

Multiple Phase Formation in the Binary System $\text{Nb}_2\text{O}_5\text{--WO}_3$. V. The Structure of $\text{W}_4\text{Nb}_{26}\text{O}_{77}$, an Ordered Intergrowth of the Adjoining Compounds $\text{WNb}_{12}\text{O}_{33}$ and $\text{W}_3\text{Nb}_{14}\text{O}_{44}$

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(Received 4 April 1966)

$\text{W}_4\text{Nb}_{26}\text{O}_{77}$ crystallizes in the monoclinic system, space group $C2$, with unit-cell dimensions $a = 29.74$, $b = 3.824$, $c = 25.97$ Å, $\beta = 92.3^\circ$. Its structure, determined by an image-seeking Patterson superposition method, and refined by two-dimensional Fourier and difference Fourier methods, contains two distinct structural elements, one characteristic of the phase $\text{WNb}_{12}\text{O}_{33}$ and the other present in $\text{W}_3\text{Nb}_{14}\text{O}_{44}$. The basis of one element is a block of octahedra sharing corners, three wide, four long and infinite in the third direction, joined with identical blocks into slabs *via* tetrahedrally coordinated tungsten atoms. The other is identical, except that each block is $4 \times 4 \times \infty$, and these two elements alternate in a regular sequence. The implications of this ordered intergrowth structure are discussed.

Introduction

A recent group of papers from this laboratory, presented as parts I to IV of the above running title (Roth & Wadsley, 1965*a, b, c, d*) described several compounds formed by reacting Nb_2O_5 and WO_3 below the liquidus at 1300–1400°C in a sealed system. By comparing their crystal structures with those of other high-temperature phases centred in composition on Nb_2O_5 , it was possible to construct a three-dimensional table (part IV) pinpointing any new compound which might subsequently be prepared, in the same or in a related system, in such a way that the details of its structure could readily be found, once its precise composition was known.

Gruehn (1966) extended this same system to wider temperature intervals, confirming these results and identifying two additional phases, one with the exact formula $13\text{Nb}_2\text{O}_5 \cdot 4\text{WO}_3$ while the other had a range of homogeneity $40\text{Nb}_2\text{O}_5 : 1\text{WO}_3$ to $20\text{Nb}_2\text{O}_5 : 1\text{WO}_3$. Neither appeared in the above mentioned table of compounds, and Gruehn kindly sent his specimens to us for further study. Roth & Waring (1966) have published a re-examination of this system in which these two new phases were also found.

We now wish to report the crystal structure determination of $\text{W}_4\text{Nb}_{26}\text{O}_{77}$ ($13\text{Nb}_2\text{O}_5 \cdot 4\text{WO}_3$), showing that it contains recognizable features of the neighbouring compounds $\text{WNb}_{12}\text{O}_{33}$ and $\text{W}_3\text{Nb}_{14}\text{O}_{44}$, and demonstrating that the principles of structure building we have developed (Roth & Wadsley, 1965*d*; Andersson, 1965) may be logically extended even further. Crystals of the other new phase proved to be twinned. Speculations about its structure suggest that the number of independent atoms in the unit cell is large, while the number of reflexions of measurable intensity will be small. Its structure may consequently be difficult to determine even when better specimens are available.

Experimental

An extremely small needle crystal of length 0.05 mm was selected from Gruehn's preparation. Approximate unit-cell dimensions and crystal symmetry were determined by moving film methods, and accurate values of $\sin^2 \theta$ for the low angle reflexions were measured with a travelling microscope from a Guinier powder film internally calibrated with potassium chloride. Indices were assigned to these by cross-referencing with the single-crystal films (Table 1), and more precise lattice parameters which are listed in Table 2 were evaluated by a least-squares fit. Intensities for $h0l$, $h1l$ and $h2l$ reflexions were gathered by the multiple film technique with $\text{Cu } K\alpha_{1,2}$ radiation on an integrating Weissenberg camera, measured with a calibrated film strip, and reduced to structure amplitudes without corrections for absorption, as the crystal was very small. All calculations were performed on the Division's Elliott 803 computer, with the programming system of Daly, Stephens & Wheatley (1963).

Table 1. Powder pattern of $\text{W}_4\text{Nb}_{26}\text{O}_{77}$ ($\text{Cu } K\alpha_1$)

<i>I</i> (obs)	$\sin^2 \theta$ (obs)	$\sin^2 \theta$ (calc)	<i>hkl</i>
<i>m</i>	0.00266	0.00269	200
<i>w</i>	0.00349	0.00352	002
<i>m</i>	0.01073	0.01075	400
<i>mw</i>	0.02417	0.02419	600
<i>w</i>	0.02536	0.02533	205
<i>m</i>	0.02698	0.02699	602
<i>w</i>	0.04124	0.04126	110
<i>vs</i>	0.04209	{ 0.04206 0.04218	{ 111 111 }
<i>mw</i>	0.04302	{ 0.04301 0.04318	{ 800 007 }
<i>mw</i>	0.04490	{ 0.04489 0.04499	{ 112 207 }
<i>vs</i>	0.04557	0.04555	802
<i>ms</i>	0.04670	0.04672	207
<i>ms</i>	0.04734	{ 0.04731 0.04752	{ 311 802 }
<i>w</i>	0.04933	0.04934	113
<i>w</i>	0.05555	0.05557	114

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Table 2. Crystallographic data for $W_4Nb_{26}O_{77}$

Symmetry: monoclinic	
Unit-cell dimensions	a 29.74 ± 0.01 Å
	b 3.824 ± 0.002
	c 25.97 ± 0.01
	β $92.3^\circ \pm 0.1^\circ$
Systematically absent reflexions	hkl with $h+k \neq 2n$
Possible space groups	$C2$ (no. 5), Cm (no. 8), $C2/m$ (no. 12)
D_m	4.9 ± 0.1 g.cm $^{-3}$
D_x	4.93 g.cm $^{-3}$
Z	2
μ	574 cm $^{-1}$

Structure determination

The a -axis length of $W_4Nb_{26}O_{77}$, 29.7 Å, appears frequently in the unit cells of high-temperature niobium oxide phases containing Ti or W as substituent elements; it corresponds to the a dimension for both $TiNb_{24}O_{62}$ and $W_5Nb_{16}O_{55}$, the $[102]$ axis of $WNb_{12}O_{33}$ and also $[110]$ for $W_3Nb_{14}O_{44}$ (Roth & Wadsley, 1965*a*, b , c). In all of these cases it is the repeat distance of

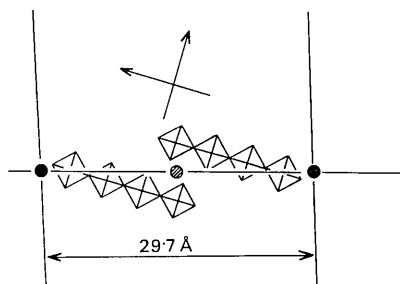


Fig. 1. The junction of two octahedral blocks at a repeat distance of 29.7 Å. Each square represents an octahedron, and the circles are tetrahedrally coordinated atoms at two levels perpendicular to the axis of projection (3.82 Å). The lines are the directions of the unit cell axes of $W_4Nb_{26}O_{77}$, and the crossed arrows give the orientation of the sub-cell, which is parallel to the diagonals of each octahedron.

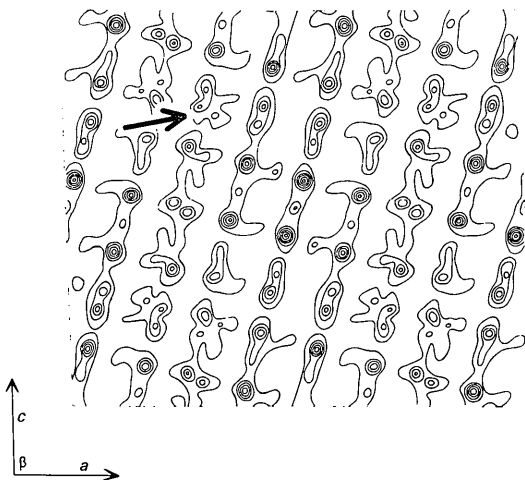


Fig. 2. Projection of the Patterson function $P(u, w)$, showing strong sub-cell development. One of the more attenuated peaks, referred to in the text, is arrowed.

two orthogonal blocks, each consisting of four octahedra joined by corners, and separated by tetrahedrally coordinated atoms occupying special positions at the origin and one or more sides of the unit cell (Fig. 1). This is evidently a feature of $W_4Nb_{26}O_{77}$ as well, and taken in conjunction with the crystal symmetry should have provided enough information for the idealized atomic positions to be determined solely from the orientation relationships of sub-cell to unit cell, as we have shown in other problems of a similar kind. Nevertheless each attempt failed or was rejected on one of two grounds. The chemical formula of every proposed structure disagreed with the composition determined by chemical synthesis, and furthermore each model was aesthetically displeasing, an intuitive criterion we have learned to respect.

With so many independent atoms in the unit cell, the Patterson projection $P(u, w)$ is bound to be difficult to unravel as the large number of vectors overlap and prominently display the sub-cell orientation (Fig. 2). The structure was nevertheless derived from it by a superposition method, where the whole structure was sought and not just the positions of the heavy atoms. When the origin of a transparent map of the function is transposed to a prominent peak of an identical underlying map, keeping the axial directions of both parallel, the positions of the coincident strong vectors are transferred elsewhere to squared paper, not just as the metals alone, but surrounded by six oxygen atoms. A square represents the idealized projected view of any octahedron, the directions of the diagonals being determined by the orientation relationships and parallel to the sub-cell axes (Fig. 1). When two coincident vectors are separated by about 3.8 Å, the octahedra they represent share corners, and when the distance between them is 2.8 Å they share an edge and partly overlap in projection (Gatehouse & Wadsley, 1964). In one superposition it proved possible to draw up the entire octahedral structure unambiguously except for those regions where two weak and extended group of vectors coincide – such a one is indicated by an arrow in Fig. 2. By plotting the strong coincidences all around these areas, however, each uncertainty was recognizable as the environment of a tetrahedrally coordinated atom, where there is no overlying oxygen. These particular atoms are the only ones in the structure which do not contribute to the sub-cell, and are consequently an inconspicuous feature of the Patterson map.

The entire contents of the unit cell were derived by this image-seeking method [Fig. 3(a)]. It contained a principle not found in other high temperature niobium oxide phases; the tetrahedral atoms occupied fourfold positions and no longer appeared in twofold sites at the origin or sides of the unit cell. There were also two different sizes of orthogonal octahedral block, the one three octahedra long, four wide and infinite out of the plane of the paper as in $WNb_{12}O_{33}$ [Fig. 3(b)], and the other was the $4 \times 4 \times \infty$ block characteristic of $W_3Nb_{14}O_{44}$ [Fig. 3(c)]. These units alternate regularly,

or as we will discuss below, are intergrown with each other.

The model produced by this method is the ideal one. The real one differs from it by the displacement of the metal atoms from these regular positions in the octahedra with common edges, which in turn affects the oxygen atoms in their immediate vicinity. Atomic parameters for the trial model were taken from a composite drawing of WNb₁₂O₃₃ and W₃Nb₁₄O₄₄, both structures having been previously refined (Roth & Wadsley, 1965*b*, *c*). The tetrahedral atoms were assumed to be tungsten, and the remaining 4W plus 52Nb were statistically distributed over the fourteen independent octahedral centres. Two oxygen atoms were in a twofold site while all of the other atoms, metal and non-metal, occupied fourfold point positions in

Table 3. Fractional atomic parameters
Space group *C*2

Atom*	<i>x</i>	<i>y</i>	<i>z</i>
W	0.2410	$\frac{1}{4}$	0.2124
B(1)	0.0422	0	0.4088
B(2)	0.0000	0	0.2665
B(3)	0.1640	0	0.3687
B(4)	0.1242	0	0.2244
B(5)	0.1000	$\frac{1}{2}$	0.1222
B(6)	0.2945	$\frac{1}{2}$	0.4919
B(7)	0.2535	$\frac{1}{2}$	0.3487
B(8)	0.2220	$\frac{1}{2}$	0.0797
B(9)	0.4200	$\frac{1}{2}$	0.4509
B(10)	0.3780	$\frac{1}{2}$	0.3076
B(11)	0.3560	0	0.2034
B(12)	0.3140	0	0.0619
B(13)	0.4785	0	0.1633
B(14)	0.4395	0	0.0195
O(1)	0.042	$\frac{1}{2}$	0.409
O(2)	0.000	$\frac{1}{2}$	0.234
O(3)	0.194	$\frac{1}{2}$	0.371
O(4)	0.122	$\frac{1}{2}$	0.201
O(5)	0.102	0	0.149
O(6)	0.271	0	0.487
O(7)	0.237	0	0.345
O(8)	0.245	0	0.077
O(9)	0.420	0	0.451
O(10)	0.377	0	0.276
O(11)	0.360	$\frac{1}{2}$	0.220
O(12)	0.289	$\frac{1}{2}$	0.056
O(13)	0.482	$\frac{1}{2}$	0.185
O(14)	0.440	$\frac{1}{2}$	0.020
O(15)	0.058	0	0.482
O(16)	0.022	0	0.339
O(17)	0.103	0	0.381
O(18)	0.064	0	0.241
O(19)	0.040	$\frac{1}{2}$	0.150
O(20)	0.187	0	0.437
O(21)	0.150	0	0.295
O(22)	0.083	$\frac{1}{2}$	0.050
O(23)	0.186	0	0.189
O(24)	0.167	$\frac{1}{2}$	0.108
O(25)	0.271	$\frac{1}{2}$	0.420
O(26)	0.229	$\frac{1}{2}$	0.273
O(35)	0.439	$\frac{1}{2}$	0.282
O(36)	0.413	0	0.191
O(37)	0.375	0	0.044
O(38)	0.458	0	0.094
O(39)	0	$\frac{1}{2}$	0

* *B* represents a disordered metal (13 Nb + W)/14. All atoms in point positions 4(*c*), except O(39) in 2(*a*).

Table 3 (*cont.*)

Atom*	<i>x</i>	<i>y</i>	<i>z</i>
O(27)	0.356	$\frac{1}{2}$	0.472
O(28)	0.316	$\frac{1}{2}$	0.321
O(29)	0.287	0	0.239
O(30)	0.247	$\frac{1}{2}$	0.156
O(31)	0.206	$\frac{1}{2}$	0.008
O(32)	0.400	$\frac{1}{2}$	0.378
O(33)	0.333	0	0.136
O(34)	0.478	$\frac{1}{2}$	0.428

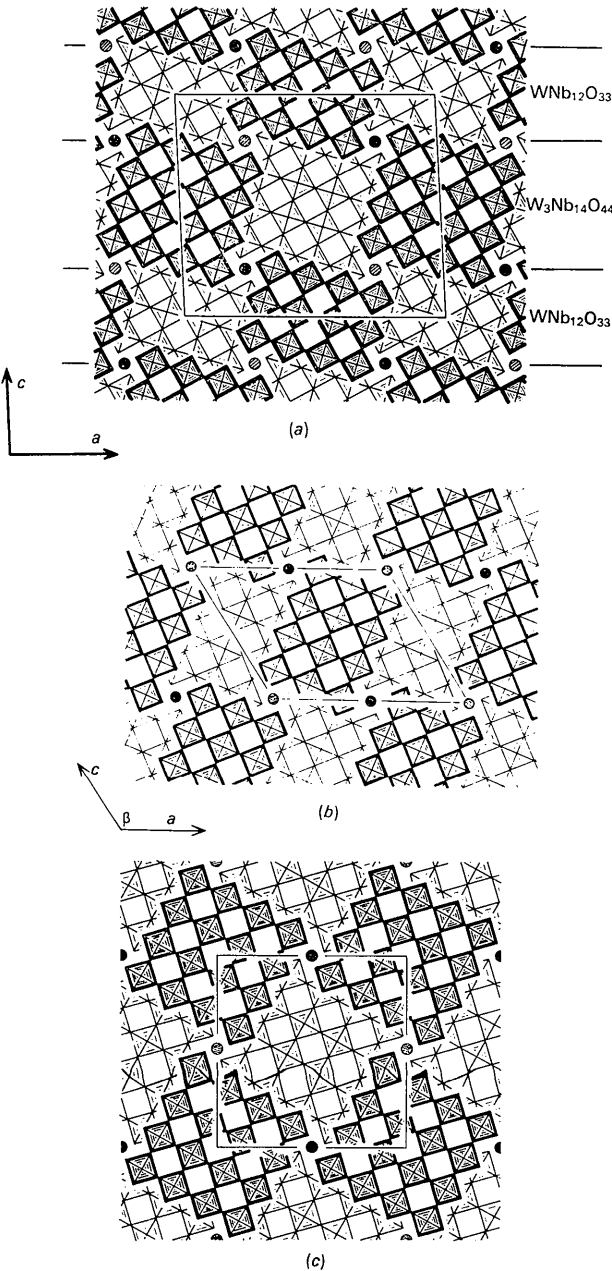


Fig. 3. (*a*) Idealized structure of W₄Nb₂₆O₇₇. The heavier and lighter squares are octahedra at *y*=0 and $\frac{1}{2}$ respectively, and the black and hatched circles are W atoms at *y*= $\frac{1}{4}$ and $\frac{3}{4}$. This diagram shows how the structure is built from alternating slabs of WNb₁₂O₃₃ (*b*) and W₃Nb₁₄O₄₄ (*c*).

one of the space groups $C2/m$ or $C2$, both of which are centred in projection on to (010). The initial R value for the $h0l$ data was 26%, and the model clearly had considerable merit.

Refinement procedures in structures such as this one pose special problems, as there are 53 independent atoms in general positions and fewer than 400 observable reflexions. The octahedral metal atoms and all the oxygen atoms were placed in planes at $y=0$ and $\frac{1}{2}$, but the tetrahedral metals must be at or near $y=\pm\frac{1}{4}$. There is no fourfold point position in $C2/m$ which allows x , y and z simultaneously to vary, and the space group must therefore be $C2$. Attempted least-squares treatment using all the data invariably 'blew up', since y for all atoms will now vary and with our computing programs there is no way to hold some of them. Consequently refinement was restricted to two-dimensional Fourier and difference Fourier syntheses projected on to (010). For the $h0l$ data the R value fell to 12.4%, and with the parameters in Table 3 the $h1l$ and $h2l$

terms gave $R=15.7$ and 16.1% respectively, assuming $y=0$ and $\frac{1}{2}$ for the oxygen atoms and the octahedral metals and $y=\frac{1}{4}$ and $\frac{3}{4}$ for the tetrahedral tungsten (Table 5).

The main objective in this study, which is the assignment of structure, was virtually reached when the ideal model was deduced from the Patterson function, the purpose of the refinement being to prove it beyond all reasonable doubt, rather than to give accurately determined interatomic distances, temperature factors and limits of precision. The octahedral interatomic distances listed in Table 4 show no anomalies, and are consistent with the other Nb–W oxides reported earlier (Roth & Wadsley, 1965*b*, *c*, *d*). The average W–O distance in the tetrahedron is 1.85 ± 0.10 Å with an estimate of accuracy taken from the final difference projection. A ball-and-spoke drawing is shown in Fig. 4.

Intergrowth

$W_4Nb_{26}O_{77}$ has certain major features common also to other mixed oxides of Nb and W. These are the blocks of octahedra $3 \times 4 \times \infty$ present in $WNb_{12}O_{33}$ and the $4 \times 4 \times \infty$ blocks in $W_3Nb_{14}O_{44}$. Slabs or layers of both kinds run throughout the structure of the new phase parallel to (001), and alternate regularly in a completely ordered solid, which is therefore a hybrid of the other two. This is made possible by the one feature common to both of them, the identical rows of four octahedra shown in Fig. 1 terminating adjacent blocks and separated by the tetrahedrally coordinated atoms. Likewise the chemical composition can be derived by summing the other two formulae. Instead of forming a mixture, as one might well expect, the experimental conditions resulted in this one compound containing the essential elements of both of the others. For this reason we regard it as an *intergrowth* of the adjoining structures, and an equilibrium phase in its own right.

This common unit of the four terminal octahedra could also be expected to give an additional phase $W_8Nb_{30}O_{99}$ ($W_3Nb_{14}O_{44} + W_5Nb_{16}O_{55}$), where $4 \times 4 \times \infty$

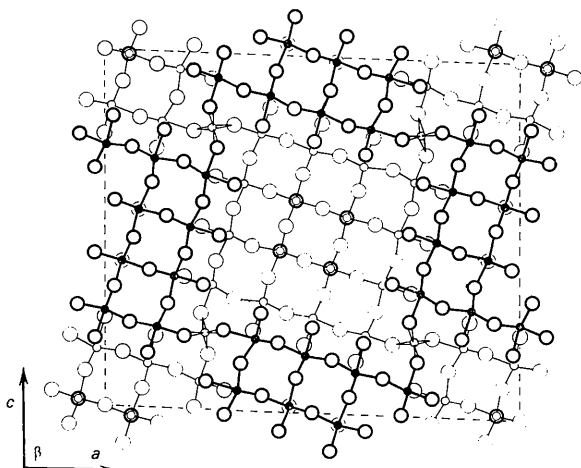


Fig. 4. Real structure of $W_4Nb_{26}O_{77}$. Small hatched circles are tetrahedral W, small open and black circles are octahedral metals, and largest circles oxygen. The heavier (or blacker) circles denote the level $y=0$, and the lighter at $y=\frac{1}{2}$.

Table 4. Interatomic distances for the octahedral atoms in $W_4Nb_{26}O_{77}$

Metal	Bonded oxygen atoms*	Distances (Å)	Average	O–O distances (Å)		
		(Same order as column 2)		Max.	Min.	Av.
B(1)	1(2); 15, 16, 17, 34'	1.91(2); 1.94, 1.89, 1.98, 1.99	1.94	3.00	2.60	2.74
B(2)	2(2); 13', 16, 18, 35'	2.09(2); 2.15, 1.96, 2.04, 1.87	2.03	3.36	2.35	2.84
B(3)	3(2); 7, 17, 20, 21	2.11(2); 2.30, 1.85, 1.88, 1.95	2.03	3.33	2.42	2.83
B(4)	4(2); 5, 18, 21, 23	2.00(2); 2.04, 1.86, 1.95, 2.08	1.99	3.17	2.41	2.78
B(5)	5(2); 4, 19, 22, 24	2.04(2); 2.14, 1.94, 1.92, 2.04	2.02	3.24	2.41	2.82
B(6)	6(2); 6', 20, 25, 27	2.03(2); 2.07, 1.94, 1.98, 1.93	2.00	3.20	2.43	2.80
B(7)	7(2); 3, 25, 26, 28	1.97(2); 1.88, 1.90, 2.08, 2.01	1.97	3.09	2.42	2.80
B(8)	8(2); 12, 24, 30, 31	2.03(2); 2.11, 1.82, 2.10, 1.90	2.00	3.14	2.39	2.79
B(9)	9(2); 15', 27, 32, 34	1.97(2); 1.89, 2.00, 1.97, 1.85	1.94	2.84	2.61	2.72
B(10)	10(2); 11, 28, 32, 35	2.09(2); 2.31, 1.90, 1.91, 1.96	2.04	3.32	2.43	2.84
B(11)	11(2); 10, 29, 33, 36	1.96(2); 1.95, 2.28, 1.85, 1.72	1.95	3.05	2.43	2.76
B(12)	12(2); 8, 31', 33, 37	2.05(2); 2.11, 1.89, 1.99, 1.89	2.00	3.22	2.39	2.80
B(13)	13'(2); 2', 19', 36, 38	2.00(2); 1.96, 1.87, 2.12, 1.87	1.97	3.10	2.35	2.77
B(14)	14(2); 22', 37, 38, 39	1.91(2); 1.90, 2.05, 1.99, 1.89	1.94	2.80	2.69	2.75

* Given by numbers. The first, followed by (2), are the two oxygen atoms lying over and under the metal. E.S.D.'s of metal–oxygen distances are ± 0.06 Å; for oxygen–oxygen 0.10 Å.

blocks are combined with $4 \times 5 \times \infty$. Other units similar to Fig. 1(a) but of different sizes are found in several $\text{Nb}_2\text{O}_5\text{-WO}_3$ or $\text{Nb}_2\text{O}_5\text{-TiO}_2$ mixed oxides and could, in principle at least, generate structures of the same kind. Any two phases with blocks five octahedra across might intergrow, and $\text{W}_{13}\text{Nb}_{34}\text{O}_{124}$ would be the compound intermediate between $\text{W}_5\text{Nb}_{16}\text{O}_{55}$ ($4 \times 5 \times \infty$) and $\text{W}_8\text{Nb}_{18}\text{O}_{69}$ ($5 \times 5 \times \infty$). Neither this nor $\text{W}_8\text{Nb}_{30}\text{O}_{99}$ could be made by heating mixtures of the pure oxides in sealed platinum containers and are not reported by Gruhn or by Roth & Waring (1966) in their detailed phase studies, and why it is that $\text{W}_4\text{Nb}_{26}\text{O}_{77}$ alone of these phases is formed is one of the puzzles of crystal chemistry.

The structural principles in the high temperature niobium oxide phases are not so straightforward when the blocks in them are three octahedra wide. The composition extends to regions where the average metal ion valency is less than five, and is represented by the system $\text{Nb}_2\text{O}_5\text{-TiO}_2$ where a number of phases have been reported. In order to diminish the oxygen to metal ratio, the blocks pack together with additional octahedral edge sharing, either in pairs as in $\text{TiNb}_{24}\text{O}_{62}$ (Roth & Wadsley, 1965), as infinitely joined slabs in TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ (Wadsley, 1961), or partly as infinite slabs joined up with more familiar isolated blocks in Nb_2O_5 and $\text{Nb}_{22}\text{O}_{54}$ (Gatehouse & Wadsley, 1964). Gruhn, Bergner & Schäfer (1965) recently pre-

Table 5. *Calculated and observed structure factors* ($\times 100$)

|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|

pared more compounds with the empirical compositions $(\text{Ti,Nb})\text{O}_{2.466}$, $\text{NbO}_{2.460-2.466}$, $\text{NbO}_{2.482}$, as well as $(\text{W,Nb})\text{O}_{2.506-2.512}$, but made no detailed crystallographic study of them. Waring & Roth (1965) reported monoclinic $(\text{V,Nb})\text{O}_{2.482}$ which appears to be identical with $\text{NbO}_{2.482}$. None of these phases can be identified as a member of the three-dimensional tables of possible structural formulae listed independently by us for the high temperature niobium oxide phases (Andersson, 1965; Roth & Wadsley, 1965), and in all probability they are intergrowths of two already known structural types.

Fig. 5 shows how the hypothetical compound $\text{Ti}_2\text{Nb}_{30}\text{O}_{79}$ $[(\text{Ti,Nb})\text{O}_{2.469}]$ could be derived from pairs of $3 \times 3 \times \infty$ blocks and single $3 \times 4 \times \infty$ blocks. $\text{TiNb}_{34}\text{O}_{87}$ $[(\text{Ti,Nb})\text{O}_{2.486}]$ might similarly be formed if the single blocks were $3 \times 5 \times \infty$, and $\text{WNb}_{40}\text{O}_{103}$ $[(\text{W,Nb})\text{O}_{2.512}]$ from pairs $3 \times 4 \times \infty$ interleaved with $3 \times 5 \times \infty$. The number of ways of putting these units together, however, is very large indeed and none of these suggestions constitutes a proof, which must be provided by a structure analysis of each phase.

Lest a good deal of the foregoing should appear fanciful, it must be borne in mind that there are many other well-documented solid state systems with a similar proliferation of closely spaced phases, the best known belonging to two different classes both of which have hexagonal or rhombohedral symmetry. The first, exemplified by the SiC and CdI_2 polytypes, involves different stacking sequences between blocks of structure of the one kind. Much the same behaviour is found in the second type, except that the blocks may be of two or more varieties having a different composition, and consequently each member of a family has its own particular formula. Jeffrey & Wu (1963) showed that a number of aluminum carbonitrides were ordered intergrowths of AlN and Al_4C_3 units, each one having its particular sequence, and an infinite number of related phases in principle is possible. The hexagonal ferrites afford similar examples, and recent studies by Kohn & Eckhardt (1964) extended the original list of

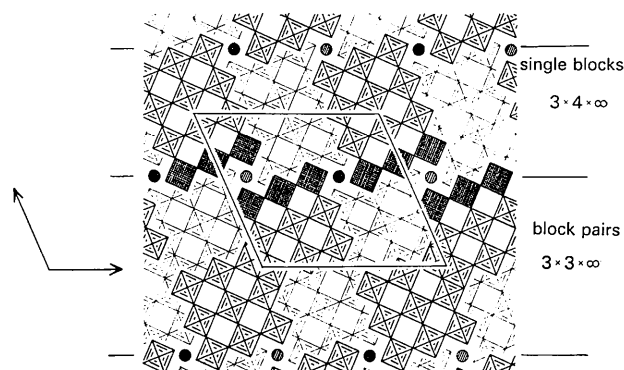


Fig. 5. Shows how intergrowth structures could be generated when the common unit is a block three octahedra wide (cross-hatched). Block pairs, each $3 \times 3 \times \infty$, alternating with single blocks, $3 \times 4 \times \infty$, form the structure of a hypothetical compound $\text{Ti}_2\text{Nb}_{30}\text{O}_{79}$ $[(\text{Ti,Nb})\text{O}_{2.469}]$.

six phases (Braun, 1957; Jonker, 1958) to include a large number of predictable new compounds containing three basic building blocks of different thicknesses stacked in various ways.

These four examples of iso- or heteropolytypes are readily distinguished by the period of the six- or three-fold axes, and once the structural principles are known, the stacking mode is determined from a limited number of possibilities which can be evaluated satisfactorily by unidimensional methods of X-ray analysis. Not all intergrowths or polytypes are so simply recognized, and the studies of the Nb-Ti-W oxides and oxyfluorides pose special problems, centring on the assignment of correct indices for the reflexions in oblique unit cells where two or more of the crystallographic axes are large, and where only a small fraction of these reflexions have an appreciable intensity. The likelihood of twinning and of disordered intergrowth are further complicating factors in an area of formidable difficulty.

Ranges of homogeneity

We noted above that there are several phases with appreciable ranges of homogeneity, $\text{NbO}_{2.466-2.460}$ and $(\text{W,Nb})\text{O}_{2.506-2.512}$, while elsewhere $\text{WNb}_{12}\text{O}_{33}$ was reported to extend in composition to $\text{WNb}_{16}\text{O}_{43}$ [*i.e.* $(\text{W,Nb})\text{O}_{2.529-2.538}$] without significant changes of lattice parameters (Roth & Wadsley, 1965a).

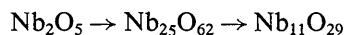
Solid solutions of metal oxides, where the metal to oxygen ratio is variable, have been widely assumed to result either from the non-periodic omission of atoms from lattice points, or from the interpolation of additional atoms into normally empty positions, *i.e.* vacancies or interstitials. The likelihood of either model being the case for the Nb/W oxides was dismissed in an earlier discussion (Roth & Wadsley, 1965d). We now ask whether the structure found for $\text{W}_4\text{Nb}_{26}\text{O}_{77}$, if only by implication, may give a realistic physical meaning to these particular cases.

One of the more surprising features in the present structure determination of $\text{W}_4\text{Nb}_{26}\text{O}_{77}$ is the long-range ordering of the two different sizes of blocks. Intergrowth having been established, it therefore remains to be asked whether disordered intergrowth could also arise. The chemical composition must remain fixed when there are equal numbers of the two kinds of block, and $\text{W}_4\text{Nb}_{26}\text{O}_{77}$ could exist either as a single ordered phase, as a disordered intergrowth of the two kinds of block, or as the two distinct phases $\text{WNb}_{12}\text{O}_{33}$ and $\text{W}_3\text{Nb}_{14}\text{O}_{44}$ present in the one single crystal. Examples of this latter phenomenon are by no means rare in crystalline minerals. Should the number of blocks of both kinds be unequal the composition will vary, and whether the crystal is a single phase of variable composition or a mixture of two adjacent structures is an order-disorder relationship which will largely depend upon its thermal history.

In very complex structures the term *solid solution* assumes a literal meaning, namely the solution of one

solid within another at the unit-cell level, and to describe it more specifically we introduced the term *intergrowth* some little time ago (Andersson & Wadsley, 1962). Subsequently this was used more generally to define a class of non-stoichiometric compound (Wadsley, 1964), and we note that the older title *anomalous* (or *hybrid*) *solid solution* (Anderson, 1946) has recently been revived (Donnay, 1965).

The number of ordered intergrowth phases in systems such as Nb₂O₅-TiO₂, Nb₂O₅-NbO₂ and Nb₂O₅-WO₃ may well depend upon the time given for materials to react. Interactions between these classes of solid have recently been considered in detail (Andersson & Wadsley, 1966). There is good evidence that the sequence



proceeds by the simultaneous diffusion of whole planes of ions throughout each structure in a preferred direction, thereby changing the size of the block. Should this process be interrupted before equilibrium is established, a partly ordered hybrid of the two adjacent structures will result. The invariance of the lattice parameters in the solid solution simply reflects the dominance of one particular size of block in the structure, which alone has sufficient long-range order coherently to scatter X-rays.

We are grateful to Dr R. Gruehn and Dr R. S. Roth for sending us their specimens.

Acta Cryst. (1966). **21**, 808

Die Struktur des As₂O₅ · $\frac{5}{3}$ H₂O*

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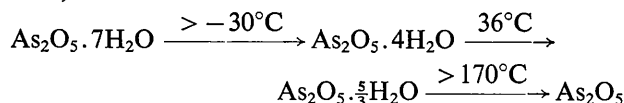
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(Eingegangen am 14. Januar 1966)

Single crystals of the dehydration product of arsenic acid 3As₂O₅ · 5H₂O are triclinic, with $a = 7.25$, $b = 5.70$, $c = 4.67$ Å, $\alpha = 99.8^\circ$, $\beta = 98.0^\circ$, $\gamma = 99.7^\circ$, space group $P\bar{1}$. The structure consists of spiro chains, formed by linked AsO₄ tetrahedra and AsO₆ octahedra. The positions of hydrogen atoms have been determined by means of three-dimensional difference electron densities.

Allgemeines

Bei der Entwässerung einer Arsensäurelösung wurden bisher folgende Zwischenprodukte eindeutig nachgewiesen und in reiner Form isoliert (Simon & Thaler, 1927):



Sowohl die Strukturen der Arsen-V-oxidhydrate, als auch die des As₂O₅ sind bisher nicht bekannt. Die vor-

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liegende Arbeit behandelt die Strukturuntersuchung des As₂O₅ · $\frac{5}{3}$ H₂O und soll ein erster Beitrag zur Klärung der Strukturen des Arsen-V-oxids und seiner Hydrate sein.

Darstellung

Genügend grosse Kristalle des As₂O₅ · $\frac{5}{3}$ H₂O erhält man durch Eindampfen einer Arsensäurelösung bei etwa 100°C.

Beim isobaren Abbau des As₂O₅ · $\frac{5}{3}$ H₂O (760 mmHg an Luft) wurde in Übereinstimmung mit früheren Arbeiten anderer Autoren (Simon & Thaler, 1927, 1941; Kolarow, 1941; Balarew, 1911) ein Diagramm erhalten, das nur eine klar erkennbare Stufe zeigt, die das Existenzgebiet der Verbindung As₂O₅ · $\frac{5}{3}$ H₂O charakte-

* Teil der Dissertation von H. Worzala, Humboldt-Universität, Berlin, 1966.