The Transposition Structure of NbAs and of Similar Monophosphides and Arsenides of Niobium and Tantalum

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NbAs crystallizes in a new structure type, which is a transposition structure variation of the WC structure type. NbAs is tetragonal with $a = 3.45_2$ Å and $c = 11.67_9$ Å. The space group is $I4_1md$ (C_{4v}^{11}) with 4Nb in $4a$ with $z = 0$ and 4As in $4a$ with $z = \frac{5}{12}$. Other isotypic compounds are TaAs with $a = 3.43_7$ Å and $c = 11.65_6$ Å and 'β-NbP' with $a = 3.33_4$ Å and $c = 11.37_8$ Å. The previously proposed structure for α and β-NbP is proved to be wrong. Stoichiometric NbP or 'β-NbP' crystallizes in the NbAs structure, but P-deficient NbP_{1-x} has a partly disordered NbAs structure. The transposition is not as regular as in stoichiometric NbP. The degree of disorder depends nearly linearly on phosphorus deficiency. The new structure type is compared with other known monophosphide structure types. The concept of a structural transposition and its cancellation offers a new viewpoint for an explanation of the occurrence of more than one crystal structure for the same compound.

Introduction

In the course of a general study of the crystal chemistry of transition metal compounds, attention had been given to compounds with the 5 B group elements: phosphorus, arsenic and antimony. In the case of monophosphides and arsenides, data for the niobium and tantalum compounds had been missing or appeared to be wrong. In particular, a proposed structure for NbP and TaP (Schönberg, 1954) assumed an improbable arrangement of atoms which involved extremely short Nb–P distances (2·35 Å). Further, this proposed structure also showed no structural relation to the other known monophosphide structure types. In view of this fact, it seemed of interest first to study the crystal structure of niobium and tantalum arsenide and, second, to reinvestigate the monophosphide structures.

Experimental procedures

The arsenides and phosphides were prepared by heating the well mixed, chemically pure components in evacuated, sealed-off silica tubes up to 1000 °C (phosphides) or 1200 °C (arsenides). To avoid explosions it was necessary to raise the temperature slowly; this applied especially to phosphorus-containing samples which had to be kept at 500 °C or 550 °C for two days before raising the temperature. The samples were annealed at the peak temperature for 24 to 48 hours and then slowly cooled down. This method of preparation gave well reproducible and homogeneous products. The alloys were investigated by X-ray powder methods with a Debye–Scherrer camera and also a diffractometer and a proportional counter.

The structure determination of NbAs

The powder pattern of alloys with the composition of NbAs could be indexed if a tetragonal unit cell was assumed with the dimensions

$$a = 3.45_2 \text{ Å and } c = 11.67_9 \text{ Å}; \ c/a = 3.38_4.$$

Reflexions occurred only for (hkl): $h + k + l = 2n$ and $2k + l = 2n + 1$ or $4n$. With these extinctions the following space groups are possible: $I4_1$ (C_4^6),

Table 1. *Intensity calculation for* NbAs

(Cu $K\alpha$ radiation)

hkl	$10^3 \sin^2 \theta_c$ for α_1 peak	$10^3 \sin^2 \theta_o$ for α_1 peak when split recognizable	I_c	Integrated I_o for α_1 and α_2
101	54·2	54·1	15	11
004	69·6	69·6	19	20
103	89·0	89·1	45	39
112	117·0	117·0	90	90
105	158·6	158·6	34	35
200	199·2	199·1	24	23
211	253·4	253·5	2	2
116	256·2	256·3	0·4	<1
107	263·0	263·0	14	13
204	268·8	268·7	8	8
008	278·4	278·5	1	2
213	288·2	287·9	12	10
215	357·8	357·7	14	13
220	398·4	398·1	6 ⎫ 9	10
109	402·2	402·4	3 ⎭	
301	452·6	—	0·4	—
217	462·2	461·9	9	9
224	468·0	468·1	3	3
208	477·6	477·6	2	2
303	487·4	487·6	2	1
312	515·4	515·7	12	12
1110	534·6	534·7	5	6
305	557·0	557·1	3	2

$I4_1/a$ (C_{4h}^6), $I4_122$ (D_4^{10}), $I4_1md$ (C_{4v}^{11}), $I\overline{4}2d$ (D_{2d}^{12}), $I4_1/amd$ (D_{4h}^{19}).

From the size of the unit cell of NbAs, it can be concluded that each unit cell contains four formula units of NbAs. The X-ray density is 8·22 g.cm^{-3}.

Placing 4Nb and 4As each in one of the only two fourfold positions in $I4_1/a$, $I4_122$, $I\overline{4}2d$ and $I4_1/amd$ leads to an unreasonable geometric arrangement in the light of spacefilling, and no agreement between calculated and observed intensities can be found (residual index $R=0\cdot64$). Thus NbAs must belong to space group $I4_1$ or $I4_1md$. The more highly symmetrical space group was assumed and 4Nb were positioned in $4a$ with $z=0$ and 4As in $4a$ with $z=\frac{5}{12}$. To obtain the z value for As one can make use of the fact that the z-sensitive 116 reflexion has almost no intensity. Geometrical considerations also suggest this value. For the intensity calculation, a temperature factor of $B=1\cdot13\times10^{-16}$ cm was used. The observed and calculated intensities can be seen in Table 1. The agreement is good (residual index $R=0\cdot07$).

The NbAs structure type, a transposition structure variation of the WC structure type

The NbAs type is an example of a structure with commutative partial structures: an interchange of the Nb- and As-partial structures does not change the structure. It may be described as an arrangement of regular, (almost) trigonal Nb prisms, with an arsenic atom in the center. Along the c axis are stacked four of these trigonal prisms, which are rotated and shifted with respect to each other as required by the symmetry operation of a fourfold screw axis (Fig. 1).

Each atom is surrounded at equal distances by six nearest neighbors of the other species. The eight shortest distances between atoms of the same type are larger and fall into two groups of four, one of which is equal in magnitude to the lattice constant a of the unit cell (Table 2), the second slightly smaller. If these eight distances were equal the above mentioned Nb prisms would be truly trigonal. The slight distortion of the trigonal prisms can be seen from the
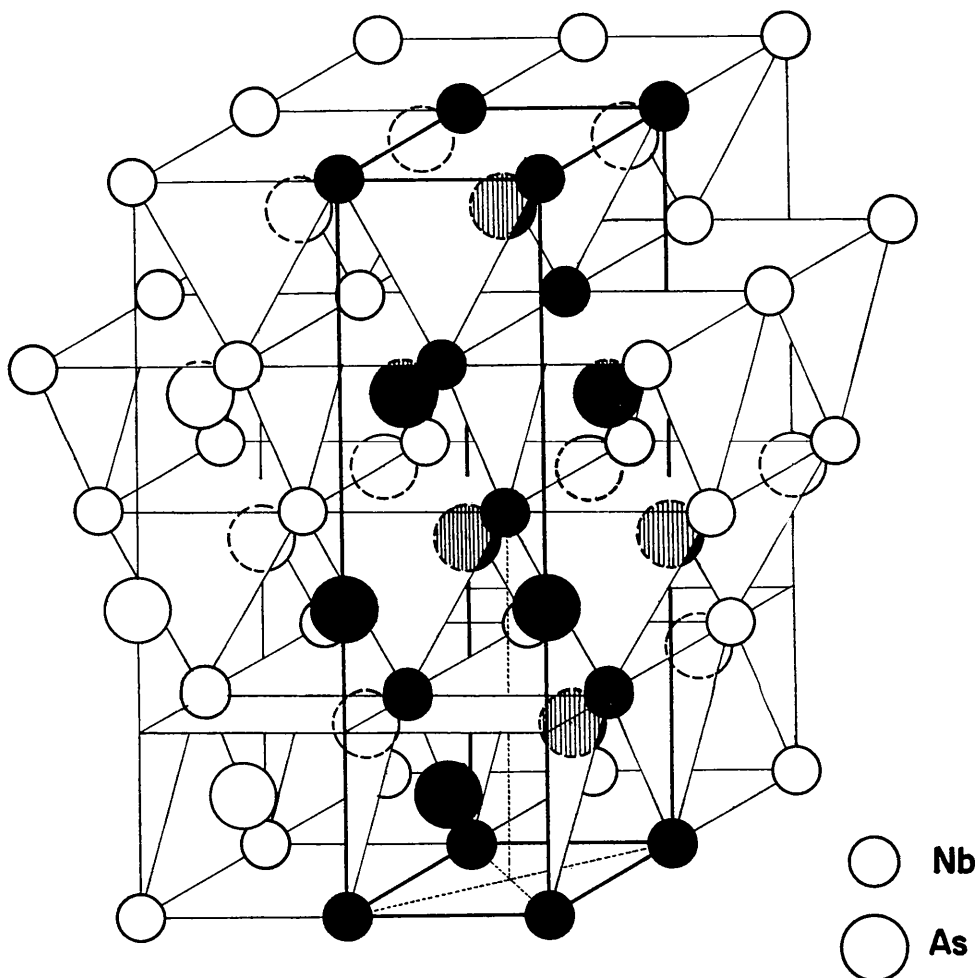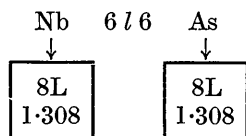

Fig. 1. Unit cell of NbAs and parts of neighboring unit cells.

Table 2. *Interatomic distances (in Å) of the nearest neighbors in compounds with NbAs-structure*

β-NbP   Nb$\Big\langle$ 4 Nb: $3\cdot33_4$
                                 4 Nb: $3\cdot29_9$ Nb–6 P: $2\cdot54_0$

NbAs   Nb$\Big\langle$ 4 Nb: $3\cdot45_2$
                                 4 Nb: $3\cdot39_2$ Nb–6 As: $2\cdot61_9$

TaAs   Ta$\Big\langle$ 4 Ta: $3\cdot43_7$
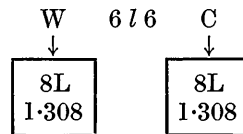   4 Ta: $3\cdot38_3$ Ta–6 As: $2\cdot61_0$

slight deviation of the c/a ratio from an ideal value. If one assumes an ideal NbAs structure with exactly trigonal prisms, one may formulate an ideal c/a ratio of $2\sqrt{3}=3\cdot46$ and an ideal z parameter for As of $\frac{5}{12}$.

To compare different crystal structure types with each other Laves devised, some 30 years ago, a so-called construction formula which can be formulated by counting the nearest neighbor atoms and calculating their relative distances (Laves, 1930, 1956; Parthé, 1961). The construction formula of an ideal NbAs structure is

$$
\begin{array}{ccc}
\text{Nb} & 6\,l\,6 & \text{As} \\
\downarrow & & \downarrow \\
\boxed{\begin{array}{c}\text{8L}\\1\cdot308\end{array}} & & \boxed{\begin{array}{c}\text{8L}\\1\cdot308\end{array}}
\end{array}
$$

A comparison of the construction formula of NbAs with that of WC shows that a geometrical correlation

exists between the two structure types. The structure of WC has been recently determined with neutron diffraction (Parthé & Sadagopan, 1962). The construction formula of WC with $c/a=1$ is given by

$$
\begin{array}{ccc}
\text{W} & 6\,l\,6 & \text{C} \\
\downarrow & & \downarrow \\
\boxed{\begin{array}{c}\text{8L}\\1\cdot308\end{array}} & & \boxed{\begin{array}{c}\text{8L}\\1\cdot308\end{array}}
\end{array}
$$

The construction formula of WC is identical with the one for NbAs. Two different structures which have identical construction formulas are called homeotect structures (Parthé, 1961). Structures which are homeotect can always be considered as different stacking variations of common structural unit slabs.

One can describe the NbAs structure type as a transposition structure (Verwerfungsstruktur; Schubert, Kiefer, Wilkens & Haufler, 1955) of the WC structure type. One unit cell of NbAs contains two slabs, each slab with an arrangement of atoms as in the WC structure. Each slab has half the height of the tetragonal c axis. These two slabs are transposed in respect to each other, the transposition vector being $\frac{1}{2}, \frac{1}{2}, 0$ for tetragonal axes. If there were no transposition, the total atomic arrangement would correspond to that of the WC structure. The point positions of the atoms in the WC structure described in terms of the tetragonal unit cell are then 4W in 000, $0\frac{1}{2}\frac{1}{4}$, $00\frac{1}{2}$, $0\frac{1}{2}\frac{3}{4}$, and 4C in $\frac{1}{2}0\frac{2}{12}$, $\frac{1}{2}\frac{1}{2}\frac{5}{12}$, $\frac{1}{2}0\frac{8}{12}$, $\frac{1}{2}\frac{1}{2}\frac{11}{12}$. All point positions with $\frac{1}{4}<z\le\frac{3}{4}$ are different
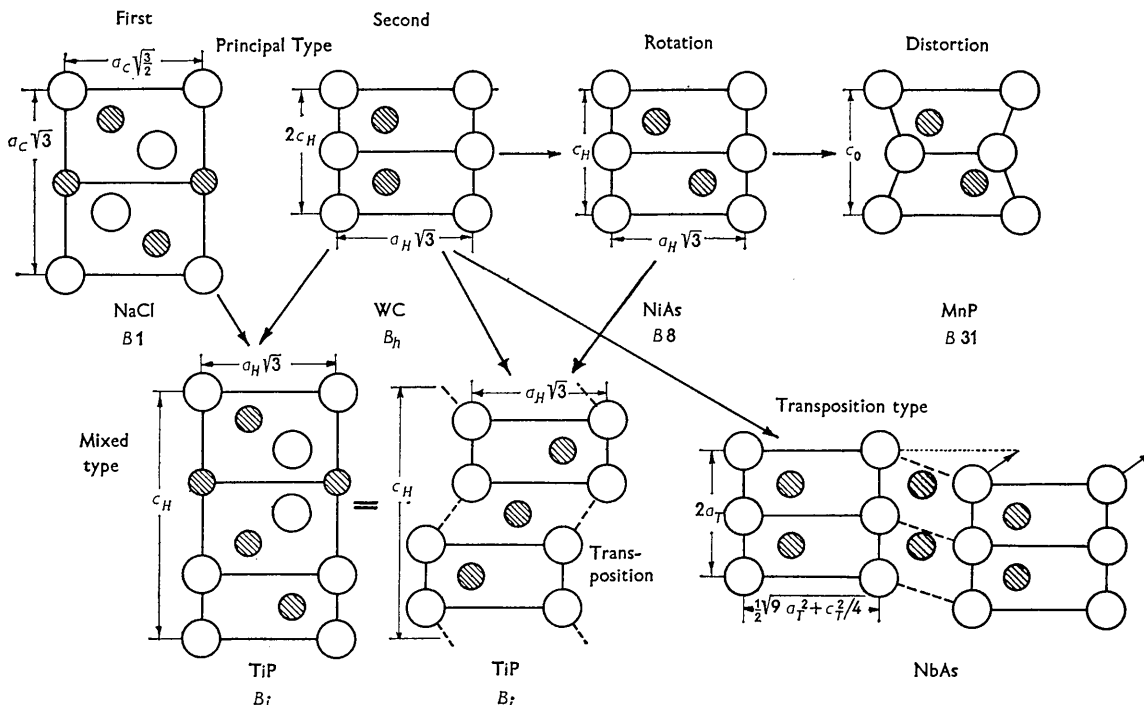

Fig. 2. The arrangement of the two kinds of hexagonal construction elements in monophosphide structure types.

from those for NbAs by the amount $\frac{1}{2}, \frac{1}{2}, 0$. The description of the NbAs structure as a transposition structure of WC will be very useful in the following discussion of the relationship between 'α-NbP' and 'β-NbP'.

To compare the NbAs structure with other monophosphide structure types, it is sometimes convenient to show the position of the atoms close to the 106 plane as demonstrated in Fig. 2. Here the unshifted WC construction element and the transposed element can be drawn into one plane.

Structure of TaAs and similar phosphides with Nb and Ta

(a) The crystal structure of TaAs

TaAs was found to be isotypic with NbAs, the lattice constants being

$$a = 3.43_7 \text{ Å}, \quad c = 11.65_6 \text{ Å}, \quad c/a = 3.39_1 .$$

The density was calculated to be 12·35 g.cm^{-3}. Table 3 shows the excellent agreement between calculated and observed intensities, assuming the same adjustable parameters as for NbAs.

(b) The niobium monophosphides

Schönberg (1954) reported two modifications of niobium monophosphides: 'α-NbP' at the approximate composition NbP$_{0.95}$ having a tetragonal face-centered unit cell, and 'β-NbP' at the composition NbP with an ordered b.c. tetragonal cell having a c axis twice as long as 'α-NbP'.

The similarity of the cell dimensions of 'β-NbP' and NbAs and the uniqueness of the 'β-NbP' type

Table 3. *Intensity calculation for* TaAs *with* NbAs *structure*

(Cu $K\alpha$ radiation)

hkl	$10^3 \sin_2 \theta_c$ for α_1 peak	$10^3 \sin^2 \theta_o$ for α_1 peaks when split recognizable	I_c	I_o for α_1 and α_2
101	54·5	54·6	48·7	s
004	69·9	70·0	31·7	ms
103	89·5	89·6	66·4	vs
112	117·8	118·0	125·2	vvs
105	159·5	159·6	46·7	s$^-$
200	200·7	200·9	35·4	s$^-$
211	255·3	255·5	11·0	mw
116	257·8	258·0	8·0	mw
107	264·3	264·6	21·1	m
204	270·7	270·9	16·9	m$^-$
008	279·8	280·1	3·5	w
213	290·3	290·5	21·3	ms
215	360·3	360·5	22·7	ms$^+$
220	401·7	401·8	10·8	mw$^+$
109	404·5	404·7	6·8	mw
301	456·4	456·4	2·2	w
217	465·4	465·5	17·4	m
224	471·8	471·8	7·2	mw$^+$
208	480·8	481·0	6·1	mw
303	491·5	491·7	4·9	mw$^-$
312	519·7	519·8	25·4	s
1110	538·0	538·1	10·3	m
305	561·2	561·4	6·8	mw

among the other monophosphide structures suggested a reinvestigation of these compounds. The extremely short NbP distance of 2·35 Å in the structure proposed by Schönberg for 'β-NbP' was particularly disturbing.

In agreement with Schönberg we found a very well crystallized phase at the composition NbP, which could be indexed tetragonal with

Table 4. *Intensity calculation for* 'β-NbP' *with* NbAs *structure*

(Cu $K\alpha$ radiation)

hkl	$10^3 \sin^2 \theta_c$ for α_1 peak	$10^3 \sin^2 \theta_o$ for α_1 peak, when split recognizable	I_c for NbAs structure type	Integrated I_o for α_1 and α_2	I_c according to Schönberg
101	58·0	57·9	43	43	31
004	73·3	73·4	23	23	41
103	94·6	94·7	42	42	16
112	125·0	125·1	73	74	74
105	168·0	168·0	26	24	7
200	213·4	213·3	19	20	16
211	271·4 ⎱	271·5	8 ⎱ 15 ⎱	17	6 ⎱ 27
116	271·7 ⎰		7 ⎰ ⎰		21 ⎰
107	278·0	278·2	11	11	3
204	286·7	286·9	11	12	19
008	293·3	293·4	2	2	5
213	308·0	308·1	12	12	5
215	381·4	381·4	13	14	3
109	424·6	424·7	4	3	1
220	426·9	426·8	11	10	5
301	484·8	485·0	2	2	1
217	491·4	491·3	10	9	2
224	500·2	500·2	5	5	8
208	506·7	506·8	4	5	8
303	521·4	521·2	3	3	1
312	551·9	552·0	14	16	14
1110	565·0	565·1	6	8	7

$a = 3.334$, $c = 11.378$ Å, $c/a = 3.412$.

While the lattice constants are almost identical with Schönberg's, a considerable discrepancy was noticed between our observed intensities and those reported by Schönberg. The intensities for 'β-NbP' were calculated on the basis of the NbAs type and the structure proposed by Schönberg. No temperature factor correction was necessary. Table 4 shows the excellent agrement between observed and calculated intensities when a NbAs structure type is assumed with the same adjustable parameters (residual index $R = 0.04$), while the structure proposed by Schönberg can be ruled out with certainty (residual index $R = 0.30$). Thus 'β-NbP' crystallizes in space group $I4_1md$ (C_{4v}^{11}), and not in space group $I4_122$ (D_4^{10}). 'β-NbP' is isotypic with NbAs.

Alloys containing less phosphorus than 50 at.%, corresponding to Schönberg's 'α-NbP', show remarkable broadening of all lines with odd l indices, while the others with even l indices remain unchanged in sharpness and intensity. With an increase of the phosphorus deficiency in NbP_{1-x} diffraction lines with odd l indices become broader and their integrated intensity decreases. This phenomenon is already noticeable at a composition corresponding to $NbP_{0.96}$ and becomes more distinct as the $NbP_{0.81}$ composition is approached. In alloys richer in niobium the b.c.c. pattern of Nb appears. The a value of the cell remains unchanged, while a slight expansion is observed of the c dimension from $c = 11.378$ Å for 'β-NbP' to $c = 11.400$ Å for $NbP_{0.81}$. Since this process is continuous and gradual, the distinction between 'α-NbP' and 'β-NbP' as different phases becomes meaningless (see also Fig. 3).
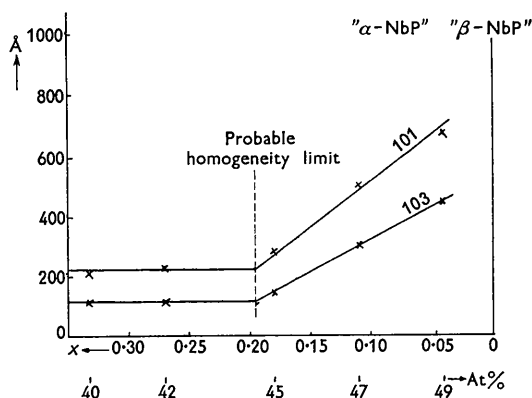

Fig. 3. Average size of undisturbed transposition structure domains in NbP_{1-x} in the [101] and [103] directions (grain size bigger than 1000 Å).

Concerning the structure of the P-deficient NbP, the data of Schönberg for his 'α-NbP' are incorrect since he obviously missed the broadened lines with odd l indices. The apparent intensities of broadened lines are generally underestimated, unless the inte-

grated intensities are measured. One may even assume that his data for the so-called 'β-NbP' correspond to a slightly P-deficient niobium monophosphide, because he reported much too small intensities for all lines with odd l indices and thus missed the correct structure type for NbP.

To account for the occurrence of sharp lines with even l and broadened lines with odd l in the same pattern, a search had to be made for a model having statistical disorder in special directions. Since it was found that the NbP is a transposition variation of the WC structure, a statistical displacement of the earlier mentioned slabs perpendicular to the c axis of the tetragonal cell was tentatively assumed. This would account for the 004 and 008 reflexions remaining sharp. But to account for the fact that all other lines with $l = 2n$ remain sharp a fixed displacement vector has to be assumed. A structure factor calculation showed that the displacement vector must be $\frac{1}{2}, \frac{1}{2}, 0$. For $l = 2n$ ($h + k = 2n$ and $2k + l = 4n$) the structure factor remains invariant if the displacement of any one slab is $\frac{1}{2}, \frac{1}{2}, 0$. This means the X-rays are reflected from these planes as if the crystal has no displacements of slabs. This is different for all other reflexions which, therefore, are broadened.

If one unit cell of NbP is considered and one slab is shifted by the displacement vector $\frac{1}{2}, \frac{1}{2}, 0$ the transposition in the NbP structure cancels out and the WC structure is obtained. This is indicated by the arrows in the drawing for the NbAs structure type in Fig. 2. In a crystal of NbP_{1-x} not every unit cell has its transposition cancelled; only a few have and these unit cells are distributed statistically over the total crystals. Thus the observed structure of NbP_{1-x} is 'half-way' between the NbAs and WC structure. This statement will become clear from the schematic drawing shown in Fig. 4.
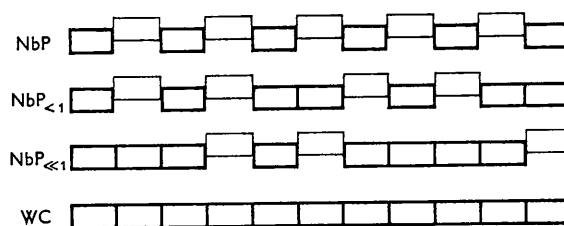

Fig. 4. Arrangements of the slabs for NbP, $NbP_{<1}$, $NbP_{\ll 1}$ and WC.

It might be surmised that with high P-deficiency the simple WC structure would be restored, but alloys up to 70% Nb have been prepared and the broadened l-odd lines did not disappear. Fig. 3 shows the change of the average size of the undisturbed NbP domains with P-deficiency. The size was determined by using Scherrer's formula and the Laue integral breadths of the 101 and 103 diffraction lines. Between 49 and 45 at.% phosphorus the domain size decreases linearly with increasing phosphorus deficiency in the direction

to (Nb_4P_3). At lower phosphorus content the domain size does not change noticeably and faint Nb lines appear on the diffraction diagram. Thus, the lower homogeneity limit of the NbP_{1-x} phase lies at about 44·5 at.% phosphorus. A more detailed and accurate Fourier analysis of the line profiles will be undertaken at a later time.

(c) Structure of 'α-TaP' and 'β-TaP'

Tantalum phosphides have not been examined by us, but in view of the fact that Schönberg reported them to be isotypic with the niobium phosphides, one may safely assume that stoichiometric TaP has the NbAs structure. P-deficient 'α-TaP' also probably crystallizes in a modified NbAs structure where a statistical cancellation of the transposition of WC unit slabs has occurred. Again the distinction between 'α-TaP' and 'β-TaP' becomes meaningless.*

The NbAs structure type in comparison with the other monophosphide types

Table 5 shows a survey of the transition metal phosphides, arsenides, and antimonides reported in the

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* *Note added in proof.* Dr Stig Rundquist from the University of Uppsala has informed us that stoichiometric TaP actually crystallizes with the NbAs structure. X-ray diffraction patterns of alloys with higher Ta content show again diffuse lines with odd l index and sharp lines with even l index.

literature. Six different structure types have been observed: the NaCl type occurs with the transition metals of the IIIA group, the lanthanides and actinides. These compounds are formed according to the valence rules, obviously having a considerable amount of ionic bonding. With the fourth group transition metals there is a competition between the NaCl, the TiP and the NiAs type. In the second and third period of the fifth group there is the NbAs type and its variation leading to the simple WC type as presented in MoP. With the rest of the transition metals, the MnP and NiAs types occur. Thus starting from the left side of the periodic table, the monophosphides and homologues occur in the following crystal structure types:

$$\text{NaCl–TiP–NbAs–WC–MnP,}$$

while representatives of the NiAs type are rather uniformly found in groups 4A through 8A.

These monophosphide structures are all geometrically closely related (Jellinek, 1959). Fig. 2 shows the geometrical arrangement of the atoms in the $(11\bar{2}0)$ plane of the NiAs type and the equivalent planes of the other monophosphides. All these types can be constructed from two kinds of principal unit: half the hexagonal NaCl cell, and the WC cell. The TiP structure takes an intermediate position. It can be regarded as a mixed structure, built up from NaCl and WC units. Actually it coexists in the fourth group with the NaCl type in the Zr–P system

Table 5. *Crystal structures of transition metal monophosphides and homologues*

IIIA	IVA	VA	VIA	VIIA	VIIIA		
ScP $\overline{B1}$	TiP $\overline{B_t}$	VP $\overline{B8}$	CrP $\overline{B31}$	MnP $\overline{B31}$	FeP $\overline{B31}$	CoP $\overline{B31}$	
ScAs $\overline{B1}$	TiAs $\overline{B8 \leftarrow B_t}$	VAs $\overline{B31}$	CrAs $\overline{B31}$	MnAs $\overline{B8}$	FeAs $\overline{B31}$	CoAs $\overline{B31}$	NiAs $\overline{B8}$
ScSb $\overline{B1}$	TiSb $\overline{B8}$	VSb $\overline{B8}$	CrSb $\overline{B8}$	MnSb $\overline{B8}$	FeSb $\overline{B8}$	CoSb $\overline{B8}$	NiSb $\overline{B8}$
YP $\overline{B1}$	ZrP $\overline{B1 \leftarrow B_t}$	NbP $\overline{(B_h) \leftarrow \text{NbAs}}$	MoP $\overline{B_h}$		RuP $\overline{B31}$		
YAs $\overline{B1}$	ZrAs $\overline{B_t}$	NbAs $\overline{\text{NbAs}}$					
YSb $\overline{B1}$						RhSb $\overline{B31}$	PdSb $\overline{B8}$
LaP $\overline{B1}$	HfP $\overline{B_t}$	TaP $\overline{(B_h) \leftarrow \text{NbAs}}$	WP $\overline{B31}$	ReP			
LaAs $\overline{B1}$	HfAs $\overline{B_t}$	TaAs $\overline{\text{NbAs}}$					
LaSb $\overline{B1}$							PtSb $\overline{B8}$

Other lanthanides and actinides with $B1$ structure: CeP, CeAs, CeSb, PrP, PrAs, PrSb, NdP, NdAs, NdSb SmP, SmAs, SmSb and ThP, ThAs, ThSb, UP, UAs, USb, PuP, PuAs.

Notation of structure types: $B1$ = NaCl type, $B8$ = NiAs type, $B31$ = MnP type, B_h = WC type, B_t = TiP type.
An arrow points to that structure type which occurs with non-metal deficiency.

(Schönberg, 1954). The structure types of NiAs, MnP, NbAs and TiP may be considered variations of the WC structure type. Rotation of two WC slabs against each other gives the NiAs type and subsequent distortion gives the orthorhombic MnP type. Transposition results in the NbAs type and also the TiP type. The TiP type may thus be considered from two viewpoints and is either a NaCl–WC mixed type or a NiAs transposition type.

Other tranposition structures

The partial cancellation of the transposition of a transposition structure with deficiency of one component observed with NbP may also occur with other compounds. Two modifications of TiAs have been reported: 'α-TiAs' with the NiAs structure, deficient in As content, and stoichiometric 'β-TiAs' with the TiP structure (Bachmayer, Nowotny & Kohl, 1955). It would be very interesting to investigate whether perhaps 'α-TiP' actually possesses a partly disordered TiP structure, because this phase was reported to be always accompanied by weak lines of the TiP phase. As in the case of NbP the deficiency of B metal tends to cancel the transposition but would produce here the NiAs structure instead of the WC structure.

Schönberg (1954) reports also two ZrP modifications: one for P-deficient 'α-ZrP' with NaCl structure and a stoichiometric 'β-ZrP' with TiP structure. A complete transition between both structure types could occur here.

It might be mentioned that the ThSi$_2$ structure type can be considered as a transposition structure based upon the $C32$ (AlB$_2$) structure. Many transition metal disilicides and digermanides crystallize in these two structure types. Often both types are reported for one disilicide or digermanide. In some cases the structures correspond to a high and low temperature modification (Mayer, Banks & Post, 1962), in others the ThSi$_2$ structure type occurs close to the stoichiometric composition, but the AlB$_2$ structure type for a compound with silicon or germanium deficiency (Tharp, Searcy & Nowotny, 1958). It might well be that the experimental data could be explained by

assuming a transition between these two structure types similar to that demonstrated for NbP.

The total experimental evidence seems to indicate that with B-element deficiency the transposition structure types or mixed structure types (NbAs, TiP, ThSi$_2$) tend to cancel the transposition and to form the principal type from which they were derived (WC, NiAs or NaCl and AlB$_2$).

The concept of a structural transposition and its cancellation offers a viewpoint to explain the often puzzling occurrence of two or more different structure types at the same or close to the same composition. Whenever two structures are reported for one compound, and when these two structures are geometrically related as transposition structure to non-transposition structure, it might be possible that a continuous transition exists between them. Both structures belong then to one phase only, being on different sides of its homogeneity range.

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