distances 1·95 and 2·76 Å between metal and anion, anion and anion respectively in NbO_2F; Vousden (1951) 2·00 and 2·82 Å for $KNbO_3$, 1·95 and 2·76 Å for $NaNbO_3$; Byström's (1944) data for the pyrochlor structure, based upon indirect methods, is not included.

Complex structures such as this one are not readily described in terms of the individual atoms of which they are composed; since it bears a close resemblance to those of the twoforms of $Ti_2Nb_{10}O_{29}$ which are found in the system TiO_2–Nb_2O_5, the three structures will be discussed together in the following paper as members of an homologous series (Wadsley, 1961).

References

ANDERSSON, S., COLLÉN, B., KUYLENSTIERNA, U. & MAGNÉLI, A. (1957a). Acta Chem. Scand. 11, 1641.

ANDERSSON, S., COLLÉN, B., KUYLENSTIERNA, U. & MAGNÉLI, A. (1957b). Acta Chem. Scand. 11, 1653.
BYSTRÖM, A. (1944). Ark. Kemi, Min. Geol. A, 18, No. 21.
DYSON, P. (1957). Acta Cryst. 10, 140.
FREVEL, L. K. & RINN, H. W. (1956). Acta Cryst. 9, 626.
HÄGG, G. & MAGNÉLI, A. (1954). Revs. Pure Appl. Chem. Australia, 4, 235.
MARINDER, B. O. & MAGNÉLI, A. (1957). Acta Chem. Scand. 11, 1635.
QURASHI, M. M. (1954). Acta Cryst. 7, 310.
ROTH, R. S. & COUGHANOUR, L. W. (1955). J. Res. Nat. Bur. Stand. Wash., 55, 209.
THOMAS, L. H. & UMEDA, K. (1957). J. Chem. Phys. 26, 293.
VIERVOLL, H. & ØGRIM, O. (1949). Acta Cryst. 2, 277.
VOUSDEN, P. (1951). Acta Cryst. 4, 373.
WADSLEY, A. D. (1955). Acta Cryst. 8, 695.
WADSLEY, A. D. (1961). Acta Cryst. 14, 664.

Mixed Oxides of Titanium and Niobium. II. The Crystal Structures of the Dimorphic Forms of Ti₂Nb₁₀O₂₉

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The structure of orthorhombic $Ti_2Nb_{10}O_{29}$, which has the lattice dimensions

$$a = 28·50, \quad b = 3·805, \quad c = 20·51 \text{ Å},$$

space group Amma, has been solved by trial and error, and refined by electron-density projections. Its monoclinic dimorph,

$$a = 15·57, \quad b = 3·814, \quad c = 20·54 \text{ Å}; \quad \beta = 113° 41'$$

has been shown, qualitatively, to have a closely related structure. Both have features which are common to $TiNb_2O_7$ as well and all three can be described as members of an homologous series $Me_{3n}O_{8n-3}$. Attempts to prepare additional homologues were not successful.

Introduction

Two intermediate phases were identified in the binary system TiO_2–Nb_2O_5 (Roth & Coughanour, 1955). The structure of one, $TiNb_2O_7$, was described in the preceding paper (Wadsley, 1961) and the second, to which the formula $TiO_2.3 Nb_2O_5$ was given, is now reported in some detail. It proved to have the formula $Ti_2Nb_{10}O_{29}$ and to exist in two crystalline modifications.

Experimental

Reaction in the solid state at 1400 °C. between TiO_2 and Nb_2O_5 in the molar ratio 1 : 3 gave αNb_2O_5 as a separate component. Roth & Coughanour (1955) believed their formula to be uncertain, and indeed their phase diagram suggested that it should perhaps be richer in TiO_2. A partial phase analysis gave the most probable formulation $2 TiO_2.5 Nb_2O_5$ which was subsequently confirmed by the structure determination.

Two preparations were then made. In the first, the weighed oxides were thoroughly ground together, pelletted, and reacted in the solid state at 1400 °C. for 36 hr. Part of this was then fused in a platinum crucible and allowed to cool slowly. Debye–Scherrer patterns of these two preparations were virtually identical, but the Guinier camera disclosed small differences between them. A single crystal of the sintered preparation proved to have a large unit cell with orthorhombic symmetry. A crystal of the fused phase, free from flaws or twinning, could not be found. Nevertheless the Weissenberg photographs clearly

showed monoclinic symmetry and with the unit cell and space groups listed in Table 1 together with those of the dimorph. The powder patterns of the two are recorded in Tables 2 and 3.

Table 1. Crystallographic data for the two modifications of $Ti_2Nb_{10}O_{29}$

		Orthorhombic	Monoclinic
Lattice dimensions	a	28·50 Å	15·57 Å
	b	3·805	3·814
	c	20·51	20·54
	β	90°	113° 41'
Systematic absent Reflexions		$hkl, k+l \neq 2n$ $h0l, l \neq 2n$ $hk0, h \neq 2n, k \neq 2n$	$hkl, k+l \neq 2n$
Space group		$Amma$ $Am2a$ $A2_1ma$	$A2/m$ Am $A2$
Density (g.cm.$^{-3}$)	Observed Calculated	$4·40 \pm 0·05$ 4·45	$4·30 \pm 0·05$ 4·33

Table 2. Guinier diffraction pattern of orthorhombic $Ti_2Nb_{10}O_{29}$

Comparison of observed and calculated data, Cu $K\alpha_1$ radiation (limited to $\sin^2 \theta < 0.18000$)

$\sin^2 \theta$ (obs.)	hkl	$\sin^2 \theta$ (calc.)	I (obs.)	Relative intensity (calc.)*
0·00564	002	0·00564	vw	0·05
0·00640	102	0·00637	m	0·23
0·01166	400	0·01169	mw	0·14
0·02251	004	0·02258	m	0·29
0·02335	104	0·02331	mw	0·14
0·02626	600	0·02630	m	0·37
0·04238	011	0·04239	s	0·45
0·04314	111	0·04312	s	0·69
0·04676	800	0·04676	vs	1·00
0·04888	311 / 604	0·04897 / 0·04888	w	0·11 / 0·01
0·05079	006	0·05080	s	0·60
0·05161	106	0·05153	mw	0·18
0·05370	013 / 206	0·05368 / 0·05372	m	0·25 / 0·01
0·05741	306	0·05738	vw	0·02
0·05843	704	0·05831 / 0·05838	vw	0·05
0·06064	511	0·06066	vw	0·03
0·06941	804	0·06954	w	0·05
0·07309	10,00	0·07306	w	0·04
0·07703	115 / 606	0·07699 / 0·07710	ms	0·52 / 0·03
0·07820	711	0·07819	m	0·36
0·08296	315	0·08284	w	0·09
0·08661	706	0·08660	m	0·08
0·08908	811	0·08915	mw	0·10
0·09103	108	0·09103	vw	0·04
0·09448	515	0·09453	w	0·10
0·09759	806	0·09756	m	0·21
0·10058	813	0·10044	vw	0·05
0·10551	12,00	0·10521	vw	0·02
0·11210	715	0·11206	m	0·23
0·13571	915	0·13544	vw	0·03
0·14131	00,10	0·14110	m	0·29
0·14306	14,00	0·14320	m	0·34
0·16373	020	0·16392	s	0·47

* The strongest reflexion (800) is given arbitrary value of 1·000.

Table 3. Guinier diffraction pattern of monoclinic $Ti_2Nb_{10}O_{29}$

Comparison of observed and calculated data, Cu $K\alpha_1$ radiation (limited to $\sin^2 \theta < 0.20000$)

$\sin^2 \theta$ (obs.)	hkl	$\sin^2 \theta$ (calc.)	I (obs.)	Relative intensity (calc.)*
0·00294	100	0·00292	vw	0·12
0·00608	10$\bar{2}$	0·00608	w	0·20
0·01166	200	0·01167	w	0·19
0·02266	10$\bar{4}$	0·02267	ms	0·54
0·02631	300	0·02625	ms	0·49
0·04251	011	0·04246	vs	1·00
0·04365	11$\bar{1}$	0·04360	w	0·16
0·04662	400	0·04667	s	0·94
0·04714	111	0·04716	vw	0·07
0·05090	20$\bar{6}$	0·05078	s	0·69
0·05242	10$\bar{6}$ / 204	0·05268 / 0·05272	vw	0·04 / 0·06
0·05367	11$\bar{3}$	0·05347	m	0·24
0·05751	211	0·05768	vw	0·04
0·07382	106	0·07398	w	0·16
0·07677	21$\bar{5}$ / 11$\bar{5}$	0·07665 / 0·07677	s	0·35 / 0·30
0·08232	015 / 41$\bar{1}$ / 31$\bar{5}$	0·08273 / 0·08203 / 0·08235	ms	0·06 / 0·36 / 0·07
0·09332	206	0·09338	w	0·19
0·10284	51$\bar{3}$	0·10220	vw	0·02
0·11128	51$\bar{5}$	0·11128	vw	0·15
0·11188	215	0·11215	vw	0·13
0·14076	30,$\overline{10}$	0·14080	m	0·38
0·14270	700	0·14293	m	0·31
0·16305	020	0·16312	s	0·46
0·17459	220	0·17479	vw	0·01
0·18641	70,$\overline{10}$ / 800	0·18643 / 0·18669	w	0·07 / 0·06

* The strongest reflexion (011) is given the arbitrary value of 1·00.

Crystal structure of orthorhombic $Ti_2Nb_{10}O_{29}$

Copper radiation was used so as to increase the resolution of the reflexions. The $h0l$ data were collected with an integrating Weissenberg goniometer and the multiple-film technique. The upper levels $h1l$ and $h2l$ were recorded without integration. Intensity readings were reduced in the normal way to $|F|$ values, specimen absorption being neglected. The same scattering curves as for $TiNb_2O_7$ (Wadsley, 1961) were used, and the techniques otherwise were the same. The run of intensities for $h0l$ and $h2l$ were virtually identical, and therefore the atoms were on, or very close to, special positions along y.

Since b is equal to 3·81 Å, the metal atoms must be clearly resolved from one another, but with an oxygen probably overlying each of them. In projection down this axis, therefore, the atoms can be in both 4(c) and 8(f) positions for $Amma$ which are identical with 4(b) and 8(c) respectively for $Am2a$. These two space groups differ only in the y co-ordinates which are general only for the latter one. This is not favoured by the intensity relationships already referred to. The 8(b) positions for $A2_1ma$ are unavailable because the condition $x, y, z; x, \bar{y}, z$) is imposed. If this is the
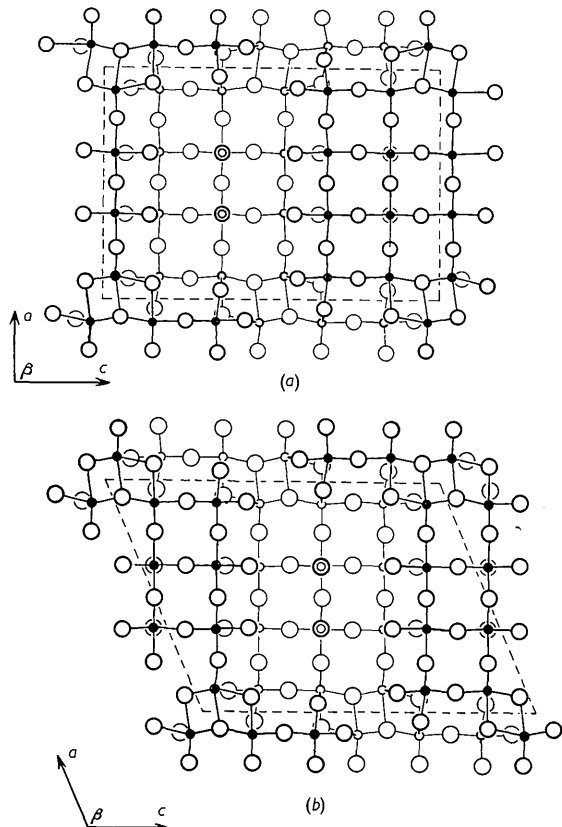
Fig. 1. (a) and (b) Structures of orthorhombic and monoclinic
Ti$_2$Nb$_{10}$O$_{29}$ respectively, as seen in projection on to (010).
One half of the unit cell is shown in (a), and the whole in (b)
as dotted lines. The metal atoms are the smaller, and
oxygen the larger circles.

Table 4. *Fractional atomic parameters for orthorhombic*
Ti$_2$Nb$_{10}$O$_{29}$

Space group *Amma**

Atom	Point position	Ideal structure x/a	y/b	z/c	Derived structure x/a	y/b	z/c
Me_1†	8(f)	0·036	0	0·050	0·0494	0	0·0375
Me_2	8(f)	0·036	0	0·650	0·0481	0	0·6674
Me_3	8(f)	0·036	0	0·850	0·0486	0	0·8518
Me_4	8(f)	0·179	0	0·050	0·1834	0	0·0371
Me_5	8(f)	0·179	0	0·650	0·1828	0	0·6675
Me_6	8(f)	0·179	0	0·850	0·1831	0	0·8521
O_1	4(c)	¼	0	0·050	¼	0	0·039
O_2	4(c)	¼	0	0·650	¼	0	0·662
O_3	4(c)	¼	0	0·850	¼	0	0·851
O_4	8(f)	0·036	0	0·550	0·043	0	0·576
O_5	8(f)	0·036	0	0·150	0·033	0	0·146
O_6	8(f)	0·036	0	0·750	0·045	0	0·757
O_7	8(f)	0·036	0	0·350	0·019	0	0·346
O_8	8(f)	0·036	0	0·950	0·037	0	0·948
O_9	8(f)	0·107	0	0·050	0·110	0	0·039
O_{10}	8(f)	0·107	0	0·650	0·114	0	0·661
O_4	8(f)	0·107	0	0·850	0·111	0	0·852
O_{12}	8(f)	0·179	0	0·550	0·182	0	0·567
O_{13}	8(f)	0·179	0	0·150	0·182	0	0·136
O_{14}	8(f)	0·179	0	0·750	0·182	0	0·758
O_{15}	8(f)	0·179	0	0·350	0·182	0	0·352
O_{16}	8(f)	0·179	0	0·950	0·181	0	0·945

* This orientation is retained to demonstrate the relation-
ship to the monoclinic form of this compound.

† Me is used to denote ($\frac{1}{6}$ Ti + $\frac{5}{6}$ Nb) as a single scattering
unit.

correct space group, the atoms must therefore be in
4(a). The alternatives are thereby reduced to $Amma$
or to $A2_1ma$. Fourier projections on to (010) should
disclose whether or not eightfold positions do exist,
or whether the electron-density maxima are com-
pounded of two independent fourfold sets which are
almost, but not quite, related by a reflexion plane.

The trial-and-error procedure outlined in the pre-
vious paper were applied to this problem. Since the
length of the z axis is the same as for TiNb$_2$O$_7$, it was
evident that the structural units in this direction must
be of the same kind. A set of parameters for a perfectly
regular structure was first obtained, and shifts of the

Table 5. *Interatomic distances for orthorhombic*
Ti$_2$Nb$_{10}$O$_{29}$

	No.	Length			No.	Length
*Me_1–O_5	1	2·27 Å		Me_4–O_9	1	2·10 Å
{ Me_1–O_8	1	1·87		Me_4–O_{16}^1	1	1·90
{ Me_1–O_8^1	1	2·47		Me_4–O_1	1	1·90
Me_1–O_9	1	1·72		Me_4–O_{13}	1	2·03
Me_1–O_4	2	2·07		Me_4–O_{12}	2	2·00
O_8–O_9	1	2·80		O_9–O_{16}^1	1	2·81
O_9–O_5	1	3·09		O_{16}^1–O_1	1	2·76
O_5–O_8^1	1	2·64		O_1–O_{13}	1	2·76
O_8–O_8^1	1	2·99		O_{13}–O_9	1	2·88
{ O_4–O_8	2	3·25		O_{12}–O_{16}^1	2	3·15
{ O_4–O_8^1	2	3·01		O_{12}–O_1	2	2·75
O_4–O_5	2	2·40		O_{12}–O_{13}	2	2·37
O_4–O_9	2	2·79		O_{12}–O_9	2	2·88
Me_2–O_4	1	1·87 Å		Me_5–O_{12}	1	2·06 Å
Me_2–O_{10}	1	1·88		Me_5–O_{10}	1	1·97
Me_2–O_6	1	1·84		Me_5–O_2	1	1·92
Me_2–O_7^1	1	1·92		Me_5–O_{14}	1	1·86
Me_2–O_5	2	2·00		Me_5–O_{13}	2	2·01
O_4–O_{10}	1	2·66		O_2–O_{14}	1	2·76
O_{10}–O_6	1	2·78		O_{14}–O_{10}	1	2·78
O_6–O_7^1	1	2·78		O_{10}–O_{12}	1	2·76
O_7^1–O_4	1	2·37		O_{12}–O_2	1	2·73
O_4–O_5	2	2·40		O_{13}–O_{12}	2	2·37
O_{10}–O_5	2	3·01		O_{13}–O_2	2	2·75
O_6–O_5	2	2·98		O_{13}–O_{14}	2	3·14
O_7^1–O_5	2	2·41		O_{13}–O_{10}	2	2·79
Me_3–O_6	1	1·95 Å		Me_6–O_{14}	1	1·93 Å
Me_3–O_{11}	1	1·77		Me_6–O_3	1	2·00
Me_3–O_8	1	2·11		Me_6–O_{16}	1	1·90
Me_3–O_5^1	1	2·33		Me_6–O_{11}	1	2·06
Me_3–O_7	2	2·09		Me_6–O_{15}	2	1·90
O_6–O_{11}	1	2·71		O_{14}–O_3	1	2·71
O_{11}–O_8	1	2·89		O_3–O_{16}	1	2·75
O_8–O_5^1	1	2·77		O_{16}–O_{11}	1	2·83
O_6–O_5^1	1	2·98		O_{11}–O_{14}	1	2·80
O_7–O_5^1	2	2·41		O_{15}–O_{14}	2	2·71
O_7–O_6	2	2·74		O_{15}–O_3	2	2·71
O_7–O_{11}	2	3·24		O_{15}–O_{16}	2	2·69
O_7–O_8	2	2·87		O_{15}–O_{11}	2	2·79

* Me represents a scattering units ($\frac{1}{6}$ Ti + $\frac{5}{6}$ Nb).

atoms, guided by the knowledge of $TiNb_2O_7$, were introduced. If Ti and Nb are assumed to occupy the metal positions at random, and with the centrosymmetrical space group *Amma*, the $h0l$ data, before any refinement, gave a discrepancy of 18%. The parameters were revised by Fourier projections on (010); by F_o, by $F_o - F_{metals}$, and finally by $F_o - F_c$ summations. No evidence for the lack of a centre of symmetry could be found. The discrepancy for $h0l$ was 11·4% and for $h1l$ 13·2%, using an overall isotropic temperature factor $B = 0·3$ Å².

The number of parameters determined by the projection is 37, and the number of observable reflexions was limited by the many non-systematic absences to 86. Consequently the accuracy of the structure cannot be regarded as high. The metal-oxygen distances are probably accurate to 0·04 Å and oxygen–oxygen to 0·06 Å. Table 4 includes the ideal positions as well as those evaluated from the Fourier analysis. A complete list of interatomic distances, and a comparison between F_o and F_c are given in Tables 5 and 6. The structure is illustrated by Fig. 1(a) as atoms and their bonds.

Crystal structure of monoclinic $Ti_2Nb_{10}O_{29}$

Although the monoclinic phase was not sufficiently well developed for single-crystal studies, the $h00$ reflexions could be identified and their intensities measured with reasonable accuracy. Within the limits of experimental error, the values were identical with $\frac{1}{2}(h00)$ reflexions* for the orthorhombic dimorph. The structures of the two were therefore undoubtedly alike as the similarity of the powder patterns had suggested

* $h00$ occurs only for $h = 2n$ in the orthorhombic phase. (200), (400) etc. can be compared with (100), (200) etc. for the monoclinic.

Table 6. *Observed and calculated structure factors for orthorhombic* $Ti_2Nb_{10}O_{29}$

Unless at variance with F_o, the non-observed reflexions are omitted

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
200	10·3	18·1	23,06	57·6	$\overline{56·9}$	10,22	69·1	76·2	31,15	57·1	54·2
400	27·3	27·2	29,06	40·5	$\overline{48·1}$	70,22	81·0	79·7	017	38·3	25·8
600	73·5	70·3	30,06	54·8	$\overline{68·0}$	15,0,22	79·2	109·4	817	33·9	$\overline{20·5}$
800	156·0	$\overline{170·6}$	31,06	22·4	34·7	00,24	23·1	28·6	14,17	19·5	$\overline{15·0}$
10,00	43·6	$\overline{50·9}$	008	28·8	$\overline{26·5}$	00,26	42·9	45·8	01,11	153·5	$\overline{134·1}$
12,00	50·6	$\overline{50·6}$	108	40·9	$\overline{32·8}$	011	79·1	79·1	11,11	93·5	$\overline{80·4}$
14,00	155·8	$\overline{167·6}$	308	16·1	$\overline{14·8}$	111	65·4	68·1	31,11	18·5	$\overline{28·6}$
16,00	94·6	94·3	708	28·6	$\overline{29·3}$	311	20·7	26·1	51,11	28·8	$\overline{30·6}$
18,00	25·3	30·8	808	20·9	19·8	511	18·8	27·0	61,11	23·4	$\overline{27·4}$
20,00	27·3	32·4	15,08	36·7	$\overline{43·8}$	611	10·2	10·8	71,11	94·9	$\overline{85·8}$
22,00	132·2	118·8	00,10	182·6	$\overline{172·1}$	711	58·8	69·7	81,11	83·4	87·1
28,00	<21·6	26·7	10,10	18·3	15·7	811	47·3	$\overline{48·2}$	91,11	20·0	18·6
30,00	98·1	$\overline{122·3}$	40,10	18·7	$\overline{16·4}$	911	12·9	$\overline{17·7}$	12,1,11	21·2	26·1
34,00	33·0	$\overline{36·3}$	60,10	44·2	$\overline{37·6}$	10,11	<13·7	$\overline{18·5}$	14,1,11	76·9	81·1
36,00	19·4	$\overline{20·0}$	70,10	<16·1	21·6	12,11	22·2	$\overline{14·8}$	15,1,11	96·1	112·0
002	9·9	$\overline{4·4}$	80,10	103·2	95·5	14,11	45·1	$\overline{44·8}$	16,1,11	45·9	49·4
102	19·8	$\overline{19·2}$	10,0,10	29·9	30·9	15,11	87·8	$\overline{95·0}$	21,1,11	23·7	21·9
15,02	23·1	22·4	12,0,10	25·7	27·7	16,11	26·4	26·7	22,1,11	62·2	$\overline{64·9}$
004	77·9	$\overline{68·3}$	14,0,10	95·9	99·2	20,11	22·0	15·5	23,1,11	61·2	$\overline{53·8}$
104	29·0	$\overline{25·6}$	15,0,10	<19·6	$\overline{22·9}$	21,11	22·7	$\overline{22·2}$	29,1,11	64·7	$\overline{70·6}$
304	11·4	$\overline{8·7}$	16,0,10	53·5	58·2	22,11	40·0	32·2	30,1,11	63·4	71·1
504	14·5	$\overline{10·9}$	22,0,10	76·1	$\overline{67·7}$	23,11	52·7	45·0	31,1,11	43·4	40·4
604	13·2	$\overline{20·0}$	30,0,10	83·1	84·1	29,11	43·9	54·4	01,13	35·1	$\overline{27·8}$
704	29·9	$\overline{22·1}$	00,12	<17·2	23·7	30,11	41·7	$\overline{34·2}$	15,1,15	51·5	56·2
804	29·0	27·0	10,12	61·2	$\overline{50·8}$	013	80·3	62·1	23,1,15	24·9	$\overline{24·2}$
14,04	38·7	35·9	70,12	64·9	$\overline{61·4}$	113	22·9	$\overline{12·3}$	01,17	107·6	$\overline{87·4}$
15,04	36·7	31·5	15,0,12	59·0	67·2	613	11·5	13·1	81,17	65·6	59·3
22,04	25·7	$\overline{18·8}$	23,0,12	56·7	$\overline{45·2}$	713	21·2	$\overline{11·6}$	14,1,17	57·3	54·9
23,04	26·4	$\overline{25·1}$	29,0,12	38·8	$\overline{42·3}$	813	28·8	$\overline{36·1}$	16,1,17	45·6	$\overline{42·0}$
006	137·3	125·4	31,0,12	18·5	27·4	14,13	24·9	$\overline{34·7}$	22,1,17	41·4	$\overline{46·9}$
106	80·1	$\overline{64·7}$	00,14	26·8	$\overline{18·9}$	15,13	18·5	13·0	11,19	33·4	27·7
306	27·5	$\overline{22·8}$	80,14	24·6	21·3	16,13	27·1	32·2	71,19	40·5	32·8
506	20·5	$\overline{24·7}$	00,16	88·2	$\overline{95·0}$	115	107·4	$\overline{89·6}$	15,1,19	36·3	33·8
606	27·5	$\overline{23·3}$	10,16	65·8	57·4	315	35·1	$\overline{35·2}$	01,21	86·1	90·5
706	69·7	$\overline{63·0}$	70,16	70·8	57·3	515	33·2	$\overline{36·4}$	11,21	41·4	43·0
806	74·8	$\overline{66·0}$	80,16	60·7	52·3	715	70·5	$\overline{74·7}$	71,21	32·7	29·1
906	19·4	22·9	14,0,16	49·3	58·2	915	36·4	29·4	81,21	53·4	$\overline{50·0}$
10,06	17·4	$\overline{21·4}$	15,0,16	76·1	84·8	15,15	121·5	136·3	14,1,21	61·7	63·3
12,06	19·1	$\overline{19·2}$	16,0,16	37·8	46·2	23,15	89·1	$\overline{74·8}$	15,1,21	61·9	64·0
14,06	70·8	$\overline{69·1}$	22,0,16	42·9	$\overline{38·4}$	25,15	39·5	$\overline{31·8}$	16,1,21	33·4	40·3
15,06	89·9	87·9	23,0,16	51·9	49·6	27,15	23·7	$\overline{17·5}$	01,23	26·8	$\overline{26·1}$
16,06	47·5	49·2	29,0,16	53·4	57·2	29,15	63·9	$\overline{77·2}$	81,23	22·0	24·5
22,06	51·7	51·2	00,20	30·8	31·0						

earlier. The differences between them were most probably due to the kind of organization, rather than to its degree.

Table 7. *Fractional atomic parameters postulated for monoclinic* $Ti_2Nb_{10}O_{29}$

Space group $A2/m$

Atom	Point position	Ideal structure		Probable distorted structure	
		x/a	z/c	x/a	z/c
Me_1*	$4(i)$	0·071	0·069	0·099	0·068
Me_2	$4(i)$	0·071	0·669	0·096	0·697
Me_3	$4(i)$	0·071	0·869	0·097	0·881
Me_4	$4(i)$	0·357	0·156	0·367	0·149
Me_5	$4(i)$	0·357	0·756	0·366	0·779
Me_6	$4(i)$	0·357	0·957	0·366	0·964
O_1	$2(c)$	$\frac{1}{2}$	0	$\frac{1}{2}$	0
O_2	$4(i)$	0·071	0·169	0·066	0·166
O_3	$4(i)$	0·071	0·369	0·038	0·358
O_4	$4(i)$	0·071	0·569	0·086	0·602
O_5	$4(i)$	0·071	0·769	0·090	0·784
O_6	$4(i)$	0·071	0·969	0·074	0·971
O_7	$4(i)$	0·214	0·113	0·220	0·106
O_8	$4(i)$	0·214	0·713	0·228	0·730
O_9	$4(i)$	0·214	0·913	0·222	0·920
O_{10}	$4(i)$	0·357	0·056	0·362	0·055
O_{11}	$4(i)$	0·357	0·256	0·364	0·247
O_{12}	$4(i)$	0·357	0·456	0·364	0·463
O_{13}	$4(i)$	0·357	0·656	0·364	0·678
O_{14}	$4(i)$	0·357	0·856	0·364	0·869
O_{15}	$4(i)$	0·500	0·190	0·500	0·188

* Me denotes ($\frac{1}{6}$ Ti + $\frac{5}{6}$ Nb) as a scattering unit. The numbering of the atoms does not necessarily correspond with Table 4.

An ideal model, fitting the crystallographic and chemical criteria, was readily devised. By this time there were two independent sets of information with which the movements of atoms from ideal positions could be assessed, and it was a matter of little difficulty to derive a set of parameters which could be expected to be a close approximation to the correct values. These are given in Table 7. Intensities, to be compared with the Guinier camera film, were calculated by means of the formula

$$I \propto [(1+\cos^2 2\theta_m . \cos^2 2\theta)/(\sin^2 \theta . \cos \theta)].p.F_{hkl}^2,$$

where θ_m is the angular setting of the monochromator* and the other symbols have their usual meaning. These are included in Table 3. This comparison does not justify the accurate structure of the monoclinic form defined by the fractional atomic parameters. All that is claimed is that it cannot be far in error, and that good single-crystal data will lead to a refined set of values which would nevertheless give a structure of the kind now proposed for it. The bond lengths have not been evaluated, as they have been made to resemble the orthorhombic form.

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* In this case, the $(10\bar{1}1)$ reflecting planes of a quartz crystal, used with a copper target, give $\theta_m = 13° 21'$.

Comparison of the structures of $Ti_2Nb_{10}O_{29}$ and of $TiNb_2O_7$

A common feature of the three structures is the disorder amongst the Ti and Nb atoms; a metal position is occupied by one or other of these elements in a random fashion. Although diffuse streaks in the single-crystal photographs of all three demonstrate that some short-range order exists, from a chemical viewpoint the compounds are *binary* oxides with formulae $Me_{12}O_{29}$ and Me_3O_7 respectively.
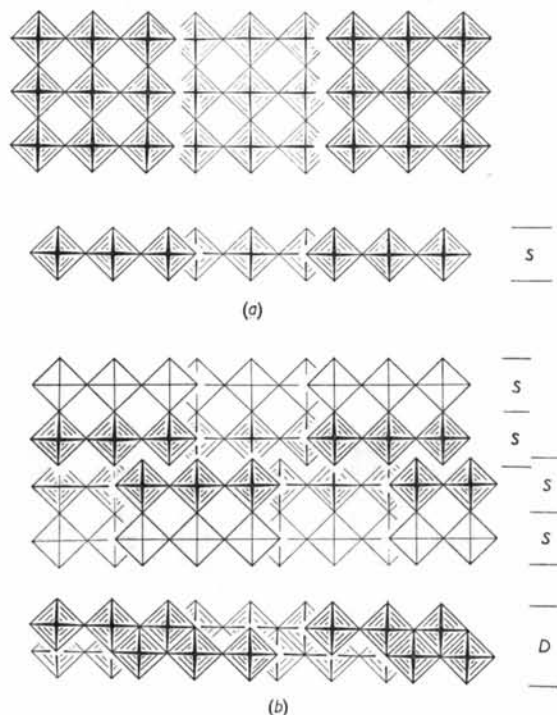

Fig. 2. (a) Blocks of the ideal ReO_3-type structure, limited in width to three. The centre block is displaced downwards by half an octahedral diagonal; each hatched square represents an octahedron in projection as viewed down a corner. Below it is a unit of the hypothetical Me_3O_8 structure formed by fusing together the blocks of octahedra. A single sheet is distinguished by the letter S. (b) In the upper part of the diagram, two Me_3O_8 blocks consisting of S units are translated sideways by $1\frac{1}{2}$ octahedral diagonals. These can then be joined together, as in the lower portion of Fig. 2(b) to form the double octahedral sheet or D unit.

Methods of description need to be devised to clarify structures as complex as these and to demonstrate their relationships to one another as well as to simpler structural types. In Fig. 2(a) are drawn blocks of the ideal ReO_3-type structure, extending parallel to the margin and out of the plane of the paper, but limited to three octahedra in width. The blocks consist of octahedra sharing corners, and each alternate one is displaced half a diagonal downwards. If these blocks are then joined together by edge sharing, a hypothetical structure of the formula Me_3O_8, and also shown in Fig. 2(a), is formed. One of the representative

two-dimensional segments of this structure will be called *single* (or *S*), to denote that it is composed of a single octahedral thickness.

Blocks of the Me_3O_8 structure are drawn in Fig. 2(*b*), the one below being translated by $1\frac{1}{2}$ octahedral diameters. If these two units are again joined together by additional edge sharing, a *double* (or *D*) row can be drawn as in the lower part of the figure.
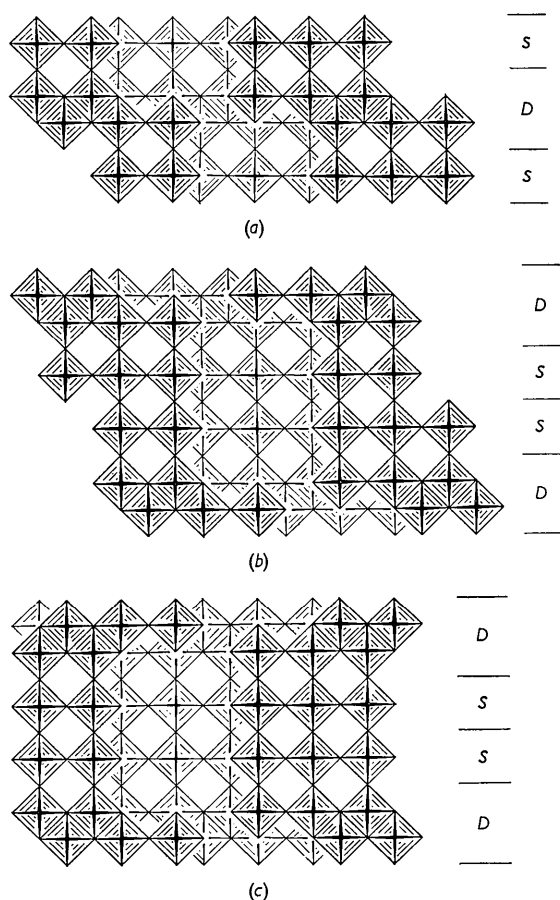

(a)

(b)

(c)

Fig. 3. (a) $TiNb_2O_7$, drawn as idealized octahedra, consists of alternating *D* and *S* units (see Fig. 2(*a*) and 2(*b*)). (b) Monoclinic $Ti_2Nb_{10}O_{29}$ consists of *D* units alternating with two *S* units. (c) Orthorhombic $Ti_2Nb_{10}O_{29}$ consists of *D* units alternating with two *S* units in the same way as its dimorph, but each alternate *D* is the mirror image of the other.

The three compounds can now be described in terms of these two units, the *D* or double, and the *S* or single sheet of octahedra. $TiNb_2O_7$ consists of *D* and *S* units alternating one with the other (Fig. 3(*a*)), and joined together by common corners (i.e. oxygen atoms). Monoclinic $Ti_2Nb_{10}O_{29}$ has *D* sheets separated by two *S* sheets, all of which are joined together by corners (Fig. 3(*b*)). Orthorhombic $Ti_2Nb_{10}O_{29}$ can also be described in the same way as its dimorph, but each alternate *D* sheet *is the mirror image of the other* (Fig. 3(*c*)). The three phases are therefore closely related to each other. The asymmetric unit of each of the two chemical types can, in fact, be given the general formula $Me_{3n}O_{8n-3}$; $TiNb_2O_7$ corresponds to $n=3$, $Ti_2Nb_{10}O_{29}$ in both its forms to $n=4$.

This is in accord with the two series of oxides which have been previously studied, $(W, Mo)_nO_{3n-1}$ (Hägg & Magnéli, 1954) and Ti_nO_{2n-1} (Andersson, Collén, Kuylenstierna & Magnéli, 1957). In all three cases a member derives its structure from that of a parent oxide, and an individual unit of a series contains features which are common to all other members of it. A characteristic is the regular occurrence of planes which form boundaries between blocks of the parent phase. These have been called *crystallographic shears* (Wadsley, 1958) and the formation of the *D* unit from blocks of the Me_3O_8 structure, which is the parent for this new series, can be described in this way (Fig. 2(*b*)).

The possibility of additional homologues

The phase diagram of Roth & Coughanour (1955) showed that only two congruently melting intermediate compounds were formed between TiO_2 and Nb_2O_5. The two series $(W, Mo)_nO_{3n-1}$ (Hägg & Magnéli, 1954) and Ti_nO_{2n-1} (Andersson *et al.*, 1957) each contain several members with the shear representing a discontinuity between large blocks of the WO_3 and TiO_2 (rutile) structures respectively. If additional members of the $Me_{3n}O_{8n-3}$ group exist, they will be limited in number to three; $n=2$, 5, and 6 will give Me_6O_{13} (i.e. $Ti_4Nb_2O_{13}$), $Me_{15}O_{37}(TiNb_{14}O_{37})$ and $Me_{18}O_{45}(Nb_2O_5)$. Me_6O_{13} would be constructed solely from *D* units sharing corners, $Me_{15}O_{37}$ from *D* groups separated by three *S* groups, and $Me_{18}O_{45}$ by four *S* units. In each case dimorphs could be expected, as *D* can also be present systematically as its mirror

Table 8. *Predicted unit cell dimensions of additional homologues**

n in $Me_{3n}O_{8n-3}$	Compound		*a*	*b*	*c*	*β*	System
2	$Ti_4Nb_2O_{13}$	$\Big\{$ or	8·70 Å	3·80 Å	20·50 Å	135° 0′	$A2/m$
			8·70	3·80	15·61	113° 12′	$P2/m$†
			12·30	3·80	20·50	90°	$Amma$
5	$TiNb_{14}O_{37}$		19·45	3·80	20·50	108° 26′	$A2/m$
			36·90	3·80	20·50	90°	$Amma$
6	$Nb_{18}O_{45}(=Nb_2O_5)$		23·37	3·80	20·50	105° 15′	$A2/m$
			45·10	3·80	20·50	90°	$Amma$

* *b* and *c* were arbitrarily chosen to have equal values for all members.
† A new orientation to give a primitive unit cell is possible. This is related to the centred cell by the transform 100/010/101.

image, as we have seen in orthorhombic $Ti_2Nb_{10}O_{29}$. The unit-cell dimensions (which are listed in Table 8) together with the ideal and the probable distorted atomic arrangements for each can readily be predicted, and it is therefore a simple problem to compute theoretical Guinier diffraction patterns to compare with those made from laboratory preparations. Such an aid is considered indispensable in a problem of this kind.

Attempts were made to prepare the two intermediates $n=2$ and 5. The low temperature forms of Nb_2O_5 and Ti_2O_5 were weighed and heated together at small temperature intervals from 700 °C. through to the quenched liquidus. $Ti_4Nb_2O_{13}$ (i.e. $n=2$) was not found in any of these, and all specimens consisted of $TiNb_2O_7$ plus rutile. $TiNb_{14}O_{37}$ ($n=5$) gave a bewildering variety of diffraction patterns bearing considerable similarities to one another as well as to αNb_2O_5, the high temperature form, but containing diffuse regions and many additional lines. At no time could it be stated that the Guinier patterns consisted solely of one or other of the two predicted forms, and evidently considerable crystalline disorder was present as well.

In some respects the cell dimensions reported for Nb_2O_5 in certain of its forms resemble those for $Me_{18}O_{45}$ in Table 8, the high-temperature form to the

monoclinic and the γ form to the orthorhombic.* Similarities between the γ form and an Me_3O_8 oxide (U_3O_8) have also been noted (Holser, 1956). Disorder as well as distortion undoubtedly plays an important role in these structures, and additional reference to this will be made elsewhere.

It appears, therefore, that $TiNb_2O_7$ and $Ti_2Nb_{10}O_{29}$ are the only representatives of the series $Me_{3n}O_{8n-3}$ which can be identified with certainty within $TiO_2–Nb_2O_5$. Other members may eventually be found in chemical systems of a related kind.

References

ANDERSSON, S., COLLÉN, B., KUYLENSTIERNA, U. & MAGNÉLI, A. (1957). Acta Chem. Scand. **11**, 1641.
HÄGG, C. & MAGNÉLI, A. (1954). Revs. Pure Appl. Chem. Australia, **4**, 235.
HOLSER, W. T. (1956). Acta Cryst. **9**, 196.
ROTH, R. S. & COUGHANOUR, L. W. (1955). J. Res. Nat. Bur. Stand. Wash. **55**, 209.
WADSLEY, A. D. (1958). J. Proc. Roy. Soc. N.S.W. **92**, 25.
WADSLEY, A. D. (1961). Acta Cryst. **14**, 660.
ZVINCHUK, R. A. (1959). Soviet Physics, Crystallography, **3**, 750.

* The nomenclature is that of Zvinchuk (1959) who has tabulated the unit-cell dimensions of several polymorphs of Nb_2O_5. His setting for αNb_2O_5 is in striking agreement with 'monoclinic $TiNb_{14}O_{37}$'.

Piezo-Optic Birefringence in NaCl Structure Crystals. Part I. Theory

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Following Bragg's method, expressions for continuum, dipole and Coulomb anisotropies as well as ionic polarizability and density changes are given for the piezo-optic birefringence in crystals. Certain simplified assumptions lead to the evaluation of the strain-optical coefficients P_{11} and P_{12} from the observed difference $(P_{11}–P_{12})$. Expressions for Mueller's strain polarizibility constants are seen to depend on wavelength and temperature.

1. Introduction

Attempts have been made by Banerjee (1927), Herzfeld (1928), Herzfeld & Lee (1933) and Mueller (1935a) to explain the photoelastic effect in cubic crystals. Banerjee developed a theory on the lines suggested by Bragg (1924a, b), Herzfeld & Lee adopted the lattice sum method of Madelung, and Mueller based his calculations on Born's theory of crystal lattices. While all these investigators considered the anisotropies arising from the Lorentz–Lorentz and Coulomb forces, Mueller considered the additional effect of strain on ionic polarizabilities. Mueller's

treatment shows that Bragg's & Born's methods are equivalent. All these attempts, however, have had a limited success. Discussions (Poindexter, 1955) based on quantum-mechanical considerations also do not lead to a satisfactory solution of the problem.

Mueller has drawn attention to the serious errors found in Banerjee's work. Banerjee's approach though essentially sound, does not take into account all possible factors that contribute to the observed birefringence. Mueller's work, in spite of its distinctive advance over the work of Banerjee and of others, neverthelsss itself suffers from certain serious draw-