final R values were 4·0% and 4·5% respectively and the standard deviations of the S–O bonds were 0·002 Å and 0·003 Å (the value of g was $6·4 \times 10^{-5}$). A perhaps more dramatic effect of this correction can be seen by examination of weak reflections along a lattice row containing some quite strong reflections. Table 9 presents the data for the $00l$ lattice row. The agreement of the 006 and 0011 reflections can be seen to be much improved after correcting for the white radiation.

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Mixed Oxides of Titanium and Niobium: The Crystal Structure of $TiNb_{24}O_{62}$ ($TiO_2.12Nb_2O_5$)

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$TiNb_{24}O_{62}$ is monoclinic, with $a = 29·78$, $b = 3·821$, $c = 21·12$ Å, $\beta = 94·9°$, space group $C2$. The structure, refined by two-dimensional Fourier methods, contains ReO_3-type blocks of metal–oxygen octahedra, 3×4 and infinite in extension along b. These join up in pairs, and the double blocks pack together by additional edge sharing, with metals in tetrahedral coordination at each of the junctions. The relationship to the structure of high-temperature Nb_2O_5, as well as to other known and hypothetical compounds formed from blocks of the same size, is examined.

Introduction

The phase equilibrium relations, and the crystal structures of the phases in the system TiO_2–Nb_2O_5, have been independently studied by the present authors (Roth & Coughanour, 1955; Wadsley, 1961*a*, *b*). Both of us concluded that only two compounds existed, $TiNb_2O_7$ ($TiO_2.Nb_2O_5$) and a second identified by structure-analysis as $Ti_2Nb_{10}O_{29}$ ($2TiO_2.5Nb_2O_5$) occurring in two forms, orthorhombic and monoclinic. These are closely related to each other, and can be described as the members $n = 3$ and 4 of a 'homologous series' of oxides with the general formula $B_{3n}O_{8n-3}$, their structures being derived from that of a parent compound B_3O_8, at the time unknown, but now reported by Andersson (1964) for the oxyfluoride Nb_3O_7F. Attempts to prepare the additional homologue $n = 5$ ($TiNb_{14}O_{37}$, or $TiO_2.7Nb_2O_5$), and to identify the member $n = 6$ ($Nb_{18}O_{45}$) with one of the polymorphs of Nb_2O_5, were unsuccessful (Wadsley, 1961*b*). This particular series of oxides appeared to contain only the two compounds, unlike the reduced tungsten-molybdenum oxides $(W, Mo)_nO_{3n-1}$ (Magnéli, 1953) and the titanium oxides Ti_nO_{2n-1} (Andersson & Jahnberg, 1963) where both have six or more members each related by a common structural principle. Likewise Kihlborg (1963) found only three members of a series Mo_nO_{3n-m+1}.

The high temperature form of Nb_2O_5, and the reduced phase $Nb_{22}O_{54}$ found by Norin & Magnéli (1961), can be grouped together by another series-type general formula $B_{3n+1}O_{8n-2}$; Nb_2O_5 corresponds to $n = 9$ and $Nb_{22}O_{54}$ to $n = 7$ (Gatehouse & Wadsley, 1964). A new

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compound in the TiO_2–Nb_2O_5 system, reported by Gruehn & Schäfer (1963) to have the empirical composition (Ti, Nb)$O_{2\cdot482}$, was shown by Roth, Wadsley & Gatehouse (1964) to be $TiNb_{24}O_{62}$ ($TiO_2 . 12Nb_2O_5$). Although its formula is that of the member $n=8$ of the new series, its structure could not be predicted from those of the other two, where n must necessarily be an odd number.

The appearance of all of these ordered phases of fixed composition, whether reduced, or with the lower valency elements Ti,Al, or Ni substituting for Nb (Roth, Wadsley & Gatehouse, 1964), is in direct conflict with the earlier work of Brauer (1941), who claimed that Nb_2O_5 appeared as a single phase over the composition interval $NbO_{2\cdot5}$–$NbO_{2\cdot4}$. Indeed Roth & Coughanour (1955) concluded that Nb_2O_5 could take up to 10 mol. % TiO_2 in solid solution, and it was only the appearance of the compound $VNb_{24}O_{62}$ in the system V_2O_5–V_2O_4–Nb_2O_5 (Waring & Roth, 1965) that prompted a reappraisal of this earlier work. A new preparation with the composition $TiO_2 . 12Nb_2O_5$ proved to be a definite compound, while $TiO_2 : 19Nb_2O_5$, when slow-cooled, consisted of the two phases Nb_2O_5 and $TiNb_{24}O_{62}$, in essential agreement therefore with the independent study of Gruehn & Schäfer (1963). Since the diffraction patterns of these two phases were so alike, it seemed worth while to compare their crystal structures so as to obtain fresh evidence for the present controversy over the status of non-stoichiometric compounds (Wadsley, 1964) in a case where equilibrium conditions are readily established. No attempt has been made in the present study to refine the structure beyond the limits of two-dimensional Fourier methods, the emphasis being placed upon structural principles and their significance.

Experimental

Colorless crystals of $TiNb_{24}O_{62}$ were readily picked from a specimen of the same composition, heated in a sealed platinum tube at 1450 °C for 19 hours, and quenched by dropping into water. The symmetry and unit-cell size were determined by single-crystal methods, and the refined dimensions in Table 1 obtained from an indexed Guinier film internally calibrated with potassium chloride. Intensities were collected by the integrated Weissenberg multiple-film method with filtered copper radiation, for the zero and first levels taken around the short axis of symmetry, and measured with a calibrated film strip. No absorption corrections were considered necessary, as the crystal measured less than 0·03 mm in the maximum dimension. Scattering curves for Nb^{5+} (Thomas & Umeda, 1957) and Ti^{4+} (*International Tables for X-ray Crystallography*, 1962) corrected for dispersion, and Suzuki's (1960) data for O^{2-}, were used for the structure factor calculations, modified by an overall isotropic temperature factor of 0·3 Å² obtained graphically.

Table 1. *Crystallographic data for* $TiNb_{24}O_{62}$

Symmetry: monoclinic
Unit-cell dimensions: $a=29{\cdot}78$, $b=3{\cdot}821$, $c=21{\cdot}12$ Å, $\beta=94{\cdot}9°$
Systematically absent reflexions: hkl with $h+k\neq 2n$
Possible space groups: $C2$ (No. 5), Cm (No. 8), $C2/m$ (No. 12).
D_m: $4{\cdot}5\pm0{\cdot}1$ g.cm^{-3}
D_x: $4{\cdot}53$ g.cm^{-3}
$Z=2$
$\mu=503$ cm^{-1}

The zero-layer Weissenberg film was very similar to that of high-temperature Nb_2O_5, and had the examination been taken no further, there would have been few doubts that the two compounds had identical structures, apart from variations of lattice parameters and minor changes of atomic position to be expected from a classic picture of a solid solution. However, the $h1l$ data proved that $TiNb_{24}O_{62}$ is side-centred with the choice of space groups, $C2$, Cm, $C2/m$. Nb_2O_5, on the other hand, is primitive with the space group $P2$, and significant differences evidently exist between them.

The diffraction data contained an orthogonal subcell of 3·8 Å inclined at angles of 16° and 106° to the positive direction of the a axis. Sub-cells of this kind are present in most of the titanium-, tungsten- and molybdenum-substituted niobium pentoxides, and provide a powerful means for solving their crystal structures. For example, all of the known members of the two series $B_{3n}O_{8n-3}$ and $B_{3n+1}O_{8n-2}$ are built up of finite blocks of BO_6 octanedra, sharing corners as in ReO_3 (Fig. 1*a*). These blocks are three octahedra wide, three, four, or five long, depending upon the compound, and infinite in the third direction corresponding to the 3·8 Å axis of symmetry. In the present instance it is safe to assume that $TiNb_{24}O_{62}$ contains blocks of this kind, and the sub-cell gives the average directions in which they are oriented.

The ideal structure (Fig. 2) was readily obtained by methods that are fully discussed elsewhere (Andersson

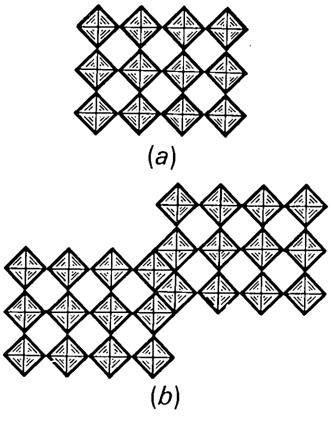

Fig. 1. (*a*) Idealized octahedral block 3 octahedra by 4 and infinite out of the plane of the paper. Octahedra joined by sharing corners as in ReO_3. (*b*) Double block of $3\times4\times\infty$ octahedra, made up of two of the blocks in (*a*) by having some edges in common.

& Wadsley, 1962; Gatehouse & Wadsley, 1964). At this stage we note that the blocks, three octahedra by four in projection, are joined in pairs with edges in common (Fig. 1*a*, *b*), and with tetrahedral positions, two of which are created at each of the junctions of four double blocks, occupied by a single metal atom. This arrangement also fulfils the additional criteria of the method, whereby the unit cell must have the correct symmetry, and the numbers of atoms within it must correspond exactly with the chemical formula of the compound.

The positions of the metals in octahedral coordination were adjusted to give distances between them in projection of 3·8 and 2·8 Å, depending upon whether they were joined by corners or edges. These positions were then refined by successive F_o, F_o-F_{metal}, and F_o-F_c electron-density projections on to (010) utilizing 230 non-zero $h0l$ reflexions. Ti^{4+} was originally assumed to be the tetrahedrally coordinated atom, but the first F_o-F_{metal} projection showed a relatively large positive area at the origin where this atom had been placed, and negative areas in the remaining metal positions. Much better agreement was reached by assuming that the metals all had the same scattering power, (24Nb+Ti)/25, and were therefore disordered as in the titanoniobates $TiNb_2O_7$ and $Ti_2Nb_{10}O_{29}$ (Wadsley, 1961*a*, *b*).

After two complete difference syntheses, the reliability index had dropped to 13·0%. The background of the map showed that the shifts were less than the estimated standard deviations of their positions, and the structure would therefore refine no further by two-dimensional Fourier methods. Extinction appears to be responsible for large discrepancies between F_o and F_c for several of the strong reflexions (Table 5).

The x and z parameters were next combined with y values for all atoms in two different sets of $h1l$ structure factors. In one set the tetrahedral atoms were placed in the position 2(*a*) of the space group *C*2 at 0, y, 0 with $y=\frac{1}{4}$. As there are actually two tetrahedral positions at both the origin and the side, the atoms in these could be disordered and present, instead, in the fourfold position 4(*g*) of the space group $C2/m \pm 0, y, 0$, with $y=\frac{1}{4}$. The reliability indices obtained from both sets were 17·3% for *C*2, and 18·3% for *C*2/*m*. Except for the slightly better overall agreement with the polar space group, there is evidently very little difference between the two possibilities. An unambiguous decision between them could undoubtedly be reached with further refinement of the complete three-dimensional data, but this is beyond our immediate objective.

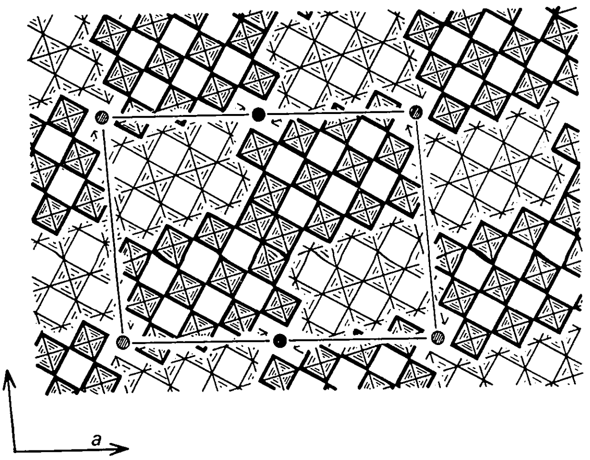

Fig. 2. Idealized structure of $TiNb_{24}O_{62}$. The double blocks of Fig. 1(*b*) are packed into a three-dimensional network, with the tetrahedrally coordinated metals (circles) at the junctions. The unit cell in projection is outlined.

Table 2. *Fractional atomic parameters*

Space group *C*2

Atom*	Point position	x	y	z
B(1)	2(*a*)	0	$\frac{1}{4}$	0
B(2)	4(*c*)	0·1144	0	0·0130
B(3)	4(*c*)	0·2411	0	0·0629
B(4)	4(*c*)	0·3684	0	0·1128
B(5)	4(*c*)	0·4978	0	0·1630
B(6)	4(*c*)	0·0911	0	0·1882
B(7)	4(*c*)	0·2192	0	0·2379
B(8)	4(*c*)	0·3466	0	0·2874
B(9)	4(*c*)	0·4754	0	0·3381
B(10)	4(*c*)	0·0687	0	0·3626
B(11)	4(*c*)	0·1954	0	0·4125
B(12)	4(*c*)	0·3218	0	0·4620
B(13)	4(*c*)	0·4479	0	0·5146
O(1)	4(*c*)	0·377	0	0·016
O(2)	4(*c*)	0·178	0	0·033
O(3)	4(*c*)	0·312	0	0·091
O(4)	4(*c*)	0·107	0	0·101
O(5)	4(*c*)	0·440	0	0·132
O(6)	4(*c*)	0·230	0	0·149
O(7)	4(*c*)	0·012	0	0·151
O(8)	4(*c*)	0·364	0	0·195
O(9)	4(*c*)	0·150	0	0·227
O(10)	4(*c*)	0·498	0	0·249
O(11)	4(*c*)	0·288	0	0·263
O(12)	4(*c*)	0·068	0	0·281
O(13)	4(*c*)	0·416	0	0·315
O(14)	4(*c*)	0·207	0	0·324
O(15)	4(*c*)	0·338	0	0·378
O(16)	4(*c*)	0·127	0	0·395
O(17)	4(*c*)	0·476	0	0·442
O(18)	4(*c*)	0·264	0	0·443
O(19)	4(*c*)	0·038	0	0·460
O(20)	4(*c*)	0·392	0	0·485
O(21)	4(*c*)	0·187	0	0·510
O(22)	4(*c*)	0·314	0	0·559
O(23)	4(*c*)	0·449	0	0·615
O(24)	4(*c*)	0·008	0	0·661
O(25)	4(*c*)	0·139	0	0·729
O(26)	4(*c*)	0·265	0	0·751
O(27)	4(*c*)	0·433	0	0·826
O(28)	4(*c*)	0·122	0	0·915
O(29)	4(*c*)	0·483	0	0·934
O(30)	4(*c*)	0·253	0	0·970
O(31)	4(*c*)	0·042	0	0·982

* *B* represents a disordered metal (24Nb+Ti)/25.

The average standard deviations for the metal atoms are $\sigma(x)=0{\cdot}0005$, $\sigma(z)=0{\cdot}0007$; for oxygen, $\sigma(x)=0{\cdot}002$, $\sigma(z)=0{\cdot}003$.

Table 3. *Octahedral metals. Interatomic distances in* Å

Metal	Bonded oxygen atoms*					Distances (same order as in previous column)					Distances	O–O distances		
											Average	Max.	Min.	Average
B(2)	1′(2);	2,	4,	31,	28	2·03(2);	1·89,	1·89,	2·19,	2·10	2·02	3·29	2·40	2·80
B(3)	30′(2);	3,	6,	2,	30	2·05(2);	2·13,	1·87,	1·94,	2·03	2·01	3·23	2·31	2·81
B(4)	28′(2);	5,	8,	3,	1	2·03(2);	2·15,	1·75,	1·72,	2·08	1·96	3·06	2·40	2·74
B(5)	7′(2);	27,	10,	5,	29	1·98(2);	2·03,	1·82,	1·78,	2·17,	1·96	2·88	2·53	2·73
B(6)	27′(2);	9,	12,	7,	4	2·06(2);	1·86,	2·13	2·41,	1·94	2·08	3·24	2·53	2·91
B(7)	26′(2);	11,	14,	9,	6	1·98(2);	2·06,	1·88,	2·06,	1·94	1·98	3·20	2·46	2·79
B(8)	25′(2);	13,	15,	11,	8	1·99(2);	2·12,	1·96,	1·79,	2·06	1·99	3·08	2·50	2·79
B(9)	24′(2);	23,	17,	13,	10	1·97(2);	2·39,	2·20,	1·78,	2·05	2·06	3·18	2·47	2·84
B(10)	23′(2);	16,	19,	24,	12	2·04(2);	1·83,	2·32,	2·29,	1·73	2·04	3·11	2·54	2·84
B(11)	22′(2);	18,	21,	16,	14	2·03(2);	2·08,	2·09,	2·03,	1·94	2·03	3·23	2·40	2·85
B(12)	21′(2);	20,	22,	18,	15	2·03(2);	2·09,	2·08,	1·74,	1·87	1·97	3·17	2·40	2·78
B(13)	19′(2);	17′,	23,	20,	17	2·02(2);	2·37,	2·11,	1·75,	1·81	2·01	3·01	2·55	2·78

* Given by numbers only (Table 2 and Fig. 3). The first, followed by (2) and a semicolon, are the two oxygen atoms lying over and under the metal *B*, the distances between them having e.s.d.'s of ±0·12 Å. The remaining metal–oxygen distances are in error by ±0·06 Å.

Table 4. *Tetrahedral interatomic distances and angles*

Nb(1) -O(29′)	1·70±0·05 Å
Nb(1) -O(31)	1·65±0·05
O(29)-O(29′)	2·82±0·10
O(31)-O(31′)	2·69±0·10
O(29)-O(31)	2·76±0·07
O(29) -Nb(1) -O(29′)	112·1°
O(31) -Nb(1) -O(31′)	108·6°
O(29′)-Nb(1) -O(31)	110·0°
O(29) -Nb(1) -O(31)	110·0°

Atomic positions are given in Table 2 for the space group *C*2, interatomic distances in Tables 3 and 4, and a list of observed and calculated structure factors, omitting unobserved reflexions, in Table 5. The structure is illustrated by a ball-and-spoke drawing in Fig. 3, and as an assemblage of ideal octahedra in Fig. 2. Although individual Nb–O octahedral bonds vary widely between real distances of 2·41 ±0·06 Å and 1·72±0·06 Å, the six bond lengths for each metal average between 1·96 and 2·08 Å, or 2·01 Å for the seventy-two independent determinations. This compares with an average value of 1·99 Å in Nb_2O_5 (Gatehouse & Wadsley, 1964). The distances between oxygen atoms also vary widely, from 2·31 to 3·23 Å with an average of 2·80 Å. The tetrahedral distances between metal and oxygen (Table 4) are 1·65 and 1·70 Å, and are of the same order of magnitude as in Nb_2O_5.

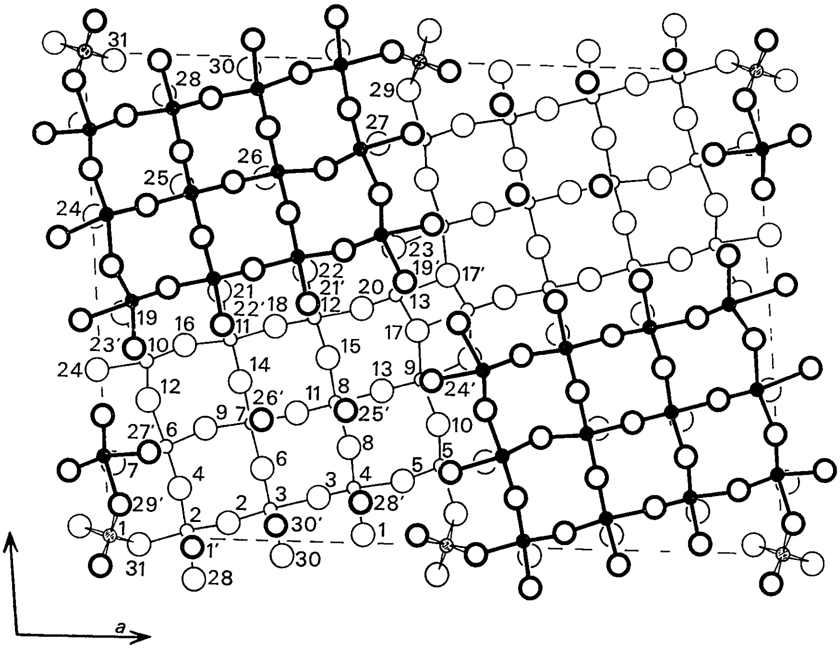

Fig. 3. Structure of $TiNb_{24}O_{62}$. Small circles metals, larger circles oxygen. Atoms in heavier outlines at $y=\frac{1}{2}$, and lighter at $y=0$. Small circles hatched are tetrahedral metal atoms at $y=\frac{1}{4}$. The unit cell is outlined.

Table 5. *Comparison of observed and calculated intensities*

Unobserved terms omitted.

h k l	F_o	$\lvert F_c\rvert$	h k l	F_o	$\lvert F_c\rvert$	h k l	F_o	$\lvert F_c\rvert$	h k l	F_o	$\lvert F_c\rvert$	h k l	F_o	$\lvert F_c\rvert$
2 0 0	128	137	18 0 6	433	481	4 0 13	410	402	9 1 1	155	87	3 1 $\overline{10}$	133	184
4 0 0	157	164	2 0 7	128	110	6 0 13	222	195	11 1 1	118	136	5 1 $\overline{10}$	191	159
6 0 0	156	148	4 0 7	440	401	12 0 13	219	215	13 1 1	222	133	7 1 $\overline{10}$	196	172
8 0 0	206	208	6 0 7	712	763	26 0 13	166	135	15 1 1	866	987	9 1 $\overline{10}$	287	323
10 0 0	154	99	8 0 7	280	290	12 0 $\overline{13}$	178	145	1 1 $\bar{1}$	1330	900	11 1 $\overline{10}$	802	952
12 0 0	141	85	10 0 7	213	253	14 0 $\overline{13}$	184	120	3 1 $\bar{1}$	196	132	13 1 $\overline{10}$	560	631
14 0 0	155	125	12 0 7	173	150	22 0 $\overline{13}$	233	171	15 1 $\bar{1}$	307	263	15 1 $\overline{10}$	162	171
16 0 0	319	382	14 0 7	278	240	24 0 $\overline{13}$	200	159	17 1 $\bar{1}$	257	295	1 1 $\overline{11}$	198	238
32 0 0	253	236	16 0 7	221	163	26 0 $\overline{13}$	249	270	29 1 $\bar{1}$	249	213	3 1 $\overline{11}$	659	706
4 0 1	211	209	18 0 7	201	201	28 0 $\overline{13}$	432	513	5 1 2	96	109	5 1 $\overline{11}$	1192	1265
6 0 1	525	565	20 0 7	313	289	30 0 $\overline{13}$	268	290	7 1 2	864	779	7 1 $\overline{11}$	326	294
8 0 1	905	1553*	28 0 7	190	142	10 0 14	503	467	15 1 2	140	130	9 1 $\overline{11}$	149	137
10 0 1	312	310	6 0 $\bar{7}$	115	120	26 0 14	546	620	23 1 2	533	629	21 1 $\overline{11}$	182	225
12 0 1	188	240	8 0 $\bar{7}$	122	138	6 0 $\overline{14}$	223	179	7 1 $\bar{2}$	144	155	3 1 12	1043	1223
16 0 1	244	249	10 0 $\bar{7}$	270	258	14 0 $\overline{14}$	190	148	9 1 $\bar{2}$	346	345	13 1 $\overline{12}$	235	254
24 0 1	196	259	12 0 $\bar{7}$	179	155	20 0 $\overline{14}$	436	447	17 1 $\bar{2}$	149	110	29 1 $\overline{12}$	217	340
6 0 $\bar{1}$	94	131	24 0 $\bar{7}$	199	160	22 0 $\overline{14}$	557	598	25 1 $\bar{2}$	628	807	7 1 13	164	159
8 0 $\bar{1}$	206	251	26 0 $\bar{7}$	534	628	2 0 15	181	144	13 1 3	175	237	9 1 13	238	355
24 0 $\bar{1}$	298	300	34 0 $\bar{7}$	152	136	18 0 15	444	409	15 1 3	764	807	11 1 13	995	1187
32 0 $\bar{1}$	180	143	0 0 8	116	171	26 0 15	142	145	17 1 3	153	234	5 1 $\overline{13}$	349	331
0 0 2	208	202	10 0 8	189	170	14 0 $\overline{15}$	686	753	23 1 3	178	149	21 1 $\overline{13}$	315	412
8 0 2	183	127	12 0 8	839	933	10 0 16	231	199	25 1 3	182	160	9 1 14	179	219
10 0 2	226	156	14 0 8	395	404	24 0 16	195	207	27 1 3	255	203	15 1 14	257	195
12 0 2	370	383	16 0 8	177	194	26 0 16	231	262	29 1 3	386	478	17 1 14	444	578
14 0 2	1112	1395	28 0 8	304	284	6 0 $\overline{16}$	800	932	1 1 $\bar{3}$	761	566	19 1 14	553	626
16 0 2	814	828	2 0 $\bar{8}$	300	293	8 0 $\overline{16}$	191	166	17 1 $\bar{3}$	966	1146	21 1 $\overline{15}$	640	727
18 0 2	268	212	4 0 $\bar{8}$	361	357	0 0 17	489	457	5 1 4	231	124	23 1 $\overline{15}$	297	197
32 0 2	175	132	12 0 $\bar{8}$	839	933	2 0 17	541	494	7 1 4	291	286	29 1 $\overline{15}$	534	648
2 0 $\bar{2}$	124	142	14 0 $\bar{8}$	153	142	26 0 17	106	59	21 1 4	300	341	7 1 15	176	114
16 0 $\bar{2}$	466	402	16 0 $\bar{8}$	251	250	2 0 $\overline{17}$	274	245	23 1 4	440	420	23 1 15	213	161
32 0 $\bar{2}$	552	634	18 0 $\bar{8}$	742	830	14 0 $\overline{17}$	260	251	5 1 $\bar{4}$	102	119	25 1 15	608	839
6 0 3	132	157	20 0 $\bar{8}$	400	320	2 0 18	200	134	7 1 $\bar{4}$	238	215	27 1 15	155	247
20 0 3	231	154	34 0 $\bar{8}$	283	342	4 0 18	201	185	9 1 $\bar{4}$	602	605	9 1 $\overline{15}$	175	161
22 0 3	814	975	4 0 9	332	309	6 0 18	349	315	11 1 $\bar{4}$	298	371	13 1 $\overline{16}$	444	412
6 0 $\bar{3}$	102	78	20 0 9	695	736	8 0 18	709	813	13 1 $\bar{4}$	131	197	15 1 $\overline{16}$	546	500
8 0 $\bar{3}$	230	255	10 0 $\bar{9}$	377	375	10 0 18	307	260	25 1 $\bar{4}$	257	254	9 1 17	315	372
10 0 $\bar{3}$	204	227	12 0 $\bar{9}$	707	794	24 0 18	165	185	1 1 5	267	233	7 1 $\overline{17}$	764	811
14 0 $\bar{3}$	157	102	14 0 $\bar{9}$	244	196	6 0 $\overline{18}$	230	185	3 1 5	147	116	23 1 $\overline{17}$	273	301
18 0 $\bar{3}$	161	168	16 0 $\bar{9}$	169	165	10 0 19	197	135	13 1 5	342	246	1 1 18	704	752
22 0 $\bar{3}$	214	243	26 0 $\bar{9}$	329	272	14 0 19	262	167	15 1 5	211	185	17 1 18	224	227
24 0 $\bar{3}$	516	508	28 0 $\bar{9}$	300	291	16 0 19	624	715	29 1 5	475	528	15 1 $\overline{18}$	398	314
26 0 $\bar{3}$	367	368	12 0 10	366	450	18 0 $\overline{19}$	191	135	1 1 $\bar{5}$	862	742	7 1 19	309	381
0 0 4	181	207	24 0 10	198	162	22 0 $\overline{19}$	173	128	3 1 $\bar{5}$	851	774	9 1 19	582	602
14 0 4	221	181	26 0 10	268	255	24 0 $\overline{19}$	205	179	5 1 $\bar{5}$	317	313	11 1 19	171	160
28 0 4	198	239	28 0 10	481	601	26 0 $\overline{19}$	162	127	7 1 $\bar{5}$	191	183	7 1 $\overline{19}$	362	365
30 0 4	723	816	4 0 $\overline{10}$	957	1392*	28 0 $\overline{19}$	213	200	17 1 $\bar{5}$	306	347	23 1 $\overline{19}$	626	779
2 0 $\bar{4}$	466	578	18 0 $\overline{10}$	212	210	20 0 $\overline{20}$	127	123	1 1 6	186	162	1 1 20	178	173
4 0 $\bar{4}$	121	111	20 0 $\overline{10}$	483	480	8 0 $\overline{20}$	232	184	3 1 6	289	186	15 1 20	435	523
6 0 $\bar{4}$	121	62	36 0 $\overline{10}$	171	211	10 0 $\overline{20}$	199	175	5 1 6	633	622	17 1 20	295	273
8 0 $\bar{4}$	103	54	0 0 11	310	269	12 0 $\overline{20}$	198	144	7 1 6	317	285	1 1 $\overline{20}$	253	235
10 0 $\bar{4}$	133	103	2 0 11	412	399	22 0 $\overline{20}$	293	319	21 1 6	251	189	15 1 $\overline{20}$	522	570
12 0 $\bar{4}$	146	112	4 0 11	701	794	24 0 $\overline{20}$	548	672	1 1 $\bar{6}$	149	151	17 1 $\overline{20}$	275	345
14 0 $\bar{4}$	226	172	18 0 11	198	173	16 0 $\overline{21}$	632	748	3 1 $\bar{6}$	151	93	7 1 21	366	350
16 0 $\bar{4}$	513	521	20 0 11	233	265	8 0 $\overline{22}$	660	750	5 1 $\bar{6}$	156	102	7 1 $\overline{21}$	297	390
18 0 $\bar{4}$	740	789	28 0 11	191	163	10 0 $\overline{22}$	370	378	7 1 $\bar{6}$	164	188	9 1 $\overline{21}$	609	715
20 0 $\bar{4}$	202	223	2 0 $\overline{11}$	234	168	0 0 23	385	384	9 1 $\bar{6}$	211	217	11 1 $\overline{21}$	166	265
34 0 4	242	238	4 0 $\overline{11}$	204	158	2 0 $\overline{23}$	548	611	11 1 $\bar{6}$	182	142	23 1 $\overline{21}$	184	265
6 0 5	295	291	6 0 $\overline{11}$	190	131	4 0 $\overline{23}$	207	169	13 1 7	982	1116	15 1 22	193	148
10 0 5	127	71	12 0 $\overline{11}$	599	614	18 0 $\overline{23}$	199	194	29 1 7	227	248	1 1 $\overline{22}$	142	172
12 0 5	138	118	28 0 $\overline{11}$	246	260	6 0 24	669	799	3 1 $\bar{7}$	277	262	17 1 $\overline{22}$	231	222
30 0 5	259	184	0 0 12	249	239	8 0 24	139	110	27 1 $\bar{7}$	180	148	5 1 23	144	207
10 0 $\bar{5}$	780	968	2 0 12	237	222	10 0 $\overline{24}$	241	146	5 1 8	309	288	7 1 23	580	751
26 0 $\bar{5}$	329	350	4 0 12	317	247	2 0 $\overline{25}$	169	157	13 1 8	153	158	9 1 $\overline{23}$	327	288
0 0 6	271	274	6 0 12	298	295	6 0 26	132	189	17 1 8	169	126	7 1 $\overline{24}$	118	149
2 0 6	233	237	8 0 12	426	455	10 0 $\overline{26}$	301	339	21 1 8	651	734	13 1 24	400	437
4 0 6	213	209	10 0 12	748	915				11 1 $\bar{8}$	195	105			
6 0 6	208	152	12 0 12	462	428	1 1 0	158	241	27 1 $\bar{8}$	757	949			
8 0 6	200	157	26 0 12	304	318	3 1 0	411	261	13 1 9	224	201			
12 0 6	310	346	2 0 $\overline{12}$	249	203	5 1 0	446	312	21 1 9	182	136			
14 0 6	253	163	4 0 $\overline{12}$	625	710	7 1 0	735	660	23 1 9	182	190			
20 0 6	188	137	6 0 $\overline{12}$	220	168	9 1 0	406	393	25 1 9	304	280			
2 0 $\bar{6}$	873	1463*	12 0 $\overline{12}$	171	165	23 1 0	249	222	27 1 9	468	632			
4 0 $\bar{6}$	213	209	14 0 $\overline{12}$	178	122	1 1 1	793	519	29 1 9	366	378			
10 0 $\bar{6}$	124	103	20 0 $\overline{12}$	256	291	3 1 1	378	259	9 1 $\bar{9}$	178	185			
12 0 $\bar{6}$	134	88	34 0 12	139	115	5 1 1	231	146	19 1 $\bar{9}$	1104	1128			
34 0 $\bar{6}$	473	531	2 0 13	324	300	7 1 1	143	141	1 1 $\overline{10}$	133	158			

* Affected by extinction.

Relationship to Nb_2O_5 and to other titanoniobates

The blocks of octahedra in $TiNb_{24}O_{62}$, three wide, four long and infinite out of the plane of the paper (Fig. 1*a*), are joined in pairs by edge-sharing (Fig. 1*b*). Some of the peripheral octahedral edges are common to neighbouring double blocks above and below, and the junctions at the corners and (001) face of the unit cell contain tetrahedrally coordinated metal atoms (Fig. 2). High temperature Nb_2O_5, on the other hand, is built up from two different block sizes, $3\times5\times\infty$ and $3\times4\times\infty$ (Gatehouse & Wadsley, 1964). The former are joined at the same level along *b* to similar units on both sides, and extend throughout the structure. The $3\times4\times\infty$ blocks cement these sheets together, and also leave tetrahedral holes for a metal atom (Fig. 4).

The similarity between the diffraction data of the two substances arises from a close but fortuitous relationship between their unit cells. The approximate dimensions of $TiNb_{24}O_{62}$ can be derived from those of Nb_2O_5 by the axial transform $102/010/\bar{1}00$, and the directions of the sub-cells in both then become the same (Figs. 2 and 4). One might have expected that the partial replacement of Nb^{5+} by Ti^{4+} would lead to a non-stoichiometric solid solution $(Ti_xNb_{2-x})O_{5-x/2}$, where a density measurement could be used to decide whether oxygen leaves the structure $(Ti, Nb)\,O_{2\cdot48}$, or additional metal atoms adopt interstitial positions, $(Ti, Nb)_{1\cdot08}O_{2\cdot50}$. Instead $TiNb_{24}O_{62}$ and Nb_2O_5 differ not only in the sizes of the blocks of which they are both composed, but also in the way they are arranged. There can be no question that the substitution of the lower valency ion for niobium does indeed reduce the oxygen-to-metal ratio, but the number of oxygen atoms in the unit cell remains a whole number. In other words there are no empty oxygen positions requiring local changes of coordination number.

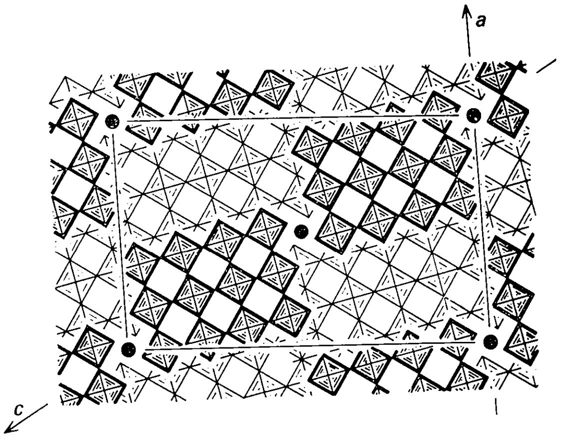

Fig. 4. Structure of high-temperature Nb_2O_5, drawn in the same orientation as Fig. 2. The transformed "unit cell" (see text) which approximates that of $TiNb_{24}O_{62}$ is outlined. The arrows *a* and *c* refer to the real axial directions of Nb_2O_5.

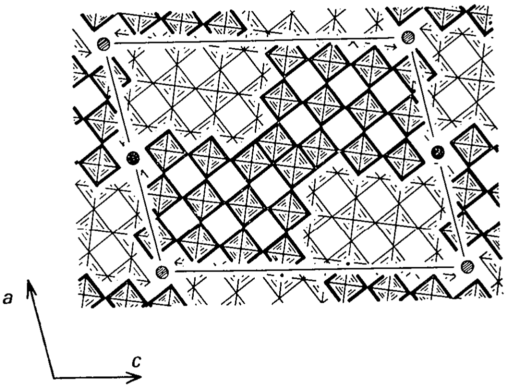

Fig. 5. Hypothetical dimorph of $TiNb_{24}O_{62}$, drawn as idealized octahedra.

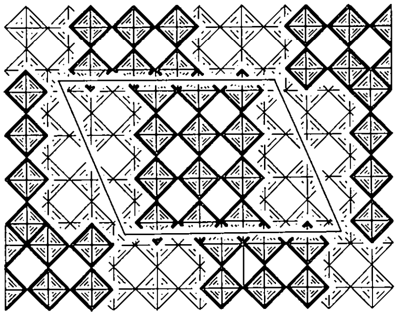

Fig. 6. Ideal structure of monoclinic $Ti_2Nb_{10}O_{29}$ (Wadsley, 1961*b*). The $3\times4\times\infty$ blocks pack together with no tetrahedral positions between them.

What other kinds of structure can be formed by the $3\times4\times\infty$ blocks of octahedra? Firstly it is possible to construct a hypothetical dimorph of $TiNb_{24}O_{62}$ with the doubled blocks joined in a slightly different way (Fig. 5), but still retaining all the essential features of the other. There is no obvious relationship to the unit cell of Nb_2O_5, and the diffraction data from it would have been less likely to be misinterpreted as a defect solid solution if this structure had been adopted.

A second way to join the blocks is in larger groups of three, four, five and so on, but there is no evidence that these phases can form within the TiO_2–Nb_2O_5 system. Nevertheless if they are joined on both sides to form infinite groups of blocks, which share corners with identical sheets *b*/2 upwards and downwards, a structure is formed with no tetrahedral positions (Fig. 6). This was found for monoclinic $Ti_2Nb_{10}O_{29}$, while a different stacking sequence of the same blocks was present in its orthorhombic dimorph (Wadsley, 1961*b*). Single $3\times4\times\infty$ units can be grouped around tetrahedral metals at the junctions (Fig. 7). This structure is adopted by $WNb_{12}O_{33}$, one of several new compounds we will shortly be describing (Roth & Wadsley, 1964).

In all cases the metal-to-oxygen ratios are not fractional, but correspond to exact, if cumbersome, chemical formulae arising from the ways in which blocks of the one size can be packed, the tetrahedral sites providing considerable flexibility. Whether a compo-

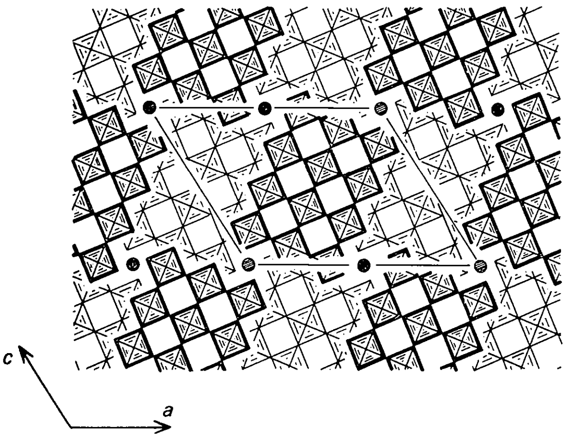

Fig. 7. Ideal structure of $WNb_{12}O_{33}$ (Roth & Wadsley, 1964). The $3\times4\times\infty$ blocks are single groups of Nb–O octahedra, which pack around the tetrahedral W atoms.

sition corresponds to a single phase, or to a mixture of two different phases, depends upon whether or not a logical method exists for blocks of given sizes to pack together in a way which will correspond to a formula with an integral number of atoms.

It should be noted that up to about 5 mol.% of TiO_2 can enter into solid solution with Nb_2O_5 at high temperature. The $TiO_2:19Nb_2O_5$ preparation, forming two phases in approximately equal amounts when slow cooled, shows a large increase of Nb_2O_5 in the powder pattern and a corresponding decrease of $TiNb_{24}O_{62}$ when it is quenched from about 1360 °C, with little or no change in the unit-cell dimensions of either. This may be due either to a small number of excess cations present in the vacant tetrahedral positions in Nb_2O_5, or to an intimate intergrowth of the two structures at the unit cell level. The nature of a solid solution of this kind, however, cannot be deduced without a good deal of additional single-crystal work.

Structural homologues

The concept of homologous series of transition metal oxides was introduced by Magnéli (1953) in his study of the reduced Mo/W oxides. Any member of a particular series contains blocks of a parent phase, with a characteristic and finite size, terminated by some discontinuity. In all other respects the homologues of a given series are identical with each other.

Nb_2O_5 and $Nb_{22}O_{54}$ are the members $n=9$ and 7 of the series $B_{3n+1}O_{8n-2}$ (Gatehouse & Wadsley, 1964), an unusual case where both compounds have ReO_3-type blocks of two different sizes. Although the formula of $TiNb_{24}O_{62}$ corresponds to $n=8$, its structure is very different from these two, and it is questionable whether it should be labelled as a homologue in the accepted sense. There should be other phases where n is even. For example $B_{19}O_{46}$, $n=6$, should resemble $TiNb_{24}O_{62}$, but with the block size $3\times3\times\infty$, instead of $3\times4\times\infty$. Attempts to prepare $Ti_3Nb_{16}O_{46}$ ($3TiO_2 . 8Nb_2O_5$) or $ZnNb_{18}O_{46}$ ($ZnO . 9Nb_2O_5$) with the expected structure were unsuccessful. The $3\times3\times\infty$ blocks are nevertheless known, in tetragonal PNb_9O_{25} (Roth, Wadsley & Andersson, 1965) arranged as single units around tetrahedral phosphorus atoms, and also in $TiNb_2O_7$ (Wadsley, 1961*a*) where, as in the case of $Ti_2Nb_{10}O_{29}$, there are no tetrahedral positions.

The building block principle, $3\times n\times\infty$, is illustrated by many different kinds of structure, but blocks smaller than $3\times3\times\infty$, or larger than $3\times5\times\infty$ have not as yet been found in any mixed valency oxide of niobium. Blocks can pack together in a great number of ways in addition to those we have discussed, and could, perhaps, arise under different thermal conditions or in different chemical systems not yet examined. This principle has proved to be rather more useful in the present case than that of the homologous series, and we will augment the number of examples of it, in due course, with a study of the stoichiometric phases identifiable at the Nb_2O_5 end of the binary system Nb_2O_5–WO_3.

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