# Mixed Oxides of Titanium and Niobium. I.*

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$TiNb_2O_7$ crystallizes as monoclinic needles, space group $A2/m$, and with the unit-cell dimensions

$$a = 11 \cdot 93, \quad b = 3 \cdot 81, \quad c = 20 \cdot 44 \text{ Å}; \quad \beta = 120° \, 10'.$$

The structure, solved by a trial-and-error procedure and then refined by Fourier methods, contains
a random distribution of both Ti and Nb in the metal positions of an octahedral structure of a new
kind.

## Introduction

The existence of series of metallic oxides which are
closely related to one another, chemically and struc-
turally, is now well recognized. A particular series is
derived from a simple structure by the reduction of
the valency of the metal ion, and this is reflected in
each member by features which are common to all
of them. Perhaps the best known is the series
$(W, Mo)_nO_{3n-1}$ based upon the $ReO_3$ type lattice
(Hägg & Magnéli, 1954) in which $n$ can have values
from 8 to 14 inclusive, and $Ti_nO_{2n-1}$ ($4 \leq n \leq 10$;
Andersson, Collén, Kuylenstierna & Magnéli, 1957$a$, $b$)
and the related compounds which are derived from
the rutile form of $TiO_2$.

$Ti^{4+}$ and $Nb^{5+}$ are ions which can be expected to
substitute isomorphously for one another in crystalline
solids; they have approximately the same ionic radii,
and both form bonds to oxygen which are pre-
dominantly octahedral. Two intermediate compounds
which were found in the system $TiO_2$–$Nb_2O_5$ (Roth
& Coughanour, 1955) were considered likely to be
members of a structural series, and the crystal struc-
ture of one of them, $TiNb_2O_7$, is now described. An
examination of the other is reported in the following
paper (Wadsley, 1961).

## Experimental

$TiNb_2O_7$ is readily prepared by the reaction in the
solid state of equimolar proportions of reagent grade
$TiO_2$ and $Nb_2O_5$ from temperatures of 1000 °C. up to
the solidus. It melts congruently at about 1500 °C.
and forms transparent yellow monoclinic needles on
cooling. The unit-cell dimensions, determined from a

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powder pattern taken with a Guinier-type focusing
camera were

$$a = 11 \cdot 93, \quad b = 3 \cdot 81, \quad c = 20 \cdot 44 \text{ Å}, \quad \beta = 120° \, 10'.$$

The systematic absences, $hkl$ with $k + l \neq 2n$, gave the
space group alternatives $A2/m$, $A2$ or $Am$. With six
formula units in the unit cell, the calculated density
is 4·29 g.cm.$^{-3}$ which may be compared with the value
$4 \cdot 25 \pm 0 \cdot 05$ g.cm.$^{-3}$ measured on a torsion micro-
balance. Dyson (1957), who determined the dielectric
properties and lattice constants of $TiNb_2O_7$, gave
figures corresponding to these, but the side-centring
was overlooked. His suggestion of four formula units
for his unit cell led to poor agreement between the
density values.

Intensity data were recorded by the multiple film
technique with molybdenum radiation. The $h0l$ re-
flexions were collected with an integrating Weissen-
berg goniometer, and measurements made with a
standard series of spots of the same shape and size,
obtained with the direct beam suitably reduced in
intensity and appropriately masked. The $h1l$ and $h2l$
series were recorded without integration. The measure-
ments were all reduced to the $|F|$ terms with the usual
correction factors, specimen absorption being neg-
lected. Structure factors were computed with the $Nb^{5+}$
scattering curve derived from the tables of Thomas &
Umeda (1957), $Ti^{4+}$ from Qurashi (1954) and $O^{2-}$ from
Viervoll & Øgrim (1949). These were eventually
modified by an overall isotropic temperature factor
$B = 1 \cdot 19$ Å$^2$ obtained experimentally. Calculations were
made on SILLIAC at the University of Sydney through
the courtesy of Dr J. E. W. L. Smith.

## Structure determination

The distribution of $h0l$ and $h2l$ intensities, with due
regard for observational errors and for the effects of

Table 1. *Observed and calculated structure factors*

The non-observed reflexions, unless at variance with $F_c$, are omitted

| hkl | $F_o$ | $F_c$ | hkl | $F_o$ | $F_c$ | hkl | $F_o$ | $F_c$ | hkl | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 100 | 15·5 | $\overline{21·9}$ | 308 | 26·9 | $\overline{29·0}$ | $\bar{6}$0,16 | 17·6 | $\overline{20·1}$ | $\bar{2}$15 | 78 | 53 |
| 200 | 65·8 | 51·6 | 108 | 16·7 | $\overline{16·4}$ | $\bar{7}$0,16 | 35·2 | 30·1 | $\bar{3}$15 | 29 | $\overline{32}$ |
| 300 | 119·0 | 116·7 | 008 | 12·7 | 11·9 | $\bar{8}$0,16 | 36·2 | 26·3 | $\bar{4}$15 | 49 | 34 |
| 400 | 33·1 | $\overline{38·5}$ | $\bar{1}$08 | 12·1 | $\overline{8·7}$ | $\overline{10}$,0,16 | 54·7 | 50·9 | $\bar{5}$15 | 27 | 24 |
| 500 | 113·7 | 127·5 | $\bar{2}$08 | 33·1 | 27·5 | $\overline{13}$,0,16 | 37·7 | 38·0 | $\bar{7}$15 | 64 | 84 |
| 600 | 52·2 | 48·8 | $\bar{3}$08 | 21·9 | $\overline{18·0}$ | $\overline{16}$,0,16 | 25·0 | 26·3 | $\overline{10}$,15 | 52 | 48 |
| 800 | 68·6 | 73·2 | $\bar{5}$08 | 24·1 | $\overline{23·4}$ | 20,22 | 25·0 | 20·6 | $\bar{2}$17 | 17 | 18 |
| 11,00 | 51·6 | 51·8 | $\bar{8}$08 | 31·5 | $\overline{28·1}$ | $\overline{10}$,2,2 | 39·9 | 44·7 | $\bar{5}$17 | 19 | 24 |
| 14,00 | 30·9 | 29·7 | $\bar{9}$08 | 17·0 | 15·5 | $\overline{40}$,2,2 | 43·3 | 47·8 | $\bar{8}$17 | 25 | 17 |
| 502 | 22·6 | $\overline{24·3}$ | 11,0,10 | 26·3 | 27·2 | $\overline{60}$,2,2 | 36·8 | 36·4 | $\overline{10}$,17 | 26 | 19 |
| 202 | 12·1 | 16·5 | 8,0,10 | 38·9 | 43·1 | $\overline{70}$,2,2 | 36·8 | 39·8 | 81,11 | 26 | 27 |
| 002 | 11·4 | 10·8 | 5,0,10 | 50·4 | 47·3 | $\overline{90}$,2,2 | 46·1 | 45·9 | 71,11 | 26 | 28 |
| $\bar{1}$02 | 16·7 | 16·4 | 3,0,10 | 37·7 | 39·9 | $\overline{120}$,2,2 | 46·1 | 48·1 | 51,11 | 44 | 52 |
| 704 | 30·6 | 27·2 | 2,0,10 | 64·0 | 67·3 | $\overline{150}$,2,2 | 30·9 | 27·8 | 21,11 | 79 | 87 |
| 404 | 51·9 | 48·3 | 1,0,10 | 21·3 | 21·0 | | | | $\bar{0}$1,11 | 49 | 42 |
| 204 | 15·8 | 19·5 | 0,0,10 | 68·3 | 70·3 | 811 | 31 | 28 | $\bar{1}$1,11 | 55 | 60 |
| 104 | 33·1 | 24·9 | $\bar{1}$0,10 | 27·2 | 22·7 | 511 | 57 | 59 | $\bar{2}$1,11 | 28 | $\overline{33}$ |
| 004 | 17·6 | $\overline{15·4}$ | $\bar{3}$0,10 | 105·4 | 119·5 | 411 | 15 | $\overline{12}$ | $\bar{3}$1,11 | 94 | 108 |
| $\bar{1}$04 | 49·8 | 54·4 | $\bar{4}$0,10 | 16·4 | 15·4 | 311 | 23 | 26 | $\bar{4}$1,11 | 30 | 32 |
| $\bar{2}$04 | 13·0 | 10·4 | $\bar{5}$0,10 | 30·9 | 30·9 | 211 | 31 | 40 | $\bar{6}$1,11 | 84 | 87 |
| $\bar{4}$04 | 28·7 | 28·1 | $\bar{6}$0,10 | 67·5 | 60·5 | 111 | 23 | $\overline{27}$ | $\bar{8}$1,11 | 34 | 39 |
| $\bar{7}$04 | 21·0 | 18·3 | $\bar{7}$0,10 | 21·3 | $\overline{21·2}$ | 011 | * | 79 | $\bar{9}$1,11 | 72 | 68 |
| 12,06 | 25·0 | 26·5 | $\bar{8}$0,10 | 62·1 | 65·1 | $\bar{1}$11 | * | 33 | $\overline{10}$,1,11 | 26 | $\overline{26}$ |
| 906 | 37·1 | 38·7 | $\bar{9}$0,10 | 17·3 | 20·1 | $\bar{2}$11 | 9 | 12 | $\overline{11}$,1,11 | 36 | 42 |
| 706 | 26·6 | 28·8 | $\overline{11}$,0,10 | 38·3 | 38·7 | $\bar{3}$11 | 47 | 62 | $\overline{12}$,1,11 | 25 | 30 |
| 606 | 28·1 | 27·0 | $\overline{14}$,0,10 | 22·6 | 22·7 | $\bar{5}$11 | 25 | 25 | $\overline{14}$,1,11 | 36 | 27 |
| 506 | 16·4 | 22·1 | $\bar{2}$,0,12 | 27·5 | 30·3 | $\bar{6}$11 | 58 | 64 | 11,15 | 26 | 31 |
| 406 | 61·2 | 65·7 | $\bar{1}$0,12 | 34·3 | 40·7 | $\bar{7}$11 | 23 | $\overline{22}$ | 01,17 | 25 | 26 |
| 306 | 31·5 | 24·4 | $\bar{3}$0,12 | 32·8 | 33·2 | $\bar{8}$11 | 31 | 26 | $\bar{2}$1,17 | 44 | 31 |
| 006 | 10·8 | $\overline{17·4}$ | $\bar{4}$0,12 | 34·3 | 36·4 | $\bar{9}$11 | 26 | 32 | $\bar{5}$1,17 | 58 | 51 |
| $\bar{1}$06 | 37·1 | 32·2 | $\bar{6}$0,12 | 40·5 | 39·2 | $\overline{11}$,11 | 36 | 40 | $\bar{8}$1,17 | 41 | 44 |
| $\bar{2}$06 | 95·8 | 98·8 | $\bar{9}$0,12 | 42·7 | 43·3 | $\overline{14}$,11 | 26 | 30 | $\overline{10}$,1,17 | 36 | 33 |
| $\bar{3}$06 | 25·7 | $\overline{26·9}$ | $\overline{12}$,0,12 | 28·7 | 27·3 | 113 | 37 | $\overline{45}$ | $\overline{11}$,1,17 | 25 | 27 |
| $\bar{4}$06 | 46·4 | 35·2 | $\overline{14}$,0,12 | 22·6 | 19·2 | 613 | 22 | $\overline{28}$ | $\overline{13}$,1,17 | 31 | 37 |
| $\bar{5}$06 | 47·9 | 45·2 | $\overline{17}$,0,12 | 26·3 | 19·2 | 12,15 | 29 | 34 | 21,21 | 32 | 34 |
| $\bar{6}$06 | 19·2 | $\overline{21·0}$ | 9,0,16 | 27·8 | 26·4 | 10,15 | 30 | 23 | $\bar{1}$1,21 | 36 | 47 |
| $\bar{7}$06 | 82·5 | 85·3 | 6,0,16 | 34·3 | 39·2 | 915 | 43 | 38 | $\bar{4}$1,21 | 25 | 35 |
| $\overline{10}$,06 | 57·8 | 57·8 | 4,0,16 | 22·3 | 25·4 | 715 | 62 | 54 | $\bar{6}$1,21 | 44 | 51 |
| $\overline{12}$,06 | 20·7 | 21·0 | 3,0,16 | 21·3 | 24·5 | 415 | 104 | 85 | $\bar{9}$1,21 | 36 | 42 |
| $\overline{13}$,06 | 34·9 | 37·6 | 1,0,16 | 48·2 | 55·4 | 215 | 26 | 23 | $\overline{12}$,1,21 | 26 | 29 |
| $\overline{14}$,06 | 23·2 | $\overline{19·7}$ | 0,0,16 | 23·2 | 15·6 | 115 | 49 | 36 | $\bar{5}$1,27 | 27 | 23 |
| $\overline{15}$,06 | 24·4 | 24·1 | $\bar{2}$0,16 | 50·4 | 54·4 | 015 | 26 | $\overline{28}$ | $\bar{8}$1,27 | 32 | 34 |
| | | | $\bar{4}$0,16 | 24·4 | 25·6 | $\bar{1}$15 | 73 | 58 | $\overline{11}$,1,27 | 27 | 33 |
| | | | $\bar{5}$0,16 | 62·4 | 60·5 | | | | | | |

\* Unobservable.

thermal motion, were identical. All the atoms comprising the structure were therefore situated in, or very close to, two planes normal to the $y$ axis and $b/2$ Å apart, making $A2/m$ the most probable space group. Since there are six formula units, the atoms must be in both fourfold and twofold sites, and one of the latter can be the origin. The Patterson function will therefore contain within it direct evidence of the detailed structure.

The projection $P(u, w)$ consisted essentially of strong positive regions parallel to the $z$ direction and centred in the sections $x/a = 0$ and $\frac{3}{8}$. Between these, at $x/a = \frac{7}{32}$ and $\frac{1}{2}$ and also parallel to $z$ were smaller positive ridges. Analytical methods of solving this problem proved to be inconclusive, and a simple trial-and-error procedure which was adopted was more successful.

Octahedra may share corners to form an endless linear string (Fig. 1(a)) or edges to form a zig-zag string (Fig. 1(b)), and the structure of many metallic oxides consist of these two kinds of simple unit grouped together in various ways. For $TiNb_2O_7$ the numerical value $a \sin \beta$ is almost identical with the distance $c/2$. If the metal–oxygen bond distance is assumed to be 2·0 Å, then five octahedral diameters are equal in length to the $c$ axis, and $2\frac{1}{2}$ to the height of the unit cell, $a \sin \beta$. With the additional criteria provided by the space group, by the numbers of atoms within the unit cell, and with the Patterson function, it was a matter of trial with the units of Fig. 1 to find an arrangement which was satisfactory. The ideal parameters of the model selected by this means are given in Table 3.

Oxide structures, however, are seldom, if ever, ideal at room temperature as the metal atoms can introduce distortions in one of two ways.

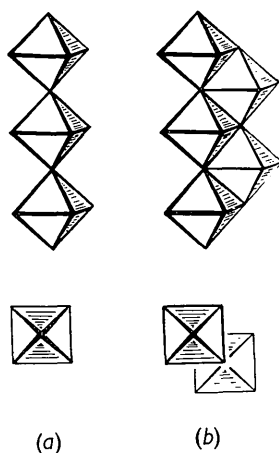(a) If they have an excess of valency electrons, they

(a)    (b)

Fig. 1. Octahedra joined by corners (Fig. 1(a)) and edges (Fig. 1(b)) to form endless strings, linear and zig-zag respectively. In perspective (upper) and as seen in projection (lower).

may attract one another to form short bonds (Marinder & Magnéli, 1957). In its ideal form Fig. 1(b) does have such a short distance.

(b) If the valencies are satisfied, the metals may repel one another if they are strongly ionized (Wadsley, 1955).

$TiNb_2O_7$ crystals are pale yellow and valency anomalies should not exist. For the trial structure it was assumed that the metals of the more closely coordinated polyhedra are moved 0·4 Å from the octahedral centres and away from one another. This would undoubtedly influence the positions of some of the oxygens, but no additional assumptions were made at that stage.

The proposed structure made it possible to provide special positions for both kinds of metal atom. With Ti occupying sites 1 and 2, Nb 3, 4 and 5, the discrepancy factor for the $h00$ reflexions was 37%. By assuming random occupancy, the figure dropped to 15% and it was clear, therefore, that there was little or no difference between the scattering of any of the metal atom positions. The model was then refined by
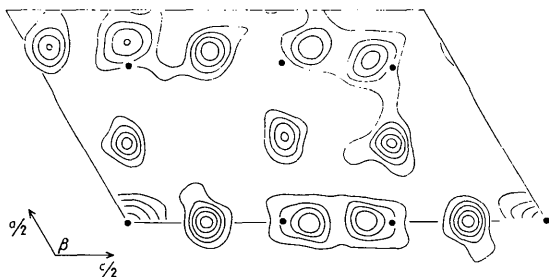


Fig. 2. Electron density projection onto (010) in which the contributions of the metals, the positions of which are shown as small black circles, were subtracted from the observed data. This shows the oxygens, drawn at intervals of 2 e.Å⁻².

Fourier projections on (010) assuming the plane group $p2$, the summations being successively $F_o$, $F_o - F_{metals}$ (Fig. 2) and finally $F_o - F_c$ until there was no detectable improvement.

The experimental data contain many non-systematic absent reflexions, and no attempt was made to introduce individual thermal parameters, particularly as the reliability factor had dropped finally to 8·9%. The structure, at this stage, may be regarded as centrosymmetric in projection.

The remaining ambiguity lay between the choice of the groups $A2$ or $A2/m$. This is not an easy matter to resolve when two axes are long and the other short.

If it is $A2$, the atoms are no longer all in particular planes characteristic of $A2/m$, but are slightly displaced from them. Fourier analysis of the $0kl$ data would be of little use as the $a$ axis is large, and considerable overlap would occur.

Comparison between $F_o$ and $F_c$ for the $h1l$ reflexions based upon $A2/m$ gave a discrepancy of 15·6%. Several attempts were made to improve this by trial and error. The introduction of $y$ parameters for some,

Table 2. *Interatomic distances*

| | No. | Length | | No. | Length |
|---|---|---|---|---|---|
| $Me_1-O_1$ | 2 | 1·90 Å | $O_8-O_9$ | 2 | 2·77 Å |
| $Me_1-O_2$ | 2 | 1·94 | $O_8-O_{10}$ | 2 | 2·58 |
| $Me_1-O_4$ | 2 | 2·07 | $O_9-O_{10}$ | 1 | 2·98 |
| $O_1-O_2$ | 4 | 2·70 | | | |
| $O_1-O_4$ | 4 | 2·82 | $Me_4-O_5$ | 1 | 1·64 Å |
| $O_2-O_4$ | 2 | 2·86 | $Me_4-O_8$ | 1 | 2·16 |
| $O_2-O_4^1$ | 2 | 2·79 | $Me_4-O_9$ | 1 | 1·86 |
| | | | $Me_4-O_{10}$ | 2 | 2·08 |
| $Me_2-O_2$ | 1 | 1·85 Å | $Me_4-O_{11}$ | 1 | 2·09 |
| $Me_2-O_3$ | 1 | 2·04 | $O_5-O_{11}$ | 1 | 2·69 |
| $Me_2-O_3^1$ | 2 | 2·01 | $O_5-O_{10}$ | 2 | 2·88 |
| $Me_2-O_5$ | 1 | 2·16 | $O_5-O_9$ | 1 | 2·68 |
| $Me_2-O_6$ | 1 | 2·08 | $O_8-O_9$ | 1 | 2·93 |
| $O_2-O_6$ | 1 | 2·80 | $O_8-O_{10}$ | 2 | 2·58 |
| $O_3-O_6$ | 1 | 2·86 | $O_8-O_{11}$ | 1 | 2·60 |
| $O_3^1-O_6$ | 2 | 2·59 | $O_9-O_{10}$ | 2 | 3·20 |
| $O_3-O_5$ | 1 | 2·96 | $O_{10}-O_{11}$ | 2 | 2·36 |
| $O_3^1-O_5$ | 2 | 3·00 | | | |
| $O_2-O_5$ | 1 | 2·87 | $Me_5-O_6$ | 1 | 1·71 Å |
| $O_2-O_3$ | 2 | 3·14 | $Me_5-O_7$ | 1 | 2·30 |
| $O_3^1-O_3$ | 2 | 2·36 | $Me_5-O_7^1$ | 1 | 1·77 |
| | | | $Me_5-O_{10}$ | 1 | 2·00 |
| $Me_3-O_4$ | 1 | 1·70 Å | $Me_5-O_{11}$ | 2 | 2·00 |
| $Me_3-O_7$ | 1 | 2·14 | $O_6-O_7$ | 1 | 2·84 |
| $Me_3-O_8$ | 2 | 2·00 | $O_6-O_{10}$ | 1 | 2·89 |
| $Me_3-O_9$ | 1 | 1·97 | $O_6-O_{11}$ | 2 | 2·72 |
| $Me_3-O_{10}$ | 1 | 2·34 | $O_7-O_7^1$ | 1 | 2·59 |
| $O_4-O_9$ | 1 | 2·90 | $O_7-O_{10}$ | 1 | 2·52 |
| $O_4-O_7$ | 1 | 2·96 | $O_7-O_{11}$ | 2 | 3·00 |
| $O_4-O_8$ | 2 | 2·98 | $O_7^1-O_{11}$ | 2 | 2·89 |
| $O_7-O_8$ | 2 | 2·78 | $O_{10}-O_{11}$ | 2 | 2·36 |
| $O_7-O_{10}$ | 1 | 2·52 | | | |

Braces denote symmetry related pairs.

or all, of the metals in their various combinations only made matters worse, and changes from special positions, if indeed they are required, would be restricted to some of the oxygens. This proved too formidable a problem for this simple procedure, and the matter is deferred until programmes for high speed computing by least-squares are available in this country.

Table 3. *Fractional atomic parameters for* $TiNb_2O_7$

Space group $A2/m$ $(0, 0, 0; 0, \frac{1}{2}, \frac{1}{2})+$

| Atom | Point position | Ideal structure $x/a$ | $z/c$ | Refined parameters $x/a$ | $z/c$ |
|---|---|---|---|---|---|
| $Me_1$* | $2(a)$ | 0 | 0 | 0 | 0 |
| $Me_2$ | $4(i)$ | 0 | 0·200 | 0·004$_0$ | 0·185$_5$ |
| $Me_3$ | $4(i)$ | 0·400 | 0·125 | 0·365$_8$ | 0·108$_6$ |
| $Me_4$ | $4(i)$ | 0·400 | 0·325 | 0·372$_3$ | 0·294$_6$ |
| $Me_5$ | $4(i)$ | 0·600 | 0·083 | 0·636$_9$ | 0·077$_1$ |
| $O_1$ | $2(c)$ | 0 | 0·500 | 0 | 0·500 |
| $O_2$ | $4(i)$ | 0 | 0·100 | 0·002 | 0·094 |
| $O_3$ | $4(i)$ | 0 | 0·300 | 0·003 | 0·285 |
| $O_4$ | $4(i)$ | 0·200 | 0·058 | 0·201 | 0·055 |
| $O_5$ | $4(i)$ | 0·200 | 0·258 | 0·213 | 0·248 |
| $O_6$ | $4(i)$ | 0·800 | 0·133 | 0·803 | 0·129 |
| $O_7$ | $4(i)$ | 0·400 | 0·017 | 0·414 | 0·021 |
| $O_8$ | $4(i)$ | 0·600 | 0·375 | 0·577 | 0·378 |
| $O_9$ | $4(i)$ | 0·400 | 0·217 | 0·402 | 0·214 |
| $O_{10}$ | $4(i)$ | 0·600 | 0·175 | 0·590 | 0·158 |
| $O_{11}$ | $4(i)$ | 0·400 | 0·417 | 0·379 | 0·399 |

* The Ti and Nb atoms occupy the metal positions at random. The symbol $Me$ represents ($\frac{1}{3}$ Ti + $\frac{2}{3}$ Nb) as a single scattering unit.

With this reservation the structure is now sufficiently established to justify description. The standard deviations, assuming $A2/m$ are 0·025 Å for the metal–oxygen distances, and $\pm$0·040 Å for oxygen–oxygen. Observed and calculated structure factors are given in Table 1, the interatomic distances in Table 2 and the atomic parameters in Table 3.

## Discussion

The structure of $TiNb_2O_7$ is illustrated in Fig. 3. The two kinds of metal atom are disordered, and as ($\frac{1}{3}$ Ti + $\frac{2}{3}$ Nb) represents the average population of
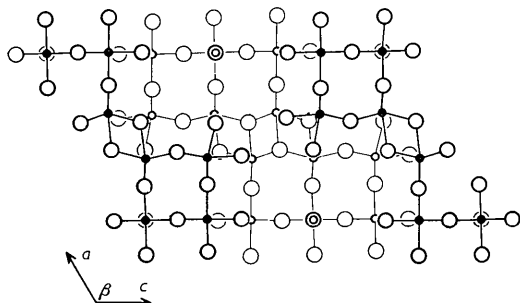


Fig. 3. Structure of $TiNb_2O_7$ projected on to (010). The smaller circles, filled and open, are the metals, and the larger open circles, oxygen.

any one position, the compound, in the strictest sense, is a binary oxide $Mo_3O_7$. The same structure could perhaps be expected in which titanium occupies sites 1 and 2, niobium the remainder. This ordered substance would undoubtedly have a unit cell almost identical in size, and could be distinguished from the present one only by minor variations of intensity in the reflexions. Attempts to prepare it by prolonged annealing at temperatures between 700 and 1000 °C., however, met with no success.

Each metal atom is co-ordinated to six oxygens forming an octahedral grouping. In the ideal structure in which no distortions occur (Table 1) the distances between the metals range from 2·79 to 4·12 Å. There is a pronounced move towards equality in the real structure (Table 4), the shifts bringing with them considerable distortion of the oxygen framework. The octahedron centred upon $Me_1$ shares its six corners with adjacent octahedra, and is almost regular. The $Me_2$ octahedron is related by symmetry to an identical one to form a single zig-zag string, and there is now a pronounced distortion leading to a very short distance $O_3$–$O_3^1$ of 2·36 Å.* $Me_3$, $Me_4$ and $Me_5$ form a triad of metal atoms, and the associated octahedra are even more irregular. Once again the very short distance of 2·36 Å is found, this time between $O_{10}$ and $O_{11}$ which are independent of one another.

Table 4. *Distances between nearest neighbour metal atoms*

Comparison between the ideal and the actual structures

| Atom | Nearest neighbour (number and kind) | Distance Ideal | Actual | Type* of neighbour |
|---|---|---|---|---|
| $Me_1$ | $2 \times Me_2$ | 4·09 Å | 3·77 Å | $A$ |
| | $2 \times Me_3$ | 4·12 | 3·77 | $A$ |
| $Me_2$ | $1 \times Me_2'$ | 2·79 | 3·28 | $B$ |
| | $1 \times Me_4$ | 4·12 | 3·79 | $A$ |
| | $1 \times Me_5$ | 4·12 | 3·78 | $A$ |
| $Me_3$ | $1 \times Me_4$ | 4·09 | 3·77 | $A$ |
| | $1 \times Me_4'$ | 2·81 | 3·33 | $B$ |
| | $1 \times Me_5$ | 4·09 | 3·78 | $A$ |
| | $1 \times Me_5'$ | 2·91 | 3·60 | $B$ |
| $Me_4$ | $1 \times Me_5$ | 2·79 | 3·29 | $B$ |
| $Me_5$ | $1 \times Me_5'$ | 3·01 | 3·20 | $B$ |

* Type $A$. The octahedral grouping for the neighbours have a corner (i.e. one oxygen atom) in common.

Type $B$. The groupings have one or more edges in common.

Although there is wide variation between metal–oxygen and oxygen–oxygen distances, the average for both in any one octahedron is quite uniform. The values are 1·99 Å for $Me$–O, and 2·77 Å for O–O, and from these the metal and oxygen 'radii' are 0·61 and 1·38 Å. There are very few data with which to compare these. Frevel & Rinn (1956) found

* This pair of atoms is related by the symmetry elements present in $A2/m$ and $A2$. If the correct space group is $Am$, they do not have any such relationship. Evidence for this in the $F_o - F_c$ syntheses was not found.

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).

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# 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

$$a = 28\cdot50, \quad b = 3\cdot805, \quad c = 20\cdot51 \text{ Å},$$

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

$$a = 15\cdot57, \quad b = 3\cdot814, \quad c = 20\cdot54 \text{ Å}; \quad \beta = 113° \, 41'$$

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 $\alpha Nb_2O_5$ 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