35, and 50 kV. The variation observed was less than the standard deviation of the measurements. For the 444 reflection with Cu radiation at 20, 35 and 50 kV, there was no difference in the values of a, the difference in measured θ_{444} being only 1·0 sec.

In the same way, and using the same germanium crystal, determination was made of the ratio of the Co $K\alpha_1$ wavelength and of the Fe $K\alpha_1$ wavelength to Cu $K\alpha_1$. λ Co $K\alpha_1$ was computed from the 333 reflection for which $\theta = 55{\cdot}2°$. λ Fe $K\alpha_1$ was measured from the 333 reflection at $\theta = 62{\cdot}7°$. A summary of the calculation and corrections is given in Table 1. The calculated wavelengths and wavelength ratios are shown in Table 2 where they are compared with the values of Siegbahn.

Table 2. *Calculated wavelengths and ratios*

	Cooper	Siegbahn
Cu $K\alpha_1$	1·537395 kX (assumed)	1·537395 kX
Mo $K\alpha_1$	0·707840 ± 0·000005	0·707831
Co $K\alpha_1$	1·78528 ± 0·00002	1·78529
Fe $K\alpha_1$	1·93204 ± 0·00001	1·932076
λ(Mo)/λ(Cu)	0·460415	0·460409
λ(Co)/λ(Cu)	1·16124	1·16124
λ(Fe)/λ(Cu)	1·25670	1·25672

The Co/Cu ratio is identical with Siegbahn's, while the Fe/Cu ratio differs by 16 ppm, and the Mo/Cu ratio differs by 13 ppm.

I am indebted to W. L. Bond and to J. W. M. DuMond for helpful advice and discussion.

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New intermediate phases in transition metal systems. II.

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This report is a continuation of a former abstracted communication (Giessen & Grant, 1964) on intermediate phases encountered in the course of an examination of binary transition metal systems containing a refractory metal component. Detailed descriptions of this work have been published, or submitted for publication (Giessen, Ibach & Grant, 1964; Ritter, Giessen & Grant, 1964; Giessen, Kane & Grant, 1965). Since, additional binary and ternary systems have been investigated and 18 new ordered phases have been found. Detailed descriptions of this work will again be published elsewhere.

The structures were all derived from powder patterns taken with an XRD 5 diffractometer or with a 114·6 mm camera and Cu $K\alpha$ radiation; this was made possible by the fact that the complex close-packed structures are related, and that their powder patterns show typical coincid-

Table 1. *New binary and ternary transition metal phases*

Compositional designation	Crystal system	Structure type	Layer structure symbol	a_0	b_0	c_0
MoIr	Orthorhombic	*B*19 – AuCd	AB(2)	2·752 Å	4·804 Å	4·429 Å
WIr	Orthorhombic	*B*19 – AuCd	AB(2)	2·760	4·811	4·452
α – VIr	Orthorhombic	α – VIr	—	5·791	6·756	2·796
$(V_{0{\cdot}96}Ir_{0{\cdot}04})Ir : (\beta - VIr)$	Tetragonal	$L1_0$ – AuCu	AB(3)	3·887		3·651
$TaNi_2$	Tetragonal	$MoSi_2$	—	3·154		7·905
$MoIr_3$	Hexagonal	DO_{19} – $MgCd_3$	$AB_3(2)$ sh 0	5·487		4·385
WRh_3	Hexagonal	DO_{19} – $MgCd_3$	$AB_3(2)$ sh 0	5·453		4·350
β – $TaNi_3$	Monoclinic	β – $NbPt_3$*	$AB_3(12)$ sh ½	5·11	4·54 $\alpha = 90°38'$	$25{\cdot}5_0$
$Ta(Pd_{0{\cdot}92}Rh_{0{\cdot}08})_3$	Orthorhombic	β – $NbPd_3$†	$AB_3(6)$ sh ½‡	5·492	4·829	13·54
$Ta(Pd_{0{\cdot}72}Rh_{0{\cdot}28})_3$	Rhombohedral	β – Ta(Pd, Rh)$_3$ (ordered Sm)	$AB_3(9)$ sh 0	5·517		20·26
$Ta(Pd_{0{\cdot}88}Ru_{0{\cdot}12})_3$	Rhombohedral	β – Ta(Pd, Rh)$_3$	$AB_3(9)$ sh 0	5·531		$20{\cdot}25_2$
$Ta(Pd_{0{\cdot}67}Rh_{0{\cdot}33})_3$	Hexagonal	γ – Ta(Pd, Rh)$_3$	$AB_3(10)$ sh 0	$5{\cdot}52_0$		$22{\cdot}4_3$
$Ta(Pd_{0{\cdot}5}Rh_{0{\cdot}5})_3$	Hexagonal	$PuAl_3(VCo_3)$	$AB_3(6)$ sh 0	5·530		$13{\cdot}49_3$
$Ta(Pd_{0{\cdot}75}Ru_{0{\cdot}25})_3$	Hexagonal	$PuAl_3(VCo_3)$	$AB_3(6)$ sh 0	5·509		13·44
$Ta(Pd_{0{\cdot}725}Rh_{0{\cdot}225})_3$(H.T.)	Hexagonal	DO_{24} – $TiNi_3$	$AB_3(4)$ sh 0	5·517		8·978
$Ta(Pd_{0{\cdot}78}Ru_{0{\cdot}22})_3$(H.T.)	Hexagonal	DO_{24} – $TiNi_3$	$AB_3(4)$ sh 0	5·525		9·027
$Ta(Pd_{0{\cdot}5}Ru_{0{\cdot}5})_3$	Cubic	$L1_2$ – $AuCu_3$	$AB_3(3)$ sh 0	3·893		
$(Ta_{0{\cdot}5}Al_{0{\cdot}5})Ni_3$	Hexagonal	DO_{24} – $TiNi_3$	$AB_3(4)$ sh 0	5·112		8·340

* Giessen, Kane & Grant (1965).
† Giessen & Grant (1964).
‡ Shift density not certain.

Table 2. *New structure types*

α-VIr

Orthorhombic, space group *Cmmm* (D_{2h}^{19}); $N=8$ atoms per cell.

V in $4(g) \pm (x, 0, 0)$; $x \sim 0{\cdot}28$;
Ir in $4(j) \pm (0, y, \frac{1}{2})$; $y \sim 0{\cdot}22$.

β-Ta(Pd, Rh)$_3$

Rhombohedral, space group $R\bar{3}m$ (D_{3d}^{5}); $N=36$ atoms per hexagonal cell; stacking sequence: *ababcbcac, ababcbcac.*

Ta in $3(a)$ $(0, 0, 0)$;
$6(c) \pm (0, 0, z)$; $z_c \sim \frac{2}{9}$;
$Pd_{0{\cdot}72}Rh_{0{\cdot}28}$ in $9(e)$ $(\frac{1}{2}, 0, 0;\ 0, \frac{1}{2}, 0;\ \frac{1}{2}, \frac{1}{2}, 0)$;
$18(h) \pm (x, \bar{x}, z;\ x, 2x, z;\ 2\bar{x}, \bar{x}, z)$;
$x \sim \frac{1}{2}$; $z_h \sim \frac{2}{9}$.

γ-Ta(Pd, Rh)$_3$

Hexagonal, space group $P6_3/mmc$ (D_{6h}^{4}); $N=40$ atoms per unit cell; stacking sequence: *abcbcacbcb, abcbcacbcb.*

Ta in $2(b) \pm (0, 0, \frac{1}{4})$;
$2 \times 4(f) \pm (\frac{1}{3}, \frac{2}{3}, z;\ \frac{2}{3}, \frac{1}{3}, \frac{1}{2}+z)$; $z_{f_1} \sim \frac{3}{20}$;
$z_{f_2} \sim -\frac{1}{20}$;
$Pd_{0{\cdot}67}Rh_{0{\cdot}33}$ in $6(h) \pm (x, 2x, \frac{1}{4};\ 2\bar{x}, \bar{x}, \frac{1}{4};\ x, \bar{x}, \frac{1}{4})$; $x_h \sim \frac{1}{2}$;
$2 \times 12(k) \pm (x, 2x, z;\ 2\bar{x}, \bar{x}, z;\ x, \bar{x}, z;$
$\bar{x}, 2\bar{x}, \frac{1}{2}+z;\ 2x, x, \frac{1}{2}+z;\ \bar{x}, x, \frac{1}{2}+z)$;
$x_{k_1} \sim -\frac{1}{6}$; $z_{k_1} \sim \frac{3}{20}$;
$x_{k_2} \sim \frac{1}{6}$; $z_{k_2} \sim -\frac{1}{20}$.

ing lines. Error limits are $< 5{\cdot}10^{-4}$, except for β-$TaNi_3$ and $Ta(Pd_{0.67}Rh_{0.33})_3$, where they are $2{\cdot}10^{-3}$, and $1{\cdot}10^{-3}$, respectively. Table 1 lists the new intermediate phases, including again a layer structure symbol as introduced previously (Giessen & Grant, 1964). Table 2 presents three new structure types.

In addition to the phases listed in Table 1, ordered WIr_3 of the $MgCd_3$ type probably exists, but this could not be proved conclusively owing to the similar scattering powders of W and Ir. The structure of α-VIr is related to *B*2-CsCl by a distortion of the atom positions and approximate doubling of two *B*2-cell edges. Most of the ternary AB_3 phases of the types $Ta(Pd_x,Rh_{1-x})_3$ and $Ta(Pd_x,Ru_{1-x})_3$ are related in such a fashion that a similar valence electron concentration in both series causes identical structures to appear; in this context the occurrence of $Ta(Pd_{0.5}Ru_{0.5})_3$ with the $L1_2$-$AuCu_3$ structure of $TaRh_3$ is remarkable. The significance of the valence electron concentration in relation to the structure type is also borne out by the occurrence of $(Ta_{0.5}Al_{0.5})Ni_3$ with the $TiNi_3$ structure, where equal parts of Ta and Al substitute for Ti.

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MX_4 compounds of alkaline earth metals with IIIB group elements.

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In the course of a study on the equilibrium diagrams of alkaline earth metals with the elements of the IIIB group of the periodic system, intermediate phases of the type MX_4 have been found in the systems Ca–Ga, Sr–Ga, Ba–Ga, Ba–In, Ba–Tl.

The gallium alloys were prepared by fusion under argon atmosphere in Phytagoras and those of indium and thallium in sealed iron crucibles. The chemical analysis showed that the compositions of the specimens were in agreement (± 1 %) with the stoichiometric values. The (Ca, Sr, Ba)Ga_4 compounds are grey and brittle; $BaIn_4$ and $BaTl_4$ are white and rather soft. These MX_4 phases, except $BaTl_4$ (whose different structure type was not determined), show the tetragonal $D1_3$ structure type ($I4/mmm-D_{4h}^{17}$) known so far for aluminum compounds (Andress & Alberti, 1935; Nowotny & Wesenberg, 1939; Nowotny, Wormnes & Mohrnheim, 1940, 1942). The atomic positions are: $[0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}]+$: $2M(0,0,0)$; $4X' \pm (0,0,z)$; $4X''(0,\frac{1}{2},\frac{1}{4})(\frac{1}{2},0,\frac{1}{4})$; (M = alkaline earth atom). The unit cell is shown in Fig. 1.

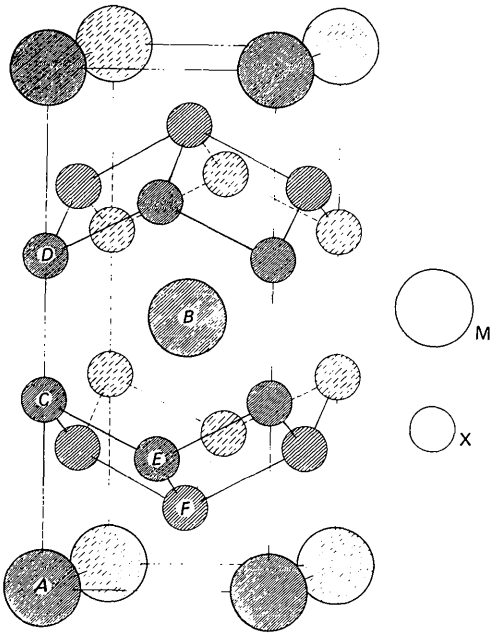

Fig. 1. Unit cell of MX_4 (M = Ca, Sr, or Ba; X = Ga, In or Tl).

The powder patterns obtained with the Straumanis method using copper *K*α radiation gave the values of the lattice constants recorded in Table 1. The best agreement of the observed intensities with those calculated for *z* between

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