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Multiple Phase Formation in the Binary System Nb_2O_5—WO_3
II. The Structure of the Monoclinic Phases $WNb_{12}O_{33}$ and $W_5Nb_{16}O_{55}$

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The unit-cell dimensions of $WNb_{12}O_{33}$ are $a=22{\cdot}37$, $b=3{\cdot}825$, $c=17{\cdot}87$ Å, $\beta=123{\cdot}6^\circ$, space group $C2$. The structure consists of ReO_3-type blocks of Nb–O octahedra three wide, four long, and infinite in the third direction, which are joined by sharing edges, and with tetrahedrally coordinated W atoms ordered at the junctions of every four blocks. $W_5Nb_{16}O_{55}$ has the dimensions $a=29{\cdot}79$, $b=3{\cdot}820$, $c=23{\cdot}08$ Å, $\beta=126{\cdot}5^\circ$ and the space group $C2$. It also contains octahedral blocks, but of a different size, four wide, five long and infinite along the third direction. These blocks are grouped as in $WNb_{12}O_{33}$, with W occupying similar tetrahedral positions. The structures of both were deduced by trial-and-error, and refined by two-dimensional Fourier methods.

Introduction

The preparation and identification of five phases in part of the equilibrium system Nb_2O_5–WO_3 was reported in the preceding paper (Roth & Wadsley, 1965*b*). Although the ideal structures of four of them in principle can be solved by geometrical reasoning, it is particularly important to examine each one in some detail, since there are potentially a very large number of related structures in the same composition range which might instead be adopted (see part IV of the present series, Roth & Wadsley, 1965*d*).

The ideal structure of a compound of this type contains perfectly regular metal–oxygen octahedra joined up by edge- or corner-sharing without irregularities or distortions of any kind. Refinement by crystallographic techniques must provide the proof, and requires at least partial solutions to three problems posed by this simplification:

(*a*) The real positions of the atoms.
(*b*) The way oxygen atoms are coordinated to the metals.
(*c*) The distribution of Nb and W over the metal positions, and in particular whether tetrahedrally coordinated atoms are ordered.

All four compounds contain an axis of symmetry 3·82 Å long corresponding to an octahedral body diagonal, and overlap is therefore limited to the oxygen atoms overlying the metal atoms with this particular coordination. The answers to these questions can be readily provided by two-dimensional methods of X-ray analysis, where the objectives are to establish these points beyond all reasonable doubt, rather than to attempt ultra-refinement which, for compounds of the present kind, poses many problems and may have little or no immediate significance.

The crystal structures of the two monoclinic compounds $WNb_{12}O_{33}$ and $W_5Nb_{16}O_{55}$ are described in this paper, and the two tetragonal compounds in part III (Roth & Wadsley, 1965*c*).

Experimental

Both compounds formed very small but well-shaped needles, with the crystallographic constants summarized in Table 1. The *h0l* and *h1l* intensity data for both were recorded with filtered copper radiation on multiple films by the integrating Weissenberg method, and measured with a standard scale. The crystals were about 0·1 mm long, but only 5 microns in the average cross-section, so that absorption corrections could be neglected. Scattering curves for Nb^{5+} were taken from the data of Thomas & Umeda (1957), W^{6+} from *Inter-*

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national Tables for X-ray Crystallography (1962), both corrected for dispersion, and O^{2-} from Suzuki (1960). Calculations were made on the C.S.I.R.O. Elliott 803 computer with programs written in machine code, which were kindly made available by Dr P. J. Wheatley and Dr F. Stephens, Monsanto Research S.A., Zürich, Switzerland.

Table 1. *Crystallographic data for* $WNb_{12}O_{33}$ *and* $W_5Nb_{16}O_{55}$

Symmetry: monoclinic

		$WNb_{12}O_{33}$	$W_5Nb_{16}O_{55}$
Unit-cell dimensions	a	22·37 Å	29·79 Å
	b	3·825	3·820
	c	17·87	23·08
	β	123·6°	126·5°

Systematically absent reflexions: hkl with $h+k\neq 2n$

Possible space groups: $C2$(No. 5), Cm(No. 8), $C2/m$(No. 12)

	$WNb_{12}O_{33}$	$W_5Nb_{16}O_{55}$
D_m	$4·7\pm 0·1$ g.cm^{-3}	$5·0\pm 0·1$ g.cm^{-3}
D_x	4·76 g.cm^{-3}	5·17 g.cm^{-3}
Z	2	2
μ	543 cm^{-1}	623 cm^{-1}

Method of structure determination

For each compound the reflexions of measurable intensity were only a fraction of the whole, but contained a strongly developed cubic sub-cell of side 3·8 Å common also to many of the high temperature niobium oxide phases. Instead of attempting to find the positions of individual atoms *ab initio*, it is more practicable to assume that octahedra are joined by corners into finite sized blocks as in the ReO_3-type structure, to find how big the blocks are and how they unite to form the ideal arrangement. The orientation of the blocks is determined by the sub-cell, while the way they are joined must give a unit cell with the correct size and symmetry, containing the numbers of atoms which correspond as closely as possible to the experimentally determined composition and density (Gatehouse & Wadsley, 1964).

The positions of the atoms in the real structure are considerably different from the ideal ones. A safe rule is to place them 3·8 Å apart within a block, and 3·4 Å at the junctions of two blocks where octahedra share edges. Most of the phase angles will then be determined, and the structure can be refined by Fourier methods with the two-dimensional space group alternatives $p1$ or $p2$, one of which must be eliminated. Because the axis of symmetry is short, the octahedral atoms must either lie within, or else be very close to two planes perpendicular to it at $y=0$ and $\frac{1}{2}$. Since each compound has a considerable number of atoms in the asymmetric unit, it is a most difficult task to decide between the two possibilities by attempting to shift some or all of them by small amounts from the special positions along y. Formal solutions requiring complete three-dimensional data can undoubtedly be found by suitable refinement procedures, but it is debatable whether they have any real meaning (Cruickshank, Lynton & Barclay, 1962), and in any case will have little relevance in this study. Consequently upper level data are used solely to confirm each structure in three dimensions, *i.e.* whether an atom is at $y=0$, $\frac{1}{4}$ or $\frac{1}{2}$.

The structure of $WNb_{12}O_{33}$

The sub-cell axes were oriented at angles of 68° and 158° to the positive direction of the a axis of the side-centred unit cell. The hypothetical number $n=4$ of the series $B_{3n+1}O_{8n+1}$, related in structure to PNb_9O_{25}, had been expected at the composition $WNb_{12}O_{33}$ ($=B_{13}O_{33}$, Roth & Wadsley, 1965*b*), and the predicted orientation of the sub-cell as well as the size and symmetry of the unit cell were exactly confirmed. The ideal structure most likely contained $3\times 4\times\infty$ blocks, not $3\times 3\times\infty$ as in PNb_9O_{25} (Roth, Wadsley & Andersson, 1965), with edges common to similar blocks on all four sides transposed $b/2$ upwards, and with tetrahedrally coordinated metals at the junctions.

The atoms were moved from their ideal positions to those they were likely to adopt in the real structure, and refined by F_o Fourier projections on to (010) in the two-dimensional space group $p2$, the symmetry present in the trial model. The best agreement between F_o and F_c was obtained by placing tungsten at the origin and the niobium atoms in the octahedral positions, in contrast to the titanoniobates $TiNb_2O_7$, $Ti_2Nb_{10}O_{29}$ (Wadsley, 1961*a*, 1961*b*) and $TiNb_{24}O_{62}$ (Roth & Wadsley, 1965*a*) where the two metals Ti and Nb were disordered. Refinement continued with two oxygen-only syntheses (Fig. 1) and finally with two

Table 2. *Fractional atomic parameters for* $WNb_{12}O_{33}$

Space group $C2$

Atom	Point position	x	y	z
W	2(*a*)	0	$\frac{1}{4}$	0
Nb(1)	4(*c*)	0·3663	0	0·0423
Nb(2)	4(*c*)	0·2475	0	0·1358
Nb(3)	4(*c*)	0·1282	0	0·2298
Nb(4)	4(*c*)	0·4165	0	0·3793
Nb(5)	4(*c*)	0·2957	0	0·4715
Nb(6)	4(*c*)	0·4619	0	0·7122
O(1)	2(*b*)	0	$\frac{1}{2}$	$\frac{1}{2}$
O(2)	4(*c*)	0·1573	0	0·0147
O(3)	4(*c*)	0·3051	0	0·0836
O(4)	4(*c*)	0·0324	0	0·0937
O(5)	4(*c*)	0·4554	0	0·1583
O(6)	4(*c*)	0·1836	0	0·1789
O(7)	4(*c*)	0·0563	0	0·2569
O(8)	4(*c*)	0·3321	0	0·2572
O(9)	4(*c*)	0·4720	0	0·3247
O(10)	4(*c*)	0·2080	0	0·3498
O(11)	4(*c*)	0·3572	0	0·4294
O(12)	4(*c*)	0·2384	0	0·5188
O(13)	4(*c*)	0·3789	0	0·5937
O(14)	4(*c*)	0·0835	0	0·6207
O(15)	4(*c*)	0·4070	0	0·7570
O(16)	4(*c*)	0·2936	0	0·9217
O(17)	4(*c*)	0·4320	0	0·9867

The average standard deviations for the niobium atoms are $\sigma(x)=0·0002$, $\sigma(z)=0·0002$; for oxygen $\sigma(x)=0·0029$, $\sigma(z)=0·0036$.

F_o–F_c projections, the final factor for the $h0l$ terms being 13·1%, with an overall isotropic temperature factor B=0·3 Å^{-2}.

The oxygen atoms in Fig. 1 are clearly resolved, although O(2), O(7), O(12), O(15) and O(16) overlying some of the metals are rather elongated. An attempt was made to determine whether half an oxygen atom was present at both ends of each of these peaks, in effect introducing an anisotropic temperature factor. This raised the R index about 3% more than by assigning the atom positions to the peak centres, and was not considered any further.

Two sets of hll structure factors were then computed, with all of the atoms except for tetrahedral

Table 3. *Observed and calculated structure factors for* $WNb_{12}O_{33}$ ($X10^{-1}$)

h k l	F_o	$\lvert F_c\rvert$	h k l	F_o	$\lvert F_c\rvert$	h k l	F_o	$\lvert F_c\rvert$	h k l	F_o	$\lvert F_c\rvert$	h k l	F_o	$\lvert F_c\rvert$	h k l	F_o	$\lvert F_c\rvert$
0 0 2	26	30	6 0 $\bar{3}$	41	45	12 0 10	19	15	18 0 $\bar{19}$	30	29	3 1 $\bar{7}$	51	42	13 1 $\bar{4}$	23	29
0 0 3	25	32	6 0 $\bar{4}$	103	166*	12 0 11	16	13	18 0 $\bar{20}$	48	45	3 1 $\bar{8}$	28	33	13 1 $\bar{5}$	127	125
0 0 4	43	49	6 0 $\bar{6}$	13	24	12 0 $\bar{1}$	27	21	18 0 $\bar{21}$	60	45	3 1 $\bar{9}$	22	28	13 1 $\bar{9}$	37	44
0 0 5	15	17	6 0 $\bar{7}$	21	27	12 0 $\bar{2}$	26	26	20 0 1	17	16	3 1 $\bar{10}$	28	31	13 1 $\bar{16}$	27	27
0 0 6	12	14	6 0 $\bar{8}$	42	40	12 0 $\bar{3}$	21	24	20 0 $\bar{2}$	31	29	3 1 $\bar{15}$	22	22	13 1 $\bar{17}$	74	64
0 0 7	19	19	6 0 $\bar{10}$	15	18	12 0 $\bar{4}$	57	47	20 0 $\bar{3}$	43	35	3 1 $\bar{16}$	19	24	13 1 $\bar{18}$	26	19
0 0 8	63	66	6 0 $\bar{11}$	36	30	12 0 $\bar{5}$	58	61	20 0 $\bar{2}$	24	22	3 1 $\bar{17}$	38	33	15 1 2	20	29
0 0 12	38	31	6 0 $\bar{12}$	83	96	12 0 $\bar{6}$	46	52	20 0 $\bar{5}$	24	24	3 1 $\bar{18}$	56	62	15 1 6	41	31
0 0 13	44	43	6 0 $\bar{13}$	52	46	12 0 $\bar{7}$	49	49	20 0 $\bar{6}$	82	82	5 1 1	46	43	15 1 $\bar{2}$	113	135
0 0 17	27	20	6 0 $\bar{17}$	19	21	12 0 $\bar{8}$	82	101	20 0 $\bar{7}$	44	40	5 1 4	20	27	15 1 $\bar{3}$	26	34
2 0 0	6	12	6 0 $\bar{21}$	10	8	12 0 $\bar{10}$	23	20	20 0 $\bar{8}$	28	29	5 1 5	122	117	15 1 $\bar{11}$	26	43
2 0 1	12	7	8 0 0	45	41	12 0 $\bar{11}$	24	25	20 0 $\bar{9}$	34	26	5 1 6	36	35	15 1 $\bar{12}$	19	31
2 0 2	45	50	8 0 1	39	40	12 0 $\bar{12}$	30	32	20 0 $\bar{14}$	34	31	5 1 7	24	33	15 1 $\bar{13}$	27	29
2 0 3	109	175*	8 0 2	44	52	12 0 $\bar{14}$	19	18	20 0 $\bar{15}$	20	21	5 1 9	47	38	15 1 $\bar{14}$	58	45
2 0 4	43	42	8 0 4	23	27	12 0 $\bar{15}$	39	31	20 0 $\bar{16}$	19	18	5 1 $\bar{2}$	28	31	15 1 $\bar{15}$	52	34
2 0 5	32	30	8 0 5	21	26	12 0 $\bar{16}$	60	62	20 0 $\bar{18}$	68	57	5 1 $\bar{3}$	97	88	15 1 $\bar{19}$	34	23
2 0 6	23	21	8 0 6	22	23	12 0 $\bar{17}$	60	49	20 0 $\bar{19}$	17	14	5 1 $\bar{4}$	91	89	17 1 0	48	57
2 0 7	56	57	8 0 7	27	26	14 0 0	18	19	22 0 0	14	14	5 1 $\bar{5}$	38	44	17 1 1	67	69
2 0 8	22	27	8 0 8	20	24	14 0 1	27	29	22 0 1	38	23	5 1 $\bar{6}$	32	35	17 1 5	21	25
2 0 9	17	20	8 0 9	28	26	14 0 2	27	29	22 0 $\bar{3}$	54	60	5 1 $\bar{7}$	32	34	17 1 $\bar{1}$	27	30
2 0 10	18	17	8 0 10	27	26	14 0 5	28	28	22 0 $\bar{4}$	26	21	5 1 $\bar{12}$	25	29	17 1 $\bar{4}$	19	29
2 0 11	57	55	8 0 11	70	74	14 0 6	27	29	22 0 $\bar{5}$	19	12	5 1 $\bar{16}$	88	80	17 1 $\bar{11}$	33	26
2 0 15	44	42	8 0 $\bar{1}$	29	46	14 0 7	64	53	22 0 $\bar{15}$	79	69	7 1 0	42	40	17 1 $\bar{12}$	88	68
2 0 16	16	19	8 0 $\bar{2}$	34	19	14 0 $\bar{1}$	28	25	22 0 $\bar{16}$	48	39	7 1 3	39	36	17 1 $\bar{16}$	43	33
2 0 $\bar{1}$	30	34	8 0 $\bar{4}$	19	23	14 0 $\bar{2}$	91	93	22 0 $\bar{17}$	21	22	7 1 4	27	34	17 1 $\bar{20}$	85	86
2 0 $\bar{3}$	7	12	8 0 $\bar{5}$	37	45	14 0 $\bar{3}$	56	60	22 0 $\bar{18}$	16	15	7 1 7	26	41	19 1 2	28	26
2 0 $\bar{4}$	15	23	8 0 $\bar{8}$	19	24	14 0 $\bar{4}$	52	49	22 0 $\bar{20}$	30	26	7 1 8	75	63	19 1 3	82	86
2 0 $\bar{5}$	35	49	8 0 $\bar{9}$	46	54	14 0 $\bar{5}$	74	73	22 0 $\bar{21}$	20	18	7 1 9	39	30	19 1 $\bar{5}$	20	41
2 0 $\bar{6}$	29	17	8 0 $\bar{10}$	75	73	14 0 $\bar{6}$	23	16	24 0 $\bar{12}$	51	37	7 1 10	33	35	19 1 $\bar{9}$	83	69
2 0 $\bar{8}$	19	6	8 0 $\bar{11}$	15	7	14 0 $\bar{7}$	16	19	24 0 $\bar{13}$	68	59	7 1 11	32	39	19 1 $\bar{13}$	44	39
2 0 $\bar{9}$	44	36	8 0 $\bar{14}$	46	49	14 0 $\bar{8}$	23	27	24 0 $\bar{14}$	30	25	7 1 $\bar{1}$	71	70	19 1 $\bar{17}$	57	59
2 0 $\bar{10}$	73	89	8 0 $\bar{18}$	23	23	14 0 $\bar{9}$	33	35	24 0 $\bar{15}$	17	13	7 1 $\bar{2}$	31	32	19 1 $\bar{18}$	48	37
2 0 $\bar{11}$	21	20	8 0 $\bar{21}$	17	14	14 0 $\bar{11}$	18	20	24 0 $\bar{17}$	34	29	7 1 $\bar{3}$	17	26	19 1 $\bar{19}$	22	24
2 0 $\bar{12}$	18	18	10 0 1	76	73	14 0 $\bar{12}$	22	24	24 0 $\bar{18}$	18	14	7 1 $\bar{4}$	17	25	19 1 $\bar{20}$	20	22
2 0 $\bar{14}$	34	37	10 0 2	68	71	14 0 $\bar{13}$	26	33	24 0 $\bar{19}$	13	10	7 1 $\bar{5}$	27	29	21 1 $\bar{6}$	85	69
2 0 $\bar{18}$	79	80	10 0 3	38	32	14 0 $\bar{14}$	64	56	26 0 $\bar{6}$	13	10	7 1 $\bar{13}$	123	137	21 1 $\bar{7}$	33	27
2 0 $\bar{19}$	18	15	10 0 4	31	25	14 0 $\bar{20}$	17	10	26 0 $\bar{9}$	15	15	9 1 2	104	112	21 1 $\bar{11}$	27	25
4 0 0	8	13	10 0 5	32	36	16 0 0	34	31	26 0 $\bar{10}$	82	81	9 1 6	27	33	21 1 $\bar{14}$	42	45
4 0 4	33	21	10 0 6	20	13	16 0 1	63	64	26 0 $\bar{11}$	22	19	9 1 10	70	68	21 1 $\bar{15}$	68	71
4 0 5	104	120	10 0 7	24	21	16 0 4	19	22	26 0 $\bar{12}$	15	13	9 1 11	33	33	21 1 $\bar{16}$	25	31
4 0 6	98	117	10 0 8	20	22	16 0 5	31	31	26 0 $\bar{14}$	21	26	9 1 12	20	16	21 1 $\bar{17}$	21	25
4 0 7	39	37	10 0 10	31	28	16 0 7	14	37	26 0 $\bar{15}$	14	11	9 1 $\bar{2}$	50	41	21 1 $\bar{18}$	22	25
4 0 8	24	23	10 0 11	23	25	16 0 8	28	26	26 0 $\bar{18}$	44	44	9 1 $\bar{6}$	30	32	21 1 $\bar{19}$	20	17
4 0 10	43	37	10 0 12	31	29	16 0 $\bar{1}$	27	24	28 0 $\bar{11}$	18	22	9 1 $\bar{8}$	20	31	23 1 $\bar{1}$	21	19
4 0 11	20	21	10 0 13	34	38	16 0 $\bar{2}$	42	40	28 0 $\bar{15}$	17	23	9 1 $\bar{9}$	40	39	23 1 $\bar{8}$	43	32
4 0 14	54	52	10 0 $\bar{1}$	17	16	16 0 $\bar{3}$	56	45	1 1 0	48	76	9 1 $\bar{10}$	105	108	23 1 $\bar{12}$	62	66
4 0 15	20	21	10 0 $\bar{2}$	23	24	16 0 $\bar{6}$	18	24	1 1 1	70	52	9 1 $\bar{11}$	65	58	23 1 $\bar{16}$	39	31
4 0 16	19	21	10 0 $\bar{3}$	22	10	16 0 $\bar{11}$	81	82	1 1 2	66	53	9 1 $\bar{15}$	28	30			
4 0 $\bar{1}$	17	20	10 0 $\bar{4}$	13	9	16 0 $\bar{12}$	27	29	1 1 3	84	79	9 1 $\bar{19}$	46	40			
4 0 [illegible]	[illegible]	[illegible]	10 0 $\bar{5}$	[illegible]	[illegible]	16 0 [illegible]	[illegible]	[illegible]	1 1 [illegible]	[illegible]	[illegible]	9 1 [illegible]	[illegible]	[illegible]			
4 0 $\bar{7}$	90	98	10 0 $\bar{6}$	29	28	16 0 $\bar{14}$	24	23	1 1 6	14	26	11 1 1	53	42			
4 0 $\bar{8}$	18	19	10 0 $\bar{7}$	108	122	16 0 $\bar{15}$	28	29	1 1 7	36	42	11 1 2	25	32			
4 0 $\bar{9}$	20	24	10 0 $\bar{9}$	15	13	16 0 $\bar{16}$	20	21	1 1 8	23	27	11 1 3	26	31			
4 0 $\bar{10}$	22	27	10 0 $\bar{10}$	19	17	16 0 $\bar{17}$	24	22	1 1 12	82	71	11 1 5	61	58			
4 0 $\bar{11}$	62	58	10 0 $\bar{11}$	67	73	16 0 $\bar{20}$	29	28	1 1 $\bar{1}$	129	91	11 1 9	25	33			
4 0 $\bar{12}$	18	19	10 0 $\bar{13}$	18	19	16 0 $\bar{21}$	25	23	1 1 $\bar{4}$	19	29	11 1 $\bar{3}$	26	31			
4 0 $\bar{14}$	20	23	10 0 $\bar{14}$	19	23	16 0 $\bar{22}$	36	26	1 1 $\bar{5}$	37	38	11 1 $\bar{5}$	20	29			
4 0 $\bar{15}$	77	81	10 0 $\bar{15}$	34	35	18 0 0	52	44	1 1 $\bar{9}$	110	123	11 1 $\bar{6}$	39	40			
4 0 $\bar{20}$	12	11	10 0 $\bar{18}$	33	26	18 0 4	56	55	3 1 2	92	90	11 1 $\bar{7}$	95	90			
6 0 1	25	32	10 0 $\bar{19}$	57	58	18 0 $\bar{5}$	19	17	3 1 3	24	27	11 1 $\bar{8}$	122	129			
6 0 2	17	23	10 0 $\bar{20}$	23	17	18 0 $\bar{8}$	47	36	3 1 4	18	25	11 1 $\bar{9}$	31	35			
6 0 3	13	17	12 0 0	23	17	18 0 $\bar{9}$	51	55	3 1 5	31	34	11 1 $\bar{12}$	31	40			
6 0 4	20	8	12 0 1	17	18	18 0 $\bar{10}$	39	40	3 1 6	90	94	11 1 $\bar{16}$	52	59			
6 0 8	79	82	12 0 2	18	19	18 0 $\bar{11}$	27	30	3 1 10	23	29	11 1 $\bar{20}$	58	44			
6 0 9	43	43	12 0 4	61	54	18 0 $\bar{12}$	34	31	3 1 13	33	28	13 1 3	24	23			
6 0 10	20	22	12 0 5	34	29	18 0 $\bar{13}$	20	19	3 1 14	59	63	13 1 4	34	24			
6 0 13	25	22	12 0 6	20	19	18 0 $\bar{14}$	20	23	3 1 15	55	48	13 1 5	27	25			
6 0 14	16	13	12 0 7	20	17	18 0 $\bar{15}$	20	21	3 1 $\bar{2}$	78	66	13 1 6	42	34			
6 0 $\bar{1}$	29	45	12 0 8	23	29	18 0 $\bar{17}$	33	29	3 1 $\bar{5}$	13	27	13 1 7	47	55			
6 0 $\bar{2}$	31	42	12 0 9	17	14	18 0 $\bar{18}$	26	25	3 1 $\bar{6}$	69	71	13 1 8	36	39			

Observed data only.
* Probably affected by extinction.

Table 4. *Interatomic distances for the octahedral* Nb *atoms in* $WNb_{12}O_{33}$

		Distances (Å)		O–O distances (Å)		
Metal	Bonded oxygen atoms*	(Same order as in column 2)	Average	Max.	Min.	Average
Nb(1)	2′(2); 16, 17, 5, 3	2·09(2); 1·85, 2·18, 1·92, 1·88	2·00	3·31	2·19	2·81
Nb(2)	16′(2); 2, 3, 8, 6	2·12(2); 1·98, 1·96, 1·94, 1·97	2·02	3·40	2·19	2·81
Nb(3)	15′(2); 4, 6, 10, 7	2·13(2); 2·18, 1·90, 1·88, 1·92	2·02	3·41	2·15	2·88
Nb(4)	14′(2); 8, 9, 1, 11	1·91(2); 1·94, 1·96, 1·92, 1·97	1·94	2·83	2·66	2·74
Nb(5)	12′(2); 10, 11, 13, 12	2·10(2); 1·97, 1·90, 1·93, 1·86	1·98	3·36	2·18	2·72
Nb(6)	7′(2); 5, 15, 13, 9	2·09(2); 2·01, 1·80, 1·89, 1·92	1·97	3·35	2·15	2·76

* Given by numbers only (Table 2, Fig. 2). The first, followed by (2) and a semicolon, are the two oxygen atoms lying over and under the metal. E.s.d's of metal–oxygen distances are ±0·07 Å, for oxygen–oxygen 0·09 Å.

tungsten placed in the special positions $y=0$ or $y=\frac{1}{2}$ given by the idealized model. In the first set the centrosymmetric space group $C2/m$ was assumed, with the two tetrahedral W distributed over the 4(*g*) positions $\pm(0, y, 0)$ with $y=\frac{1}{4}$ while in the second set they were placed in 2(*a*) for $C2$, $(0, y, 0)$ with $y=\frac{1}{4}$. The R index for the former was 17·0%, and for the latter 15·7%, favouring the ordered polar structure as in Nb_2O_5 (Gatehouse & Wadsley, 1964) and other related niobates. Fractional atomic parameters are given in Table 2, F_o and F_c in Table 3, and octahedral and tetrahedral bond distances in Tables 4 and 5. The positions of the atoms are illustrated in Fig. 2.

Table 5. *Tetrahedral interatomic distances and angles*

$WNb_{12}O_{33}$	
W–O(4)	1·70 ± 0·07 Å
W–O(17)	1·70 ± 0·07
O(4)–O(17′)	2·77 ± 0·09
O(4)–O(17)	2·75 ± 0·09
O(4)–O(4′)	2·83 ± 0·13
O(17)–O(17′)	2·81 ± 0·13
O(4)–W–O(17′)	108·1°
O(4)–W–O(17)	107·0
O(4)–W–O(4′)	111·7
O(17)–W–O(17′)	110·5

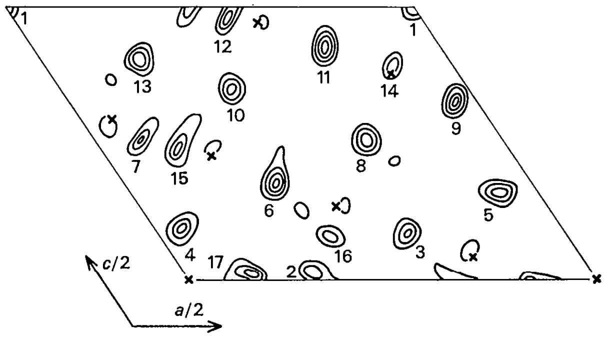

Fig. 1. $F_o - F_{\text{metal}}$ electron-density projection on to (010) for $WNb_{12}O_{33}$, zero contour omitted. The numbering of the oxygen atoms corresponds to Table 2. Crosses are the positions of the metals; some small shifts were still to be made.

The structure of $W_5Nb_{16}O_{55}$

The orthogonal sub-cell in this compound was oriented at angles of 74° and 164° to the *a* axis, the unit cell again being centred on (001). Although the axial dimensions were considerably larger than those of $WNb_{12}O_{33}$, the two structures were undoubtedly related, but not by any of the relationships expressed in part I (Roth & Wadsley, 1965*b*). The simplest guess was to increase the size of the blocks to $4\times5\times\infty$, which then were packed together in exactly the same way as the smaller blocks of $WNb_{12}O_{33}$, with tetrahedral atoms once more at the junctions. The sub-cell orientation, the unit-cell size and the chemical formula of this ideal model agreed perfectly with the experimentally determined values.

The number of W atoms in the formula greatly exceeded the number of tetrahedra, and the initial structure factor calculations assumed that W and Nb were disordered over all metal sites. It soon became clear that the model would refine to R values below 25% only if some or all of the metals were ordered. There are ten non-equivalent octahedrally coordinated metal atoms occupying general positions in the asymmetric unit and only one tetrahedral metal present at the origin in projection on to (010). The first F_o–F_{metal} synthesis showed negative regions around the octahedral positions and a large residual peak at the origin. If W is ordered in this latter position, then either the eight Nb and the remaining two W atoms have preferred octahedral sites of their own in a fully ordered structure, or they are disordered. Peak heights in F_o Fourier syntheses are not always able to resolve uncertainties of this kind when the number of observed data is only a fraction of the whole (Roth & Wadsley, 1965*d*). However, by placing W at the origin and disordering Nb and the remaining W to give simulated atoms (8Nb+2W)/10, an F_o–F_{metal} synthesis showed well-defined oxygen atoms (Fig. 3) with a good background in the neighbourhood of the metal positions. After two F_o–F_c projections R dropped to 12·3%. The shifts of all the atoms were then less than half the

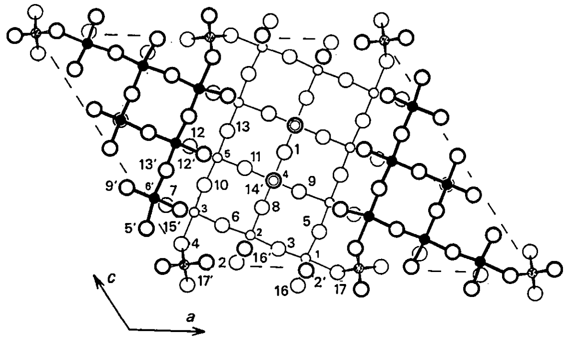

Fig. 2. Atom positions in $WNb_{12}O_{33}$, small circles Nb, larger circles oxygen. The lighter ones are at $y=0$, the heavier at $y=\frac{1}{2}$. The tetrahedral W is hatched.

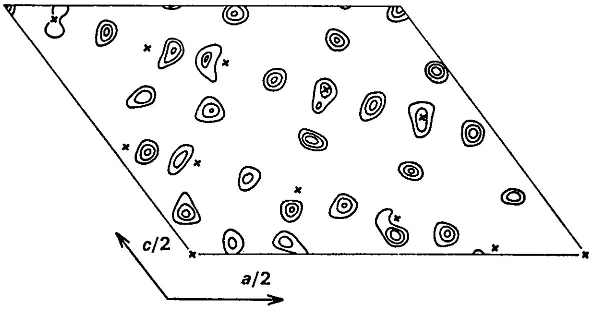

Fig. 3. The oxygen atoms in $W_5Nb_{16}O_{55}$, shown by an F_o-F_{metal} electron density projection on to (010), zero contour omitted. Crosses are the metal positions.

Table 6. *Fractional atomic parameters for* $W_5Nb_{16}O_{55}$, Space group *C*2

Atom	Point position	*x*	*y*	*z*
W(1)	2(*a*)	0	$\frac{1}{4}$	0
B(1)*	4(*c*)	0·3904	0	0·0152
B(2)	4(*c*)	0·2931	0	0·0732
B(3)	4(*c*)	0·1950	0	0·1298
B(4)	4(*c*)	0·0959	0	0·1864
B(5)	4(*c*)	0·4214	0	0·2747
B(6)	4(*c*)	0·3250	0	0·3311
B(7)	4(*c*)	0·2256	0	0·3868
B(8)	4(*c*)	0·4519	0	0·5277
B(9)	4(*c*)	0·3528	0	0·5855
B(10)	4(*c*)	0·4812	0	0·7839
O(1)	2(*b*)	0	$\frac{1}{2}$	$\frac{1}{2}$
O(2)	4(*c*)	0·1253	0	0·0200
O(3)	4(*c*)	0·3422	0	0·0403
O(4)	4(*c*)	0·0318	0	0·0792
O(5)	4(*c*)	0·2410	0	0·0979
O(6)	4(*c*)	0·4639	0	0·1152
O(7)	4(*c*)	0·1420	0	0·1508
O(8)	4(*c*)	0·3557	0	0·1651
O(9)	4(*c*)	0·0399	0	0·2035
O(10)	4(*c*)	0·2606	0	0·2281
O(11)	4(*c*)	0·4720	0	0·2452

Table 6 (*cont.*) Space roup *C*2

Atom	Point position	*x*	*y*	*z*
O(12)	4(*c*)	0·1591	0	0·2892
O(13)	4(*c*)	0·3725	0	0·3041
O(14)	4(*c*)	0·2686	0	0·3505
O(15)	4(*c*)	0·4840	0	0·3679
O(16)	4(*c*)	0·1695	0	0·4114
O(17)	4(*c*)	0·3867	0	0·4318
O(18)	4(*c*)	0·0481	0	0·4723
O(19)	4(*c*)	0·2790	0	0·4852
O(20)	4(*c*)	0·3965	0	0·5493
O(21)	4(*c*)	0·2976	0	0·6049
O(22)	4(*c*)	0·1750	0	0·6689
O(23)	4(*c*)	0·4114	0	0·6845
O(24)	4(*c*)	0·0786	0	0·7253
O(25)	4(*c*)	0·4298	0	0·8111
O(26)	4(*c*)	0·3301	0	0·9065
O(27)	4(*c*)	0·2217	0	0·9605
O(28)	4(*c*)	0·4383	0	0·9759

* *B* represents a 'hybrid' metal $\frac{1}{5}$ (W + 4Nb).

The average standard deviations for the metal atoms are $\sigma(x) = 0·0002$, $\sigma(z) = 0·0003$; for oxygen $\sigma(x) = 0·0018$, $\sigma(z) = 0·0023$.

Table 7. *Observed and calculated structure factors for* $W_5Nb_{16}O_{55}$ ($X10^{-1}$)
Observed data only

h k l	F_o	$\lvert F_c\rvert$
0 0 2	42	36
0 0 3	58	36
0 0 4	45	31
0 0 5	69	60
0 0 6	37	33
0 0 7	29	23
0 0 8	22	19
0 0 9	24	25
0 0 10	103	95
0 0 11	28	19
0 0 12	30	23
0 0 15	133	140
0 0 20	97	103
0 0 21	29	33
2 0 2	43	41
2 0 3	134	113
2 0 4	290	338
2 0 5	83	68
2 0 6	61	54
2 0 7	55	39
2 0 9	97	90
2 0 10	48	44
2 0 11	30	36
2 0 14	77	76
2 0 15	35	31
2 0 16	36	27
2 0 19	155	171
2 0 20	30	28
2 0 21	37	43
2 0 22	43	42
2 0 $\bar{4}$	19	18
2 0 $\bar{5}$	27	27
2 0 $\bar{6}$	65	65
2 0 $\bar{11}$	136	145
2 0 $\bar{12}$	68	68
2 0 $\bar{15}$	47	31
2 0 $\bar{16}$	98	91
2 0 $\bar{17}$	86	77
4 0 3	17	13
4 0 5	21	27
4 0 6	87	89
4 0 7	241	280
4 0 8	233	235
4 0 9	68	58
4 0 10	42	43
4 0 11	31	27
4 0 13	60	47
4 0 14	35	37
4 0 18	45	56
4 0 19	30	27
4 0 $\bar{1}$	17	16
4 0 $\bar{2}$	50	47
4 0 $\bar{3}$	27	35
4 0 $\bar{6}$	23	30
4 0 $\bar{7}$	57	62
4 0 $\bar{8}$	95	79
4 0 $\bar{10}$	23	23
4 0 $\bar{11}$	50	47
4 0 $\bar{12}$	120	103
4 0 $\bar{13}$	164	161
4 0 $\bar{14}$	30	31
4 0 $\bar{18}$	50	49
6 0 2	32	24
6 0 6	35	22
6 0 10	31	25
6 0 11	196	222
6 0 12	84	88
6 0 $\bar{1}$	15	24
6 0 $\bar{2}$	25	25
6 0 $\bar{3}$	47	41
6 0 $\bar{4}$	113	120
6 0 $\bar{9}$	204	200
6 0 $\bar{12}$	26	29
6 0 $\bar{14}$	93	93
6 0 $\bar{15}$	31	29
6 0 $\bar{19}$	71	81
6 0 $\bar{24}$	190	237
8 0 0	32	29
8 0 1	26	17
8 0 2	35	27
8 0 3	37	30
8 0 4	24	34
8 0 6	27	35
8 0 7	29	30
8 0 8	31	34
8 0 10	67	66
8 0 13	50	55
8 0 14	35	43
8 0 15	182	216
8 0 $\bar{1}$	56	46
8 0 $\bar{2}$	54	55
8 0 $\bar{3}$	53	52
8 0 $\bar{4}$	68	65
8 0 $\bar{5}$	278	324
8 0 $\bar{6}$	30	12
8 0 $\bar{8}$	34	34
8 0 $\bar{9}$	36	34
8 0 $\bar{10}$	78	68
8 0 $\bar{12}$	25	20
8 0 $\bar{13}$	27	31
8 0 $\bar{14}$	41	36
8 0 $\bar{15}$	105	113
8 0 $\bar{19}$	50	56
8 0 $\bar{20}$	175	203
10 0 0	78	66
10 0 1	68	68
10 0 2	79	70
10 0 3	84	76
10 0 5	40	39
10 0 6	52	34
10 0 7	44	38
10 0 8	33	32
10 0 9	48	38
10 0 10	50	38
10 0 11	36	35
10 0 14	82	87
10 0 15	44	37
10 0 16	40	49
10 0 17	65	76
10 0 18	57	93
10 0 $\bar{1}$	204	195
10 0 $\bar{2}$	104	85
10 0 $\bar{4}$	19	21
10 0 $\bar{5}$	33	23
10 0 $\bar{6}$	79	67
10 0 $\bar{7}$	28	13
10 0 $\bar{9}$	21	25
10 0 $\bar{10}$	32	26
10 0 $\bar{11}$	87	76
10 0 $\bar{14}$	28	31
10 0 $\bar{15}$	67	73
10 0 $\bar{16}$	189	208
10 0 $\bar{17}$	135	152
10 0 $\bar{18}$	34	22
10 0 $\bar{20}$	36	27
10 0 $\bar{21}$	36	47
10 0 $\bar{22}$	49	53
12 0 1	25	30
12 0 2	210	210
12 0 3	153	153
12 0 4	66	55
12 0 5	53	42
12 0 6	56	50
12 0 7	47	34
12 0 8	35	27
12 0 9	35	31
12 0 10	36	32
12 0 11	35	31
12 0 $\bar{2}$	32	15
12 0 $\bar{6}$	30	27
12 0 $\bar{7}$	57	59
12 0 $\bar{8}$	73	69
12 0 $\bar{11}$	35	38
12 0 $\bar{12}$	96	73
12 0 $\bar{13}$	202	203
12 0 $\bar{14}$	29	29
12 0 $\bar{16}$	31	34
12 0 $\bar{17}$	46	41
12 0 $\bar{18}$	96	95
14 0 1	40	26
14 0 6	168	179
14 0 7	61	57
14 0 10	50	31
14 0 $\bar{1}$	26	25
14 0 $\bar{2}$	25	23
14 0 $\bar{3}$	25	28
14 0 $\bar{4}$	54	41
14 0 $\bar{5}$	24	32
14 0 $\bar{6}$	23	25
14 0 $\bar{7}$	24	23
14 0 $\bar{8}$	24	28
14 0 $\bar{9}$	152	183
14 0 $\bar{10}$	43	20
14 0 $\bar{14}$	160	157
14 0 $\bar{19}$	35	37
14 0 $\bar{24}$	46	34
16 0 0	52	45
16 0 3	33	39
16 0 4	34	43
16 0 8	61	53
16 0 9	60	67
16 0 10	170	191
16 0 $\bar{1}$	58	54
16 0 $\bar{2}$	40	33
16 0 $\bar{3}$	27	23
16 0 $\bar{5}$	127	116
16 0 $\bar{6}$	143	122
16 0 $\bar{7}$	96	91
16 0 $\bar{8}$	77	75
16 0 $\bar{9}$	86	88
16 0 $\bar{10}$	219	217
16 0 $\bar{11}$	27	18
16 0 $\bar{12}$	28	20
16 0 $\bar{13}$	40	35
16 0 $\bar{14}$	42	38
16 0 $\bar{15}$	43	54
16 0 $\bar{18}$	34	36
16 0 $\bar{19}$	35	37
16 0 $\bar{20}$	50	45
16 0 $\bar{24}$	57	63
16 0 $\bar{25}$	125	151
16 0 $\bar{26}$	75	79
18 0 1	34	28
18 0 2	48	38
18 0 3	50	64
18 0 6	35	27
18 0 7	35	35
18 0 8	47	40
18 0 11	36	34
18 0 12	61	59
20 0 0	35	33
20 0 1	61	55
20 0 2	123	132
20 0 6	34	28
20 0 7	64	67
20 0 $\bar{1}$	48	41
20 0 $\bar{2}$	81	84
20 0 $\bar{3}$	149	163
20 0 $\bar{10}$	30	26
20 0 $\bar{11}$	30	20
20 0 $\bar{12}$	31	36
20 0 $\bar{15}$	32	39
20 0 $\bar{16}$	33	27
20 0 $\bar{17}$	48	35
20 0 $\bar{18}$	170	179
22 0 1	139	166
22 0 6	94	109
22 0 $\bar{4}$	39	30
22 0 $\bar{9}$	32	35
22 0 $\bar{14}$	210	220
22 0 $\bar{15}$	75	61
22 0 $\bar{16}$	48	38
22 0 $\bar{18}$	35	27
22 0 $\bar{19}$	61	56
24 0 3	45	47
24 0 4	73	81
24 0 5	150	149
24 0 $\bar{5}$	35	39
24 0 $\bar{6}$	35	44
24 0 $\bar{10}$	118	97
24 0 $\bar{11}$	132	136
24 0 $\bar{12}$	68	76
24 0 $\bar{13}$	59	50
24 0 $\bar{14}$	60	52
24 0 $\bar{15}$	85	75
24 0 $\bar{17}$	35	34
24 0 $\bar{18}$	36	30
24 0 $\bar{19}$	36	38
24 0 $\bar{21}$	35	51
24 0 $\bar{26}$	64	72
24 0 $\bar{27}$	37	42
24 0 $\bar{28}$	39	52
24 0 $\bar{29}$	59	76
26 0 3	47	52
26 0 $\bar{2}$	61	72
26 0 $\bar{6}$	62	57
26 0 $\bar{7}$	185	200
26 0 $\bar{8}$	71	81
26 0 $\bar{9}$	50	50
26 0 $\bar{10}$	61	51
26 0 $\bar{11}$	86	79
26 0 $\bar{13}$	35	37
26 0 $\bar{14}$	35	33
26 0 $\bar{15}$	35	34
26 0 $\bar{17}$	36	44
26 0 $\bar{18}$	36	26
26 0 $\bar{19}$	36	29
26 0 $\bar{20}$	35	27
26 0 $\bar{22}$	59	56
26 0 $\bar{23}$	33	46
26 0 $\bar{24}$	32	52
26 0 $\bar{25}$	60	75
26 0 $\bar{26}$	87	100
26 0 $\bar{27}$	130	154
28 0 2	83	78
28 0 $\bar{3}$	155	153
28 0 $\bar{4}$	34	32
28 0 $\bar{7}$	35	36
28 0 $\bar{8}$	50	58
28 0 $\bar{18}$	61	50
28 0 $\bar{23}$	187	197
1 1 0	138	81
1 1 1	138	81
1 1 2	111	70
1 1 3	103	76
1 1 4	182	140
1 1 5	70	51
1 1 9	48	64
1 1 18	53	58
1 1 19	91	128
1 1 $\bar{1}$	270	156
1 1 $\bar{5}$	36	44
1 1 $\bar{6}$	38	38
1 1 $\bar{16}$	149	156
3 1 3	221	174
3 1 4	60	40
3 1 7	39	43
3 1 8	40	43
3 1 $\bar{2}$	125	93
3 1 $\bar{7}$	47	53
3 1 $\bar{12}$	229	196
5 1 2	83	75
5 1 7	252	245
5 1 12	62	66
5 1 $\bar{3}$	111	90
5 1 $\bar{8}$	151	137
5 1 $\bar{9}$	109	75
7 1 1	60	45
7 1 5	42	49
7 1 6	50	60
7 1 10	61	76
7 1 11	140	145
7 1 $\bar{3}$	43	49
7 1 $\bar{4}$	159	153
7 1 $\bar{5}$	184	169
7 1 $\bar{6}$	69	68
7 1 $\bar{7}$	38	49
7 1 $\bar{8}$	40	44
7 1 $\bar{9}$	52	42
7 1 $\bar{20}$	55	51
7 1 $\bar{23}$	75	76
7 1 $\bar{24}$	66	108
9 1 0	79	42
9 1 4	69	78
9 1 14	120	154
9 1 15	48	66
9 1 $\bar{1}$	149	134
9 1 $\bar{2}$	47	55
9 1 $\bar{3}$	33	33
9 1 $\bar{5}$	38	35
9 1 $\bar{6}$	61	42
9 1 $\bar{21}$	165	168
11 1 3	212	201
11 1 $\bar{2}$	94	78
11 1 $\bar{17}$	227	263
13 1 2	101	105
13 1 7	100	92
13 1 $\bar{12}$	62	72
13 1 $\bar{13}$	185	201
13 1 $\bar{14}$	115	131
15 1 6	78	78
15 1 9	61	63
15 1 10	59	92
15 1 11	48	49
15 1 $\bar{8}$	48	71
15 1 $\bar{9}$	137	160
15 1 $\bar{10}$	227	251
15 1 $\bar{11}$	44	60
15 1 $\bar{20}$	45	61
15 1 $\bar{25}$	90	99
17 1 9	81	93
17 1 $\bar{6}$	211	257
17 1 $\bar{21}$	101	120
17 1 $\bar{26}$	90	83
19 1 2	211	272
19 1 $\bar{22}$	132	97
21 1 1	91	120
21 1 2	127	132
21 1 $\bar{14}$	52	74
21 1 $\bar{18}$	110	85
21 1 $\bar{19}$	101	79
23 1 4	47	60
23 1 5	139	172
23 1 $\bar{14}$	44	51
23 1 $\bar{15}$	172	144
23 1 $\bar{25}$	53	52
25 1 $\bar{11}$	155	155
25 1 $\bar{16}$	45	53
25 1 $\bar{21}$	61	70
25 1 $\bar{26}$	151	170
27 1 $\bar{7}$	148	15
27 1 $\bar{8}$	63	6
27 1 $\bar{17}$	63	65
27 1 $\bar{22}$	91	100
27 1 $\bar{23}$	87	88
29 1 $\bar{3}$	91	87
29 1 $\bar{4}$	95	102
29 1 $\bar{14}$	54	65
29 1 $\bar{18}$	61	68
29 1 $\bar{19}$	140	147
29 1 $\bar{23}$	52	45

Table 8. *Interatomic distances for the octahedral atoms B in* $W_5Nb_{16}O_{55}$

Metal	Bonded oxygen atoms*	Distances (Å)		O–O distances (Å)		
		(Same order as in column 2)	Average	Max.	Min.	Average
B(1)	2′(2); 26, 28, 6, 3	2·02(2); 2·04, 2·11, 2·03, 1·85	2·01	3·26	2·37	2·81
B(2)	27′(2); 27, 3, 8, 5	2·01(2); 2·17, 2·02, 1·81, 1·95	1·99	3·07	2·48	2·80
B(3)	26′(2); 2, 5, 10, 7	2·04(2); 2·12, 1·91, 1·92, 1·92	1·99	3·26	2·37	2·79
B(4)	25′(2); 4, 7, 12, 9	2·07(2); 2·04, 1·98, 1·97, 1·94	2·01	3·36	2·22	2·83
B(5)	24′(2); 8, 11, 15, 13	1·91(2); 2·09, 2·00, 1·83, 1·92	1·94	2·92	2·63	2·75
B(6)	22′(2); 10, 13, 17, 14	1·91(2); 1·98, 1·89, 1·93, 1·99	1·93	2·85	2·69	2·74
B(7)	21′(2); 12, 14, 19, 16	2·08(2); 1·93, 1·91, 1·84, 2·07	1·98	3·33	2·28	2·77
B(8)	18′(2); 15, 20, 17, 1	1·91(2); 1·99, 1·99, 1·89, 1·89	1·93	2·89	2·55	2·73
B(9)	16′(2); 12, 21, 19, 20	2·04(2); 1·88, 1·95, 2·03, 1·92	1·97	3·24	2·28	2·79
B(10)	9′(2); 6, 25, 23, 11	2·09(2); 1·89, 1·98, 1·98, 1·88	1·98	3·32	2·22	2·76

* Given by numbers only (Table 6, Fig. 4). The first, followed by (2) and a semicolon, are the two oxygen atoms lying over and under the metal *B*. E.s.d's of metal–oxygen distances are ±0·07 Å, for oxygen–oxygen 0·09 Å.

average estimated standard deviations, and would refine no further within the limits we have outlined. The alternative model was therefore not considered.

The *hll* data again favoured a polar structure, *R* for the space group *C*2 with W ordered in 2(*a*), (0, *y*, 0) with $y=\frac{1}{4}$ being 16·4%, while for *C*2/*m* with W statistically situated in 4(*g*), ±(0, *y*, 0) with $y=\frac{1}{4}$ it was 18·3%. Atomic parameters are given in Table 6, a comparison of F_o and F_c in Table 7, and bond distances in Tables 8 and 9, while the structure is illustrated by Fig. 4.

Table 9. *Tetrahedral interatomic distances and angles for* $W_5Nb_{16}O_{55}$

W–O(4)	1·76±0·07 Å
W–O(28)	1·85±0·07
O(4)–O(4′)	2·95±0·14
O(28)–O(28′)	3·17±0·14
O(4′)–O(28)	3·04±0·09
O(4)–O(28)	2·72±0·09
O(4)–W–O(28′)	96·8°
O(4)–W–O(28)	113·7
O(4)–W–O(4′)	112·9
O(28)–W–O(28′)	116·9

Discussion

We wish to stress the dual purpose of these structure analyses, firstly to confirm the building principles which are discussed with their implications in part IV of this series (Roth & Wadsley, 1965*d*), and secondly to derive the real positions of the atoms as well as the distribution of the metals.

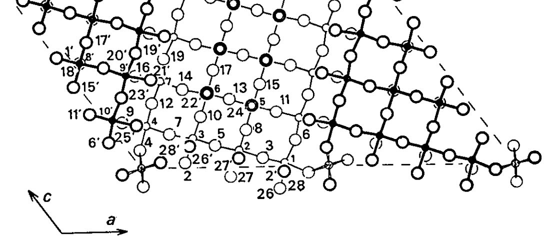

Fig. 4. Atom positions in $W_5Nb_{16}O_{55}$, small circles octahedral metals $\frac{1}{5}$(4Nb+W), larger circles oxygen. The lighter ones are at $y=0$, the heavier at $y=\frac{1}{2}$. The tetrahedral W is hatched.

In the ideal cases there are two distances between the octahedral metals. Within a block where corners are shared, they are separated by 3·8 Å, but when they are joined by edges to other blocks they are only 2·7 Å apart. Short distances of this order are possible only if there are metal-to-metal bonds, but are unlikely with Nb and W in their normal valency states. Departures from the ideal structure undoubtedly originate from the repulsion of these atoms, the 2·7 Å distance being increased to about 3·4 Å where there is then little likelihood of overlap between the orbitals of the adjacent metals. Within a block and between blocks, where there is a shear, the metals themselves form a remarkably regular group showing little or no departure from orthogonality, their linear extension being terminated only by the tetrahedral metals which are completely out of alignment.

In $WNb_{12}O_{33}$ the octahedron associated with Nb(4) is at the centre of the block, and is more nearly regular than the remainder. As each pair of metals at the edges are pushed apart, the two oxygens common to them are pulled together, resulting in normal metal–oxygen bonds but very short O(12)–O(12′), O(7)–O(15′) and O(2)–O(16′) distances of 2·18, 2·15 and 2·19, all ±0·09 Å. The elongation of the peaks corresponding to these atoms in the F_o–F_{metal} synthesis (Fig. 1) could have arisen from the presence of half an oxygen atom at each end, either statistical or ordered in the alternative space group *Cm*, just as much as through a grossly anisotropic temperature factor. This would give on an average rather more acceptable distances between these atoms, but was not confirmed by structure factor calculations.

In $W_5Nb_{16}O_{55}$ *B*(5), *B*(6) and *B*(8) are inside the blocks, and their octahedra are more nearly regular than the remainder (Fig. 4). The distances O(16)–O(21′), O(9)–O(25′), O(2)–O(26′) and O(27)–O(27′) are 2·28, 2·22, 2·37 and 2·48±0·09 Å respectively. Correspondingly short distances are not altogether rare in solid state compounds containing metal ions of Groups IV, V and VI, and have been discussed elsewhere (Gatehouse & Wadsley, 1964).

The tetrahedron in $WNb_{12}O_{33}$ is very nearly regular with four W–O bonds 1·70 ± 0·07 Å, while in $W_5Nb_{16}O_{55}$ there are two W–O bonds 1·76 Å as well as two of 1·85 ± 0·07 Å. They may be compared with values of 1·79 Å in $CaWO_4$ (Kay, Frazer & Almodovar, 1964) and 1·74 and 1·78 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 $a = 21{\cdot}02$, $c = 3{\cdot}824$ 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 $a = 26{\cdot}25$, $c = 3{\cdot}813$ 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 agreement 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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