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New intermediate phases in systems of Nb or Ta with Rh, Ir, Pd, or Pt.

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Table 1. *New intermediate phases*

Compositional designation	Crystal system	Structure type	Layer structure symbol	a_0	b_0	c_0	α
$(Nb_{0\cdot85}Rh_{0\cdot15})Rh$	orthorhombic	*B*19–AuCd	AB(2)	2·813 Å	4·808 Å	4·510 Å	
α NbPt*	orthorhombic	*B*19–AuCd	AB(2)	2·780	4·983	4·611	
$(Nb_{0\cdot96}Rh_{0\cdot04})Rh$	tetragonal	$L1_0$–AuCu	AB(3)	4·019		3·809	
$(Nb_{0\cdot95}Ir_{0\cdot05})Ir$	tetragonal	$L1_0$–AuCu	AB(3)	4·027		3·863	
$(Ta_{0\cdot79}Rh_{0\cdot21})Rh$	orthorhombic	α TaRh	AB(6)	2·822	4·742	13·551	
$(Nb_{0\cdot90}Rh_{0\cdot10})Rh$	orthorhombic	α TaRh	AB(6)	2·827	4·770	13·587	
$(Nb_{0\cdot85}Ir_{0\cdot15})Ir$	orthorhombic	α TaRh	AB(6)	2·823	4·818	13·619	
$(Ta_{0\cdot86}Ir_{0\cdot14})Ir$	orthorhombic	α TaRh	AB(6)	2·830	4·803	13·661	
$(Nb_{0\cdot75}Rh_{0\cdot25})Rh$†	monoclinic	Nb_3Rh_5	AB(9)	2·806	4·772	20·25	90° 31·5′
$NbPt_2$	orthorhombic	$NbPt_2$	$AB_2(3)$	2·801	8·459	3·951	
$TaPd_2$	orthorhombic	$NbPt_2$	$AB_2(3)$	2·896	8·397	3·790	
$TaPt_2$	orthorhombic	$TaPt_2$	$AB_2(2)$	8·403	4·785	4·744	
$TaRh_2$	orthorhombic	Co_2Si		8·179	5·454	4·027	
α $NbPt_3$	orthorhombic	DO_a–$TiCu_3$	$AB_3(2)$ sh $\frac{1}{2}$	5·534	4·873	4·564	
$Nb(Rh_{0\cdot90}Nb_{0\cdot10})_3$	hexagonal	VCo_3	$AB_3(6)$ sh 0	5·483		13·405	
β $NbPd_3$	orthorhombic	β $NbPd_3$	$AB_3(6)$ sh $\frac{1}{2}$	5·486	4·845	$13{\cdot}60_2$	
β $NbPt_3$	monoclinic	β $NbPt_3$	$AB_3(12)$ sh $\frac{1}{2}$	$5{\cdot}53_7$	$4{\cdot}87_0$	$27{\cdot}3_3$	90° 32′
β $TaPt_3$	monoclinic	β $NbPt_3$	$AB_3(12)$ sh $\frac{1}{2}$	5·537	4·869	27·33	90° 32·4′

* Measured at Nb + 52 at.% Pt.

† Possible further ordering based on Nb_3Rh_5 leads to doubling of a_0 and b_0.

Recent investigations of binary systems combining Nb or Ta with Rh, Ir, Pd, or Pt showed the existence of several new intermediate phases, in addition to those previously reported (Greenfield & Beck, 1956; Dwight & Beck, 1959; Nevitt, 1963; Darby, Downey & Norton, 1963). These new phases will be described in more detail in separate publications dealing with the respective phase diagrams.

The structures were deduced mostly from powder patterns taken with a 114·6 mm camera and Cu *K*α or Cr Kα radiation; however, α TaRh, $TaRh_2$, Nb_3Rh_5, and β $NbPt_3$ rotating crystal patterns were employed to facilitate indexing. For all powder patterns, internal standards were used. Error limits on all measurements are $< 5{\cdot}10^{-4}$. In Table 1 are listed the new intermediate phases. Besides the customary data a symbol A_mB_n (*l*) sh *x* is presented for all close-packed layer structures, listing the composition A_mB_n, the number *l* of close packed layers per unit cell, and the shift density *x* in the unit layer (for AB_3 phases), following a suggestion by Wegst & Schubert (1958). Table 2 lists the new structure types together with the layer stacking sequence.

Table 2. *New structure types*

α TaRh:

Orthorhombic, space group *Pmcm* (D^5_{2h}); $N = 12$ atoms per cell. Stacking sequence *babcac*, *babcac.*

$$\begin{array}{llllll}
\text{Ta:} & 4(i): & x_i = 0; & y_i \approx 0{\cdot}317; & z_i \approx -\frac{1}{12} = -0{\cdot}083; \\
 & 2(e): & x_e = 0; & y_e \approx 0{\cdot}05; & z_e = \frac{1}{4}; \\
\text{Rh:} & 4(j): & x_j = \frac{1}{2}; & y_j \approx 0{\cdot}817; & z_j \approx -\frac{1}{12} = -0{\cdot}083; \\
 & 2(f): & x_f = \frac{1}{2}; & y_f \approx 0{\cdot}55; & z_f = \frac{1}{4}
\end{array}$$

Table 2 (*cont.*)

Nb_3Rh_5:

Monoclinic, space group *P*2/*m* (C^1_{2h}); $N = 18$ atoms per cell. Stacking sequence *ababcbcac*, *ababcbcac.*

$$\begin{array}{lll}
Nb_{0\cdot75}Rh_{0\cdot25}: & 4\times2(m): & \pm(0, y_{1-4}, z_{1-4}) \\
 & 1(a): & (0, 0, 0) \\
\text{Rh:} & 4\times2(n): & \pm(\frac{1}{2}, y_{5-8}, z_{5-8}) \\
 & 1(e): & (\frac{1}{2}, \frac{1}{2}, 0)
\end{array}$$

$$\begin{array}{lll}
y_1 \sim \frac{2}{3}; & z_1 \sim \frac{1}{9}; & \\
y_2 \sim 0; & z_2 \sim \frac{2}{9}; & y_{5-8} \sim \frac{1}{2} + y_{1-4}; \\
y_3 \sim \frac{2}{3}; & z_3 \sim \frac{3}{9}; & z_{5-8} \sim z_{1-4}\,. \\
z_4 \sim \frac{1}{3}; & z_4 \sim \frac{4}{9}; &
\end{array}$$

$NbPt_2$:

Orthorhombic, space group *Immm* (D^{25}_{2h}); $N = 6$ atoms per cell. Stacking sequence *abc*, *abc.*

$$\begin{array}{llll}
[000; & \frac{1}{2}, \frac{1}{2}, \frac{1}{2}] & & \\
+\text{Nb:} & 2(a): & 000; & \\
+\text{Pt:} & 4(g): & \pm(0y0); & y = 0{\cdot}337 \pm 0{\cdot}001\,.
\end{array}$$

$TaPt_2$:

Orthorhombic, space group *Cmcm* (D^{17}_{2h}); $N = 12$ atoms per cell. Stacking sequence *ab*, *ab.*

$$\begin{array}{lll}
[000; & \frac{1}{2}, \frac{1}{2}, 0] & \\
+\text{Ta:} & 4(c): & \pm(0, y_c, \frac{1}{4}); \\
+\text{Pt:} & 8(g): & \pm(x_g, y_g, \frac{1}{4};\ \bar{x}_g, y_g, \frac{1}{4}); \\
 & & y_c \sim 0{\cdot}22;\quad x_g \sim \frac{1}{6};\quad y_g \sim y_c + \frac{1}{2} \sim 0{\cdot}72\,.
\end{array}$$

Table 2 (*cont.*)

β $NbPd_3$:

Orthorhombic, space group $Pmmn$ (D_{2h}^{13}); $N=24$ atoms per cell. Stacking sequence *babcac*, *babcac*.

Nb: $2(a)$: $\pm(\frac{1}{4}, y_a, \frac{1}{4})$; $y_a \sim 0$;
$4(e)$: $\pm(\frac{1}{4}, y_{e1}, z_{e1}; \ \frac{1}{4}, y_{e1}, \frac{1}{2}-z_{e1})$;
$y_{e1} \sim \frac{2}{3}$; $z_{e1} \sim -\frac{1}{12}$;
Pd: $2(b)$: $\pm(\frac{1}{4}, y_b, \frac{3}{4})$; $y_b \sim 0$;
$4(e)$: $\pm(\frac{1}{4}, y_{e2}, z_{e2}; \ \frac{1}{4}, y_{e2}, \frac{1}{2}-z_{e2})$;
$y_{e2} \sim \frac{1}{3}$; $z_{e2} \sim \frac{1}{12}$;
$4(f)$: $\pm(x_f, y_f, \frac{1}{4}; \ \frac{1}{2}-x_f, y_f, \frac{1}{4})$; $x_f \sim 0$;
$y_f \sim y_a+\frac{1}{2} \sim \frac{1}{2}$;
$8(g)$: $\pm(x_g, y_g, z_g; \ \frac{1}{2}-x_g, y_g, \frac{1}{2}-z_g; \ \frac{1}{2}-x_g, y_g, z_g;$
$x_g, y_g, \frac{1}{2}-z_g)$; $x_g \sim 0$; $y_g \sim y_{e1}-\frac{1}{2} \sim \frac{1}{6}$;
$z_g \sim z_{e1} \sim -\frac{1}{12}$.

β $NbPt_3$:

Monoclinic, space group $P2_1/m$ (C_{2h}^2); $N=48$ atoms per cell. Stacking sequence *cacabcbcabab*, *cacabcbcabab*.

Nb: $6\times2(e)$: $\pm(\frac{1}{4}, y_{1-6}, z_{1-6})$;
Pt: $6\times2(e)$: $\pm(\frac{1}{4}, y_{7-12}, z_{7-12})$;
$6\times4(f)$: $\pm(x_{13-18}, y_{13-18}, z_{13-18};$
$\frac{1}{2}-x_{13-18}, y_{13-18}, z_{13-18})$;
$y_1 \sim \frac{1}{3}$; $z_1 \sim \frac{1}{24}$;
$y_2 \sim 0$; $z_2 \sim \frac{5}{24}$; $y_{7-12} \sim \bar{y}_{1-6}$; $z_{7-12} \sim \bar{z}_{1-6}$;
$y_3 \sim 0$; $z_3 \sim \frac{9}{24}$;
$y_4 \sim \frac{2}{3}$; $z_4 \sim \frac{13}{24}$; $x_{13-18} \sim 0$; $y_{13-18} \sim \frac{1}{2}+y_{1-6}$;
$y_5 \sim \frac{2}{3}$; $z_5 \sim \frac{17}{24}$; $z_{13-18} \sim z_{1-6}$.
$y_6 \sim \frac{1}{3}$; $z_6 \sim \frac{21}{24}$;

In addition to these structures, phases of the $NbPt_2$ type were found in VNi_2, VPd_2, VPt_2, and $NbPd_2$, and an additional $TiCu_3$ type phase was encountered in α $TaPt_3$. VNi_2 and VPt_2 have also been recently reported by Schubert *et al.* (1963) who also found a phase $Nb_{40}Pd_{60}$ of the same type as $NbPd_2$.

All described AB and AB_3 phases are close-packed, as is the A_3B_5 phase. In the $NbPt_2$ type, the lattice can be regarded as composed of plane close-packed layers in the (101) plane in which each Nb atom is surrounded by 6 Pt atoms, stacked in the sequence *abc*, *abc*. The $TaPt_2$ lattice is made up of similar layers stacked in sequence *ab*, *ab*; however, there is a considerable displacement from ideal positions in this case.

In most cases where A and B belong to the same long period, lines due to ordering of the lattice were not observed with certainty. This leaves the possibility of a larger unit cell, especially for β $NbPd_3$, where a larger shift density seems possible and for $(Nb_{0 \cdot 75}Rh_{0 \cdot 25})Rh$, where a larger ordered basal plane A_3B_5 is possible.

α $NbPt_3$ ($TiCu_3$ type) is probably stabilized with respect to β $NbPt_3$ by very small amounts of interstitial impurities.

On comparing the mean atomic volumes for each phase to those calculated from a Vegard's law straight line (Massalski & King, 1961), it was found that there is a strong contraction for AB and AB_3 phases and a smaller contraction for AB_2 phases, especially $TaPt_2$ and $TaRh_2$, Nb_3Rh_5 being intermediate. This agrees with the above mentioned distortion in $TaPt_2$.

The results support the concept (*e.g.* Brewer, 1963) that the determining factor for the stability of a given layer structure is the valence electron/atom ratio, resulting in 2- or 3-layer structures, but that small changes of this quantity and of the size factor, especially by off-stoichiometry or impurities, influence the layer type and produce more complex close-packed intermediate structures.

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Crystallographic data for silver acetylide.

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Passage of acetylene into aqueous silver nitrate solution produces a precipitate, according to conditions (Vestin & Ralf, 1949), of either Ag_2C_2, $Ag_2C_2 . AgNO_3$ or $Ag_2C_2 . 6AgNO_3$. The 1:1 complex can also be made by reaction of the 1:6 complex with water (Shaw & Fisher, 1946).

Specimens of the 1:1 complex were prepared by both of the above methods, and their chemical identity established by analysis (Found: Ag 78·9%, C 6·1%, N 3·7%; $Ag_2C_2 . AgNO_3$ requires Ag 79·0%, C 5·86%, N 3·42%). Powder diffraction patterns were obtained with both a Philips Debye-Scherrer camera (diameter 114·83 mm) and a Philips recording diffractometer in conjunction with a silicon standard. The observed *d* values are listed in Table 1; these can be indexed on a body-centred tetra-