The tetrahedron in $WNb_{12}O_{33}$ is very nearly regular with four W–O bonds $1\cdot70 \pm 0\cdot07$ Å, while in $W_5Nb_{16}O_{55}$ there are two W–O bonds $1\cdot76$ Å as well as two of $1\cdot85 \pm 0\cdot07$ Å. They may be compared with values of $1\cdot79$ Å in $CaWO_4$ (Kay, Frazer & Almodovar, 1964) and $1\cdot74$ and $1\cdot78$ Å in $Eu_2(WO_4)_3$ (Templeton & Zalkin, 1963) where the isolated tungsten–oxygen tetrahedra are joined only through the Ca or Eu ions.

There is no evidence that either compound forms a defect structure with excess oxygen or with vacated metal positions, and any range of composition despite the evidence for $WNb_{12}O_{33}$ in part I, can be expected to be extremely small.

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Multiple Phase Formation in the Binary System Nb_2O_5–WO_3
III. The Structures of the Tetragonal Phases $W_3Nb_{14}O_{44}$ and $W_8Nb_{18}O_{69}$

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The unit-cell dimensions of $W_3Nb_{14}O_{44}$ are $a = 21\cdot02$, $c = 3\cdot824$ Å, space group $I4/m$ or $I\bar{4}$. The structure consists of ReO_3-type blocks of octahedra four wide, four long, and infinite along the fourfold axis, joined by sharing edges and with tetrahedral W atoms at the junctions of every four blocks. $W_8Nb_{18}O_{69}$, with the dimensions $a = 26\cdot25$, $c = 3\cdot813$ Å, most probable space group $I\bar{4}$, has an identical structure except that the blocks are five octahedra in width and length. W and Nb are randomized in the octahedral positions of both phases. The structures were deduced by trial-and-error and refined by two-dimensional Fourier methods.

Introduction

The crystal structure analyses of the two tetragonal compounds $W_3Nb_{14}O_{44}$ and $W_8Nb_{18}O_{69}$ posed problems of a special kind. In the first place the crystals were extremely small and fragile, and consequently difficult to handle. Since the specimens provided powder diffraction patterns of good quality, we had hoped to use intensities from the diffractometer to confirm the proposed structures, even although the asymmetric unit of each one contained a considerable number of atoms. The powder data, however, could not be used analytically, as the ideal structures of both compounds, although readily proposed, belonged to a symmetry group where overlapping reflexions of the same class were not equivalent. 'One shot' attempts to move the atoms to their real positions showed a general agree-

ment between observed and calculated intensities, but were not good enough to resolve all of the ambiguities outlined in the introduction to part II of the present series of papers (Roth & Wadsley, 1965).

In the second place the crystals, when eventually mounted, were so small and the sub-cell development so marked, that the number of reflexions in both cases was extremely small. The structure analyses, using the methods outlined in the preceding paper, are therefore not particularly accurate.

The structure of $W_3Nb_{14}O_{44}$

A minute needle 0·05 mm long and less than two microns in cross-section was picked from a specimen that had been heated to 1425 °C for four hours in a sealed platinum capsule and then quenched. The unit-cell dimensions are given in Table 1 with the remainder of the crystallographic constants. The systematically missing reflexions were characteristic of a body-centred

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unit cell and the absence of mirror planes, with the possible exception of one perpendicular to the fourfold axis, reduced the eight possible space groups to three, $I4$, $I\bar{4}$ and $I4/m$. Only 49 independent $hk0$ and 42 $hk1$ reflexions were recorded on prolonged multiple film exposures by the integrating Weissenberg technique with filtered copper radiation.

The orthogonal sub-cell of side 3·8 Å was inclined at angles of 29° and 119° to the a axis, and the few superlattice reflexions were difficult to index, except by plotting the Weissenberg data on to polar coordinates. Even then some ambiguities remained, which subsequently required reappraisal as the analysis proceeded.

The ideal model, which was constructed readily enough, contained octahedra joined by corners as in the ReO_3-type structure, and forming blocks 4×4 extending infinitely along the fourfold axis, with tetrahedral atoms at the junctions of adjacent blocks. This arrangement related the structure directly to that of tetragonal PNb_9O_{25} where the blocks were smaller, $3 \times 3 \times \infty$ (Roth, Wadsley & Andersson, 1965). The initial assumption that tungsten was present in the tetrahedral positions, with the remaining tungsten and all the niobium atoms statistically distributed over the octahedral sites, was subsequently confirmed. But the F_o Fourier projections on to (001) assuming the two-dimensional space group $p4$, raised considerable doubts. Although the octahedral metals and even some of the oxygen atoms were well-defined and of good shape, the tetrahedral tungsten had the appearance of a four-bladed airscrew, and the peak height at the 'hub' was not nearly large enough.

It was demonstrated elsewhere (Gatehouse & Wadsley, 1964) that the junction of four ReO_3-type blocks of the present kind consisted of four empty octahedral positions with the tetrahedron at the centre. It could be argued, therefore, that the irregular shape of this tungsten atom was due to its displacement towards one of these eightfold octahedral positions, the tetragonal symmetry of the phase being retained only because the movements in the four directions were all equally probable. This was disproved by subtracting the metals in several partial difference syntheses based upon the alternative models. The only projection giving oxygen atoms of good shape and with an acceptable background (Fig. 1) was based upon the original as-

Table 1. Crystallographic data for $W_3Nb_{14}O_{44}$ and $W_8Nb_{18}O_{69}$

Symmetry: tetragonal

		$W_3Nb_{14}O_{44}$	$W_8Nb_{18}O_{69}$
Unit-cell dimensions	a	21·02 Å	26·25 Å
	c	3·824 Å	3·813 Å

Systematically absent reflexions hkl with $h+k+l \neq 2n$
Possible space groups: $I4$ (No. 79), $I\bar{4}$ (No. 82), $I4/m$ (No. 87)

D_m	4·9±0·1 g.cm^{-3}	5·2±0·1 g.cm^{-3}
D_x	5·03 g.cm^{-3}	5·37 g.cm^{-3}
Z	2	2
μ	594 cm^{-1}	659 cm^{-1}

Table 2. Fractional atomic parameters for $W_3Nb_{14}O_{44}$

Space group $I\bar{4}$

Atom	Point position	x	y	z
W	2(c)	0	$\frac{1}{2}$	$\frac{1}{4}$
*B(1)	8(g)	0·0355	0·1237	0
B(2)	8(g)	0·1954	0·2132	0
B(3)	8(g)	0·2489	0·0552	0
B(4)	8(g)	0·3932	0·1270	$\frac{1}{2}$
O(1)	8(g)	0·0355	0·1237	$\frac{1}{2}$
O(2)	8(g)	0·0870	0·0441	0
O(3)	8(g)	0·1164	0·1800	0
O(4)	8(g)	0·2149	0·0077	0
O(5)	8(g)	0·2194	0·2357	$\frac{1}{2}$
O(6)	8(g)	0·2518	0·1417	0
O(7)	8(g)	0·3130	0·0789	$\frac{1}{2}$
O(8)	8(g)	0·3393	0·1959	$\frac{1}{2}$
O(9)	8(g)	0·3748	0·1070	0
O(10)	8(g)	0·4412	0·0383	$\frac{1}{2}$
O(11)	8(g)	0·4783	0·1564	$\frac{1}{2}$

*B represents a 'hybrid' metal atom $\frac{1}{8}(W+7Nb)$.
Average standard deviations for the metals $\sigma(x)=\sigma(y)=$ 0·0007; for oxygen $\sigma(x)=\sigma(y)=0·0060$.

Table 3. Observed and calculated structure factors for $W_3Nb_{14}O_{44}$ ($\times 10^{-1}$)

Observed data only.

h	k	l	F_o	$|F_c|$	h	k	l	F_o	$|F_c|$
10	0	0	27	30	22	5	1	25	29
12	0	0	74	67	3	6	1	18	21
11	1	0	33	34	9	6	1	61	56
13	1	0	55	52	21	6	1	26	39
25	1	0	36	37	0	7	1	18	22
4	2	0	40	41	2	7	1	50	50
14	2	0	20	22	8	7	1	22	24
24	2	0	26	33	1	8	1	19	22
5	3	0	114	124	3	8	1	34	32
17	3	0	59	58	15	8	1	64	49
4	4	0	37	27	7	10	1	87	89
6	4	0	28	28	17	10	1	20	19
8	4	0	25	20	19	10	1	54	50
3	5	0	16	24	20	11	1	21	19
7	5	0	24	21	0	13	1	39	38
9	5	0	105	99	12	13	1	61	57
2	6	0	12	19	4	15	1	89	89
10	6	0	76	72	16	15	1	45	45
22	6	0	54	56	17	16	1	37	30
3	7	0	29	26	9	18	1	60	54
7	7	0	26	15	2	19	1	29	40
9	7	0	34	38	12	19	1	22	19
2	8	0	81	80	1	20	1	49	45
8	8	0	37	37	13	20	1	35	40
14	8	0	68	69	14	21	1	33	24
1	9	0	29	29	7	22	1	29	33
5	9	0	16	14	0	23	1	21	17
7	9	0	47	47	6	23	1	37	34
15	9	0	32	28					
6	10	0	42	37					
8	10	0	18	21					
7	11	0	58	57					
19	11	0	61	60					
6	12	0	38	37					
12	12	0	49	47					
5	13	0	39	39					
11	13	0	31	34					
4	14	0	75	76					
5	15	0	47	43					
17	15	0	50	53					
4	16	0	22	24					
10	16	0	32	29					
16	16	0	29	36					
9	17	0	65	68					
1	19	0	46	45					
2	20	0	51	47					
14	20	0	63	71					
6	22	0	46	52					
7	23	0	26	24					
0	1	1	41	56					
2	1	1	47	36					
6	1	1	27	28					
12	1	1	65	76					
24	1	1	52	57					
3	2	1	43	33					
5	2	1	78	65					
11	2	1	23	25					
4	3	1	69	56					
6	3	1	15	16					
18	3	1	29	29					
17	4	1	35	37					
10	5	1	94	84					
20	5	1	28	24					

Table 4. *Interatomic distances for* $W_3Nb_{14}O_{44}$

Metal	Bonded oxygen atoms*					Distances in Å (Same order as in column 2)					O–O distances in Å			
											Average	Max.	Min.	Average
$B(1)$	1(2);	2,	2′,	4′,	3	1·91(2);	1·99,	1·84,	2·12,	2·07	1·97	2·92	2·66	2·79
$B(2)$	5(2);	5′,	6,	3,	8′	2·04(2);	2·09,	1·91,	1·80,	2·04	1·99	3·12	2·38	2·75
$B(3)$	7(2);	4,	6,	9,	11′	2·06(2);	1·78,	1·95,	2·18,	2·03	2·01	3·19	2·39	2·81
$B(4)$	9(2);	7,	8,	11,	10	2·00(2);	1·97,	1·84,	1·89,	2·12	1·97	3·08	2·39	2·75

* Given by numbers (Table 2, Fig. 3). 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 ±0·14 Å; for oxygen–oxygen 0·18 Å.

sumptions, and the one distorted peak in the F_0 projection was evidently a consequence of the limited number of observed data. This is discussed below.

After two F_o–F_c syntheses the R index for the $hk0$ reflexions dropped to 9·4% and further refinement was not considered. Two sets of hkl structure factors were then computed. The octahedral atoms in both were placed in the special planes at $z=0$ or $\frac{1}{2}$ given by the ideal model. In the first set the two tetrahedral W atoms were distributed over the $4(d)$ positions of the space group $I4/m$ $(0\ \frac{1}{4}\ \frac{1}{2})$, R being 12·5%. In the second these atoms were ordered in the $2(c)$ positions of the polar space group $I\bar{4}$, $(0\ \frac{1}{4}\ \frac{1}{2})$, for which R was 12·6%. Evidently the data are not sensitive enough to distinguish between the two possibilities. The parameters in Table 2 and the comparison between F_o and F_c which include an overall isotropic B of 0·3 Å^{-2} are given for $I\bar{4}$ (Table 3) while the bond lengths (Table 4) are the same for both space groups.

The structure of $W_8Nb_{18}O_{69}$

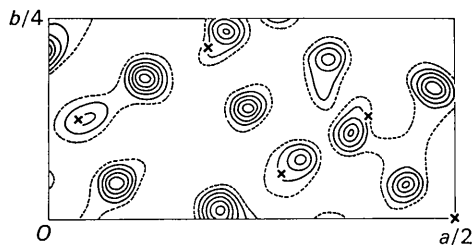The crystal, a small needle 0·03 mm long and about 2 microns thick, was selected from a specimen of the

Fig. 1. F_o-F_{metal} electron-density projection on to (001) for $W_3Nb_{14}O_{44}$; zero contours drawn as broken lines. The oxygen atoms, with the positions from which metals were extracted indicated by crosses.
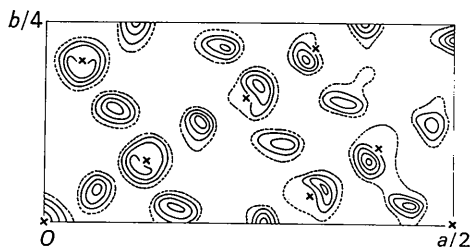

Fig. 2. F_o-F_{metal} electron-density projection on to (001) for $W_8Nb_{18}O_{69}$, showing the oxygen atoms; zero contours drawn as broken lines. The positions from which metals were extracted are indicated by crosses.

composition $9Nb_2O_5:8WO_3$ quenched from 1350 °C after heating for 18 hours in a sealed platinum tube. The crystallographic data are given in Table 1. The diffraction symmetry was identical with that of $W_3Nb_{14}O_{44}$, and the space groups were therefore limited once more to $I4$, $I\bar{4}$ or $I4/m$.

Only 47 independent $hk0$ reflexions were recorded on integrated Weissenberg films exposed with filtered copper radiation. Since there were 26 atoms in the asymmetric unit of the ideal structure, only three being in special positions, it was necessary to increase the number of data. The crystal was exposed again for two weeks, this time without integration, and an additional 27 weak $hk0$ reflexions were recorded. The two sets were then placed on the same scale.

The sub-cell was inclined at angles of 32° and 122° to the positive direction of the a axis. Since the body-centred tetragonal phases PNb_9O_{25} and $W_3Nb_{14}O_{44}$ contained blocks $3\times3\times\infty$ and $4\times4\times\infty$ respectively, the most logical ideal structure for $W_8Nb_{18}O_{69}$ would

Table 5. *Fractional atomic parameters for* $W_8Nb_{18}O_{69}$
Space group $I\bar{4}$

Atom	Point position	x	y	z
W	2(c)	0	$\frac{1}{2}$	$\frac{1}{4}$
*$B(1)$	2(a)	0	0	0
$B(2)$	8(g)	0·0448	0·2015	0
$B(3)$	8(g)	0·1230	0·0780	0
$B(4)$	8(g)	0·2474	0·1566	0
$B(5)$	8(g)	0·3259	0·0338	0
$B(6)$	8(g)	0·3308	0·2194	$\frac{1}{2}$
$B(7)$	8(g)	0·4092	0·0950	$\frac{1}{2}$
$O(1)$	2(b)	0	0	$\frac{1}{2}$
$O(2)$	8(g)	0·045	0·201	$\frac{1}{2}$
$O(3)$	8(g)	0·064	0·045	0
$O(4)$	8(g)	0·081	0·144	0
$O(5)$	8(g)	0·123	0·078	$\frac{1}{2}$
$O(6)$	8(g)	0·162	0·020	0
$O(7)$	8(g)	0·189	0·125	0
$O(8)$	8(g)	0·221	0·220	0
$O(9)$	8(g)	0·260	0·172	$\frac{1}{2}$
$O(10)$	8(g)	0·270	0·002	0
$O(11)$	8(g)	0·294	0·099	0
$O(12)$	8(g)	0·319	0·205	0
$O(13)$	8(g)	0·343	0·045	$\frac{1}{2}$
$O(14)$	8(g)	0·373	0·149	$\frac{1}{2}$
$O(15)$	8(g)	0·389	0·251	$\frac{1}{2}$
$O(16)$	8(g)	0·398	0·077	0
$O(17)$	8(g)	0·448	0·023	$\frac{1}{2}$
$O(18)$	8(g)	0·473	0·125	$\frac{1}{2}$

*B represents a 'hybrid' metal atom $\frac{1}{25}(7W+18Nb)$.
Average standard deviations for the metals $\sigma(x)=\sigma(y)=$ 0·0004; for oxygen $\sigma(x)=\sigma(y)=0·0040$.

Table 6. *Interatomic distances for* $W_8Nb_{18}O_{69}$

						Distances (Å)						O–O distances in Å			
Metal	Bonded oxygen atoms*					(same order as column 2)						Average	Max.	Min.	Average
B(1)	1(2);	3(4)				1·91(2);	2·05(4)					2·00	2·90	2·80	2·83
B(2)	2(2);	10′,	15′,	4,	6′	1·91(2);	2·18,	2·14,	1·78,	1·99		1·99	3·02	2·60	2·81
B(3)	5(2);	4,	7,	6,	3	1·91(2);	2·05,	2·13,	1·83,	1·77		1·93	2·86	2·60	2·74
B(4)	9(2);	8,	12,	11,	7	1·98(2);	1·80,	2·27,	1·94,	1·74		1·95	2·94	2·50	2·73
B(5)	13(2);	11,	16,	18′,	10	1·98(2);	1·91,	2·21,	2·05,	1·69		1·97	2·86	2·53	2·75
B(6)	12(2);	8′,	15,	14,	9	1·97(2);	2·09,	1·74,	2·15,	2·24		2·03	3·03	2·50	2·81
B(7)	16(2);	14,	18,	17,	13	1·99(2);	1·71,	1·85,	2·15,	2·18		1·98	3·02	2·53	2·78

* Given by number (Table 5, Fig. 4). The first, followed by (2), are the two oxygen atoms over and under the metal. E.s.d's of metal–oxygen distances are ±0·11 Å; for oxygen–oxygen 0·15 Å.

contain $5 \times 5 \times \infty$ blocks, packed in exactly the same way as the other two. This gave the correct formula and orientation. Rapid refinement was achieved by electron density projections on to (001) after shifting the atoms from their ideal positions to give realistic distances between the metals (Roth & Wadsley, 1965), and placing W at the tetrahedral sites, with the remaining W and the Nb disordered in the octahedral positions. The tetrahedrally coordinated atom was again very distorted, but the F_o–F_{metal} projection (Fig. 2) confirmed that this had no meaning in terms of

Table 7. *Observed and calculated structure factors for*
$W_8Nb_{18}O_{69}$ ($\times 10^{-1}$)
Unobserved data omitted

h	k	l	F_o	$|F_c|$		h	k	l	F_o	$|F_c|$		h	k	l	F_o	$|F_c|$
10	0	0	20	14		3	19	0	31	34		26	9	1	49	65
12	0	0	35	38		5	19	0	83	80		28	9	1	21	15
24	0	0	84	81		4	20	0	45	43		1	10	1	42	28
7	1	0	15	10		20	20	0	73	80		3	10	1	64	49
9	1	0	15	15		19	21	0	60	64		9	10	1	21	22
11	1	0	15	16		10	22	0	108	123		13	10	1	23	24
13	1	0	52	41		1	23	0	24	27		17	10	1	34	45
15	1	0	152	134		1	25	0	63	84		27	10	1	32	24
23	1	0	24	34		16	26	0	108	117		4	11	1	26	26
2	2	0	17	22		6	28	0	98	95		8	11	1	17	19
4	2	0	28	27		7	29	0	54	41		18	11	1	89	87
14	2	0	55	49		1	0	1	106	95		26	11	1	24	18
16	2	0	100	81		9	0	1	34	27		5	12	1	17	19
3	3	0	24	21		17	0	1	17	20		9	12	1	20	19
5	3	0	81	73		25	0	1	82	78		17	12	1	38	40
7	3	0	16	10		2	1	1	81	51		19	12	1	25	32
17	3	0	35	33		8	1	1	34	33		6	13	1	20	16
31	3	0	58	70		16	1	1	65	62		8	13	1	125	149
4	4	0	20	17		24	1	1	27	21		20	13	1	22	26
6	4	0	220	214		26	1	1	15	21		22	13	1	26	18
30	4	0	52	57		1	2	1	17	18		24	13	1	29	34
5	5	0	36	35		3	2	1	60	45		7	14	1	34	18
7	5	0	42	44		5	2	1	13	17		21	14	1	36	29
9	5	0	20	19		7	2	1	54	45		23	14	1	72	86
21	5	0	113	116		15	2	1	116	124		22	15	1	30	39
4	6	0	28	28		29	2	1	44	27		24	15	1	39	32
6	6	0	18	16		4	3	1	62	47		14	17	1	101	101
8	6	0	28	31		6	3	1	117	111		3	18	1	25	15
10	6	0	57	51		14	3	1	44	43		5	18	1	25	33
3	7	0	33	27		30	3	1	85	99		27	18	1	23	17
9	7	0	28	25		3	4	1	17	16		4	19	1	120	149
11	7	0	178	179		5	4	1	107	93		18	19	1	38	29
2	8	0	33	26		7	4	1	43	24		19	20	1	61	78
12	8	0	137	116		13	4	1	26	31		20	21	1	56	46
1	9	0	22	14		31	4	1	33	26		3	22	1	19	19
3	9	0	61	56		4	5	1	31	29		11	22	1	33	34
11	9	0	42	40		6	5	1	43	27		2	23	1	34	31
13	9	0	33	32		8	5	1	17	16		10	23	1	100	97
27	9	0	83	99		12	5	1	25	26		1	24	1	56	64
2	10	0	145	139		22	5	1	45	45		13	24	1	25	24
10	10	0	35	41		3	6	1	14	16		14	25	1	43	33
18	10	0	39	30		5	6	1	25	22		15	26	1	53	69
1	11	0	55	50		11	6	1	20	21		17	26	1	21	17
9	11	0	55	50		13	6	1	34	40		16	27	1	54	44
17	11	0	136	137		21	6	1	55	65		7	28	1	54	61
6	12	0	39	32		23	6	1	22	25		15	28	1	17	17
8	12	0	77	72		4	7	1	23	24		6	29	1	58	54
18	12	0	43	40		10	7	1	26	15		14	29	1	16	19
7	13	0	86	83		12	7	1	125	141		5	30	1	22	23
9	13	0	46	37		20	7	1	25	32		4	31	1	17	18
8	14	0	97	89		24	7	1	27	27		10	31	1	22	20
16	14	0	23	28		28	7	1	23	23		3	32	1	18	18
7	15	0	44	45		1	8	1	25	26						
15	15	0	33	35		3	8	1	35	29						
23	15	0	87	109		11	8	1	91	93						
6	16	0	42	45		13	8	1	24	30						
14	16	0	57	76		19	8	1	15	27						
3	17	0	35	34		25	8	1	43	33						
5	17	0	58	63		27	8	1	46	49						
13	17	0	57	72		2	9	1	101	94						
2	18	0	24	19		10	9	1	39	35						
4	18	0	124	123		14	9	1	22	28						
14	18	0	34	39		18	9	1	18	29						
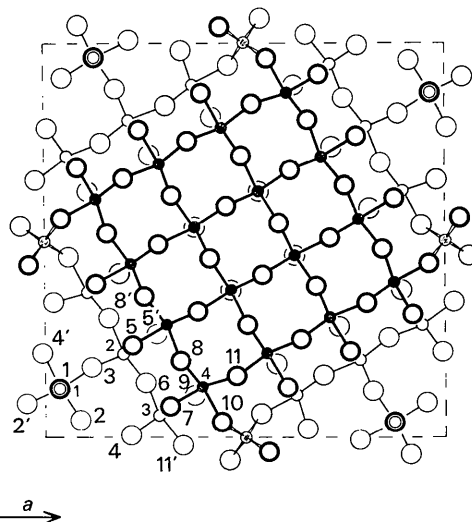
Fig. 3. Drawing of atom positions in $W_3Nb_{14}O_{44}$; small circles metals, larger circles oxygen. The tetrahedral W atoms are shaded.
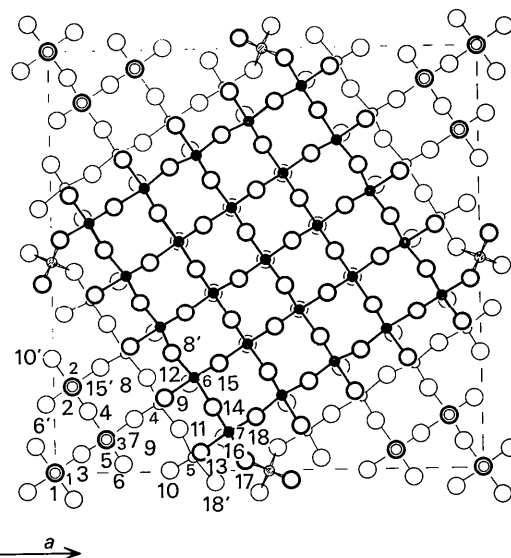
Fig. 4. Drawing of atom positions in $W_8Nb_{18}O_{69}$; small circles metals, larger circles oxygen. The tetrahedral W atoms are shaded.

physical displacements towards the neighbouring un-occupied octahedral positions. After two F_o–F_c syntheses R for the $hk0$ reflexions was 10·6%. The ambiguities of space group noted for $W_3Nb_{14}O_{44}$ apply equally to the present case for the same reasons. For the 104 observed $hk1$ data, R for $I\bar{4}$ was 16·0% and for $I4/m$ 17·8%. Parameters are listed in Table 5, bond lengths in Table 6, and F_o and F_c in Table 7 where the value for B (isotropic) is 0·3 Å^{-2}.

Discussion

The structures of the tetragonal phases are illustrated by Figs. 3 and 4. In projection, the octahedral metal atoms appearing at both levels form rows exactly parallel and at right angles to each other. These orthogonal groups, constituting the bulk of the scattering matter in both structures, are primarily responsible for the crystallographic sub-cell and contribute little or nothing to the remainder of the reflexions, most of which are below the observable limit. The tetrahedral tungsten atoms, on the other hand, are not collinear and interrupt each row at finite intervals; being in the special positions (0 ½ ¼) they contribute equally to all $hk0$ reflexions. Projections of electron density based

upon the observed data, therefore contain only a small fraction of them, and it is not surprising that the octahedral metals appeared as well shaped peaks, while the tetrahedral atoms, for which so much necessary information was missing, did not.

It is difficult to discuss variations of interatomic distance with any assurance as the standard deviations are so large. The tetrahedral dimensions are almost the same for both compounds, $1·76 \pm 0·12$ Å for the W–O distances and 106·0° and 113·3° for the O–W–O angles in $W_3Nb_{14}O_{44}$, and $1·77 \pm 0·14$ Å together with 106·7° and 115·3° for $W_8Nb_{18}O_{69}$. These can be compared with the W–O distances of $1·70 \pm 0·07$ Å for $WNb_{12}O_{33}$ and 1·76 and $1·85 \pm 0·07$ Å for $W_5Nb_{16}O_{55}$. The octahedra at the centres of the blocks, $B(1)$ for $W_3Nb_{14}O_{44}$ and $B(2)$ and $B(3)$ for $W_8Nb_{18}O_{69}$ appear to be no more regular than the others (Tables 4 and 6), but this may simply be a consequence of the large uncertainties. In all other respects the dimensions appear to be normal.

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Multiple Phase Formation in the Binary System Nb_2O_5-WO_3.
IV. The Block Principle

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The four new phases found in the Nb_2O_5-WO_3 system each contain octahedral blocks of a specific size, joined in a manner which leaves tetrahedral positions for some of the metal atoms. The many ways in which logical structures containing blocks of octahedra can be devised are briefly discussed. These can all be summarized by a general formula containing several independent variables, representing the size of block and its mode of packing.

The niobium-tungsten mixed oxide phases

At the outset of this study (Roth & Wadsley, 1965*b*) an attempt was made to predict the compositions of previously unsuspected mixed-oxide phases of niobium and tungsten. These predictions were based upon certain relationships between a number of other niobates, from which it was supposed that structurally related homologues might exist in the Nb_2O_5-WO_3 compos-

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ition region. Although one and possibly two of these new phases were found, namely $WNb_{12}O_{33}$ and $WNb_{30}O_{78}$, there were three which did not fit exactly into this preconceived pattern. Their structures were nevertheless related in a logical way, and they are now discussed in this paper.

Each metal atom in the cubic ReO_3-type structure is in octahedral coordination with oxygen, and every oxygen atom is common to two metals. The three-dimensional structure, therefore, contains octahedra all sharing corners, and is conveniently pictured as a chessboard pattern of squares each representing an