the disorder would presumably have been concealed by errors in the molecular geometry and thermal motion.

The specimen material was prepared by Mr Y. Lupien of the Division of Pure Chemistry. Computations were carried out on the IBM 1620 computer under the supervision of Dr F. R. Ahmed, using his programs and those of Dr G. A. Mair and Mrs M. E. Pippy. Drs Brown and Wallwork were kind enough to allow study of their paper before publication. The assistance of those mentioned, and the continued encouragement of Dr W. H. Barnes, are gratefully acknowledged.

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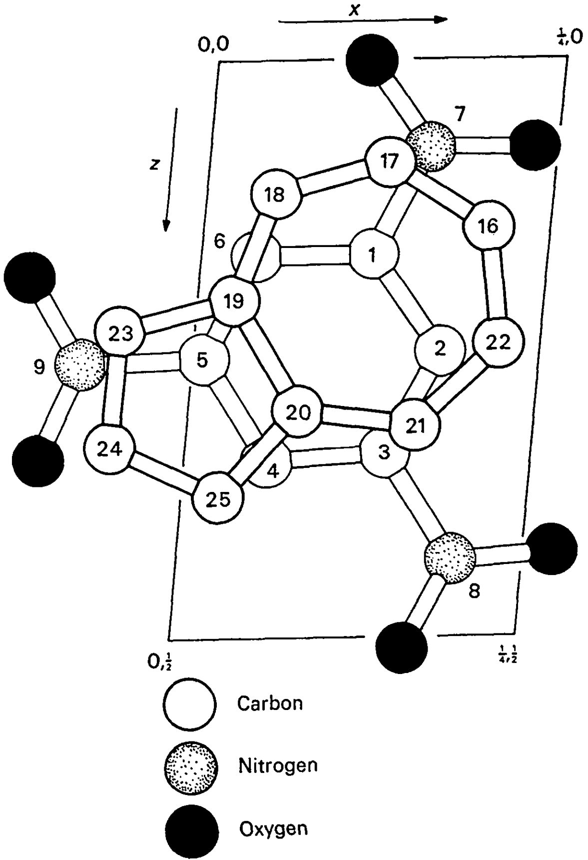

Fig. 7. Projection along **b** of the asymmetric unit, showing overlap.

Acta Cryst. (1965). **19**, 26

Multiple Phase Formation in the Binary System Nb_2O_5–WO_3.
I. Preparation and Identification of Phases

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(*Received* 26 *October* 1964)

An equilibrium study at 1300–1400°C of the system Nb_2O_5–$1Nb_2O_5:1WO_3$ led to the identification of five compounds in what had been previously reported as a region of solid solution. Three phases, $WNb_{30}O_{78}$, $WNb_{12}O_{33}$ and $W_5Nb_{16}O_{55}$ are monoclinic, while the remaining two, $W_3Nb_{14}O_{44}$ and $W_8Nb_{18}O_{69}$, are tetragonal. Each phase is characterized, and it is shown that the existence of not more than two of them could have been predicted by crystallochemical arguments.

Introduction

We have recently discussed the crystal chemistry of niobium pentoxide and the compounds, related to it, that are formed when elements with about the same ionic radii, and of the same or lower valency, are substituted for niobium (Roth & Wadsley, 1965*a*). The structures all contain metal–oxygen octahedra forming sub-units or blocks of the ReO_3-type, of finite sizes in two dimensions but infinite in the third, which condense upon themselves by edge-sharing in such a way

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that tetrahedrally coordinated atoms may, or may not, be present at the junctions. For each compound the repeat distance along the axis of symmetry is approximately 3·8 Å, and the blocks are centred about two equidistant levels in the unit cell perpendicular to it.

The six compounds whose structures have been reported can be classified into four groups.

Group A. $TiNb_2O_7$ contains blocks of octahedra $3 \times 3 \times \infty$ joined at both ends to similar blocks forming infinite ribbons. These appear at both levels and are joined by edge-sharing (Wadsley, 1961*a*). $Ti_2Nb_{10}O_{29}$ has an identical arrangement, but the blocks are larger, $3 \times 4 \times \infty$ (Wadsley, 1961*b*).

Group B. In Nb_2O_5 there are two sizes of block, $3 \times 5 \times \infty$ joined as in group *A* at one level, but cemented together by single $3 \times 4 \times \infty$ blocks at the other level, with tetrahedral metal atoms at the junctions. $Nb_{22}O_{54}$ is probably related to Nb_2O_5, but the blocks of which the ribbons are composed are $3 \times 4 \times \infty$, and the single units are $3 \times 3 \times \infty$ (Gatehouse & Wadsley, 1964).

Group C. $3 \times 4 \times \infty$ blocks are joined in pairs, appearing at both levels and with tetrahedral metals at the junctions in $TiNb_{24}O_{62}$ (Roth & Wadsley, 1965*a*).

Group D. In PNb_9O_{25} there are single $3 \times 3 \times \infty$ blocks at two levels with tetrahedral phosphorus atoms (Roth, Wadsley & Andersson, 1965).

The idea of structurally related 'homologous series' of reduced metal oxides (Magnéli, 1953) has been a particularly fruitful one. In binary systems BO_n–BO_{n-1}, where *B* is one of the elements Mo, W, or Ti, a particular series may consist of several members, and if the crystal structure of one is known, those of the remainder, in principle, can be deduced from their chemical composition. Conversely the unit-cell size of a member defines the position it adopts in a series, and its structural formula and chemical composition can thereby be established. The two compounds of group *A* are the members $n = 3$ and 4 of the series $B_{3n}O_{8n-3}$, and no other homologues have been reported. Those in group *B* form the series $B_{3n+1}O_{8n-2}$ which is limited to members where *n* is odd. Group *C*, containing only one compound, belongs to a potential series with the same formula as group *B* but where *n* is even. Finally a series $B_{3n+1}O_{8n+1}$ could possibly arise from compounds with structures related to PNb_9O_{25} of group *D*, *n* in this case being 3. Each series is derived from a parent phase B_3O_8, with a structure of the kind recently reported for Nb_3O_7F by Andersson (1964), which is broken up into the smaller units and then rearranged in these four characteristic ways. There is no simple formula containing only one variable that encompasses the six known compounds.

It appeared not unlikely that more homologues could belong to each group *B*, *C*, and *D*. The substitution of lower valency ions for Nb does not give any more phases other than those that are listed (Roth & Wadsley, 1965*a*), and the alternative, therefore, was to seek higher members of the series. These could possibly be synthesized by reacting Nb_2O_5 in the solid state with a hexavalent metal oxide, WO_3 or MoO_3, and some of the compounds that might be expected to form are given in Table 1. Their ideal structures can be derived geometrically from those already known from within the same group. The composition of each one is deduced from its particular formula, while the symmetry, space group, and close approximations to the unit-cell size are readily evaluated from the ideal model.

We have therefore examined the phase equilibria in a binary system where compound formation might be predictable. Although the approximate crystallographic data for any likely compound are known, the best possible powder diffraction patterns, used as the sole means of identification, can be misinterpreted. Where there is a sub-cell, there will be an overall similarity between the patterns of the various phases, irrespective of their composition; and where the unit cell is large and oblique, there will be difficulties in assigning the correct indices to the reflections. Optical methods of phase determination are of very little use in a system where the indices of refraction are very high, but may help in evaluating the extent of regions of homogeneity, if these exist. Consequently the use of single-crystal techniques is of the utmost importance as a phase-determining criterion, while crystal structure analysis provides the only satisfactory proof that each compound has the arrangement of atoms claimed for it.

A preliminary appraisal of the system Nb_2O_5–WO_3, dealt with here, forms the introduction to the three papers following immediately after. Five previously unknown compounds have been identified in the region Nb_2O_5–$Nb_2O_5 . WO_3$ at 1350 °C. The determination of the structures of four of them, two monoclinic and two tetragonal phases, is described in the two follow-

Table 1. *Possible compound formation in the system* Nb_2O_5–WO_3 (*below dotted line*)

$B_{3n+1}O_{8n-2}$						$B_{3n+1}O_{8n+1}$		
Group *B*, *n* odd			Group *C*, *n* even			Group *D*		
n	Formula	Composition	*n*	Formula	Composition	*n*	Formula	Composition
7	$B_{22}O_{54}$	$Nb_{22}O_{54}$						
9	$B_{28}O_{70}$	Nb_2O_5	8	$B_{25}O_{62}$	$TiO_2 . 12Nb_2O_5$	3	$B_{10}O_{25}$	PNb_9O_{25}
······	······	······	······	······	······	······	······	······
11	$B_{34}O_{86}$	$WO_3 . 8Nb_2O_5$	10	$B_{31}O_{78}$	$WO_3 . 15Nb_2O_5$	4	$B_{13}O_{33}$	$WO_3 . 6Nb_2O_5$
13	$B_{40}O_{102}$	$2WO_3 . 9Nb_2O_5$	12	$B_{37}O_{94}$	$3WO_3 . 17Nb_2O_5$	5	$B_{16}O_{41}$	$2WO_3 . 7Nb_2O_5$

ing papers, while the crystal chemistry of the whole group is discussed in the fourth (Roth & Wadsley, 1965*b*, *c*, *d*).

Previous work in the system Nb_2O_5–WO_3

Two previous attempts have been made to determine the phases in the system Nb_2O_5–WO_3. Goldschmidt (1960) surveyed a number of binary systems of Nb_2O_5 with other oxides, and concluded that more than 50 mol.% WO_3 could enter into solid solution with high-temperature Nb_2O_5. He also reported a phase at about 75 mol.% WO_3, $Nb_2O_5 . 3WO_3$, and a small amount of solid solution of Nb_2O_5 in WO_3. Kovba & Trunov (1962) considered that this compound was tetragonal with the lattice parameters $a=12\cdot19$ and $c=3\cdot934$ Å, and with a structure possibly related in some way to that of tetragonal tungsten bronze. Fiegel, Mohanty & Healy (1964) confirmed this compound, and suggested that two more were present at the compositions $3Nb_2O_5 . 2WO_3$ and $Nb_2O_5 . WO_3$. The first was formed above 1200 °C, the second was stable only at lower temperatures, and neither was prepared as a single phase. They reported that up to 33 mol.% WO_3 entered into solid solution with Nb_2O_5.

Experimental

The component oxides were weighed out to the nearest milligram in approximately one-gram batches to give the required composition, and then thoroughly mixed by hand in a pestle and mortar. A portion of each was sealed inside a small platinum capsule in order to eliminate volatilization of WO_3 upon heating, as well as to promote crystal growth. The tubes were heated in a platinum-wound vertical tube furnace, and either quenched by dropping into water, or annealed at some lower temperature.

X-ray powder diffraction patterns were taken with copper radiation on an accurately aligned Guinier-type focusing camera, internally calibrated with potassium chloride and where appropriate, single crystals were examined in a Weissenberg camera to establish the unit-cell size and space group. The approximate dimensions were then refined with the Guinier data, the complementary use of the two techniques having considerable merit in equilibrium studies of the present kind. Densities were measured with a torsion microbalance with toluene as the displaced liquid.

The results of the partial phase analysis are summarized in Table 2.

Table 2. *Experimental data for the system* Nb_2O_5–WO_3

Composition (mol ratio)		Heat treatment			Results
Nb_2O_5	WO_3	Temp. (°C)	Time (hr)	Cooling†	
30	1	1350	24	An	Nb_2O_5+15:1
15	1	1350	24	An	15:1
13	1	1350	24	An	15:1+'6:1'*
11	1	1350	24	An	15:1+'6:1'
8	1	1350	24	An	'6:1'
6	1	1350	24	An	6:1
17	3	1300	24	An	6:1
7	2	1300	24	An	6:1+7:3
		1400	18	Q	6:1+7:3
8	3	1300	24	An	6:1+7:3
7	3	1350	24	An	7:3
		1425	4	Q	7:3
		1500	1	Q	7:3 (melted)
8	5	1350	24	An	8:5
		1350	18	Q	8:5
3	2	1350	24	An	8:5+unidentified phase or phases
9	8	1350	24	An	9:8+unidentified phase or phases
		1350	18	Q	9:8
1	1	1100	72	Q	'1:1'
		1350	18	Q	9:8+'13:24'
10	11	1350	18	Q	9:8+'13:24'
11	15	1350	18	Q	9:8+'13:24'
12	19	1350	18	Q	'13:24'+9:8
13	24	1350	18	Q	'13:24'
14	29	1350	18	Q	'13:24'+'4:9'
3	7	1350	18	Q	'4:9'
16	41	1350	18	Q	'4:9'+'1:3'
17	48	1350	18	Q	'4:9'+'1:3'
1	3	1350	18	Q	'4:9'+'1:3'
19	63	1350	18	Q	'1:3'+'4:9'

† An=annealed at 1000°C for one to three days, Q=quenched by dropping from furnace into water.

* Ratio enclosed by quotation marks when the exact composition of the phase has not been established.

Description of phases

$WNb_{30}O_{78}$ ($15Nb_2O_5 . WO_3$)

A single phase $WNb_{30}O_{78}$, appearing at the predicted composition, is separated by two-phase regions from both Nb_2O_5 and $WNb_{12}O_{33}$. No measurable changes in the positions of lines in the Guinier patterns could be found, and it therefore cannot have more than a small region of homogeneity. It forms minute colorless monoclinic needles with the powder pattern given in Table 4, to which we could not give satisfactory indices.

If the phase is truly the member $n=10$ of the series $B_{3n+1}O_{8n-2}$, it will have the approximate unit-cell dimensions

$$a=39\cdot0,\ b=3\cdot82,\ c=21\cdot5\ \text{Å},\ \beta=91\cdot5$$

and the space group $C2$, Cm or $C2/m$.

We have shown elsewhere that $TiNb_{24}O_{62}$, $n=8$ of the same series, could be expected to have a dimorph where the ReO_3-type blocks are joined up in pairs in a different way (Roth & Wadsley, 1965*a*). This method of joining could also be adopted by the phase $WNb_{30}O_{78}$, and the unit cell would then be

$$a=22\cdot4,\ b=3\cdot82,\ c=38\cdot0\ \text{Å},\ \beta=106°,$$

with the same space group alternatives.

Several crystals were mounted, but in all cases the films could be interpreted only by assuming they were

Table 3. *Crystallographic data for compounds in the region* Nb_2O_5–$1Nb_2O_5:1WO_3$

Mol. ratio		Symmetry	Possible	Unit-cell dimensions in (Å)			
Nb_2O_5	WO_3		space groups	*a*	*b*	*c*	*β*
∞	–	Monoclinic	*P*2	21·16	3·822	19·35	119·8°
15	1	Monoclinic	—	—	—	—	
6	1	Monoclinic	*C*2/*m*, *C*2, *Cm*	22·37	3·825	17·87	123·6°
7	3	Tetragonal	*I*4/*m*, *I*4, $I\bar{4}$	21·02		3·824	
8	5	Monoclinic	*C*2/*m*, *C*2, *Cm*	29·79	3·820	23·08	126·5°
9	8	Tetragonal	*I*4/*m*, *I*4, $I\bar{4}$	26·25		3·813	

derived from two crystals, either a twin of the one structure, or an intergrowth of the dimorphs within the one crystal. This latter phenomenon was noted by Evans & Mrose (1960) for the case of structurally related vanadium minerals doloresite and montroseite, and is commonly found in sulphosalt minerals. In the present case an unambiguous decision between the two alternatives cannot be given from the material available, as the unit cells of both expected dimorphs are very large and not dissimilar, while the diffraction data provided by the crystal are scanty and dominated by the sub-cell reflexions.

We should point out that the zero level Weissenberg film, as well as the powder pattern, could be indexed with the unit cell

$$a=21{\cdot}62,\ b=3{\cdot}824,\ c=18{\cdot}77\ \text{Å},\ \beta=125{\cdot}8^\circ$$

if certain weak reflexions in both sets of data were ignored. For some time we believed this to be the true unit cell with a structure related to that of $WNb_{12}O_{33}$, but with excess metal atoms in the tetrahedral positions. This model did not refine, and the study was abandoned.

$WNb_{12}O_{33}$ ($6Nb_2O_5 . WO_3$)

Although the compositions ranging from 8:1 to 17:3 Nb_2O_5:WO_3 all showed a single phase with no detectable differences in the unit-cell dimensions, it is debatable whether the experimental techniques are good enough to classify this region as a solid solution.

This compound forms colorless monoclinic needles up to 0·04 mm long, providing single-crystal data of high quality. Unit-cell dimensions and indexed powder patterns are given in Tables 3 and 5. All of the evidence suggested that the compound was $WNb_{12}O_{33}$, the predicted homologue $n=4$ of the series $B_{3n+1}O_{8n+1}$, group *D*, which contains PNb_9O_{25} as the member $n=3$ (Table 1). This was subsequently confirmed by the structure analysis reported in the following paper (Roth & Wadsley, 1965*b*). The Guinier pattern was very much like that of $WNb_{30}O_{78}$, and if the films of preparations at the compositions 13:1 and 11:1 Nb_2O_5:WO_3 had not shown two sets of reflexions side by side, it would have been logical to assert that the two compounds were part of the same solid solution.

$W_3Nb_{14}O_{44}$ ($7Nb_2O_5 . 3WO_3$)

A single phase $W_3Nb_{14}O_{44}$ with no range of homogeneity was found at the composition $7Nb_2O_5 . 3WO_3$. It forms minute pale blue tetragonal needles averaging 20 microns long. The unit cell dimensions and powder pattern are given in Tables 3 and 6.

This compound is not a member of any of the homologous series in Table 1, and its structure is reported in the third paper of this group (Roth & Wadsley, 1965*c*). It should be noted that its composition corresponds to the end of the solid solution of WO_3 in Nb_2O_5 reported by Fiegel, Mohanty & Healy (1964).

$W_5Nb_{16}O_{55}$ ($8Nb_2O_5 . 5WO_3$)

The composition $3Nb_2O_5$:$2WO_3$ was found in the present study to consist of two phases (Table 2), and $8Nb_2O_5$:$5WO_3$, separated from this by less than 2 mol.%, was essentially a single phase, consisting of well-formed blue needles up to 0·1 mm long.

Table 4. *Unindexed powder pattern of* $15Nb_2O_5 . WO_3$

I(obs)	$\sin^2\theta$ (obs)
w	0·00509
vw	0·01500
ms	0·02288
m	0·02747
vs	0·04242
vw	0·04300
s	0·04492
vw	0·04531
w	0·04699
w	0·04814
s	0·04862
m	0·05274
w	0·05877

Table 5. *Powder pattern of* $WNb_{12}O_{33}$ ($6Nb_2O_5 . WO_3$), Cu $K\alpha_1$

I(obs)	$\sin^2\theta$ (obs)	$\sin^2\theta$ (calc)	*hkl*
m	0·00268	0·00268	001
m	0·00478	0·00478	$20\bar{1}$
vw	0·01073	0·01076	002
w	0·01922	0·01916	$40\bar{2}$
mw	0·02326	0·02313	$40\bar{3}$
vw	0·02423	0·02421	003
mw	0·02706	0·02708	202
ms	0·04219	0·04225	110
ms	0·04254	0·04256	$11\bar{1}$
w	0·04318	0·04304 0·04311	004 $60\bar{3}$
vw	0·04397	0·04388	$60\bar{2}$
s	0·04526	0·04527	203
mw	0·04726	0·04730	111
s	0·04802	0·04772	$60\bar{4}$
vw	0·05011	0·05002 0·05014	$60\bar{1}$ $20\bar{5}$
m	0·05249	0·05247	$31\bar{2}$
mw	0·05772	0·05775	112

Table 6. *Powder pattern of* $W_3Nb_{14}O_{44}$ ($7Nb_2O_5 . 3WO_3$), Cu $K\alpha_1$

I(obs)	$\sin^2\theta$ (obs)	$\sin^2\theta$ (calc)	*hkl*
m	0·00267	0·00269	110
m	0·01074	0·01075	220
w	0·01339	0·01343	310
mw	0·02417	0·02418	330
s	0·02686	0·02687	420
vs	0·04189	0·04192	101
m	0·04302	0·04299	440
vvs	0·04576	0·04568	530
w	0·04827	0·04836	600
m	0·05801	0·05804	321
vw	0·06716	0·06717	710
w	0·06997	0·06986	640
s	0·07422	0·07416	501
w	0·07803	0·07792	730
s	0·07948	0·07954	521
w	0·09029	0·09028	611
ms	0·09145	0·09135	820
w	0·09571	0·09566	541
w	0·10104	0·10103	631
m	0·11189	0·11178	721
ms	0·14263	0·14240	950
ms	0·16238	0·16231	020

Part of its Guinier powder pattern is given in Table 7. The unit cell is large and oblique (Table 3), and it would have been well nigh impossible to index the pattern unambiguously if good single-crystal films had not been available for cross-reference. The powder pattern, furthermore, could have been dismissed as a mixture of the two adjacent phases if no attempt had been made to examine single crystals. The compound does not belong to any of the predicted series of compounds, and its structure is reported in the following paper (Roth & Wadsley, 1965*b*).

Table 7. *Powder pattern of* $W_5Nb_{16}O_{55}$ ($8Nb_2O_5 . 5WO_3$), Cu $K\alpha_1$

I(obs)	$\sin^2\theta$ (obs)	$\sin^2\theta$ (calc)	*hkl*
mw	0·00266	0·00268	$20\bar{1}$
vvw	0·00687	0·00689	002
m	0·01073	0·01079	$40\bar{2}$
vw	0·01305	0·01303	$40\bar{3}$
vvw	0·01540	0·01551	003
vvw	0·01702	0·01739	202
mw	0·02427	0·02417	$60\bar{3}$
ms	0·02688	0·02670	$60\bar{4}$
mw	0·02911	0·02918	203
vvs	0·04184	0·04169 0·04182	110 $11\bar{1}$
w	0·04307	0·04296 0·04308	$80\bar{4}$ 005
s	0·04441	0·04442	204
mw	0·04505	0·04500	111
vs	0·04576	0·04576	$80\bar{5}$
m	0·05006	0·04997	310
m	0·05824	0·05820	$51\bar{3}$

$W_8Nb_{18}O_{69}$ ($9Nb_2O_5 . 8WO_3$)

The composition $9Nb_2O_5 . 8WO_3$ was found to be single phase when quenched from 1350 °C, but underwent a polymorphic change, or decomposed to some other phases that are as yet unidentified, when annealed for three days at 1000 °C. Its unit-cell dimensions and powder pattern are given in Tables 3 and 8.

Table 8. *Powder pattern of* $W_8Nb_{18}O_{69}$ ($9Nb_2O_5 . 8WO_3$), Cu $K\alpha_1$

I(obs)	$\sin^2\theta$ (obs)	$\sin^2\theta$ (calc)	*hkl*
vw	0·00688	0·00689	220
vw	0·01548	0·01550	330
w	0·01715	0·01722	420
m	0·02927	0·02927	530
s	0·04169	0·04166	101
vw	0·04305	0·04305	710
vs	0·04477	0·04472	640
w	0·04510	0·04511	211
w	0·05199	0·05199	321
vw	0·05859	0·05855	820
w	0·06220	0·06199 0·06233	660 501
m	0·07603	0·07610	541
vw	0·07743	0·07749	930
ms	0·07945	0·07955	631
vw	0·08642	0·08643	721
mw	0·08947	0·08954	10,2,0

This high-temperature compound crystallizes as small dark green tetragonal needles, turning yellow after several months, and like the two preceding phases its structure was not predictable with the original assumptions prompting this study. It has now been determined, and is reported together with that of $W_3Nb_{14}O_{44}$ (Roth & Wadsley, 1965*c*).

Additional phases in the system Nb_2O_5–WO_3

All of the previous workers have agreed upon the composition of tetragonal $Nb_2O_5 . 3WO_3$, although Mohanty & Fiegel (1964) reported that single-crystal patterns contained superstructure reflexions differing from one crystal to the next. We found three and possibly four phases in the composition region 65–80 mol.% WO_3. The Guinier patterns were remarkably similar to each other as well as to that reported for Nb_2O_5:$3WO_3$, but none of them indexed satisfactorily with the reported lattice parameters. Single crystals have not yet been examined, and therefore no assignments of unit cell size and symmetry are included in this paper.

The compositions at which the phases are found are approximately $13Nb_2O_5$:$24WO_3$, $4Nb_2O_5$:$9WO_3$, while the third is richer in tungsten than Nb_2O_5:$3WO_3$. The three preparations are characterized simply enough by striking colour differences between them; the first is cream, the second which is dark grey contains two phases, colourless and black, while the third is bright yellow. The crystal structure determination of these compounds may prove to be the only satisfactory way of deciding their chemical formulae, and this is now being examined by one of us (A.D.W.).

Most of the preparations have been confined to the interval 1300–1400 °C. The formation at 1100 °C of the compound at or near $Nb_2O_5 . WO_3$ was confirmed, but it did not have the B_3O_8 structure that is the progenitor of the phases in Table 1, and the examination was taken no further. A more comprehensive phase equilibrium study will be reported in due course by R.S.R.

Discussion

The results of the present partial phase equilibrium diagram together with the relevant parts of the two previous studies by Goldschmidt (1960) and by Fiegel *et al.* (1964) are represented in Fig. 1. The differences between them may be due to different methods of preparation. It is important to emphasize that reactions in the solid state at high temperatures, where one or more of the components is volatile, must be conducted in a sealed system in order to maintain the composition. The inconsistencies may also be due to different interpretations of the same diffraction data, where we have emphasized the need for the use of single-crystal techniques. The failure on our part to solve the problems posed by the compound $WNb_{30}O_{78}$ shows that the value of even these techniques is uncertain when the crystals themselves are poor. Although likely guesses of structure are made readily enough, the initial problems of assigning the correct unit cell prove embarrassingly difficult in cases where twins or intergrown crystals of two different structures are formed under the experimental conditions. It is little wonder, therefore, that systems such as this are called 'solid solutions' in a normal phase-equilibrium diagram.

Solid solutions of WO_3 in Nb_2O_5 would give a defect structure, either $(Nb_{2-x}W_x)O_{5+\frac{1}{2}x}$ requiring excess oxygen, or $(Nb_{2-6/5x}W_x \text{vac}\, ^1/_{5x})O_5$ with vacated metal positions. Needless to say this is not confirmed by the present study, where each new phase at the most can have only a very small range of homogeneity. Where equilibrium conditions are established, the widely held concepts of extensive regions of homogeneity in phase systems, whether they are called solid solutions or nonstoichiometric compounds, may in general be incorrect (Wadsley, 1964). The attempted prediction of phases on the other hand was only partly successful, and modifications to the ideas leading up to the present study will conclude this present group of papers (Roth & Wadsley, 1965*d*).

We should like to thank J. W. Asker and W. F. Donovan for their help with the experimental work, and L. J. Fiegel of the A. O. Smith Corporation, Wisconsin, U.S.A., for a preprint of his phase equilibria paper.

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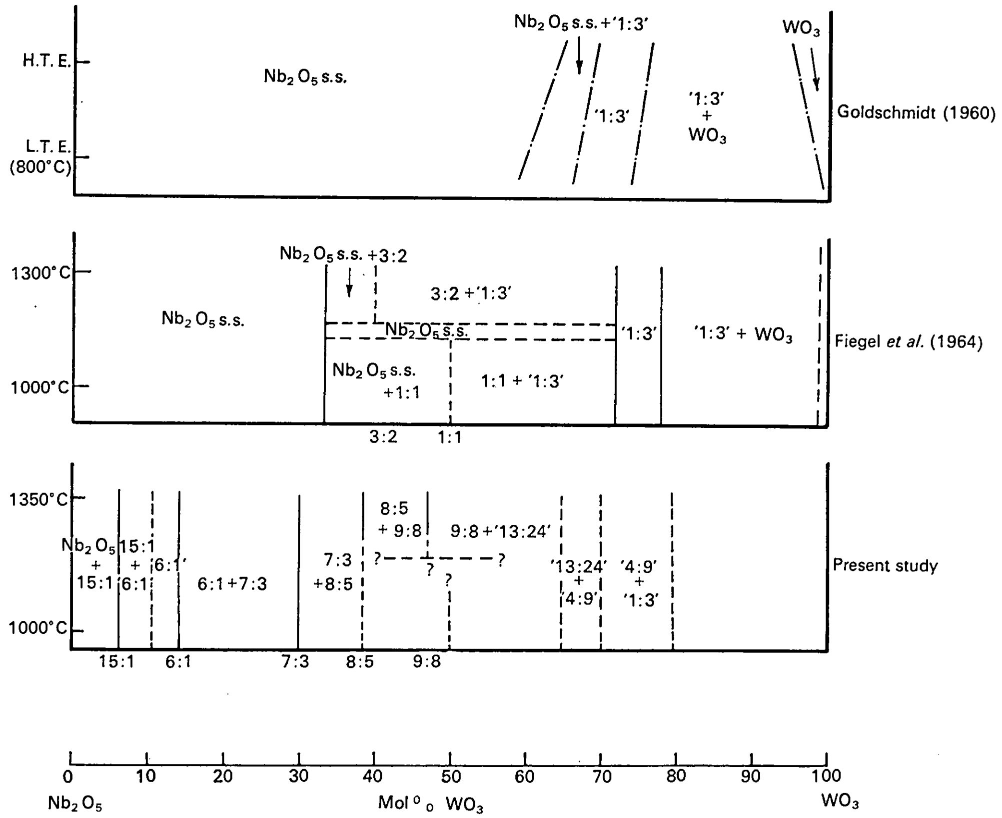

Fig. 1. Phases reported for the equilibrium system Nb_2O_5–WO_3.
The present study was confined to the temperature interval 1300–1400 °C.

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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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(*Received* 26 *October* 1964)

The unit-cell dimensions of $WNb_{12}O_{33}$ are $a=22{\cdot}37$, $b=3{\cdot}825$, $c=17{\cdot}87$ Å, $\beta=123{\cdot}6°$, 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, $\beta=126{\cdot}5°$ 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 *h*0*l* and *h*1*l* 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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