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Multiple Phase Formation in the Binary System Nb_2O_5–WO_3. V. The Structure of $W_4Nb_{26}O_{77}$, an Ordered Intergrowth of the Adjoining Compounds $WNb_{12}O_{33}$ and $W_3Nb_{14}O_{44}$

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$W_4Nb_{26}O_{77}$ crystallizes in the monoclinic system, space group $C2$, with unit-cell dimensions $a=29{\cdot}74$, $b=3{\cdot}824$, $c=25{\cdot}97$ Å, $\beta=92{\cdot}3°$. 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 $WNb_{12}O_{33}$ and the other present in $W_3Nb_{14}O_{44}$. 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 $4\times4\times\infty$, 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 $13Nb_2O_5.4WO_3$ while the other had a range of homogeneity $40Nb_2O_5{:}1WO_3$ to $20Nb_2O_5{:}1WO_3$. 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 $W_4Nb_{26}O_{77}$ ($13Nb_2O_5.4WO_3$), showing that it contains recognizable features of the neighbouring compounds $WNb_{12}O_{33}$ and $W_3Nb_{14}O_{44}$, 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 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* $W_4Nb_{26}O_{77}$ (Cu $K\alpha_1$)

I (obs)	$\sin^2\theta$ (obs)	$\sin^2\theta$ (calc)	hkl
m	0·00266	0·00269	200
w	0·00349	0·00352	002
m	0·01073	0·01075	400
mw	0·02417	0·02419	600
w	0·02536	0·02533	205
m	0·02698	0·02699	$60\bar{2}$
w	0·04124	0·04126	110
vs	0·04209	0·04206 0·04218	$11\bar{1}$ 111
mw	0·04302	0·04301 0·04318	800 007
mw	0·04490	0·04489 0·04499	112 $20\bar{7}$
vs	0·04557	0·04555	$80\bar{2}$
ms	0·04670	0·04672	207
ms	0·04734	0·04731 0·04752	$31\bar{1}$ 802
w	0·04933	0·04934	113
w	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 $\pm$0·01 Å b 3·824$\pm$0·002 c 25·97 $\pm$0·01 β 92·3°$\pm$0·1°
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$\pm$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 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.

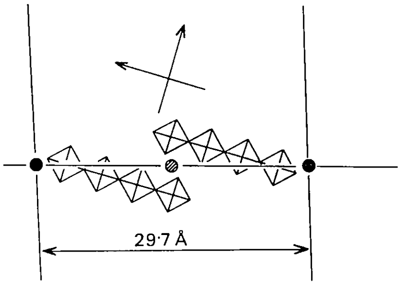

Fig. 1. The junction of two octahedral blocks at a repeat distance of 29·7 Å. Each square represents an octahedron, and the circles are tetrahedrally coordinated atoms at two levels perpendicular to the axis of projection (3·82 Å). The lines are the directions of the unit cell axes of $W_4Nb_{26}O_{77}$, and the crossed arrows give the orientation of the sub-cell, which is parallel to the diagonals of each octahedron.

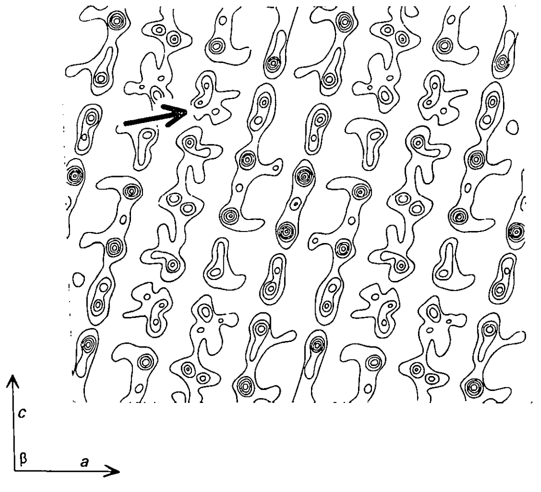

Fig. 2. Projection of the Patterson function $P(u,w)$, showing strong sub-cell development. One of the more attenuated peaks, referred to in the text, is arrowed.

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 $4\times4\times\infty$ 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 $WNb_{12}O_{33}$ and $W_3Nb_{14}O_{44}$, 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*	*x*	*y*	*z*
W	0·2410	¼	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	½	0·1222
B(6)	0·2945	½	0·4919
B(7)	0·2535	½	0·3487
B(8)	0·2220	½	0·0797
B(9)	0·4200	½	0·4509
B(10)	0·3780	½	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	½	0·409
O(2)	0·000	½	0·234
O(3)	0·194	½	0·371
O(4)	0·122	½	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	½	0·220
O(12)	0·289	½	0·056
O(13)	0·482	½	0·185
O(14)	0·440	½	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	½	0·150
O(20)	0·187	0	0·437
O(21)	0·150	0	0·295
O(22)	0·083	½	0·050
O(23)	0·186	0	0·189
O(24)	0·167	½	0·108
O(25)	0·271	½	0·420
O(26)	0·229	½	0·273
O(35)	0·439	½	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	½	0
O(27)	0·356	½	0·472
O(28)	0·316	½	0·321
O(29)	0·287	0	0·239
O(30)	0·247	½	0·156
O(31)	0·206	½	0·008
O(32)	0·400	½	0·378
O(33)	0·333	0	0·136
O(34)	0·478	½	0·428

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

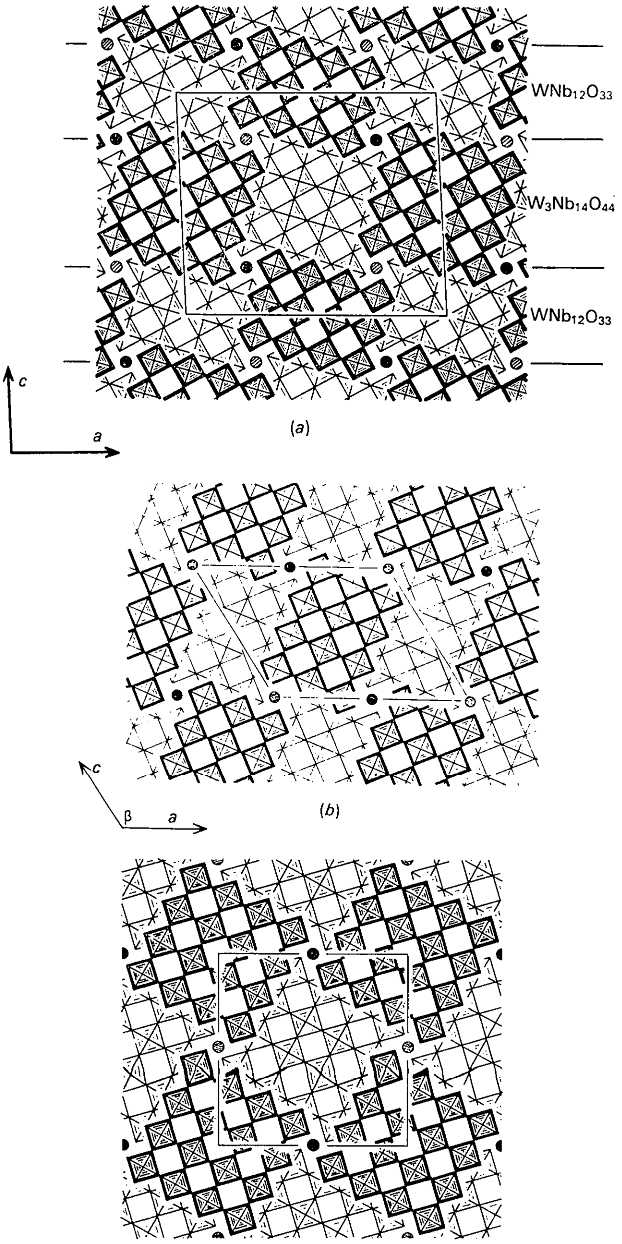

Fig. 3. (*a*) Idealized structure of $W_4Nb_{26}O_{77}$. The heavier and lighter squares are octahedra at $y=0$ and $\frac{1}{2}$ respectively, and the black and hatched circles are W atoms at $y=\frac{1}{4}$ and $\frac{3}{4}$. This diagram shows how the structure is built from alternating slabs of $WNb_{12}O_{33}$ (*b*) and $W_3Nb_{14}O_{44}$ (*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 $R=15{\cdot}7$ 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).

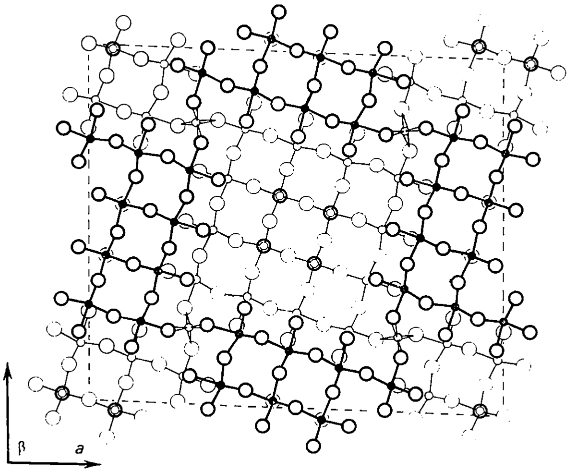

Fig. 4. Real structure of $W_4Nb_{26}O_{77}$. Small hatched circles are tetrahedral W, small open and black circles are octahedral metals, and largest circles oxygen. The heavier (or blacker) circles denote the level $y=0$, and the lighter at $y=\frac{1}{2}$.

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 $1{\cdot}85\pm0{\cdot}10$ 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 $3\times4\times\infty$ present in $WNb_{12}O_{33}$ and the $4\times4\times\infty$ 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 $4\times4\times\infty$

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

Metal	Bonded oxygen atoms*	Distances (Å) (Same order as column 2)	Average	O–O distances (Å) 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 × 5 × ∞. Other units similar to Fig. 1(*a*) but of different sizes are found in several Nb_2O_5–WO_3 or Nb_2O_5–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 $W_{13}Nb_{34}O_{124}$ would be the compound intermediate between $W_5Nb_{16}O_{55}$ (4 × 5 × ∞) and $W_8Nb_{18}O_{69}$ (5 × 5 × ∞). Neither this nor $W_8Nb_{30}O_{99}$ could be made by heating mixtures of the pure oxides in sealed platinum containers and are not reported by Gruehn or by Roth & Waring (1966) in their detailed phase studies, and why it is that $W_4Nb_{26}O_{77}$ 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 Nb_2O_5–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 $TiNb_{24}O_{62}$ (Roth & Wadsley, 1965), as infinitely joined slabs in $TiNb_2O_7$ and $Ti_2Nb_{10}O_{29}$ (Wadsley, 1961), or partly as infinite slabs joined up with more familiar isolated blocks in Nb_2O_5 and $Nb_{22}O_{54}$ (Gatehouse & Wadsley, 1964). Gruehn, Bergner & Schäfer (1965) recently pre-

Table 5. *Calculated and observed structure factors* (× 100)

h	k	l	$\|F_o\|$	$\|F_c\|$
0	0	2	2401	2731
0	0	3	2258	2283
0	0	4	2201	2155
0	0	5	2945	3564
0	0	7	4630	5291
0	0	14	5860	6205
0	0	21	7261	7670
0	0	28	5746	4322
2	0	5	5432	6401
2	0	6	3574	2662
• 2	0	7	13643	20131
2	0	8	2087	2920
2	0	9	4173	3559
2	0	10	2372	2730
2	0	12	1886	2498
2	0	14	5917	6340
2	0	21	3887	4051
2	0	28	7633	8581
2	0	-7	3830	4186
2	0	-14	7204	7775
2	0	-16	2286	3765
2	0	-21	5489	4867
2	0	-23	4001	3045
4	0	0	2600	3284
4	0	10	3002	3205
4	0	11	2229	2653
• 4	0	12	12706	15208
4	0	13	2858	3366
4	0	14	9777	11491
4	0	21	3403	3634
4	0	-7	3460	3949
4	0	-9	4545	3980
4	0	-14	6975	5971
4	0	-16	8320	8404
6	0	0	2801	3301
6	0	19	10321	9996
6	0	21	3944	3762
6	0	-2	5775	6095
6	0	-14	2144	2548
6	0	-16	5746	5899
6	0	-23	4946	3494
8	0	0	3544	4179
8	0	1	3030	2995
8	0	2	1943	2960
8	0	3	3460	3941
8	0	19	3830	5133
8	0	26	8004	8091
8	0	-1	1629	1962
• 8	0	-2	18811	21417
8	0	-9	5030	5698
8	0	-16	6804	7142
8	0	-23	8576	11300
10	0	3	4203	3239
10	0	4	2286	1480
10	0	5	11921	12542
10	0	6	3002	3380
10	0	7	3601	3916
10	0	8	4173	4512
10	0	9	1943	2618
10	0	10	5718	5565
10	0	26	5202	5396
10	0	29	3601	3020
10	0	-1	4573	1310
10	0	-9	4630	5335
10	0	-16	11378	12685
10	0	-18	6489	6885
12	0	10	10578	10497
12	0	11	2229	1903
12	0	12	8004	8527
12	0	17	3287	2976
12	0	-2	3430	3855
12	0	-4	3517	3879
12	0	-9	4946	6264
12	0	-11	10635	10840
12	0	-18	4687	3376
14	0	17	7833	8016
14	0	19	3487	2959
14	0	-2	1886	2978
•14	0	-4	13612	15388
14	0	-11	7976	7571
14	0	-18	2774	2115
16	0	0	2915	3593
16	0	1	7204	7181
16	0	2	2087	2240
16	0	3	6346	5321
16	0	8	3287	3477
16	0	22	3344	3271
16	0	24	8778	7937
16	0	-1	4630	4717
16	0	-2	5088	5068
16	0	-3	2543	2472
16	0	-4	11978	13327
16	0	-11	3830	3536
16	0	-18	3460	3156
16	0	-25	7204	7955
16	0	-27	3173	2305
18	0	3	9777	10026
18	0	4	3287	3732
18	0	5	4718	4637
18	0	6	5860	6224
18	0	7	2429	3146
18	0	8	10549	11068
18	0	15	3430	3315
18	0	22	2600	2352
18	0	27	3574	2843
18	0	-4	3230	3359
18	0	-11	2572	3097
18	0	-18	6975	7420
18	0	-20	6947	6882
20	0	8	6975	7881
20	0	10	5432	5026
20	0	13	2801	2687
20	0	15	6975	6429
20	0	22	3487	2972
20	0	-11	2686	3140
20	0	-13	7833	8363
22	0	15	7519	7505
22	0	22	5060	3921
22	0	-6	10348	10723
22	0	-8	3830	2767
22	0	-13	3460	2848
24	0	1	5489	4363
24	0	20	3258	4197
24	0	22	5974	6346
24	0	-1	6717	6644
24	0	-3	3887	4002
24	0	-4	2744	2833
24	0	-6	5575	5337
24	0	-22	3201	3816
24	0	-24	2372	1887
24	0	-25	2972	2334
26	0	1	4916	4877
26	0	4	4030	4296
26	0	6	9464	10325
26	0	13	3315	3095
26	0	20	2858	2832
26	0	-8	2858	3203
26	0	-15	3830	4187
26	0	-17	2572	2415
26	0	-18	2486	2190
26	0	-19	2401	1855
26	0	-20	5603	5500
26	0	-22	5974	4994
28	0	13	7604	7083
28	0	20	4659	3566
28	0	-8	3430	3270
28	0	-15	8805	7169
30	0	13	3201	3128
30	0	-8	9662	9335
30	0	-10	3688	2958
32	0	-2	6804	2097
32	0	-10	2343	2403
32	0	-17	3315	2476
34	0	4	9777	10646
1	1	0	1729	2102
1	1	1	14339	9851
1	1	2	5507	3699
1	1	3	6091	4893
1	1	4	6011	5187
1	1	5	2793	2498
1	1	6	10427	8964
1	1	8	2527	2536
1	1	13	3990	3575
1	1	27	6357	7207
1	1	29	5135	4322
1	1	-1	12555	9166
1	1	-5	1968	1272
1	1	-8	1941	2695
1	1	-22	8379	8578
3	1	6	11385	11588
3	1	8	4309	2658
3	1	11	2633	2983
3	1	13	9071	8259
3	1	-1	8327	6050
3	1	-8	2793	3083
3	1	-15	12369	14882
5	1	6	4123	4871
5	1	13	14391	15641
5	1	20	3670	2501
5	1	-1	6384	5947
5	1	-8	7607	8264
5	1	-10	4415	4653
7	1	6	2847	3611
7	1	13	2606	3408
7	1	18	4362	5209
7	1	20	8299	8133
7	1	25	3564	3257
7	1	-1	7873	8854
7	1	-2	2315	2386
7	1	-3	9709	10808
7	1	-4	2155	2605
7	1	-5	3138	4163
7	1	-6	2793	3362
7	1	-8	3458	3664
7	1	-29	6091	5820
7	1	-31	4469	3452
9	1	2	2261	3104
9	1	4	7795	8306
9	1	6	2473	3202
9	1	11	4123	4742
9	1	25	8884	9049
9	1	27	3803	3493
9	1	-1	2234	3328
9	1	-3	1968	2935
9	1	-24	8193	7452
11	1	4	5054	4925
11	1	11	11651	11903
11	1	-3	2447	2638
11	1	-17	11810	14162
13	1	11	6011	7055
13	1	18	6465	5081
13	1	-3	2287	3323
13	1	-10	9657	12123
13	1	-12	5081	5154
15	1	18	4603	4768
15	1	21	3645	3628
15	1	23	6384	5709
15	1	-3	8113	9804
15	1	-5	10561	13703
15	1	-26	4841	5500
17	1	23	5107	4964
17	1	2	10241	14160
17	1	-19	5293	6729
17	1	-26	5373	4113
19	1	9	10987	14746
19	1	-19	7820	7328
21	1	14	4575	5862
21	1	16	6889	6684
21	1	-12	5267	5862
21	1	-14	3751	3401
23	1	19	2739	3264
23	1	21	8406	8808
23	1	23	2287	2453
23	1	-5	3165	3843
23	1	-7	7395	7849
25	1	0	7475	8244
25	1	-7	2660	3230
25	1	-21	8379	9234
27	1	7	7341	8809
27	1	-15	4069	1927
27	1	-17	3085	1490
27	1	-21	2049	2739
29	1	12	4894	4332
29	1	14	5347	4846
29	1	-2	3138	2527
29	1	-7	3059	4084
29	1	-14	2687	2713
29	1	-9	6490	7700
31	1	5	6091	3500
31	1	-2	5852	6767
33	1	5	4921	5767
33	1	-2	5213	4726
35	1	5	4283	5155
0	2	28	5387	5948
0	2	-2	2407	1804
0	2	-4	1739	976
0	2	-5	2169	1320
0	2	-9	3861	2123
0	2	-16	2813	1548
0	2	-21	3336	3937
0	2	-26	2383	1891
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2	2	0	2955	2339
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2	2	3	4576	3781
2	2	4	3932	2989
2	2	5	8175	8365
2	2	6	2860	2138
2	2	7	12465	11900
2	2	16	2288	990
2	2	26	1930	2151
2	2	28	4267	5645
2	2	-2	4839	3481
2	2	-3	2431	1710
2	2	-4	2478	1878
2	2	-5	2502	2307
2	2	-14	3099	2812
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2	2	-18	2359	2482
2	2	-19	3360	3538
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2	2	-28	2837	2789
4	2	0	2121	1774
4	2	2	2455	2657
4	2	3	3050	2941
4	2	5	4790	3496
4	2	7	4600	4182
4	2	9	3932	3798
4	2	10	4504	5587
4	2	11	2931	2968
4	2	12	14253	15054
4	2	14	5887	6048
4	2	26	2335	2451
4	2	-2	6030	4984
4	2	-3	2145	1829
4	2	-4	3074	2513
4	2	-5	2551	2428
4	2	-9	7579	7289
4	2	-10	2002	2448
4	2	-11	4600	3533
4	2	-12	4218	4305
4	2	-13	3050	2258
4	2	-14	6983	8270
4	2	-16	5148	3929
4	2	-28	1979	2470
6	2	0	2169	1594
6	2	3	2216	2579
6	2	5	4147	3734
6	2	7	1930	1947
6	2	8	1955	1778
6	2	10	2049	2971
6	2	12	2645	1364
6	2	14	2241	2994
6	2	17	3336	3017
6	2	19	10105	11409
6	2	26	2621	3152
6	2	-2	8199	8467
6	2	-4	4075	3046
6	2	-7	4267	4227
6	2	-9	8461	7011
5	2	-16	2311	1741
6	2	-28	1930	2810
8	2	5	3313	3967
8	2	26	7961	9308
8	2	-2	11131	12609
8	2	-4	3265	3009
8	2	-23	6627	7300
8	2	-26	2621	1900
8	2	-28	1859	1739
10	2	0	2335	1869
10	2	1	2359	3001
10	2	3	5505	6687
10	2	5	6913	7131
10	2	-4	4361	3954
10	2	-11	3074	3182
10	2	-16	6673	7152
10	2	-18	7150	8233
10	2	-21	2813	2629
10	2	-23	4314	3827
12	2	1	2002	2105
12	2	3	4553	4109
12	2	8	2645	3573
12	2	10	9487	11884
12	2	12	3622	4034
12	2	-4	6125	6362
12	2	-11	10034	11949
12	2	-13	3265	3723
12	2	-14	2860	3245
12	2	-16	4099	4690
14	2	3	5219	5019
14	2	10	4600	3836
14	2	17	9105	9831
14	2	-4	11655	15193
14	2	-11	3241	3137
16	2	1	2693	2553
16	2	3	6649	7747
16	2	10	3313	3913
16	2	24	7460	9176
16	2	-4	5863	7126
16	2	-26	3765	1868
18	2	1	4553	5099
18	2	3	4290	5012
18	2	8	5769	5951
18	2	10	3742	3791
18	2	-18	3527	3805
18	2	-20	7817	8064
18	2	-25	2002	1782
20	2	1	2860	3111
20	2	8	6292	9490
20	2	15	3146	2945
20	2	-6	3336	3471
20	2	-13	9105	9898
22	2	1	3360	3814
22	2	8	3336	3787
22	2	15	8127	9073
22	2	22	1693	1411
22	2	-6	10105	11971
24	2	1	5769	6736
24	2	8	3217	3598
24	2	15	2717	2301
26	2	6	5839	6384
26	2	8	3718	3944
26	2	15	2049	1819
28	2	6	2860	4277
28	2	13	4243	4056
28	2	15	1930	1557
28	2	-16	7007	228
30	2	13	4243	4944
30	2	-1	2717	1256
30	2	-4	1906	1910
30	2	-7	2241	1509
30	2	-8	9819	10508
32	2	6	2527	2338
32	2	-1	4933	6826
32	2	-3	3265	3883

* Affected by extinction.

pared more compounds with the empirical compositions $(Ti,Nb)O_{2\cdot466}$, $NbO_{2\cdot460-2\cdot466}$, $NbO_{2\cdot482}$, as well as $(W,Nb)O_{2\cdot506-2\cdot512}$, but made no detailed crystallographic study of them. Waring & Roth (1965) reported monoclinic $(V,Nb)O_{2\cdot482}$ which appears to be identical with $NbO_{2\cdot482}$. 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 $Ti_2Nb_{30}O_{79}$ $[(Ti,Nb)O_{2\cdot469}]$ could be derived from pairs of $3\times3\times\infty$ blocks and single $3\times4\times\infty$ blocks. $TiNb_{34}O_{87}$ $[Ti,Nb)O_{2\cdot486}]$ might similarly be formed if the single blocks were $3\times5\times\infty$, and $WNb_{40}O_{103}$ $[W,Nb)O_{2\cdot512}]$ from pairs $3\times4\times\infty$ interleaved with $3\times5\times\infty$. 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 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.

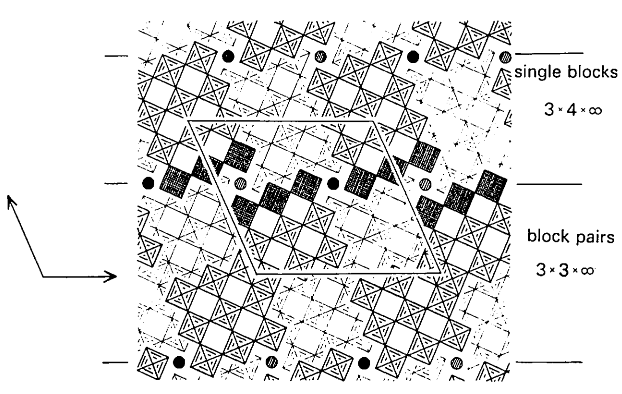

Fig. 5. Shows how intergrowth structures could be generated when the common unit is a block three octahedra wide (cross-hatched). Block pairs, each $3\times3\times\infty$, alternating with single blocks, $3\times4\times\infty$, form the structure of a hypothetical compound $Ti_2Nb_{30}O_{79}$ $[(Ti,Nb)O_{2\cdot469}]$.

These four examples of iso- or heteropolytypes are readily distinguished by the period of the six- or threefold 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, $NbO_{2\cdot466-2\cdot460}$ and $(W,Nb)O_{2\cdot506-2\cdot512}$, while elsewhere $WNb_{12}O_{33}$ was reported to extend in composition to $WNb_{16}O_{43}$ [*i.e.* $(W,Nb)O_{2\cdot529-2\cdot538}$] without significant changes of lattice parameters (Roth & Wadsley, 1965*a*).

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, 1965*d*). We now ask whether the structure found for $W_4Nb_{26}O_{77}$, 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 $W_4Nb_{26}O_{77}$ 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 $W_4Nb_{26}O_{77}$ could exist either as a single ordered phase, as a disordered intergrowth of the two kinds of block, or as the two distinct phases $WNb_{12}O_{33}$ and $W_3Nb_{14}O_{44}$ 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 Nb_2O_5–TiO_2, Nb_2O_5–NbO_2 and Nb_2O_5–WO_3 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

$$Nb_2O_5 \rightarrow Nb_{25}O_{62} \rightarrow Nb_{11}O_{29}$$

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.

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Die Struktur des $As_2O_5 . \frac{5}{3}H_2O$*

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Single crystals of the dehydration product of arsenic acid $3As_2O_5.5H_2O$ are triclinic, with $a=7{\cdot}25$, $b=5{\cdot}70$, $c=4{\cdot}67$ Å, $\alpha=99{\cdot}8$, $\beta=98{\cdot}0$, $\gamma=99{\cdot}7°$, space group $P\bar{1}$. The structure consists of spiro chains, formed by linked AsO_4 tetrahedra and AsO_6 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):

$$As_2O_5.7H_2O \xrightarrow{>-30°C} As_2O_5.4H_2O \xrightarrow{36°C} As_2O_5.\tfrac{5}{3}H_2O \xrightarrow{>170°C} As_2O_5$$

Sowohl die Strukturen der Arsen-V-oxidhydrate, als auch die des As_2O_5 sind bisher nicht bekannt. Die vorliegende Arbeit behandelt die Strukturuntersuchung des $As_2O_5.\frac{5}{3}H_2O$ und soll ein erster Beitrag zur Klärung der Strukturen des Arsen-V-oxids und seiner Hydrate sein.

Darstellung

Genügend grosse Kristalle des $As_2O_5.\frac{5}{3}H_2O$ erhält man durch Eindampfen einer Arsensäurelösung bei etwa 100°C.

Beim isobaren Abbau des $As_2O_5.\frac{5}{3}H_2O$ (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 $As_2O_5.\frac{5}{3}H_2O$ charakte-

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