

PHASE DIAGRAMS OF ALLOYS BASED ON NIOBIUM

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Abstract

The phase constitution of binary and ternary alloys of niobium has been reviewed and information is presented on the solubilities observed and the intermediate phases which are formed. This information is discussed in terms of atomic size, chemical characteristics and the structures of the phases which occur.

## Terminal Solutions

Normally, terminal solutions are large when the components of the system are similar in size (say  $\pm$  15% size difference) and of similar electronegativity. Table I gives limiting solubilities and these may be compared with the atomic sizes given in Figure 1 and the electronegativities presented in Table II.

It can be seen that niobium behaves in much the same way as other transition metals and that solubilities are high when sizes are favorable and electronegativity differences are less than 0.3. Hafnium is a minor exception in the sense that a complete series of solid solutions is observed although the size and electronegativity differences are both at the limits suggested above. Appendix I reviews the constitutional data available on binary alloys and presents phase diagrams where these are available. Phase diagrams are available on a considerable number of ternary systems (Table III) although many of the investigations cover only limited temperature and composition ranges. Terminal solid solutions in general follow the patterns that can be expected on the basis of the behavior of the binary systems e.g., Figure 2, Nb-Zr-Hf, although occasionally a miscibility gap develops in an unexpected way e.g., Figure 3, Nb-Mo-Cr.

## Intermediate Phases

Hume-Rothery, Smallman and Haworth (1) have pointed out that alloys of Groups IV, V or VI transition element with an element from Group VII or VIII often show the sequence

bcc	$\text{Cr}_3\text{Si}$	$\sigma$	$\mu$	X	cph	fcc
solid solution	+ type phase	+ phase	+ phase	+ phase	+ phase	+ solid solution

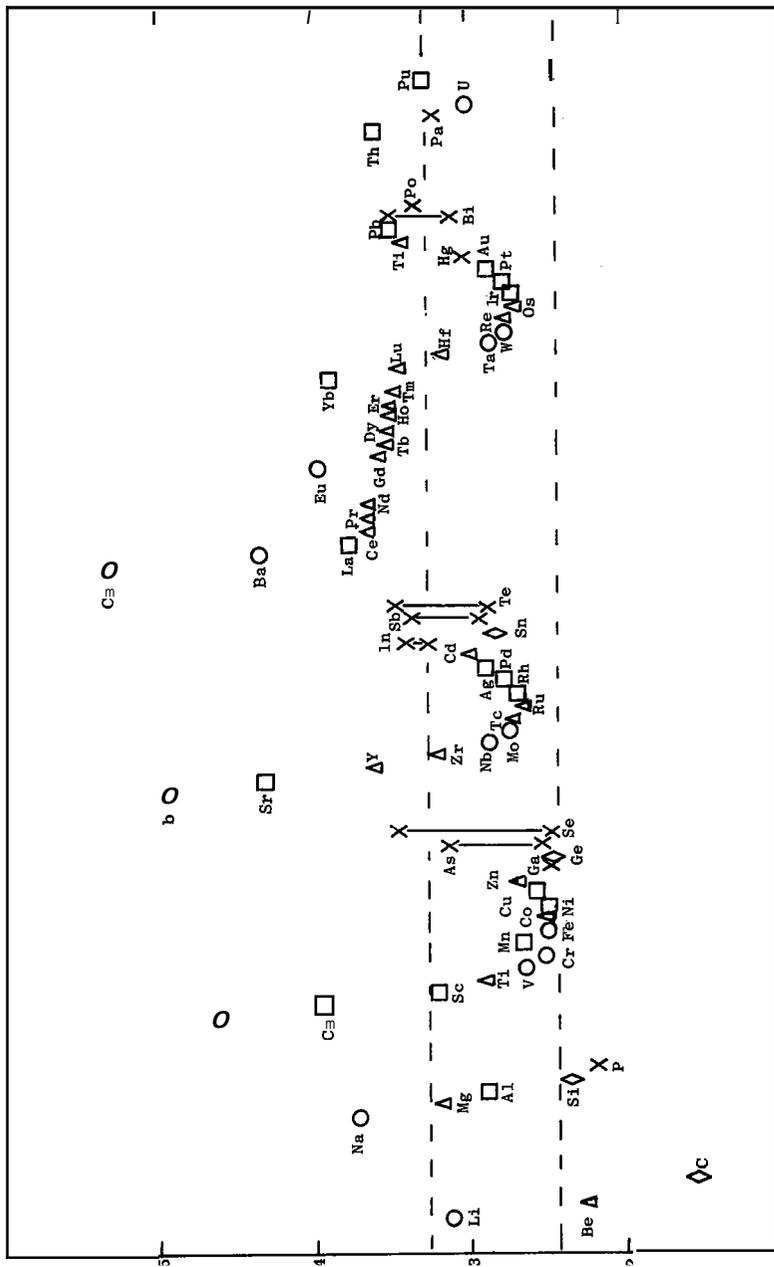
The  $\text{Cr}_3\text{Si}$  phase is markedly stoichiometric but the other phases show wide homogeneity ranges. In general the composition ranges for the phases move towards the niobium-rich side of the diagram on passing from Group 7  $\rightarrow$  8a  $\rightarrow$  8b  $\rightarrow$  8c.

The following sections describe these phases, examine their occurrence in niobium alloys and summarize the available information on the solubility of other elements in the binary phases.

### $\text{Cr}_3\text{Si}$ Type Phase

Originally called  $\beta$  tungsten or  $\text{Cr}_3\text{O}$ , it now seems that both of these assignments were due to impurity effects. The structure is formed from an ordered arrangement at the  $\text{A}_3\text{B}$  composition with the A component a transition metal from Group IV, V or VI and the B component from elsewhere. Size differences are generally  $<10$  percent. The structure (Figure 4) has the B atoms at the body centered lattice points and the A atoms forming chains lying in opposite faces of the unit cell. The A sites all have coordination number 14 and are greatly distorted.

Table IV summarizes  $\text{Cr}_3\text{Si}$  type compounds formed by niobium of the elements shown all but Pb and Ir are within 15 percent of the size of niobium.



Body-centred cube. Face-centred cube. Close-packed hexagonal. Diamond Structure.  
 Closest distance of approach in more complicated structures. Where two X's are given, it implies two well-defined sets of neighbours.

Figure 1. Closest distances of approach as a function of atomic number.  
 (After Hume-Rothery, Smallman and Haworth).

### Table 1. Solubility Limits in Binary Systems Based on Niobium

Li	Be											B	C	N	O
Na	Mg											Al	Si	P	S
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf						

Li	Be	Mo	Pb	Ni	As	B	C	N	O						
Na	Mg	Al	Si	P	S	Ga	Ge	As	Se						
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf						

• Maximum Values Except Where Temperature(°C) is Cited  
 • Amounts in Atomic %

Table II. Electronegativity Values (Pauling).

Li	Be	B											C	N	O	F
1.0	1.5	2.0											2.5	3.0	3.5	4.0
Na	Mg	Al											Si	P	S	Cl
0.9	1.2	1.5											1.8	2.1	2.5	3.0
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.6	1.8	2.0	2.4	2.8
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5
Cs	Ba	La to Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
0.7	0.9	1.1 - 1.2	1.3	1.5	1.7	1.9	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2	
Fr	Ra	Ac	Th	Pa	U	Np to No										
0.7	0.9	1.1	1.3	1.5	1.7	1.3										

Table III. Ternary Systems on which some Phase Diagram Data are available Nb-X-Y.

-Al-Ce	-B-Ge	-Cr-Ni	-H-Zr	-Ni-W	-V-Zr
-Al-Co	-B-Hf	-Cr-Si	-Hf-Mo	-Ni-Zr	-W-Zr
-Al-Cr	-B-Mn	-Cr-Ti	-Hf-N	-O-Re	
-Al-Cu	-B-Mo	-Cr-U	-Hf-O	-O-Ru	
-Al-Dy	-B-Ni	-Cr-V	-Hf-Ru	-O-S	
-Al-Fe	-B-Re	-Cr-W	-Hf-Sn	-O-Ti	
-Al-Ga	-B-Si	-Cr-Zr	-Hf-Ti	-O-v	
-Al-Gd	-B-Ti	-Cu-Ga	-Hf-Zr	-O-w	
-Al-Ge	-B-W	-Cu-H	-Ir-O	-O-Zr	
-Al-H	-B-Zr	-Cu-Mo	-Ir-Si	-Re-Ti	
-Al-Hf	-C-CO	-Cu-Sn	-Mo-N	-Re-W	
-Al-Ho	-C-Cr	-Cu-Ta	-Mo-Ni	-Ru-Ta	
-Al-Ir	-C-Fe	-Cu-W	-Mo-O	-Ru-Ti	
-Al-La	-C-Hf	-Cu-Zr	-Mo-Si	-Ru-Zr	
-Al-Lu	-C-Mo	-Fe-N	-Mo-Ta	-Sc-V	
-Al-Mo	-C-N	-Fe-P	-Mo-Ti	-Si-Sn	
-Al-No	-C-Ni	-Fe-S	-Mo-U	-Si-V	
-Al-Ni	-C-Re	-Fe-Si	-Mo-V	-Si-W	
-Al-Pr	-C-Ti	-Fe-Zr	-Mo-W	-Sn-Ti	
-Al-Rh	-C-U	-Ga-Ir	-Mo-Zr	-Sn-Zr	
-Al-Si	-C-W	-Ga-V	-N-O	-Ta-Ti	
-Al-Ta	-C-Zr	-Ga-Y	-N-Re	-Ta-V	
-Al-Tb	-Co-Pu	-Ge-Ti	-N-Ru	-Ta-W	
-Al-Ti	-Co-Pt	-H-Mo	-N-Ti	-Ta-Zr	
-Al-V	-Co-Si	-H-Ni	-N-W	-Th-Zr	
-Al-Zr	-Co-Sn	-H-Pd	-N-Zr	-Ti-U	
-B-C	-Co-U	-H-Sn	-Ni-Si	-Ti-V	
-B-Co	-Co-Zr	-H-Ta	-Ni-Sn	-Ti-W	
-B-Cr	-Cr-Cu	-H-Ti	-Ni-Ta	-Ti-Zr	
-B-Fe	-Cr-Mo	-H-V	-Ni-Ti	-U-Zr	

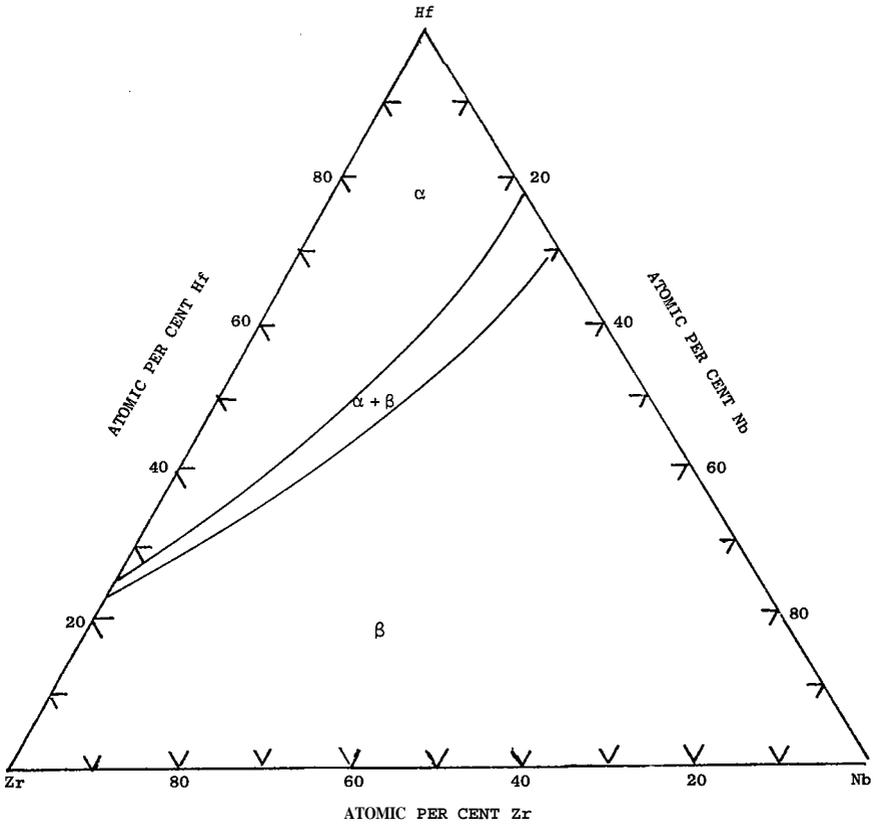


Figure 2 Isothermal section of Nb-Zr-Hf at 1000 C.

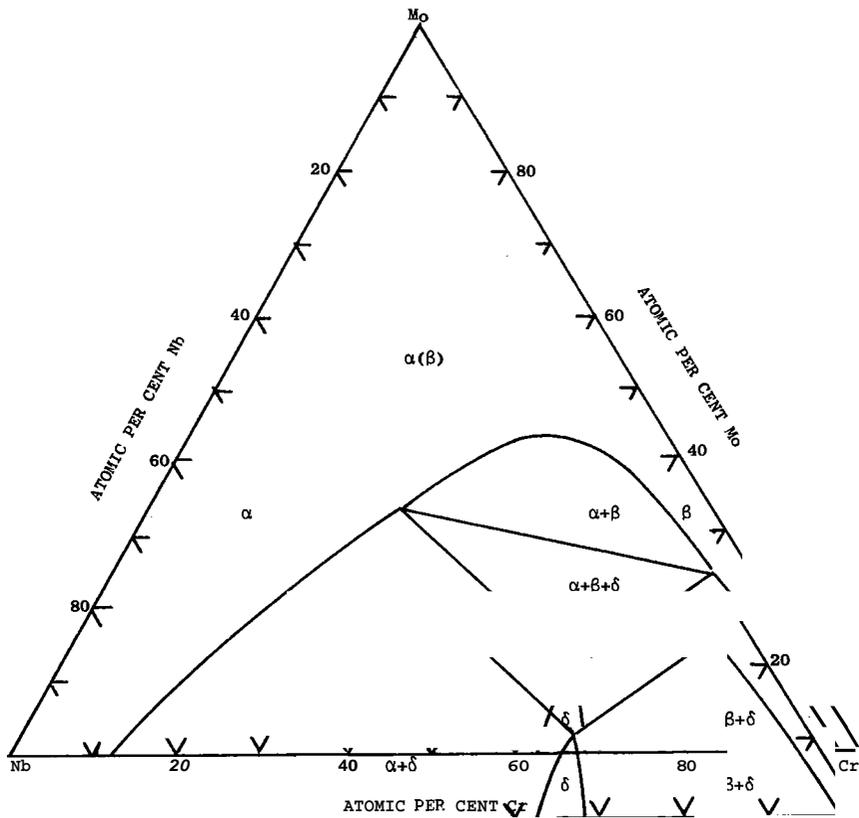


Figure 3 Isothermal section of Nb-Cr-Mo at 1200 C

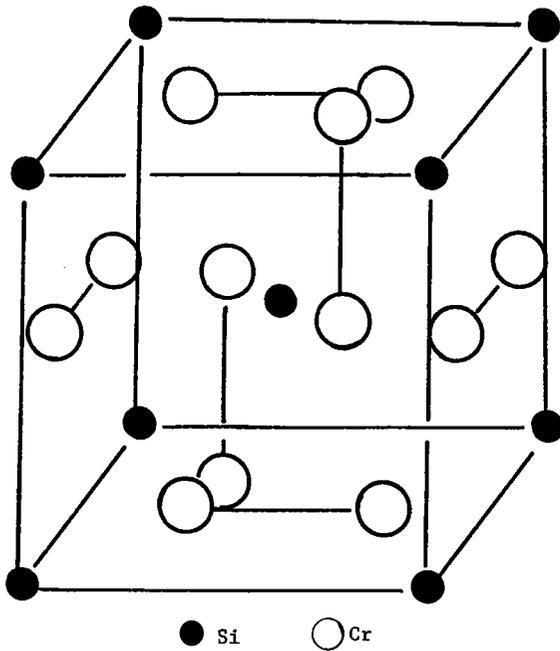
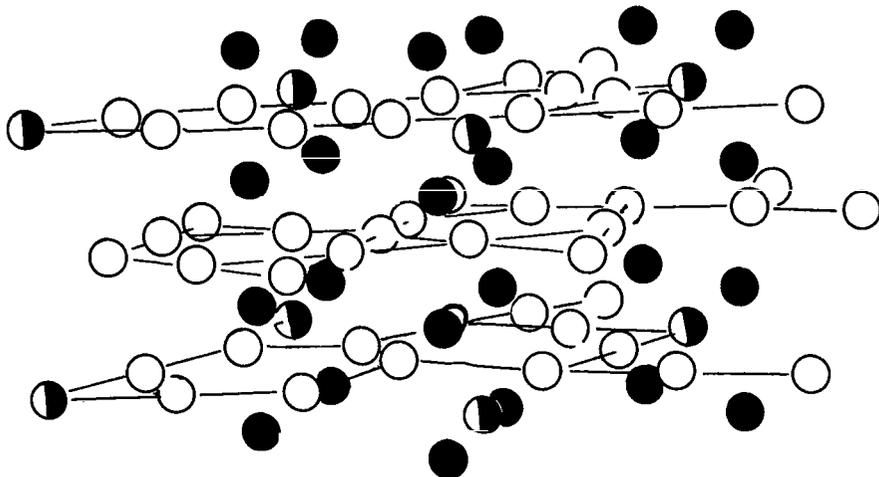


Figure 4. Crystal structure of  $\text{Cr}_3\text{Si}$ .



- Atoms forming chains of coordination number 14
- Atoms forming Kagome tile layers
- ◐ Atoms in the layers at the corners of unit cells

Figure 5. Crystal structure of the  $\sigma$  phase.

Table IV. Binary Cr<sub>3</sub>Si Type Compounds Formed by Niobium

<u>A Component</u>	<u>B Component and Groups</u>								
	8a	8b	8c	1	2	3	4	5	
Nb	-	-	-	-	-	Al	-	-	
	-	-	-	-	-	Ga	Ge	-	
	-	Rh	-	-	-	In	Sn	Sb	
	<b>Os</b>	Ir	Pt	Au	-	-	(Pb?)		

Similarly, when solubility for a third element is considered (Table V), extensive ranges are observed when the size differences are less than 15 percent. Chemical similarity is not a necessary criterion, e.g., although one might expect a complete range of solid solutions between Nb<sub>3</sub>Ga and Nb<sub>3</sub>Al, this also occurs for the system Nb<sub>3</sub>Ga - Nb<sub>3</sub>Ir.

Table V. Solubility in at%

Cr<sub>3</sub>Si Type intermediate phases based on niobium

(Temperatures /°C are given in brackets)

<u>Nb<sub>3</sub>Al</u>					
si	1.5 (1400)				
Ti	15 (1200)	Zr	4(925)	Hf	10(925)
V	10 (1000)	-		Ta	43(925)
Cr	17 (1000)	Mo	CSS(1000)		
Mn	-				
Fe	4 (1000)				
co	-	Rh	2.5(926)	Ir	2.5(1100)
Ni	2.5 (1140)				
cu	6 (1000)				
Zn	-				
Ga	CSS (900)				
Ge	CSS (800)				

Miscellaneous

Nb <sub>3</sub> Rh	2.5 41 (925)
Nb <sub>3</sub> Ir	2.5 41 (1100); CSS Ga (1000) 7 si (1200)
Nb <sub>3</sub> Ga	4 Cu (800) ; CSS Ge (900); 6V (800); CSS Al (900); CSS In(1000)
Nb <sub>3</sub> Pt	5 co (1000)
Nb <sub>3</sub> Ge	CSS Al (800) ; CSS Ga (900)
V <sub>3</sub> Ga	45 Nb (800)

σ - phase

The unit cell for σ phase is tetragonal and contains 30 atoms (Figure 5). Two similar layers of atoms each consisting of a network of hexagons and triangles can be distinguished in each cell and one layer is rotated by 90° with respect to the other but the hexagons are superimposed and centered by

chains of atoms. There are five different types of atom site in the structure and some ordering of atoms among the sites (see Table VI).

Table VI. Ordering in  $\sigma$  - phase alloys

<u>Type of site</u>	<u>No. of atoms/unit cell</u>	<u>Coordination No.</u>	<u>Occupancy</u>
I	2	12	B
II	4	15	A
III	8	14	Mixed
IV	8	12	B
V	8	14	Mixed

(After Hume-Rothery, Smallman and Hawarth) (1).

The type V sites are associated with the chains of atoms and are small and distorted. Type A atoms come from Groups Va or VIA and Type B atoms from Groups VIIA or VIII.

The  $\sigma$  - phase which is well known through its appearance in the Fe-Cr system also occurs in niobium alloys (see Table VII).

Table VII. a - phases in binary systems based on niobium

<u>A Component</u>	<u>B Component and Groups</u>						
	7	8a	8b	8c	1	2	3
	-	-	-	-	-	-	A1
Nb	-	Fe	-	-	-	-	-
	-	Xu	Rh	Pd	-	-	-
	Re	Os	Ir	Pt	-	-	-

The Average Group Number for the formation of the phase is 5.6 to 7.6 but unfortunately this is wide enough also to include a number of  $\chi$  and  $\mu$  phases. A ternary  $\sigma$  phase is found in some systems, e.g., Nb<sub>2</sub>CuGa and wide solubilities exist sometimes extending to complete intersolubility, e.g., Nb<sub>2</sub>Al and Ta<sub>2</sub>Al (Figure 6). Available data on solubilities is summarized in Table VIII and it can be seen that these are greatest when size differences are small, but again, chemical similarity is not a prerequisite for wide solubility c.f. NbRh and NbIr which form a complete series of solid solutions with NbAl.

### $\chi$ Phase

This phase is isomorphous with  $\alpha$ -manganese which has a complicated cubic structure with a unit cell containing 58 atoms. If the basic structure is considered to be body centered cubic each lattice point is replaced by a cluster of 29 atoms. There are 4 different types of site (see Table IX).

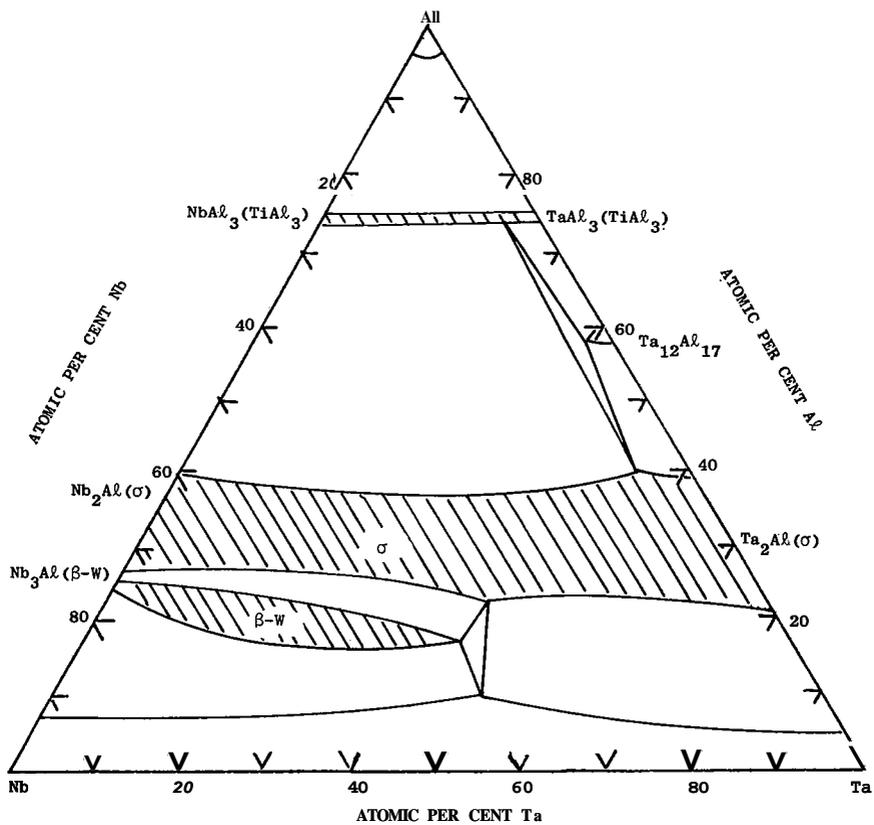


Figure 6. Isothermal section of Nb-Al-Ta at 925 C.

Table VIII. Solubilities in at% in  $\sigma$  Phases Based on Niobium

(Temperatures/ $^{\circ}$ C are given in brackets)

NbAl  $\sigma$

Al					
Si	1 (1400)				
Ti	20 (1200)	Zr	13 (925)	Hf	720 (800)
V	24 (1000)	-	-	Ta	CSS
Cr	22 (1000)	Mo	33 (1000)		
Mn					
Fe	10 (1000)				
Co	15 (1000)	Rh	CSS	Ir	CSS
Ni	5 (1140)				
Cu	10 (1000)				
Zn	-				
Ga	13 (9000)				

Miscellaneous  $\sigma$

NbIr	18 Ga (1000);	CSS Al;	12 Si (1200)
NbRh		CSS Al	
NbFe			15 Si
NbRe	CSS W (H.T.)		
NbPt	10 Co (1000)		

Table IX: Ordering in  $\chi$  Phases

<u>Type of Site</u>	<u>No. of Atoms/ unit cell</u>	<u>Coordination No.</u>	<u>Possible Occupancy</u>
I	2	16	A
II	8	16	A
III	24	13	B
IV	24	12	B

Where size differences are great, ordering of large atoms to sites I and II can lead to stoichiometric phase of the approximate formula  $AB_5$ . The

$\chi$  phase generally occurs at an Average Group Number of 6.2-7.0 and phases observed in niobium systems are given in Table IXa,

Table IXa:  $\sigma$  Phases in Binary Niobium Alloys

	Group			
	<u>7</u>	<u>8a</u>	<u>8b</u>	<u>8c</u>
Nb	Tc	---	---	Pd
	Re	Os	---	--

Ternary  $\chi$  phases have also been observed e.g. NbCoB (Figure 7) and ZrNbAl.

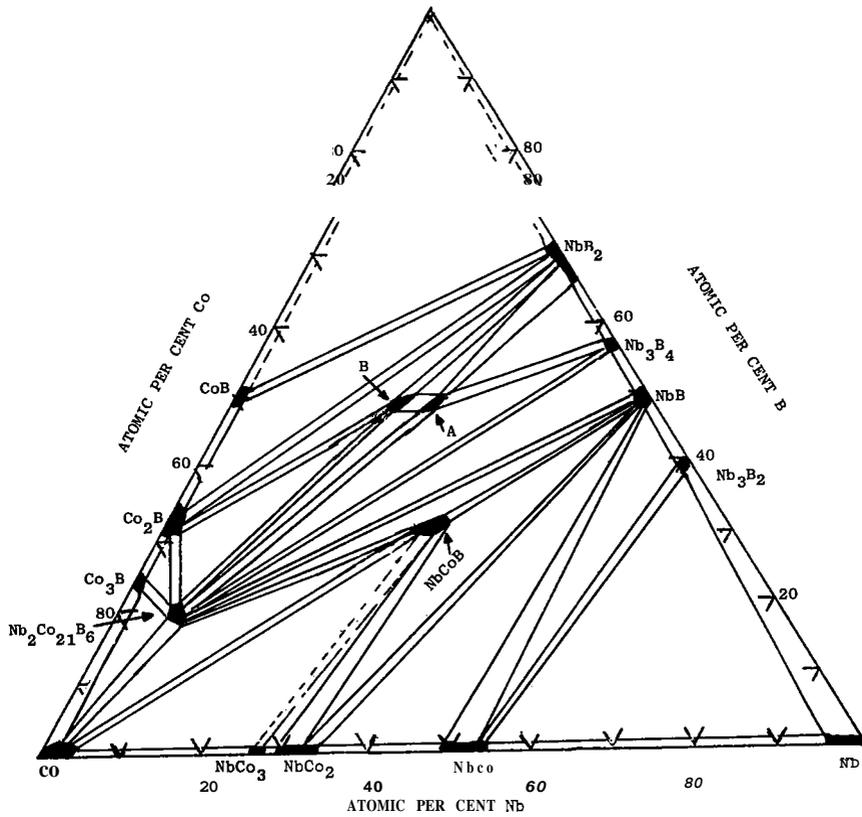


Figure 7. Isothermal section of Nb-Co-B at 800 C.

## R and $\mu$ Phases

The R phase is related to the  $\sigma$  phase and has a rhombohedral unit cell containing 53 atoms and atomic sites of coordination numbers 12, 14, 15 and 16. The larger sites are probably occupied by the large atoms of groups IV<sub>A</sub>, V<sub>A</sub> or VI<sub>A</sub> whereas the manganese, cobalt, nickel and iron probably take up the smaller sites.

$\mu$  phase or the W<sub>6</sub>Fe<sub>7</sub> type structure (A<sub>6</sub>B<sub>7</sub>) has the A component chosen from Nb, Mo, Ta or W and the B component from Fe, Co or Ni. Its structure is hexagonal with a c/a of  $\sim 5.4$  and its unit cell contains 41 atoms (see Figure 8). The layer formation is similar to the MgZn<sub>2</sub> Laves phase with a different stacking sequence. Five different types of site can be distinguished in the structure (Table X).

Table X: Ordering in  $\mu$  Phases

<u>Type</u>	<u>Number of atoms/ unit cell</u>	<u>Coordination No.</u>	<u>Occupancy</u>
I	6	16	A
II	6	15	A
III	6	14	A
IV	3	12	A or B
V	18	12	B

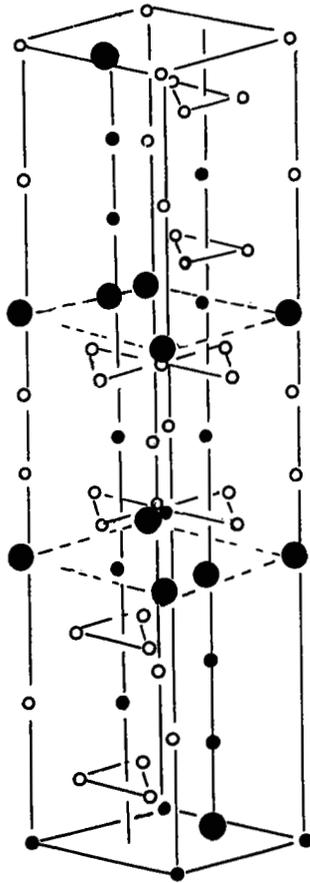
Again, the larger atoms occupy the sites with high coordination numbers. R and  $\mu$  phases are found in some systems containing niobium e.g. R in the system Nb-Si-Mn and  $\mu$  in the binary systems Nb-Fe, Nb-Co, Nb-Ni and the ternary systems Nb-Al-Fe, ( $\mu$ )<sup>1</sup>, (Figure 9), Nb-Al-Co, Nb-Al-Cu (Nb<sub>2</sub>CuAl) and Nb-Al-Zr (Nb<sub>2</sub>Zr<sub>5</sub>Al<sub>6</sub>). Solubility in binary  $\mu$  phases are given in Table XI.

Table XI: Solubilities in at% in Binary  $\mu$  Phases Based on Niobium

(Temperature/°C in brackets)

Nb <sub>19</sub> Fe <sub>20</sub>	20	Al (1000)		
	35	si (1000)		
Nb Co	30	Al (1000)		15 Pt (1000)
	12	Si (800)		
Nb Ni	30	Al (1140)		
	10	Si (800)		
	6	Ti (1000)	3 Zr (800)	
			5 Mo (900)	12 W (1000)

Figure 9 illustrates the wide solubility of Al in Nb<sub>19</sub>Fe<sub>20</sub> and the way in which substitution is by exchange of aluminum for iron.



○ Fe atom      ● W atom (CN 16)  
 ● W atom (CN 14,15)

Figure 8. Unit cell for  $\mu$  phase.

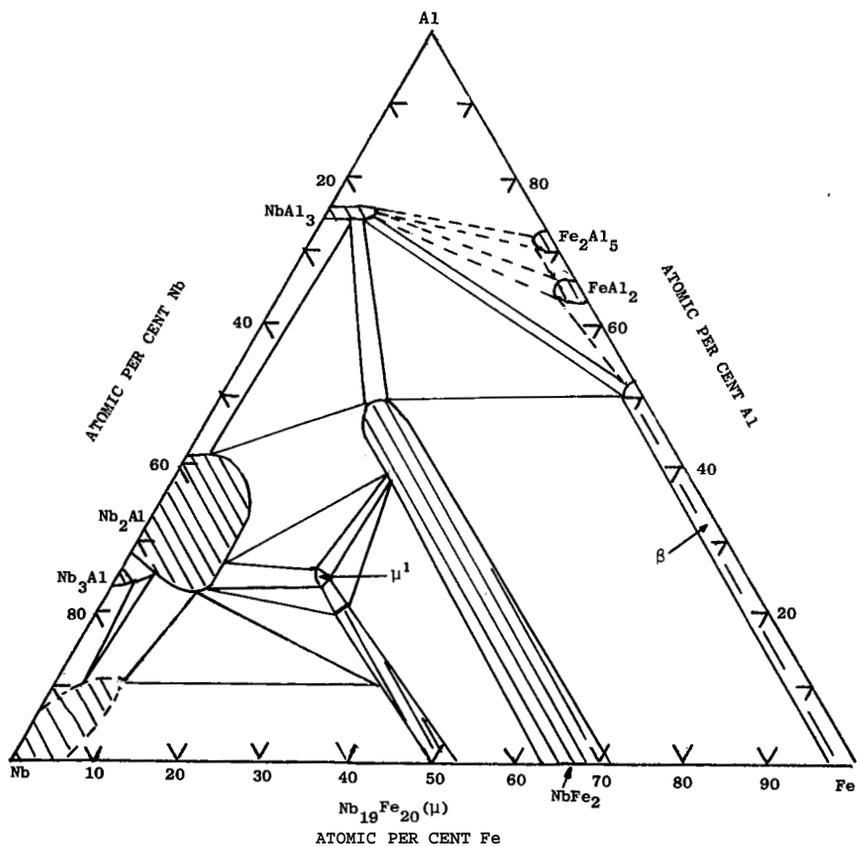


Figure 9. Isothermal section of Nb-Al-Fe at 1000 C.

Close Packed Ordered Structures

These structures are based on ordering of the close packed layers in the face centered cubic and close packed hexagonal structures. The most common stoichiometry for these phases is  $AB_3$  and the structures are built up of different arrangements of the close packed layers shown in Figure 10 which give either triangular or rectangular arrangements of the A atoms. The A atoms are surrounded by 6 B atoms in the close packed phase and the stacking sequence is such that an A atom is surrounded by a total of 12 B atoms in the overall structure. Stacking sequences are shown in Table XII.

Table XII: Stacking Sequences in Close Packed Phases

<u>Structure Type</u>	<u>Lattice Type</u>	<u>Atoms/ Unit Cell</u>	<u>Type of Close Packed Layer</u>	<u>Stacking Sequence</u>
AuCu <sub>3</sub>	Cubic	4	triangular	ABCABC
VCo <sub>3</sub>			triangular	ABCACBABCACB
TiNi <sub>3</sub>	hexagonal	16	triangular	ABACABAC
MgCd <sub>3</sub>	hexagonal	8	triangular	ABAB
TiCu <sub>3</sub>	orthorhombic	8	rectangular	ABAB
TiAl <sub>3</sub>	tetragonal	8	rectangular	ABCA <sup>1</sup> B <sup>1</sup> C <sup>1</sup> ABCA <sup>1</sup> B <sup>1</sup> C <sup>1</sup>

The Cu<sub>3</sub>Au type structure is shown in Figure 11, MgCd<sub>3</sub> in Figure 12 and the TiNi<sub>3</sub> type structure combines the stacking sequence of AuCu<sub>3</sub> and MgCd<sub>3</sub>.

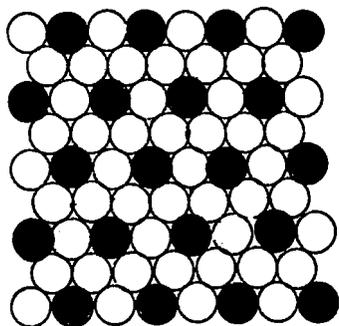
TiCu<sub>3</sub> and TiAl<sub>3</sub> structures involve orthorhombic and tetragonal distortion due to the ordering within the close packed layers.

Examples of binary ordered phases containing niobium are given in Table XIII.

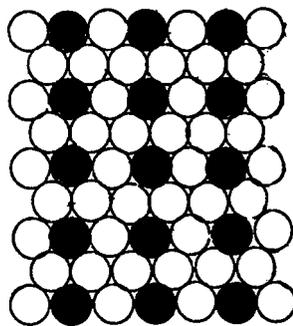
Table XIII: Ordered Binary Phases Based on Niobium

<u>Structure Type</u>	<u>Example</u>
AuCu <sub>3</sub>	NbRh <sub>3</sub> NbIr <sub>3</sub>
TiCu <sub>3</sub>	NbNi <sub>3</sub> NbPt <sub>3</sub>
TiAl <sub>3</sub>	NbPd <sub>3</sub> NbAl <sub>3</sub> NbGa <sub>3</sub>
VCo <sub>3</sub>	η phase in Nb-Rh

So far TiNi<sub>3</sub> type phases have only been found in systems between Group IVa and Group 8c elements and no reports of binary phases of the MgCd<sub>3</sub> type containing Nb have been noted.



(a)



(b)

Figure 10. Ordering in close packed layers at the  $AB_3$  composition.  
a. Triangular; b. Rectangular

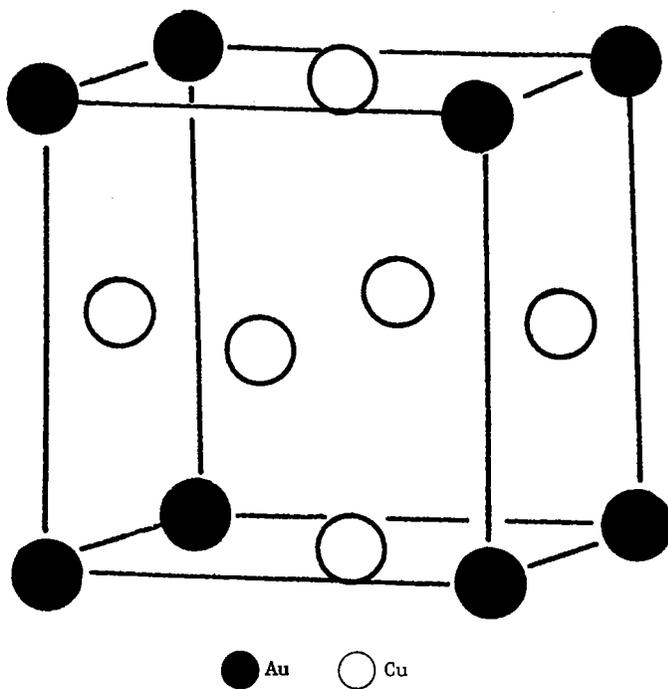


Figure 11. The  $Cu_3Au$  Structure.

Table XIV shows the solubility of a number of elements in  $\text{NbAl}_3$  and  $\text{NbNi}_3$ . In cases of close chemical similarity e.g.  $\text{NbAl}_3$  and  $\text{TaAl}_3$  there may be a complete series of solid solutions (Figure 6) but generally solubilities are not very great.

Table XIV. Solubilities in at% of Various Elements in Close Packed Binary Phases Based on Niobium

(Temperature/°C in brackets)

$\text{NbAl}_3$

Ti	4 (1200)	Zr	17 (925)	Ta	css(925)
V	css(1000)	Mo	14 (1000)		
Cr	5 (1000)				
Mn	---				
Fe	5 (1000)				
Co	---				
Ni	0 (1140)				
Cu	5 (1000)				
Zn	---				
Ga	css (900)				

$\text{NbNi}_3$

Al	2 (1140)	Zr	15 (800)	W	7 (900)
Ti	5 (1000)	Mo	css (900)		

Ordered Structures of the  $\text{Cu}_2\text{MnAl}$  Type

This structure is based on the ordering in  $\text{Fe}_3\text{Al}$ . Figure 13 shows eight simple body centered cubic cells with 4 sets of equivalent sites, Al atoms occupy the d sites, Mn atoms the b sites while the a and c sites are occupied by copper atoms. These Heusler alloy type structures are found in ternary alloys containing niobium, e.g.  $\text{Co}_2\text{NbAl}$ ,  $\text{Ni}_2\text{NbAl}$  and  $\text{Co}_2\text{NbSn}$ . The close stoichiometry of the  $\text{Ni}_2\text{NbAl}$  "H" phase is illustrated in Figure 14.

Laves Phases  $\text{AB}_2$

Comparisons of this type have the stoichiometric composition  $\text{AB}_2$  and the ratio of diameter  $d_A/d_B$  is  $\sim 1.2:1$ . The phases form in one of 3 related structures which differ in stacking sequence of 2 layers in an analogous way to  $\text{AuCu}_3$ ,  $\text{MgCd}_3$  and  $\text{TiNi}_3$  (Table XV). The two planar networks are a simple triangular arrangement and a Kagomé tile network.

The structures of  $\text{MgCu}_2$ ,  $\text{MgZn}_2$  and  $\text{MgNi}_2$  are shown in Figures 15, 16 and 17. Figure 17 shows the arrangement of. (a) tetrahedra of small B atoms and (b) large A atoms in  $\text{MgNi}_2$ . The large atoms are accommodated in the holes of the skeleton of small atoms.

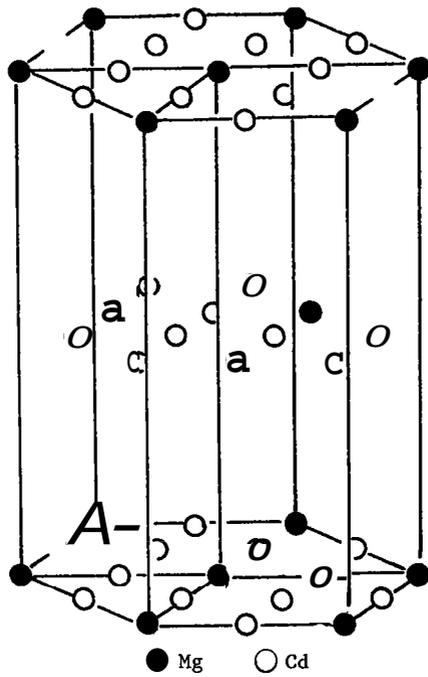


Figure 12. The  $\text{MgCd}_3$  structure.

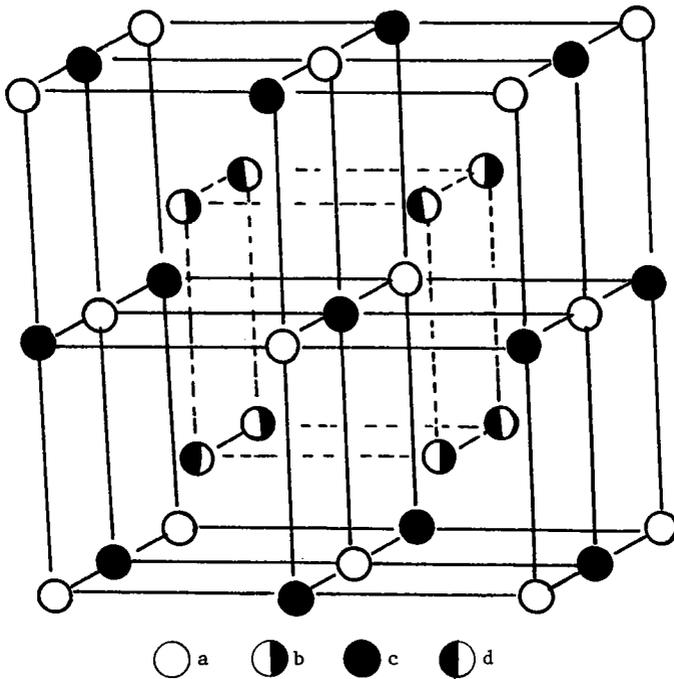


Figure 13. The  $\text{Fe}_3\text{Al}$  structure with Al atoms in b sites.

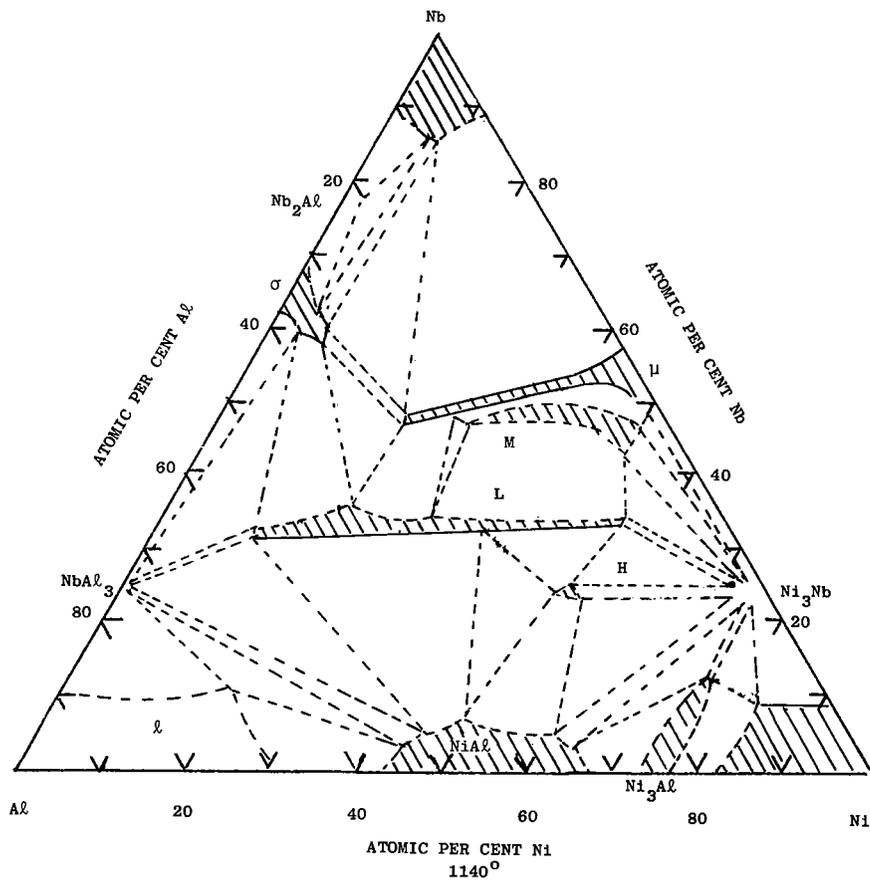
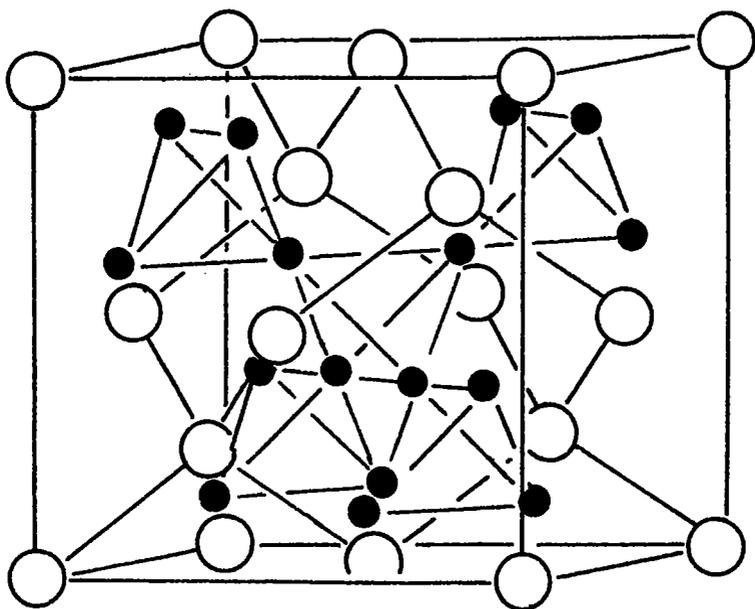
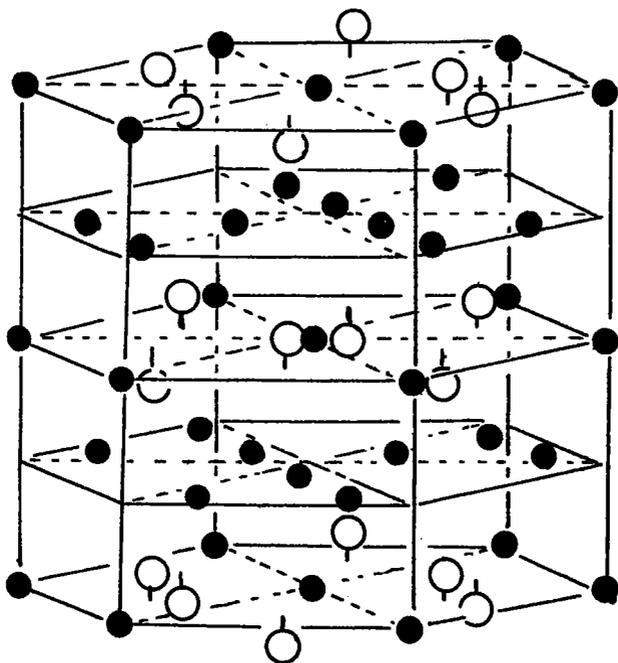


Figure 14. Isothermal section of Nb-Al-Ni at 1140 C.



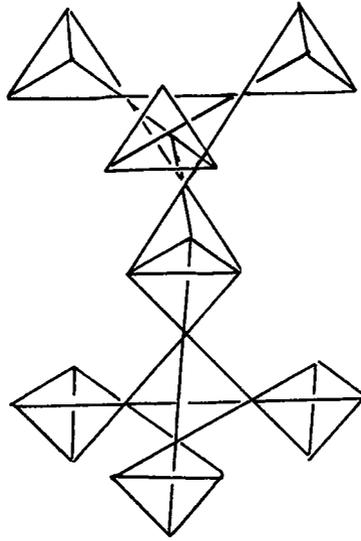
○ Mg      ● Cu

Figure 15. The  $\text{MgCu}_2$  structure.

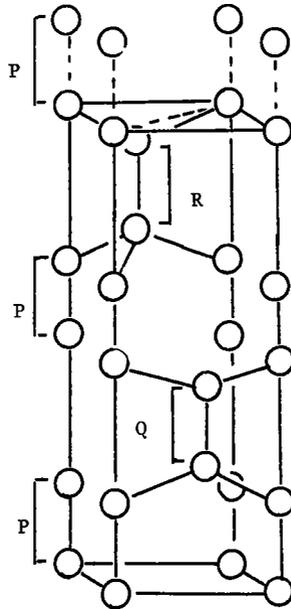


○ Mg      ● Zn

Figure 16. The  $\text{MgZn}_2$  structure.



(a)



(b)

Figure 17. Arrangement of tetrahedra of small B atoms (a), and large A atoms (b) in  $\text{MgNi}_2$ .

Table XV. Stacking Sequences for Laves Phases

<u>Structure Type</u>	<u>Lattice Type</u>	<u>Atoms/Unit Cell</u>	<u>Stacking Sequence</u>
MgCu <sub>2</sub>	Cubic	8A + 16B	PQRPQR
MgZn <sub>2</sub>	Hexagonal		PQPQ
MgNi <sub>2</sub>	Hexagonal		PQPRPQPR

Examples of all three structure types are found in the alloys of niobium, viz.

<u>MgCu<sub>2</sub></u>	<u>MgNi<sub>2</sub></u>	<u>MgZn<sub>2</sub></u>
NbCo <sub>2</sub>	NbCo <sub>2</sub>	NbFe <sub>2</sub>
NbCr <sub>2</sub>		NbMn <sub>2</sub>

They are also found in ternary systems when no equivalent phase is observed in the constituent binary systems e.g. MgZn<sub>2</sub> type phases are found in NbCuGa, NbCuAl and NbNiAl (Figure 14), Nb<sub>2</sub>Co<sub>3</sub>Si ( $\lambda_1$ , Figure 18). However, sometimes the appearance in a ternary section is due to the stabilization of a high temperature structure to a lower temperature e.g. stabilization of the MgZn<sub>2</sub> structure ( $\epsilon$  in the Nb-Cr-Ni ternary system to) temperatures where only the MgCu<sub>2</sub> form of Cr<sub>2</sub>Nb ( $\beta$ ) is present in the binary system (Figure 19) or the Laves phase  $\rho$  Cr<sub>5</sub>Nb<sub>3</sub>Si<sub>2</sub> in the Cr-Nb-Si system (Figure 20). Solubilities of various elements in MgCu<sub>2</sub> and MgZn<sub>2</sub> Laves phases are given in Table XVI

#### Silicide Structures

A considerable number of binary and ternary silicides of varying complexity occur in Nb-base systems. Details of their structure may be found in H. J. Goldschmidt's "Interstitial Alloys" (2). The disilicides of which NbSi<sub>2</sub> is a typical example have two dimensional close packed layers of both silicon and metal atoms (Figure 21) with 4, 3 or 2 fold repeat structures. Examples of phases with binary silicide structures are given in Table XVII.

The ternary  $\beta$  phase shown in Figure 20 is the  $\beta$  form of Nb<sub>5</sub>Si<sub>3</sub> stabilized by chromium. More complex ternary silicides e.g. "E" (TiNiSi type) FeNbSi, CoNbSi (E), NiNbSi, CoNbGe and NiNbGe or "G" (Ti<sub>6</sub>Ni<sub>16</sub>Si<sub>7</sub> type), Co<sub>16</sub>Nb<sub>6</sub>Si<sub>7</sub> (T), Ni<sub>16</sub>Nb<sub>6</sub>Si, Ni<sub>16</sub>Nb<sub>6</sub>Ge<sub>7</sub> and Co<sub>16</sub>Nb<sub>6</sub>Ge<sub>7</sub> are also observed. Figure 18 shows limited stoichiometry of CoNbSi and Co<sub>16</sub>Nb<sub>6</sub>Si<sub>7</sub>.

Qualitative information on solubilities in silicides is given in Table XVIII.

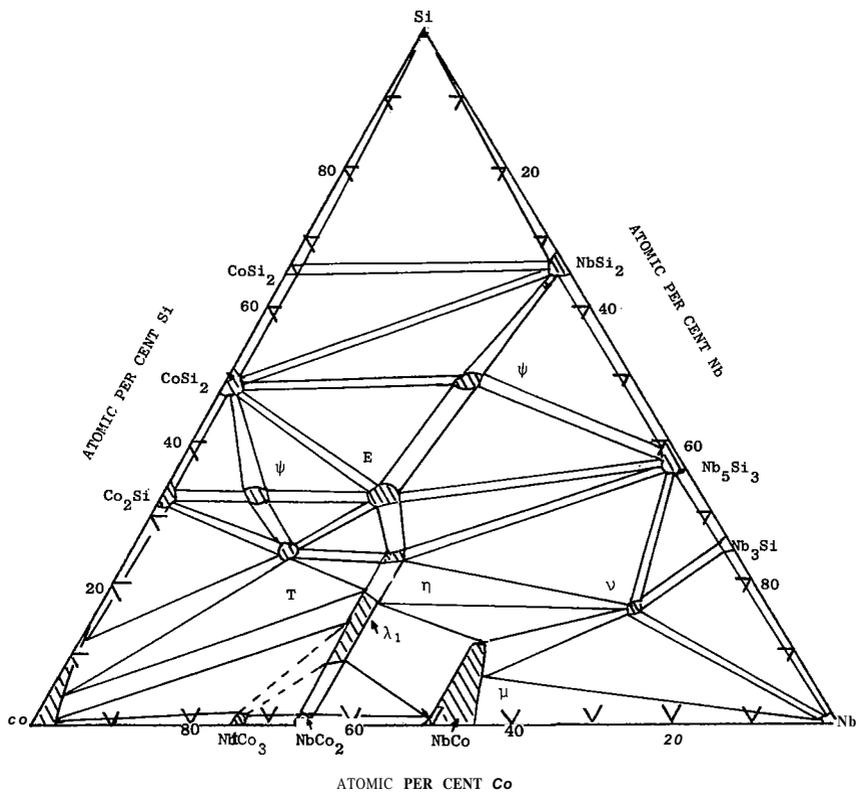


Figure 18. Isothermal section of Nb-Co-Si at 800 C.

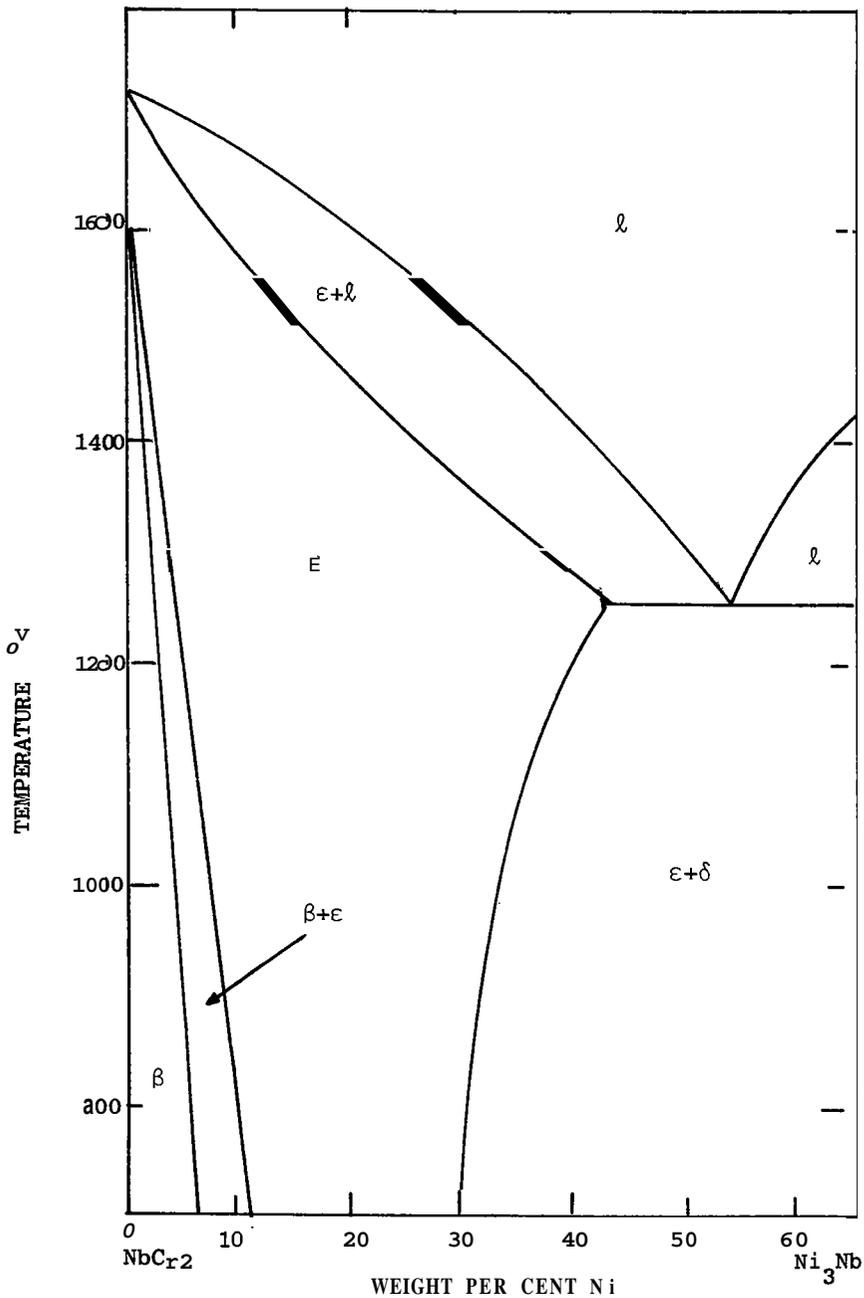


Figure 19. Vertical section of Nb-Ni-Cr.

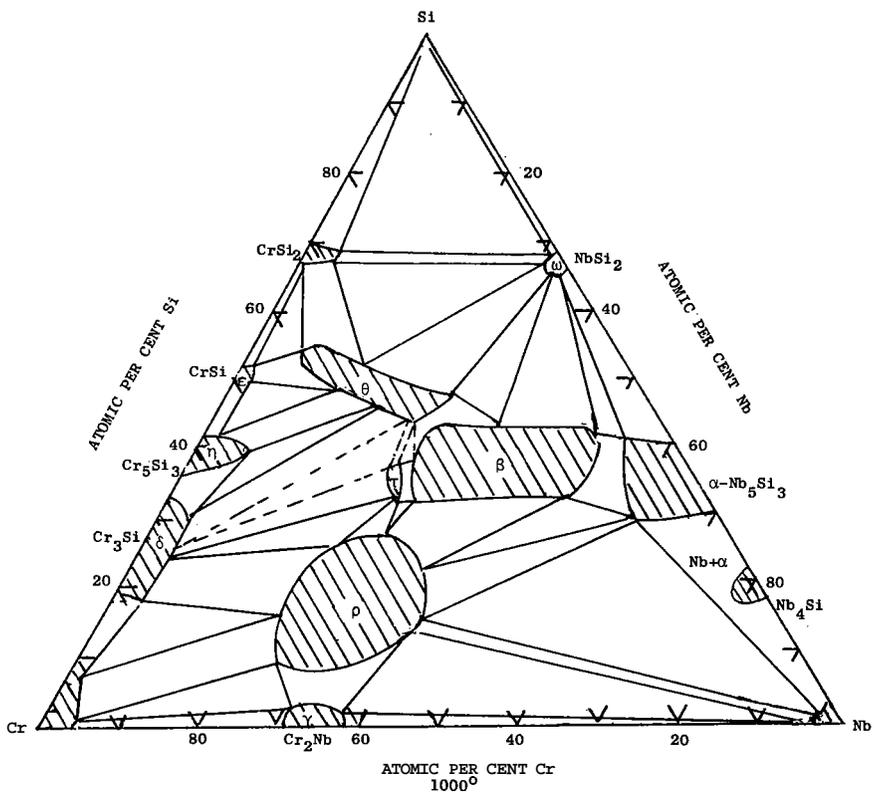
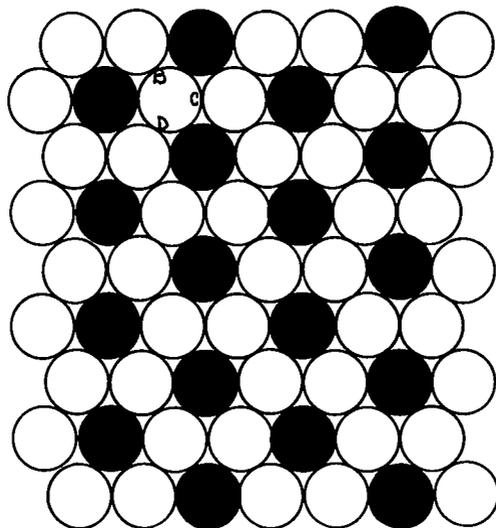


Figure 20. Isothermal section of Nb-Cr-Si at 1000 C



Layer A; layers B, C, D similar but metal atoms above spaces B, C, D.

● Metal atom    ○ Silicon atom

Figure 21. Close packed plane in disilicides.

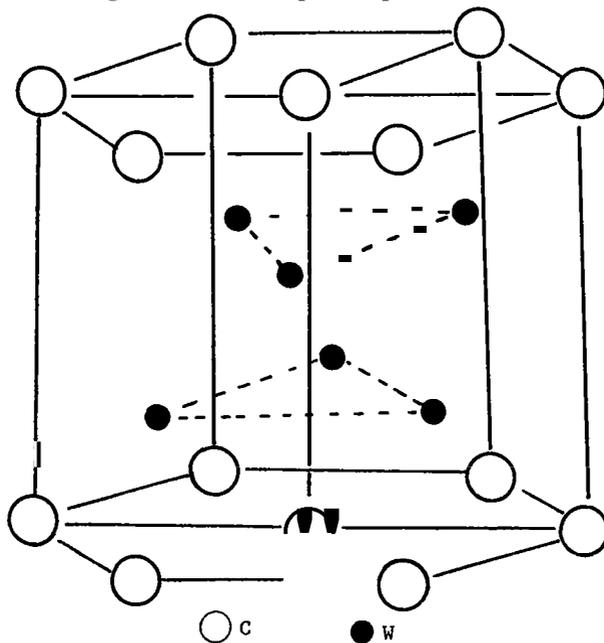


Figure 22. Structure of  $W_2C$ .

Table XVI Solubilities of various elements in at% in binary  
Laves phases containing niobium

(Temperature/°C in brackets)

MgCu<sub>2</sub> Type

NbCr <sub>2</sub>	3	si (1000)	
	40	V (1000)	10%Mo
	5	Ni (1000)	
NbCo <sub>2</sub>			css Zr
NbSn <sub>2</sub>	~ 2	Co (500)	
	< 2	Ni (500)	

MgZn<sub>2</sub> Type

(a) Derived from binary system

NbCr <sub>2</sub>	3-47	Al (mainly exchanging for Cr)	(1000)	
	8-28	Si (22-40 Nb, 40-60 Cr)	(1000)	
	css	Ti (H.T.)		css Zr (H.T.)
	7-35	Ni (exchanging for Cr)	(1000)	
NbFe <sub>2</sub>	50	Al (exchanging for Fe)	(1000)	
	33	Si (exchanging for Fe)	(1000)	
NbCo <sub>2</sub>	46	Al (exchanging for Co)	(1000)	12 Pt (1000)

(b) When no comparable phase exists in the binary systems

Nb (Co <sub>(1-x)</sub> Si <sub>x</sub> ) <sub>2</sub>		x = 0.25
Nb (Ni <sub>(1-x)</sub> Si <sub>x</sub> ) <sub>2</sub>		x = 0.25
Nb (Ni <sub>(1-x)</sub> Al <sub>x</sub> ) <sub>2</sub>	when	0.19 < x < 0.83 at 1000
Nb (Ir <sub>(1-x)</sub> Al <sub>x</sub> ) <sub>2</sub>	when	0.73 < x < 0.81 at 1100
Nb (Cu <sub>(1-x)</sub> Al <sub>x</sub> ) <sub>2</sub>	when	0.5 < x < 0.68 at 1000
Nb (Cu <sub>(1-x)</sub> Ga <sub>x</sub> ) <sub>2</sub>		x = 0.5

Table XVII Phases with binary silicide structures

<u>Structure</u>	<u>Examples</u>
CrSi <sub>2</sub>	NbSi <sub>2</sub> , NbGe <sub>2</sub>
W <sub>5</sub> Si <sub>3</sub>	Nb <sub>5</sub> Ge <sub>3</sub> , β Nb <sub>5</sub> (Si, Al) <sub>3</sub>
Cr <sub>5</sub> B <sub>3</sub>	α Nb <sub>5</sub> Si <sub>3</sub>
Mn <sub>5</sub> Si <sub>3</sub>	Nb <sub>5</sub> Ge <sub>3</sub> , Zr <sub>35</sub> Nb <sub>30</sub> Al <sub>35</sub>
U <sub>3</sub> Si <sub>2</sub>	Nb <sub>3</sub> B <sub>2</sub> , Nb <sub>3</sub> Ga <sub>2</sub>

Table XVIII. Information on Solubilities in certain Binary Silicides

<u>System</u>	<u>Information</u>
V-Nb-Si	Wide solubility for Nb in $VSi_2$ , $V_5Si_3$ & $V_3Si$ .
Nb-Cr-Si	Limited solubility in binary silicides.
Nb-W-Si	Partial solubility between $Nb_5Si_3$ - $W_3Si_3$ , large solubility W in $NbSi_2$ .
Nb-Fe-Si	Slight solubility in binary silicides.

Interstitial Compounds

For atomic size ratios of 0.41 to 0.59 structures of close packed metal atoms are formed in:

- NbC - Face centered cubic metal atom structure in carbide giving an overall NaCl structure when carbon atoms are placed interstitially.
- Nb<sub>2</sub>C - Close packed hexagonal metal atom structure giving a hexagonal carbide (Figure 22).

Intersolubility of the carbides varies considerably (Table XIX) for example, Figure 23 shows the continuous series of solid solutions formed between NbC and ZrC, Figure 24 shows the very limited solubilities in the Fe-Nb-C system and Figure 25 shows the formation of a ternary  $\eta_1$  carbide  $Nb_3Co_3C$ . Two complex carbide structures are found  $M_6C$  and  $M_{23}C_6$  e.g.  $Nb_3Cr_3C$  ( $\eta_1$ ) and  $Nb_2Ni_{21}B_6$  ( $\eta_2$ ) or  $Nb_2Co_{21}B_6$  (Figure 7) and  $Nb_2Ni_{21}B_6$ .

Table XIX. Carbide Solubilities

<u>Carbide Systems</u>	<u>NbC</u>	<u>Nb<sub>2</sub>C</u>
<u>Soluble</u>		
TiC - NbC	$V_2C$ - Nb <sub>2</sub> C	
ZrC - NbC	$Ta_2C$ - Nb <sub>2</sub> C	
HfC - NbC		
VC - NbC		
TaC - NbC		$R_{M_1}/R_{M_2} = 1.0 \mp 0.1$
MoC <sup>cubic</sup> - NbC		
UC - NbC		
<u>Partially Soluble</u>		
NbC - $Cr_3C_2$ ( $Cr_{23}C_6$ )		
NbC - Mo <sub>2</sub> C		$R_{M_1}/R_{M_2} = 1.0 \mp 0.15$
NbC - WC		
<u>Not Soluble</u>		
NbC - Mn carbides		
NbC - Fe <sub>3</sub> C		
NbC - (Co, Ni-C)		

$A_4B_2C/A_3B_3C$  [where A = Ti, V, Mn, Fe, Co, Ni and B = Mo, W, Nb, Zn (Ta, Hf)]

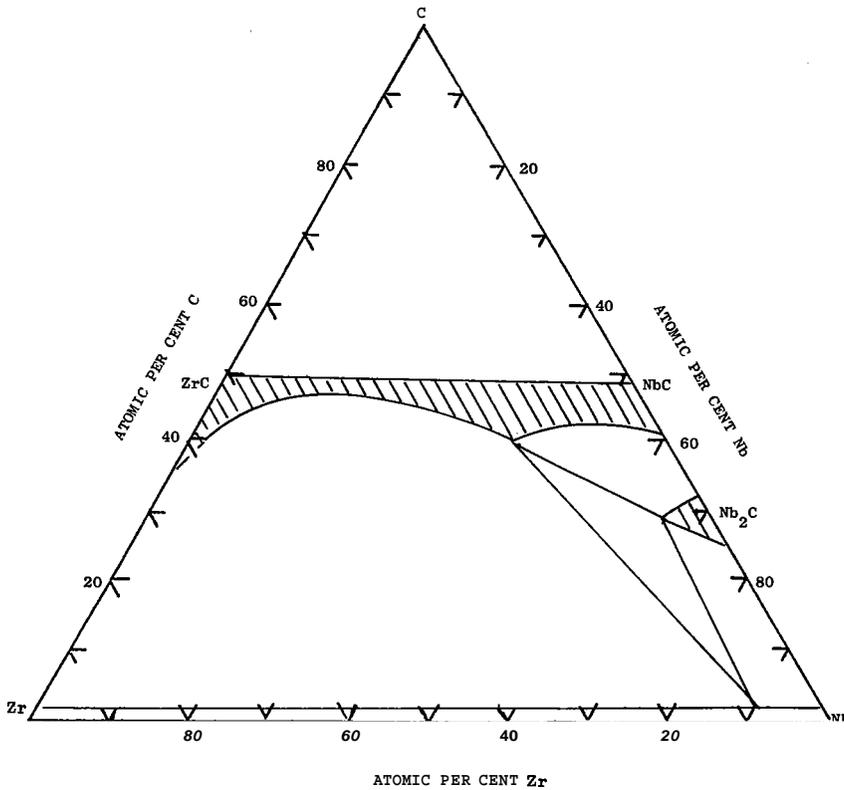


Figure 23. Isothermal section of Nb-Zr-C at 1700 C.

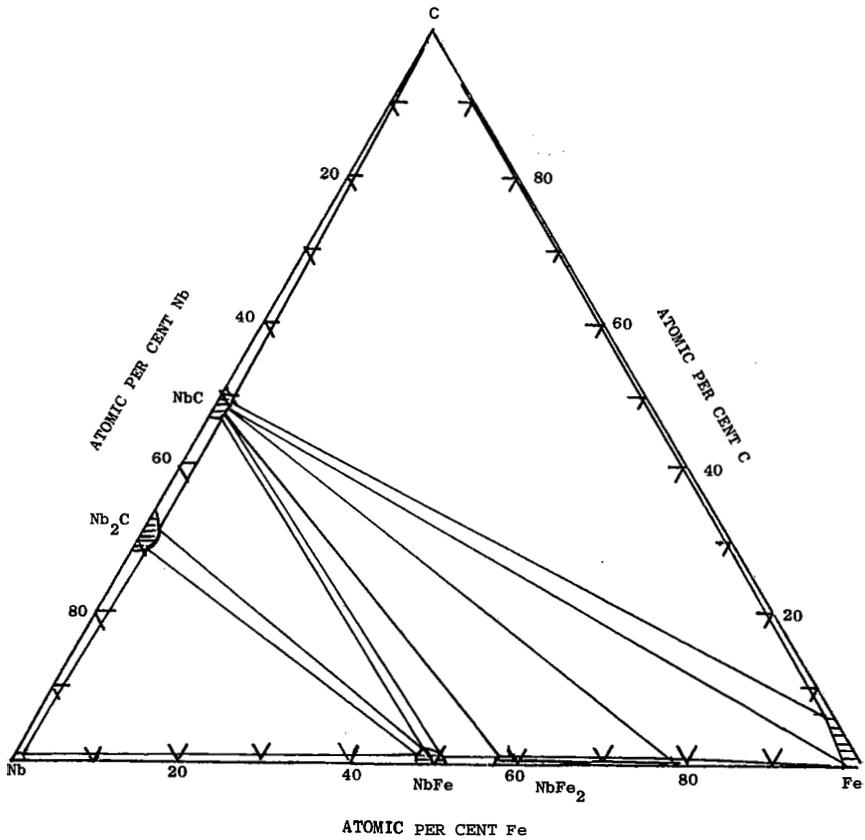


Figure 24. Isothermal section of Nb-Fe-C at 1000 C.

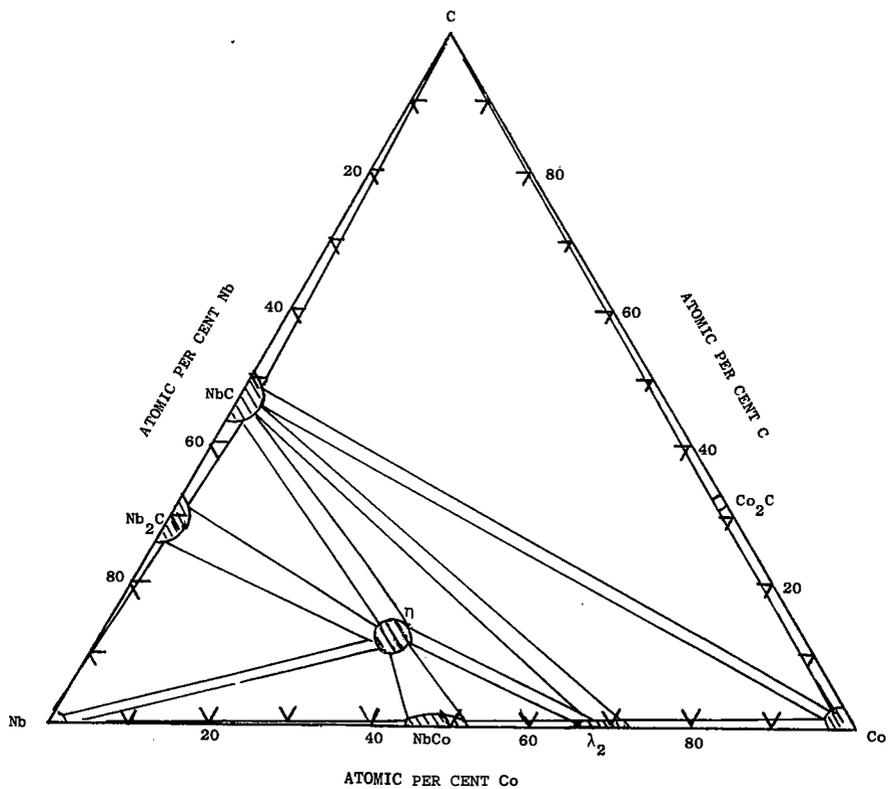


Figure 25. Isothermal section of Nb-Co-C at 1000 C.

$\eta_1$  carbide has 112 atoms per unit cell. The structure consists of octahedral and tetrahedral units, the former occupied by metal atoms A and B and the latter by A atoms alone. Carbon atoms are located centrally between any two octahedra (Figure 26).  $\eta_2$  carbides are similar to  $\eta_1$  but with different arrangements of the A and B atoms and a stoichiometry of  $A_2B_4C$ .

The  $M_{23}C_6$  carbide is cubic with 92 metal and 34 carbon atoms. The unit cell (Figure 27) may be divided into 8 octants in each of which the corners are alternately surrounded by cubo-octahedra (48 positions) and simple cubes (32 positions). An additional metal atom occupies the center of the cubo-octahedra (4 positions) and one at the center of each octant (8 positions). The latter positions are particularly large and those occupied by Nb in  $Nb_2Co_{21}B_6$ .

Another type of ternary carbide is also observed, the "H" type phases. These involve transition and non-transition metals combined in the proportions  $A_2BC$  e.g.  $Nb_2AlC$ ,  $Nb_2SnC$ ,  $Nb_2GaC$  and  $Nb_2InC$ .

### Oxides, Nitrides and Borides

Niobium forms several compounds in each binary system  $Nb_2O$ ,  $NbO$ ,  $NbO_2$  and  $Nb_2O_5$ ;  $Nb_2N$ ,  $Nb_{14}N_{11}$  and  $NbN$ ;  $Nb_3B$ ,  $Nb_2B$ ,  $Nb_3B_2$ ,  $NbB$ ,  $Nb_3B_4$  and  $NbB_2$  and information on the solubility of some of these compounds for other oxides, nitrides and borides is given in Tables XX, XXI and XXII. The intersolubility of the niobium and molybdenum borides is illustrated in Figure 28.

### Effect of Alloying Elements on Gas Solubility

Tables XXIII, XXIV and XXV show the effects of various alloying elements on the solubility of hydrogen, oxygen and nitrogen in niobium.

### Discussion and Conclusions

From the vast amount of information available on the phase diagrams of niobium only three simple rules have wide validity. Wide solubility is not observed when size differences are large although if they are large enough size factor compounds, interstitial compounds or interstitial solutions may be observed. Substitution of chemically similar elements in a compound is generally possible e.g. Ta for Nb in NbC but dissimilar elements generally do not substitute to any large extent e.g. Nb in the chromium carbides. Ternary compounds can sometimes be predicted from analogous systems but occasionally their absence in a system that is chemically similar may not be a reliable guide e.g. the appearance of  $TiNbAl_3$  (Figure 29) would not be expected from the Zr-Nb-Al system.

Work reported in the literature has inevitably been carried out using materials of quite widely differing purities and consequently the temperatures given for fixed points such as the melting point of niobium differ over quite wide ranges (in this case 2410 to 2475 C compared with the more generally accepted 2468 C). The diagrams presented in Appendix 1 and in the main text do not attempt to reconcile these differences as they reflect the purity of the materials and it is known that the appearance or absence of an

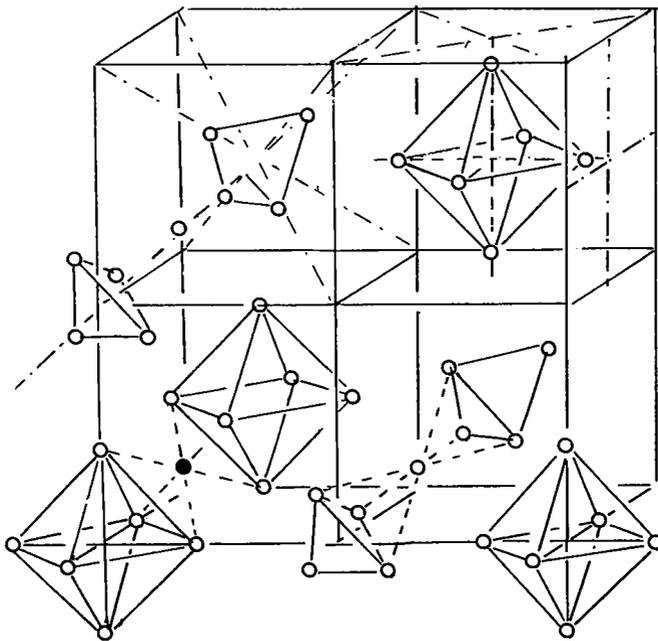
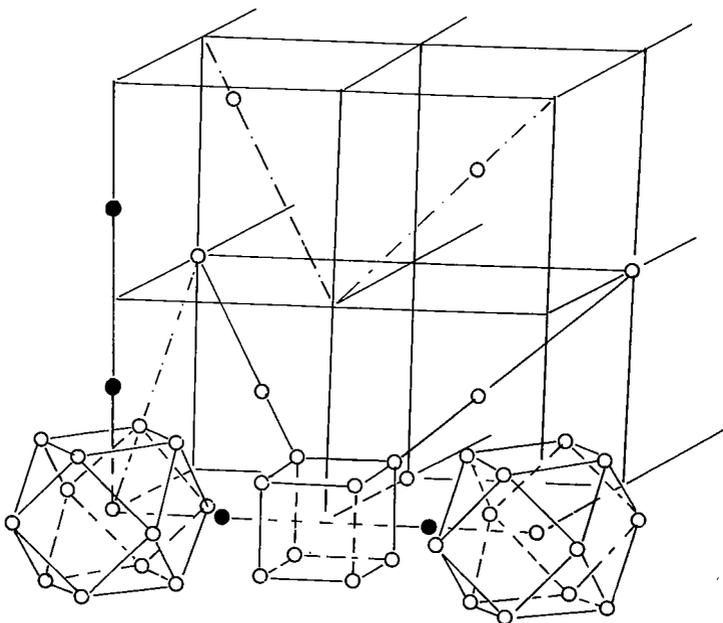


Figure 26. Structure of  $M_6C$  (After K. W. Andrews).



○ Metal atoms A, B or D      ● Carbon atoms C

Figure 27. Structure of  $M_{23}C_6$  (After K. W. Andrews).

Table XX. Oxide Solubilities

<u>System</u>	
Nb-Ti-O	(a) pseudo binary $\text{Nb}_2\text{O}_5\text{-TiO}_2$ , extensive series of solid solutions, compounds $\text{TiO}_2 \cdot \text{Nb}_2\text{O}_5$ , $\text{TiO}_2 \cdot 3\text{Nb}_2\text{O}_5$ . (b) pseudo binary $\text{NbO}_2\text{-TiO}_2$ complete series of solid solutions.
Nb-Zr-O	(a) pseudo binary $\text{ZrO}_2\text{-Nb}_2\text{O}_5$ limited solubilities; compound $6\text{ZrO}_2 \cdot \text{Nb}_2\text{O}_5$ . (b) partial solubility $\text{NbO}_2\text{-ZrO}_2$ .
V-Nb-O	Extensive partial solubility $\text{V}_2\text{O}_5\text{-Nb}_2\text{O}_5$ , compounds $\text{V}_2\text{O}_5 \cdot \text{Nb}_2\text{O}_5$ and $\text{V}_2\text{O}_4 \cdot \text{Nb}_2\text{O}_5$ .
Nb-Ta-O	Complete series of solid solutions $\beta \text{Nb}_2\text{O}_5\text{-Ta}_2\text{O}_5$ ; compound $2\text{Nb}_2\text{O}_5 \cdot \text{Ta}_2\text{O}_5$ .
Nb-Cr-O	Partial solid solubility $\beta \text{Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$ ; extensive rutile series $\text{NbO}_2 + \text{NbCrO}_4 + \text{CrO}_2$ .
Nb-Mo-O	Partial solid solubility $\beta \text{Nb}_2\text{O}_5\text{-MoO}_3$ ; rutile series $\text{MoO}_2$ .
Nb-W-O	Extensive partial solid solubility $\beta \text{Nb}_2\text{O}_5\text{-WO}_3$ ; compound $\text{Nb}_2\text{O}_5 - 3\text{WO}_3$ ; rutile series $\text{NbO}_2 - \text{WO}_2$ .
Nb-Fe-O	Partial solubility $\beta \text{Nb}_2\text{O}_5 - \text{Fe}_2\text{O}_3$ .
Nb-Co-O	Partial solubility $\beta \text{Nb}_2\text{O}_5 - \text{Co}_3\text{O}_4$ .
Nb-Ni-O	Partial solubility $\beta \text{Nb}_2\text{O}_5 - \text{NiO}$ .

Table XXI. Nitride Solubilities

<u>System</u>	<u>Information</u>
Nb-Ti-N	Wide solubility $\text{TiN} - \text{NbN}$
Nb-Zr-N	Wide solubility $\text{ZrN} - \text{NbN}$
Nb-V-N	Wide solubility $\text{VN} - \text{NbN}$

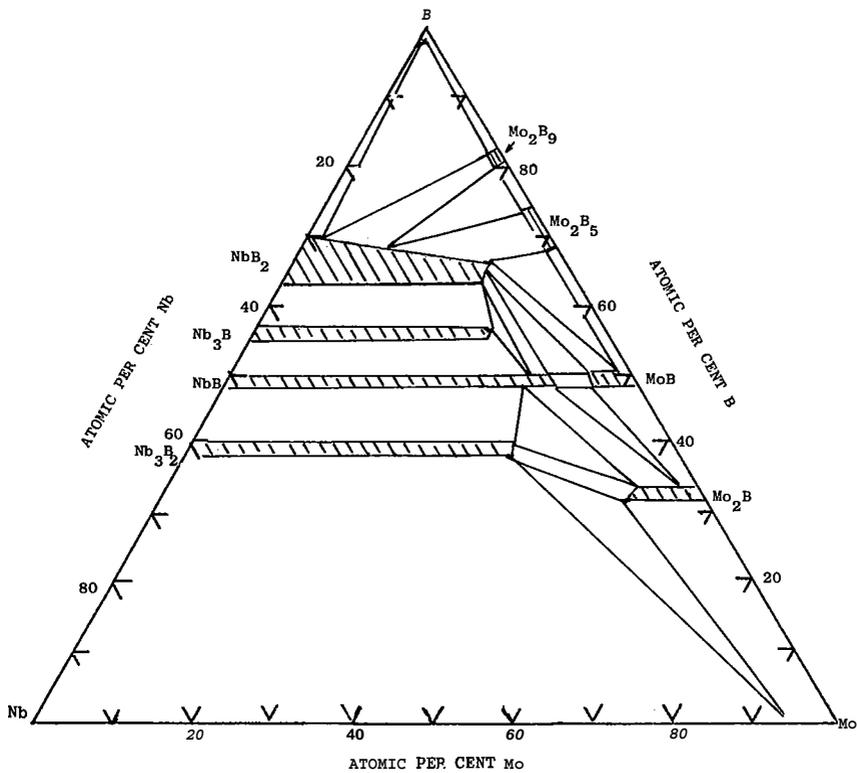


Figure 28. Isothermal section of Nb-Mo-B at 1400 C.

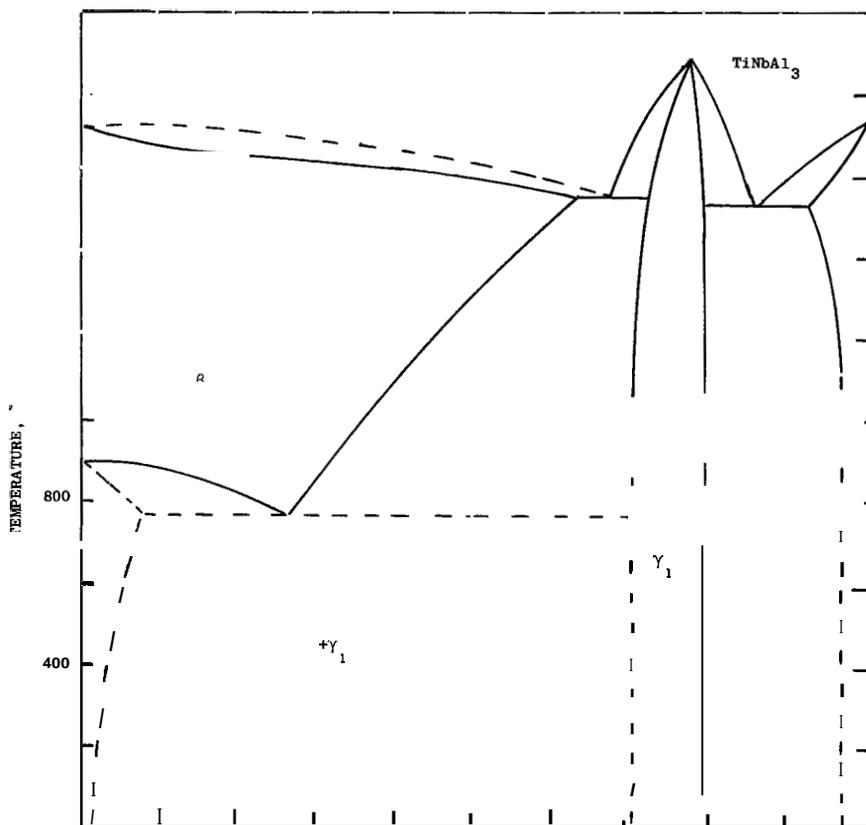


Figure 29. Vertical section of Nb-Ti-Al.

Table XXII. Boride Solubilities

<u>System</u>	<u>Information</u>
Nb-Ti-B } Nb-Zr-B }	(complete series of solutions) $TiB_2-NbB_2$ $ZrB_2-NbB_2$
Nb-Cr-B	Limited solubility $CrB_2-NbB_2$ .
Nb-Mo-B	$NbB_2$ ) $Nb_3B_4$ ) Wide solubility for Mo-exchanging $NbB$ ) for Nb. $Nb_3B_2$ )
Nb-W-B	$NbB$ ) $Nb_3B_2$ ) Wide solubility for W.

It should be noted that there is also complete series of solid solutions between NbC and NbN, TiN and VN; the intersolubility of NbC with ZrN and HfN is small.

Table XXIII. Effect of Alloying Elements on Hydrogen Solubility in Niobium at 823K and 400 mm pressure

<u>Alloy</u>	<u>H/M Ratio</u>
Pure Nb	0.17
Nb-5 a/oAl	0.12
Nb-25 a/oTi	0.30
Nb-50 a/oTi	0.60
Nb-75 a/oTi	1.00
Nb-5 a/o Ni	0.12
Nb-5 a/o Cu	0.13
Nb-10 a/o Mo	0.06
Nb-5 a/oPd	0.075
Nb-10 a/oPd	0.05

intermediate phase can also be related to quite small variations in trace element contents. In a similar way it has not been possible to reconcile the binary and ternary diagrams with regard to phase constitution. For example, even for a system as commercially important as Fe-Nb, investigators are not agreed on whether the Laves phase  $Fe_2Nb$ ,  $\sigma$  phase,  $\eta$  phase  $Fe_{20}Nb_{19}$ , the  $Ti_2Ni$  type phase  $Fe_2Nb_3$  and an unidentified  $Fe_xNb_y$  are all characteristic of the equilibrium system of pure components. Many investigators of the ternary systems at 1000 C, where 3 or 4 binary phases should be present, choose to show only the Laves and  $\eta$  or Laves and  $\sigma$  phases.

Although much work has been done on the phase constitution of niobium alloys, much more needs to be done on commercially significant systems. The impression given by the literature is that there is an adequate coverage of carbide, nitride, boride and silicide systems for most of our present needs, that a good start has been made on Al-base alloys, systems between refractory metals and systems of relevance to superconducting materials applications, but that more work is needed on ternary systems relevant to steels, nickel, cobalt and precious metal alloys. For example, there is only information on systems between iron and niobium with Al, B, C, N, P, S, Si and Zr. A good start on this area would be to cover the systems formed by niobium and chromium with iron, cobalt and nickel.

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## Appendix - Binary Phase Diagrams

### Group Ia

Hydrogen. At temperatures above -171 C niobium shows a large solubility for hydrogen; at lower temperatures phase separation occurs with a critical temperature of 171 C and a reported eutectoid at 74 C giving a b.c.c. solid solution based on Nb containing up to -10 at % H at 100 C and a face centered orthorhombic NbH with a homogeneity range extending from 41 at % H to at least 48.5 at % H. The higher hydride NbH<sub>2</sub> dissociates on heating to 300 C.

Alkali Metals. None of the systems Nb-Li, Nb-Na, Nb-K show compound formation. The solubility of niobium in metals is given in Table I.

Table A1. Solubility of Nb in Alkali Metals at 1000 C.

<u>Li</u>	<u>Na</u>	<u>K</u>
$<7.5 \times 10^{-6}$ a/o	low	$<8 \times 10^{-4}$ a/o
{n.b. for solubility in Li: $-\log_{10} x_{\text{Nb}} = -4.77 - \frac{1094}{T}$ (760 - 1540 C)}		

### Group IIa

Alkaline Earth Metals. Beryllium forms a number of compounds with niobium; agreement exist on Be<sub>12</sub>Nb (bct) Be<sub>3</sub>Nb (rhombohedral) Be<sub>2</sub>Nb (fcc MgCu<sub>2</sub> type) and Be<sub>2</sub>Nb<sub>3</sub> (tetragonal U<sub>3</sub>Si<sub>2</sub> type), a rhombohedral phase is variously reported as Nb<sub>2</sub>Be<sub>17</sub> or NbBe<sub>8</sub> and an NbBe<sub>5</sub> has also been suggested. Conflicting evidence exists about the nature of the reaction forming the compounds and the invariant temperatures involved.

### Group IIIa

Scandium, Yttrium and Lanthanum. The phase diagrams with Sc, Y and La all show very limited solid solubilities and no compound formation. The systems with yttrium and lanthanum show liquid immiscibility.

Rare Earths. Limited information was found on systems with Ce, Nd, Sm, Gd, Dy, Er, Yb. All showed limited solid solubility, no compounds and, in the case of Ce, Gd, Er and Yb liquid immiscibility.

Actinides: - Thorium, Uranium and Plutonium. A significant amount of information is available on the systems with Th, U and Pu. The solubilities for niobium are limited viz. for Nb-Th  $< 0.25$  a/o at  $< 1375$  C Nb-U, aU negligible - 1.9 a/o depending on investigation; Nb-Pu 1.1 a/o in liquid Pu at 700 C. The solubility of uranium in niobium is high ~ 26.9 a/o at the  $\gamma$ -eutectoid temperature.

#### Group IVa

Titanium, Zirconium and Hafnium. All three systems show complete inter-solubility in the b.c.c. phase with minima in the solidus curves for Nb-Zr and Nb-Hf. The cph-b.c.c. transition temperatures are depressed and in the case of the Nb-Zr system, there is a monotectoid reaction -610 C. Differences between the results of different investigators can largely be attributed to the purity of the materials particularly with regard to oxygen content.

#### Group Va

Vanadium and Tantalum. The phase diagrams for both systems show complete inter-solubility in the solid state with, however, a minimum in the solidus for Nb-V alloys.

#### Group VIa

Chromium, Molybdenum and Tungsten. Whereas complete inter-solubility in the solid state is exhibited by the Nb-Mo and Nb-W systems, the Nb-Cr system shows an intermetallic compound  $\text{NbCr}_2$  which is of the f.c.c.  $\text{MgCu}_2$  type structure at low temperatures with the possibility of transformation at high temperatures to hexagonal  $\text{MgZn}_2$  type. Considerable uncertainty exists about the transformation temperatures which have been placed at between 1600 and 1717 C on the Nb-rich side of  $\text{NbCr}_2$  and 1600 to 1660 C on the chromium-rich side. Uncertainty exists about whether a minimum exists in the melting curve for Nb-Mo alloys; two sets of Russian workers variously report a minimum of 22 a/o Mo and 2345 C or 34 a/o and 2290 C, whereas an American compilation reports monotonically increasing solidus curves for both Nb-Mo and Nb-W. The latter observation is in agreement with earlier work but still leaves considerable uncertainty about the melting points which may be related to the purity of the materials used.

#### Group VIIa

Manganese, Technetium and Rhenium. There is a very extensive solubility of Re in Nb (maximum solubility 42.5 a/o to 48 a/o Re). The solubility of Nb-Re reaches a maximum of 4 a/o and for Nb-Mn 2.4 a/o. Phases of a Mn structure have been reported for Nb-Re and Nb-Tc; in both cases wide homogeneity ranges have been observed including the compositions  $\text{NbX}_3$ . A  $\sigma$  phase exists at high temperatures in the Nb-Re system decomposing eutectoidally at a temperature variously reported as 2162 C or >2300 C. An  $\text{MgZn}_2$  type Laves phase  $\text{NbMn}_2$  exists in the Nb-Mn system but little is known of the Nb-rich alloys which are difficult to investigate at high temperatures because of the high vapor pressure of manganese.

### Group VIIa

Iron, Ruthenium, Osmium. The iron and osmium systems both show sigma phases; in the case of iron the phase breaks down eutectoidally at ~600 C.  $Fe_2Nb$  is hexagonal isomorphous with  $MgZn_2$ ,  $Fe_2Nb_3$  cubic of the  $Ti_2Ni$  type structure and another high temperature high Nb phase  $Nb_xFe_y$  has also been postulated. The Os system has  $Nb_3Os$  of the  $Cr_3Si$  ( $\beta$ -W type) structure, a  $\sigma$  phase and  $\chi$  phase of the **a-Mn** structure. The ruthenium system has been less well investigated and cph, bct and fcc orthorhombic phases have all been reported. Considerable intersolubility exists in the osmium and ruthenium systems (up to 27 a/o sol. of Nb in Os and 29 a/o in Ru; up to 19 a/o Os and possibly 58% Ru in Nb).

### Group VIIb

Cobalt, Rhodium and Iridium. These systems are characterized by a large number of intermetallic compounds. For example, Nb-Co shows  $NbCo_2$  Laves phase of the  $MgCu_2$  and **MgNi<sub>2</sub>** type, and possibly also of the  $MgZn_2$  type. NbCo is of the  $W_6Fe_7$  or  $\mu$  phase structure. Nb-Rh shows  $Cr_3Si$  ( $\alpha$ ), **a**, orthorhombic ( $\delta$  and  $\epsilon$ ), monoclinic  $\zeta$ , hexagonal  $VCu_3$  ( $\eta$ ),  $AuCu_3$  ( $\kappa$ ) phases and an unidentified  $\beta$  phase. Nb-Ir shows  $\sigma$ ,  $Cr_3Si$  ( $Nb_3Ir$ ),  $AuCu$  ( $\alpha_1$ ), orthorhombic ( **$\alpha_2$** ) and  $AuCu_3$  ( $NbIr_3$ ) type phases. Inter-solubility of cobalt and niobium is limited to a maximum of <5 a/o Nb in cobalt and <3 a/o Co in Nb whereas the maximum solubility of Nb in Rh is -16.5 a/o and in Ir -16 a/o; the maximum solubility of Rh in Nb is 20.5 a/o and of Ir in Nb is 12 a/o.

### Group VIIc

#### Nickel, Palladium and Platinum

Many intermetallic compounds are also found in these systems; the simplest system is Nb-Ni which shows  $Nb_7Ni_6$ , a phase of the  $W_6Fe_7$  type structure,  $NbNi_3$  of the orthorhombic  $TiCu_3$  type structure and  $Ni_8Nb$  a face centered tetragonal 9-layer structure. Nb-Pd has three compounds, NbPd (cubic Cu type),  $NbPd_2$  (orthorhombic  $MoPt_2$ ) and  $NbPd_3$  with 2 modifications (tetragonal  $TiAl_3$  with a 3-layer sequence) or (orthorhombic with a 6-layer sequence). Nb-Pt has four phases  $Nb_3Pt$  ( $Cr_3Si$  type),  $Nb_2Pt$  (tetragonal  $\sigma$  or  $\beta$ ),  $NbPt_3$  ( $\alpha TiCu_3$  type, monoclinic) NbPt (orthorhombic AuCd type) with the possibility of a body centered orthorhombic  $MoPt_2$  type NbPt<sub>2</sub> phase. The maximum intersolubilities are quite large thus for Nb 12.7 a/o in Ni >25 a/o in Pd and >25 in Pt (in the latter cases solubility is restricted by the appearance of ordered  $Nb_3$  phases) and for solubility in Nb 4.6 a/o Ni, 36 a/o Pd, <1 a/o Pt.

### Group Ib

Copper, Silver and Gold. Copper and silver show very little solubility with no compounds (solubility of Nb in Cu -0.6 a/o at 1050 C). However, gold forms a number of intermetallic compounds viz,  $\text{AuNb}_3$  ( $\text{Cr}_3\text{Si}$  type),  $\text{Nb}_3\text{Au}_2$  (body centered tetragonal type),  $\text{NbAu}_2$  (hexagonal  $\text{AlB}_2$  type) with the possibility of  $\text{Nb}_{11}\text{Au}_9$  (cubic  $\beta$  Mn type).

### Group IIb

Zinc, Cadmium and Mercury. Information is available for the Nb-Zn system and shows 6 intermetallic phases, three of these -  $\text{Nb}_2\text{Zn}_3$  (hexagonal),  $\text{NbZn}_2$  (hexagonal  $\text{MgNi}_2$  type) and  $\text{NbZn}_3$  (cubic  $\text{CuAu}_3$ ) - have been identified crystallographically and three  $\text{NbZn}$ ,  $\text{NbZn}_7$  and  $\text{NbZn}_{15}$  await identification. The  $\text{Cr}_3\text{Si}$  type structure has not been observed at  $\text{Nb}_3\text{Zn}$ . The solubility of Nb in Zn at -500 C is -0.05 a/o.

### Group IIIb

Boron, Aluminium, Gallium, Indium, Thallium. Little information is available on Nb-In and Nb-Tl except that a  $\text{Cr}_3\text{Si}$  type phase has been identified at  $\text{Nb}_3\text{In}$  but not at  $\text{Nb}_3\text{Tl}$ . The Nb-B system shows four compounds,  $\text{Nb}_3\text{B}_2$  (tetragonal  $\text{U}_3\text{Si}_2$  type),  $\text{NbB}$  (orthorhombic),  $\text{Nb}_2\text{B}_4$  (body centered orthorhombic isomorphous with  $\text{Ta}_3\text{B}_4$ ) and  $\text{NbB}_2$  (hexagonal) and a solubility of -2 a/o boron in niobium is indicated at 2165 C. In contrast to this the Nb-Al system shows only three compounds  $\text{Nb}_3\text{Al}$  (cubic  $\text{Cr}_3\text{Si}$  type),  $\text{Nb}_2\text{Al}$  (tetragonal  $\sigma$ ,  $\text{FeCr}$  type) and  $\text{NbAl}_3$  ( $\text{TiAl}_3$  type, tetragonal) with a solubility of -21.5 a/o aluminum in niobium at 2060 C and <0.3 Nb in Al at 661 C. The Nb-Ga system shows many compounds:  $\text{Nb}_3\text{Ga}$  (cubic,  $\text{Cr}_3\text{Si}$  type),  $\text{Nb}_5\text{Ga}_3$  (body centered tetragonal  $\text{W}_5\text{Si}_3$  type),  $\text{Nb}_3\text{Ga}_2$  ( $\text{U}_3\text{Si}_2$  type),  $\text{Nb}_5\text{Ga}_4$  (hexagonal  $\text{Ti}_5\text{Ga}_4$  type),  $\text{Nb}_5\text{Ga}_{13}$  (a centered orthorhombic) and  $\text{NbGa}_3$  (body centered tetragonal  $\text{TiAl}_3$  type).

The maximum solubility of gallium in niobium is -15 a/o at 1720 C

### Group IVb

Carbon, Silicon, Germanium, Tin and Lead. Apart from Nb-Pb which is reported by two sets of investigations to show immiscibility and no compounds, the other systems show several compounds. It should, however, be noted that the compound  $\text{Nb}_3\text{Pb}$  ( $\text{Cr}_3\text{Si}$  type) has been reported by another group. The system Nb-C shows a hexagonal  $\text{Nb}_2\text{C}$  and a cubic NaCl type NbC with a solubility of -8.5 a/o C in Nb at 2393 C Nb-Si has three compounds  $\text{Nb}_5\text{Si}_3$  (tetragonal  $\text{Cr}_5\text{B}_3$  type)  $\text{NbSi}_2$  (hexagonal  $\text{CrSi}_2$  type) and  $\text{Nb}_4\text{Si}$  (hexagonal), the solubility of Si in Nb is -3 a/o at 1000 C but the solubility of Nb in Si is very small. In the case of Nb-Ge there are four compounds: a  $\beta$  phase

(Cr<sub>3</sub>Si type but at -15 a/o Ge), NbGe<sub>2</sub> (hexagonal CrSi<sub>2</sub> type), Nb<sub>3</sub>Ge<sub>2</sub> (hexagonal Mn<sub>5</sub>Si<sub>3</sub> type) and Nb<sub>5</sub>Ge<sub>3</sub> (tetragonal); the solubility of Ge in Nb is -7 a/o at 1980 C whilst the solubility of Nb in Ge is very small. The Nb-Sn system has a Cr<sub>3</sub>Si type phase at Nb<sub>3</sub>Sn, a body centered orthorhombic phase at Nb<sub>6</sub>Sn<sub>5</sub> and a face centered orthorhombic Mg<sub>2</sub>Cu type phase NbSn<sub>2</sub>; the maximum solid solubility of Sn in Nb is -12 a/o at 2130 C with negligible solid solubility of niobium in Sn.

#### Group Vb

Nitrogen, Phosphorus, Arsenic, Antimony, Bismuth. The Nb-Bi system shows negligible solid solubility and no compounds. All of the other systems in this group show a number of compounds. Nb-N shows a hexagonal Nb<sub>2</sub>N and an NaCl type NbN with a maximum solid solubility for nitrogen of -13 a/o. The Nb-P system exhibits a body centered tetragonal NbP phase and a monoclinic (NbAs<sub>2</sub> type) NbP<sub>2</sub> phase. Six compounds have been reported for Nb-As, As<sub>3</sub>Nb<sub>4</sub>, As<sub>3</sub>Nb<sub>5</sub>, As<sub>4</sub>Nb<sub>7</sub> (monoclinic), AsNb<sub>3</sub>, As<sub>2</sub>Nb (monoclinic) and AsNb (body centered tetragonal). The Nb-Sb system shows four compounds, Nb<sub>3</sub>Sb (Cr<sub>3</sub>Si type), Nb<sub>3</sub>Sb<sub>2</sub>, NbSb and Nb<sub>4</sub>Sb<sub>3</sub>; and Nb<sub>5</sub>Sb<sub>4</sub> has been reported as tetragonal Ti<sub>5</sub>Te<sub>4</sub> type and NbSb<sub>2</sub> as monoclinic. The solid solubility of Sb in Nb reaches 20 a/o at 1760 C whereas the Nb solubility in Sb is very small. The conflicting information on the compounds suggests more work is required on this system.

#### Group VIb

Oxygen, Sulphur, Selenium, Tellurium, Polonium. Three oxides are reported for the system Nb-O, NbO, NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>; NbO is cubic, NbO<sub>2</sub> is tetragonal and Nb<sub>2</sub>O<sub>5</sub> monoclinic. The maximum solid solubility of oxygen in Nb is -9 a/o at 1915 C. Two sulphide phases NbS and NbS<sub>2</sub> have been described and there are a considerable number of selenides. NbSe (hexagonal), NbSe<sub>2</sub> (hexagonal of NbS<sub>2</sub>), Nb<sub>5</sub>Se<sub>4</sub> (body centered tetragonal Ta<sub>5</sub>Te<sub>4</sub>), Nb<sub>3</sub>Se<sub>4</sub> (hexagonal) and NbSe<sub>4</sub>, and tellurides Nb<sub>5</sub>Te<sub>4</sub> (body centered tetragonal), NbTe (rhombohedral), Nb<sub>3</sub>Te<sub>4</sub> (hexagonal), NbTe<sub>2</sub> (rhombohedral), NbTe<sub>4</sub> (tetragonal).

