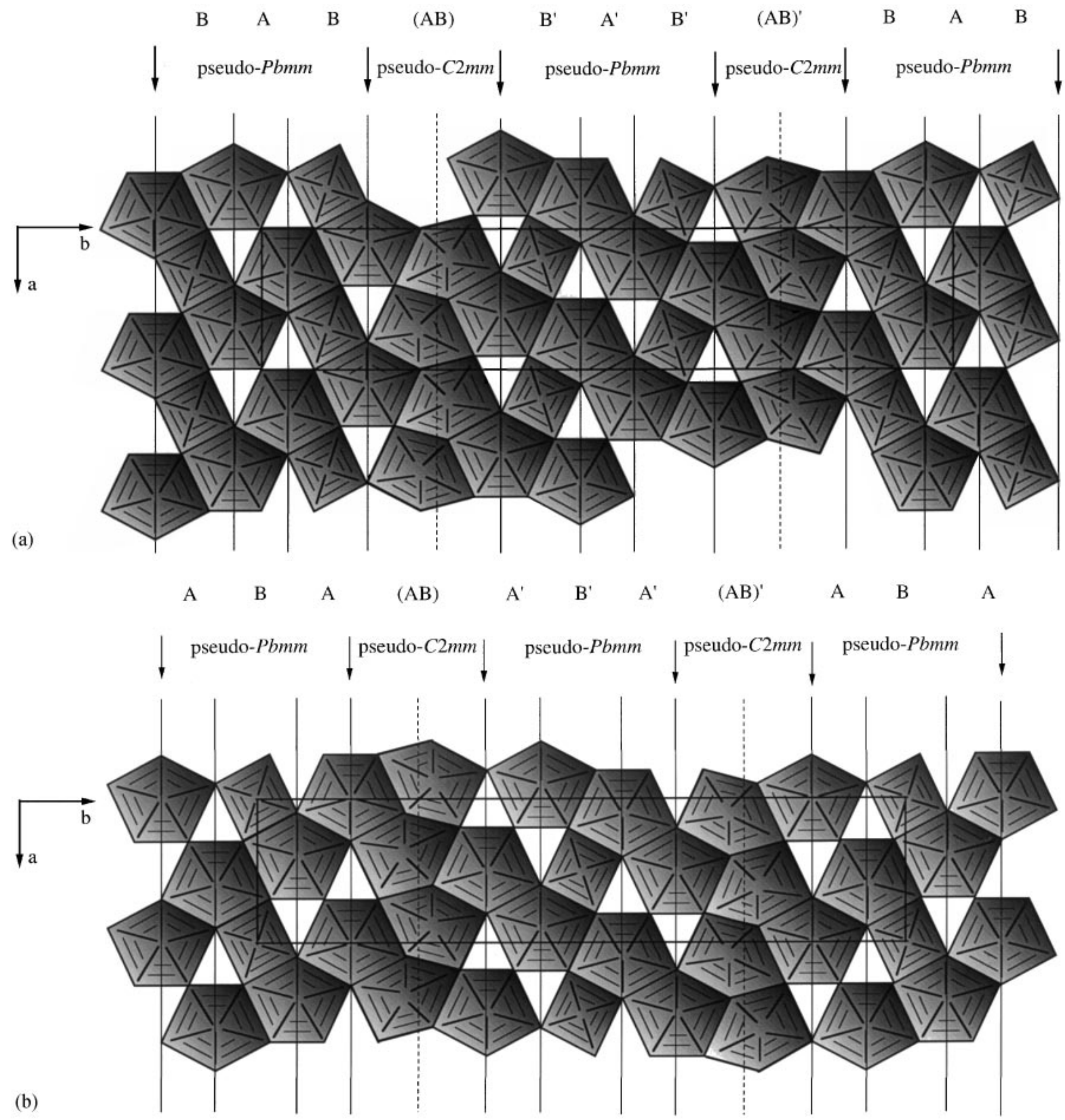

FIG. 3. (a) The crystal structure of T-Nb_2O_5 shown as being built up of *A*, *B* and (*AB*) modules or as strips of structure of pseudo-*C2mm* symmetry of M_3X_8 composition, and of pseudo-*Pbmm* symmetry of M_5X_{13} composition. (b) The crystal structure of $Zr_7O_9F_{10}$ shown as built up of *A*, *B*, and (*AB*) modules or as strips of structure of pseudo-*C2mm* symmetry of M_3X_8 composition and pseudo-*Pbmm* symmetry of M_4X_{11} composition.

through a mirror plane, as are *B* and *B*′). It is found that this structure is better described by a somewhat modified module called (*AB*), shown in Fig. 2b, where the left and right part of the module are related through a glide perpendicular to the plane of the paper. The composition of (*AB*) is M_3X_8, with three seven-coordinated metal atoms. This yields a structure model of α-U_3O_8 that can be denoted as $(AB)(AB)'(AB)\ldots$, where all the U atoms are seven-coordinated, as found from a single-crystal structure determination (15).

We will demonstrate the use of this module by describing two structures, T-Nb_2O_5 (16) of type I and $Zr_7O_9F_{10}$ (17) of type II, determined by X-ray single-crystal investigations (see Table 1). The unit cell content of the first one is $[Nb_{16}O_{42}]^{4-}$, with 0.8 Nb^{5+} as interstitial ions (16). The $Nb_{16}O_{42}$ arrangement corresponds to $2[(AB) + A + 2B]$ modules per unit cell, with $m = 2 \times 1.5 + 2 \times 0.5 + 4 \times 1$, which gives $m = 8$, as shown in Fig. 3a (the contributions to m by the modules *A*, *B*, and (*AB*) are 0.5, 1, and 1.5, respectively). The four *B* modules contribute four $M^{[6]}$. The

TABLE 2a
Arrangement of Modules, Composition, and Real Multiplicity m of Type-I Structures as a Function of n, the Number of B Modules between the (AB) Modules

n	Arrangement of modules in the unit cell	Composition	Real multiplicity, $m = 3n + 2$	$q_{\mathrm{I}} =$ $(2n + 1)/(3n + 2)$	$f_{\mathrm{oct}} =$ $n/(3n + 2)$
—	$(AB)(AB)$	M_6X_{16} (α-U_3O_8 type)	—	—	—
1	$B/2(AB)B(AB)B/2$	$M_{10}X_{26}$ ($U_5O_{12}Cl$)[a]	5	$\frac{3}{5}$	$(\frac{1}{5})$
2	$A/2B(AB)BAB(AB)BA/2$	$M_{16}X_{42}$ (T-Nb_2O_5)	8	$\frac{5}{8}$	$\frac{1}{4}$
3	$B/2AB(AB)BABAB(AB)BAB/2$	$M_{22}X_{58}$ (L-Ta_2O_5)	11	$\frac{7}{11}$	$\frac{3}{11}$
4	$A/2BAB(AB)BABABAB(AB)BABA/2$	$M_{28}X_{74}$	14	$\frac{9}{14}$	$\frac{2}{7}$
.	.	.	.	.	.
n	$(A_{n-1}B_n)/2(AB)\underbrace{A_{n-1}B_n}_{M_{3n-1}X_{8n-3}}(AB)\ (A_{n-1}B_n)/2$	$M_{6n+4}X_{16n+10}$ or	$3n + 2$	$(2n + 1)/(3n + 2)$	$n/(3n + 2)$
		$M^{[7]}_{4n+4}M^{[6]}_{2n}X_{16n+10}$			
.	.	.	.	.	.
∞	M_3X_8 (β-U_3O_8 type)	M_6X_{16} (β-U_3O_8 type)	3	$\frac{2}{3}$	$\frac{1}{3}$

Note. Also shown are theoretical values of q_{I} and f_{oct}, the proportion of metal atoms with octahedral surroundings, according to the model. The contributions to m by A, B, and (AB) are 0.5, 1, and 1.5, respectively.
[a]All uranium atoms are seven-coordinated in the real structure (21).

cell content of the second structure is $Zr_{14}X_{38}$ (17), whose composition relates to $2[(AB) + 2A + B]$ modules with $m = 2 \times 1.5 + 4 \times 0.5 + 2 \times 1$, which gives $m = 7$, as shown in Fig. 3b. Two B modules contribute one $M^{[6]}$ each. Note that both structures contain the same part of the α-U_3O_8 structure, i.e., the (AB) module. While T-Nb_2O_5 uses the sequence BAB from the β-U_3O_8 structure type with Nb_5O_{13} composition (Table 2a), $Zr_7O_9F_{10}$ uses the sequence ABA, also from the β-U_3O_8 structure type, with Zr_4X_{11} composition (Table 2b). The two structures consist in fact of ordered intergrowths of α-U_3O_8 type and parts of the β-U_3O_8 type structure, as discussed in Ref. (18).

The structural features of $Zr_7O_9F_{10}$ have been discussed by O'Keeffe and Hyde (19) as units of M_4O_{11} intergrown with units of M_3O_8 of α-U_3O_8 structure.

It should be noted that the arrangement of modules in type I structures in general is

$$\ldots B(AB)A_{n-1}B_n(AB)B\ldots,$$

giving an X/M value less than 2.67. For T-Nb_2O_5, n is 2 (see Table 2a). The arrangement in type II structures is

$$\ldots A(AB)A_nB_{n-1}(AB)A\ldots,$$

TABLE 2b
Arrangement of Modules, Composition, and Real Multiplicity m of Type II Structures as a Function of n, the Number of A Modules between the (AB) Modules

n	Arrangement of modules in the unit cell	Composition	Real multiplicity, $m = 3n + 2$	$q_{\mathrm{I}} =$ $(2n + 1)/(3n + 1)$	$f_{\mathrm{oct}} =$ $(n - 1)/3n + 1$
—	$(AB)(AB)$	M_6X_{16} (α-U_3O_8 type)	—	—	—
1	$A/2(AB)A(AB)A/2$	M_8X_{22}	4	$\frac{3}{4}$	0
2	$B/2A(AB)ABA(AB)AB/2$	$M_{14}X_{38}$ ($Zr_7O_9F_{10}$)	7	$\frac{5}{7}$	$\frac{1}{7}$
3	$A/2BA(AB)ABABA(AB)ABA/2$	$M_{20}X_{54}$	10	$\frac{7}{10}$	$\frac{1}{5}$
4	$B/2ABA(AB)ABABABA(AB)ABAB/2$	$M_{26}X_{70}$	13	$\frac{9}{13}$	$\frac{3}{13}$
5	$A/2BABA(AB)ABABABABA(AB)ABABA/2$	$M_{32}X_{86}$	16	$\frac{11}{16}$	$\frac{1}{4}$
.	.	.	.	.	.
n	$(A_nB_{n-1})/2(AB)\underbrace{A_nB_{n-1}}_{M_{3n-2}X_{8n-5}}(AB)\ (A_nB_{n-1})/2$	$M_{6n+2}X_{16n+6}$ or	$3n + 1$	$(2n + 1)/(3n + 1)$	$(n - 1)/(3n + 1)$
		$M^{[7]}_{4n+4}M[6]_{2n-2}X_{16n+6}$			
.	.	.	.	.	.
∞	M_3X_8 (β-U_3O_8 type)	M_6X_{16} (β-U_3O_8 type)	3	$\frac{2}{3}$	$\frac{1}{3}$

Note. Also shown are theoretical values of q_{II} and f_{oct}, the proportion of metal atoms with octahedral surroundings, according to the model. The contributions to m by A, B and (AB) are 0.5, 1 and 1.5, respectively.

giving an X/M value larger than 2.67. For $Zr_7O_9F_{10}$, n is 2 (see Table 2b).

FURTHER COMPARISON BETWEEN STRUCTURES OF TYPES I AND II

Table 1 shows some L-Ta_2O_5-related structures reported in the literature. Type I structures have either simple multiplicities, such as 5, 8, 11, and so on, or a mixture of these multiplicities, like 13, 19, etc. (2, 3).

Besides T-Nb_2O_5, with $m = 8$, the crystal structure of an isotypic compound, $Ta_{74}W_6O_{203}$ ($Z = 0.2$, similar unit cell dimensions and the same space group *Pbam*, also given as $Ta_{30}W_2O_{81}$ (3, 4)), has been determined (20). This structure has been described as consisting of strips of structure perpendicular to **b**, with pseudo-*C2mm* and pseudo-*Pbmm* symmetry. The width of the pseudo-*C2mm* strips is invariant with composition M_3O_8. This corresponds to the description given above of T-Nb_2O_5 as containing (AB) modules of α-U_3O_8 structure type. The width and the composition of the pseudo-*Pbmm* strips are given by the formula $M_{3n-1}O_{8n-3}$, $n = 1, 2, 3\ldots$ (cf. Table 2a, where the composition of the structure between the (AB) modules is derived, giving the same expression). $Ta_{74}W_6O_{203}$ contains only pseudo-*Pbmm* strips with $n = 2$, i.e., M_5O_{13}, to be compared with the BAB sequence in T-Nb_2O_5, with Nb_5O_{13} composition.

$Ta_{22}W_4O_{67}$ ($m = 13$) is an example of a structure with mixed multiplicity. As shown in Table 1 it can be thought of as composed of one structure with $2(AB) + 2A + 4B$, $m = 8$, and one with $2(AB) + 2B$, $m = 5$. It can be regarded as an ordered intergrowth of these two structures in the following arrangement:

$$(AB)BAB(AB)B(AB)BAB(AB)B(AB)\ldots .$$

or $4(AB) + 2A + 6B$, as shown in Table 1. This structure has been described (20) as being composed of pseudo-*C2mm* strips of constant width (cf. the (AB) module) and pseudo-*Pbmm* strips of $M_{3n-1}O_{8n-3}$ composition. Strips with $n = 1$ and $n = 2$ alternate in the structure. This corresponds to the B and BAB sequences with M_2X_5 and M_5X_{13} composition, respectively, shown in the arrangement above.

From the number and kind of modules, the amount of seven- and six-coordinated metal atoms per unit cell in these structures can be derived and is found to agree with what is known from X-ray single-crystal structure determinations. One exception, however, is the compound with $m = 5$, i.e., $U_5O_{12}Cl$, where all the uranium atoms are seven-coordinated (21), presumably due to the presence of the large Cl atom.

T-Nb_2O_5 has been described (16) with 8 $Nb^{[7]}$ and 8 $Nb^{[6]}$, although it is stated that small changes in the oxygen positions may alter the coordination from six to seven or vice versa. According to Table 2a it is assumed that the four B modules contribute four $M^{[6]}$ per unit cell. In the isostructural $Ta_{76}W_6O_{203}$, 4 of 16 metal atoms are six-coordinated according to a crystal structure determination (20). As regards $Ta_{22}W_4O_{67}$ (20), the number of six-coordinated metal atoms in the unit cell is six. This is in accordance with the model (see Table 1).

According to Papiernik *et al.* (9, 10), type II structures have either simple multiplicities m, like 3, 4, 7, 10, 13, etc., or complex ones like 17 (7 + 10), 23 (10 + 13), and 29 (13 + 16). Only one compound of type II seems to have been studied by X-ray single-crystal techniques, namely $Zr_7O_9F_{10}$ (17). As mentioned above, it can be thought of as built up of (AB) modules intergrown with ABA modules, or, to use the nomenclature of (20), of pseudo-*C2mm* strips and pseudo-*Pbmm* strips of Zr_4X_{11} composition, corresponding to $M_{3n-2}X_{8n-5}$ with $n = 2$ (cf. Table 2b).

Similarly, the complex $m = 17$ structure in Table 1 can be thought of as composed of one structure with $2(AB) + 4A + 2B$, $m = 7$, and one with $2(AB) + 6A + 4B$, $m = 10$. The $m = 17$ structure is then an ordered intergrowth of these two in the following arrangement:

$$(AB)ABA(AB)ABABA(AB)ABA(AB)ABABA(AB)\ldots$$

or $4(AB) + 10A + 6B$, as shown in Table 1. Alternatively, it is built up of pseudo-*C2mm* strips and pseudo-*Pbmm* strips of $M_{3n-2}X_{8n-5}$ composition (see Table 2b), with $n = 2$ and $n = 3$ alternating.

As regards the coordination of the metal atoms in $Zr_7O_9F_{10}$ (cf. Tables 1 and 2b and Fig. 3), it is found that the modules used to describe the structure correctly represent the coordination found experimentally (17).

q AND THE PROPORTION OF METAL SITES WITH OCTAHEDRAL CHARACTER, f_{oct}

According to Ref. (20), the ratio of in-plane O atoms to M atoms is $1 + q$ for structures of type I. The general composition expression of a type I compound is $M_{6n+4}X_{16n+10}$ (see Table 2a). If this is rewritten as $M_{6n+4}X(\text{top})_{6n+4}X(\text{in-plane})_{10n+6}$, we obtain $(10n + 6)/(6n + 4) = 1 + q_I$ or $q_I = (4n + 2)/(6n + 4)$ or $(2n + 1)/(3n + 2)$. Similarly, the general composition expression of a type II compound is $M_{6n+2}X_{16n+6}$ (see Table 2b). If this is rewritten as $M_{6n+2}X(\text{top})_{6n+2}X(\text{in-plane})_{10n+4}$, we obtain $(10n + 4)/(6n + 2) = 1 + q_{\mathrm{II}}$ or $q_{\mathrm{II}} = (4n + 2)/(6n + 2)$ or $(2n + 1)/(3n + 1)$. q_{I} and q_{II} are shown in Tables 2a and 2b, respectively.

Let the proportion of metal sites that have octahedral character be f_{oct} and assume, as in (20), a linear relationship between f_{oct} and q. With data from $Ta_{22}W_4O_{67}$ and Nb_3O_7F (hp) of β-U_3O_8 type (23, 24), we obtain very nearly

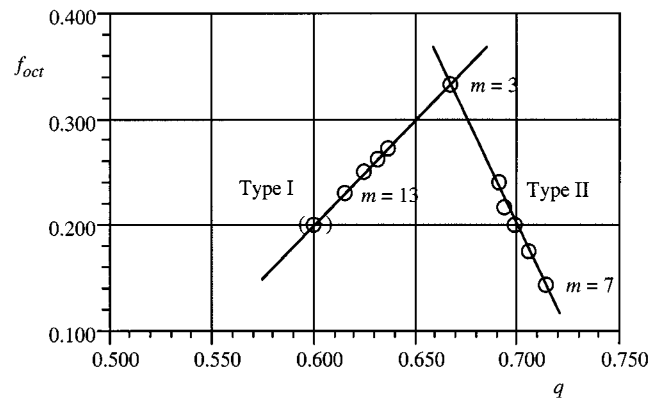

FIG. 4. A plot of f_{oct}, the proportion of M sites with octahedral surroundings, *versus* q for type I and type II structures.

the following equation for type I structures:

$$f_{\mathrm{oct}} = 2q - 1. \qquad [4]$$

Similarly, data from $Zr_7O_9F_{10}$ and Nb_3O_7F(hp) give

$$f_{\mathrm{oct}} = -4q + 3 \qquad [5]$$

for type II structures. A plot of Eqs [4] and [5] for the data of Table 1 (i.e., f_{oct} taken from the models and q values calculated from powder patterns) is shown in Fig. 4. The graphs are both linear to a fairly good approximation, implying that knowledge of the magnitude of the wave vector can be used for estimating the distribution of seven- and six-coordinated metal atoms in structures of types I and II.

CONCLUSION

This study of L-Ta_2O_5-related structures is chiefly based on published X-ray powder diffraction data for the compounds concerned. Using these data we have in each case identified and refined a basic subcell of Lehovec type. We have then assumed the presence of a commensurate modulation wave vector along the **b*** direction. The unit cell dimensions, including the magnitude of the modulation vector q, with standard deviations of the subcell, were obtained from Eq. [1]. It was found that $q < 2/3$ for type I and $q > 2/3$ for type II structures and that q equals 2/3 for a subcell of β-U_3O_8 type like that of Nb_3O_7F (hp).

The apparent multiplicity m' as defined in Eq. [2] depends on q as shown in Eq. [3] for both structure types.

In order to describe the structures concerned, a new kind of module (AB), with M_3X_8 composition and with seven-coordinated metal atoms, has been introduced. It correctly depicts the α-U_3O_8-type structure, which appears to be an integral part of these phases. Using the modules A, B, and (AB), it is found that structures of types I and II can be represented by $M^{[7]}_{4n+4}M^{[6]}_{2n}X_{16n+10}$, $n = 1, 2, 3 \ldots$ and $M^{[7]}_{4n+4}M^{[6]}_{2n-2}X_{16n+6}$, $n = 1, 2, 3 \ldots$, respectively, and that $M^{[7]}_4M^{[6]}_2X_{16}$, a subcell of β-U_3O_8 type, is the limiting structure at $n = \infty$ in both cases.

The proportion, f_{oct}, of metal atoms with octahedral surrounding that can be derived from the series above agrees with what is known from X-ray single-crystal structure investigations of $Ta_{74}W_6O_{203}$ (20), $Ta_{22}W_4O_{67}$ (20), $Zr_7O_9F_{10}$ (17), and Nb_3O_7F(hp) (24). Finally, it is shown that f_{oct} depends on q as given by Eqs. [4] and [5] and as illustrated in Fig. 4. $U_5O_{12}Cl$ is an exception, with $f_{\mathrm{oct}} = 0$, presumably due to the presence of the large Cl atom.

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