

ON THE BINDING IN $A^n A_M^{8,9}$ PHASES

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Summary

According to the structures formed, the $A^n A_M^{8,9}$ mixtures may be divided into $A^{1,2} A_M^{8,9}$, the Zintl mixtures; $A^{3...7} A_M^{8,9}$, the pseudo-brass mixtures with non-Ekmanian electron count; and $A^{8,9} A_M^{8,9}$, the brass-like mixtures with Ekmanian electron count. The Zintl mixtures either do not form intermediate phases or form phases which have close-packed structures mainly determined by the considerable difference of the component radii. The pseudo brasses have a large atomic volume and correspondingly weak core interaction characterizing the structures of the Cr_3Si -family and the 3,4-coalescence structures. For $A^{n \geq 5}$ the 3,4-coalescence structures (including the Friauf-Laves phases) are replaced by homeotypes of Cu as the size of A^n has decreased. However, the non-Ekmanian electron count is conserved up to A^7 and causes there various replacement- and stacking-homeotypes of Cu. For $A^{n > 7}$ mainly structures occur which are homeotypic to elements, as quasi homologous mixing takes place.

Analysis

$A_M^{12,8}$ phases. The \underline{b} electron expansion energy of both components is too weak to cause intermediate phases. An exception is the mixture $MgRu_M$. Here the electron count $Mg^{2,8} Ru_M^{0,8}$ may be assumed, and the \underline{b} electron concentration in $Mg_3 Ru_2 (Mn.h_1)$ is then near 1.5 so that the favourable FF2 binding of $Mn.h_1$ (82cSch) may be assumed. The CHT2 binding for $Mg_{44} Ru_7$ (F88.14) can only be tentative as no use has been made of the distribution of the Ru atoms in the crystal cell.

$A_M^{3,8}$ phases. Starting from the electron count $Sc^{3,8}$, the FHFH/3 binding $\underline{a}_{Sc} = H3.31; 5.27 \underline{a} = \underline{b}_{FH} (\sqrt{2.3; 3/3}) = \underline{c}_{FH} (\sqrt{7; 5/3})$ may be assumed which yields the place number ratio $N_{p''}^{P'} = 5.2$. On the other side for $Fe^{1,7}$ the binding $\underline{a}_{Fe.r} = \underline{b}_B (1) = \underline{c}_U (2; 2.5)$ with $N_{p''}^{P'} = 9.8$ appears probable or $\underline{a}_{Fe.h1} = \underline{b}_F (1) = \underline{c}_B (\sqrt{8; 2.8})$ with $N_{p''}^{P'} = 11.3$. The place number ratio interval 5.2...9.8 is not very extended so that

A1A8M
 NaFeM(nic)see E KFeM(nic)see S RbFeM(nic)see HA CsFeM(nic)see HA
 NaRuM KRuM RbRuM CsRuM
 NaOsM KOsM RbOsM CsOsM

A2A8M
 MgFeM(nic,tm)phdM CaFeM(nic,tm)see S SrFeM(nic)see HA BaFeM(nic)seeHA
 Mg44Ru7(Mg44Rh7,SR39.82)20.19A=bC(9)=cHT(18;21/2) N=704,3264 phdM
 Mg3Ru2(Mn.h1,SR39.117)6.929A=bF(2)=cF(4)
 CaRuM SrRuM BaRuM
 MgOsM(icipossible)see HA CaOsM SrOsM BaOsM

A3A8M
 Sc3Fe phdM
 ScFe1.9(MgCu2,71Eck)7.09A=bC(3)=cC(6) N=24,192
 ScFe2(MgNi2?,SR26.237)H4.972;16.278A N=24,128 cmp
 ScFe2.1(MgZn2,71Eck)H4.92;7.90A=bCH(√2.25;6/3)=cCH(3;12/3) N=12,96
 YFe2(MgCu2,SR24.35)7.357A=idmScFe1.9 phdS
 YFe3(NbBe3,71 Eck)H5.133;24.60A=bH(2;10)=cH(4;20) N=27,288
 Y6Fe23(Th6Mn23,SR30.137)12.12A
 YFe(CaCu5,SR24.109,doubtbed,71Eck)H4.87;4.06A
 Y2Fe17(Th2Zn17,71Eck)H8.510;12.384A
 Y2Fe17.1(Th2Ni17,71Eck)H8.464;8.312A
 LaFeM(nic) phdE
 Sc11Ru4(Sc11Ir4,F22.8,SR46.132)13.367A=bHT(6;7/2)=cC(12) N=264,960 phdM
 ScRu(CsCl,SR27.342)3.203A=bHT(√2;1.6/2)=cHTK'(2) cmp
 ScRu2(MgZn2,SR23.216)H5.119;8.542A=idmScFe2.1 CC2
 Y3Ru phdM
 YRu2(MgZn2,SR23.216)H5.256;8.792A=idmScFe2.1 CC2 cmp
 La3Ru(Fe3C,SR45.123)7.468;10.032;6.555A phdM
 La5Ru2(Mn5C2,SR45.123)M95.79016.790;6.672;7.422A cmp
 LaRu2(MgCu2,SR23.215)7.702A=idmScFe1.9 CC2
 Sc11Os4(Sc11Ir4,SR46.89)13.344A=idmSc11Ru4 HTC2
 ScOs2(MgZn2,SR23.216)H5.179;8.484A=idmScFe2.1
 Y3Os phdM
 YOs2(MgZn2,SR23.216)H5.307;8.786A=idmScFe2.1 cmp
 LaOs2(MgCu2,SR23.215)7.736A=idmScFe1.9 CC2

A4A8M
 Ti2Fe.i(Ti2Ni,SR13.91)11.328A=bF(4)=cU(8;10) N=256,768
 TiFe(CsCl,SR24.134)2.98A=bF(1)=cF(2) N=4,24 phdE
 TiFe2(MgZn2,SR23.90)H4.831;7.855A=bCH(√2.25;6/3)=cCH(3;12/3)
 Zr3Fe(Q6.3,JLCM81.293)8.819;3.329;10.952A phdS
 Zr2Fe.h(CuA12,SR38.6)6.385;5.596A=bFU(3;3.7/2)=cU(√18;4.5) N=32,96
 ZrFe2(MgCu2,SR18.124)7.07A=bF(2)=cF(4) cmp
 Zr0.8Fe2.2(MgNi2,SR8.57)H4.962;16.15A
 Zr6Fe23(Th6Mn23,SR30.137)11.69A=bC(√20;4.5)=cCK'(2) N=96,928
 Hf2Fe(Ti2Ni,SR24.133)12.055A=idmTi2Fe.i phdE
 HfFe2.h(MgZn2,SR23.157)H4.912;8.001A=idmTiFe2 CC2 cmp
 HfFe2.r(MgCu2,SR18.123)7.025A=idmZrFe2 FF2
 TiRu(CsCl,SR23.77)3.076A=idmTiFe FF2 phdM cmp
 ZrRu(CsCl,SR23.77)3.25A=idmTiFe FF2 phdS
 ZrRu2.h(MgZn2,SR9.49)H5.11;8.43A=idmTiFe2 CC2
 HfRu(CsCl,SR23.77)3.225A=idmTiFe FF2 phdM
 HfRu2(Laves-phase)
 TiOs(CsCl,SR19.246)3.07A=idmTiFe FFe phdM
 Zr11Os4(Sc11Ir4,SR46.131) =bB(√32;5.6)=cF(8) N=352,960 phdM

the structural display is fairly uniform.

Unfortunately the structure of Sc_3Fe appears to be unknown as yet, and furthermore only the 3,4-coalescence phases $\text{ScFe}_{1.9}(\text{MgCu}_2)$ and $\text{ScFe}_{2.1}(\text{MgZn}_2)$ are stable. They are compatible with a CC2 binding and it appears that the MgZn_2 type is preferred by this binding, as it yields a simpler commensurability than the MgCu_2 type. $\text{YFe}_3(\text{NbBe}_3)$ might have a HH2 binding, but this makes dubious the CC2 binding of YFe_2 as it violates the rule that the density of a XX2 binding ($X=\text{C,H,B,U,F}$) becomes closer with increasing \underline{b} electron concentration. This problem requires further consideration.

$A^4_8 M^8$ phases. Here the CsCl type is more frequent than in $A^3_8 M^8$ as it permits the favourable FF2 binding. However, in ZrFe_M the CsCl type is missing. The FF2 binding stabilizes now the MgCu_2 type; also the CC2 binding stabilizes $\text{Zr}_6\text{Fe}_{23}(\text{Th}_6\text{Mn}_{23})$ instead of the MgZn_2 type. It becomes apparent once more that the binding in first line stabilizes a phase while the structure is strongly influenced by the composition of the phase.

$A^5_8 M^8$ phases. The phase $\text{VFe.h}(\text{CsCl})$ appears to have too many \underline{b} electrons for the FF2 binding, but there are various possibilities to reduce the number of V^5 electrons: absorption by Fe atoms, Hund insertion in V atoms, or presence of a b' correlation as in V metal. The strong decrease of the distance \underline{d}_b in the transformation $\text{VFe.h} \rightarrow$ following the bindings of TABLE $A^5_8 M^8$ is an indication that at higher temperatures Hund insertion is excited similarly as in Sn.r. The phase $\text{Nb}_7\text{Fe}_5(\text{Ti}_2\text{Ni})$ contains less Nb than required by the ideal structure, the cause for this must lie in the FU2 binding, which is to be assumed as in Ti_2Ni . Unfortunately the lattice constants of $\text{NbFe.h}(\text{U.h}_1)$ are not known so that the binding proposal FHH2 for $\text{Nb}_{48}\text{Fe}_{52}(\text{W}_6\text{Fe}_7)$ becomes less certain. The question may be raised why the FHH2 binding does not go to FF2 and stabilize the simpler CsCl structure of VFe.h . While $\frac{N}{C}(\text{VFe.h})=16$ it is found $\frac{N}{C}(\text{Nb}_{48}\text{Fe}_{52})=13.5$ and this conforms to the place number rule, so that the instability of " $\text{NbFe}(\text{CsCl})$ " is a consequence of a general rule. This also answers the question why the W_6Fe_7 type does not occur with V or Cr (see 64Sch p.153).

When for $\text{V}_{64}\text{Ru}_{36}(\text{CsCl})$ the FF2 binding is chosen then because of decrease of \underline{b} electron concentration for $\text{VRu}(\text{CuAu})$ a HH2 binding becomes probable and just this may generate the orthorhombic deformation of $\text{NbRu}(\text{DhtpCuAu})$ as is easily seen. In NbO_5M the Raub sequence of structures is found (see $A^5_7 M^7$), but the binding of $\text{Nb}_2\text{Os}_3(\text{Mn.r})$ is somewhat different from that of $\text{MoRe}_3(\text{Mn.r})$; it is not yet clear whether one of the assumptions must be changed.

Zr Os(CsCl,SR23.77)3.263A=idmTiFe FF2
ZrOs2(MgZn2,SR9.49)H5.189;8.526A=idmTiFe2 CC2 cmp
HfOs(CsCl,SR23.76)3.239A=idmTiFe FF2
HfOs2(MgZn2,SR23.216)H5.250;8.492A=idmTiFe2 CC2

A5A8M

VFeM.h(W) phdHA
VFe.h(CsCl,SR21.145) 2.910A=bF(1)=cF(2)
VFe.r(U.h1,SR29.179)8.956;4.627A=bHT(5;3/2)=cU($\sqrt{50}$;4.5)
Nb9Fe phdE
Nb7Fe5(Ti2Ni,SR21.129)11.262A=bF(4)=cU(8;10) N=280,768
NbFe.h(U.h1,SR21.139)
Nb48Fe52(W6Fe7,SR32.139)H4.928;26.83A=bFH($\sqrt{5.25}$;18/3)=cH($\sqrt{21}$;25) N=30,312
NbFe2(MgZn2,SR24.165)H4.811;7.857A=bCH($\sqrt{2.25}$;6/3)=cCHK'(2) N=20,96 cmp
Ta6Fe7(W6Fe7,SR32.139)H4.919;27.00A=idmNb6Fe7 FF2 phdE
TaFe2(MgZn2,SR17.111)H4.816;7.868A=idmNbFe2 CC2 cmp
V64Ru36(CsCl,SR28.49)2.997A=idmVFe.h FF2 phdM
VRu(CuAu.r,SR20.76)2.96;3.09A=bHT($\sqrt{2}$;1.6/2)CHT($\sqrt{8}$;3.2/2)
Nb68Ru32(CsCl,SR28.48)3.19A=idmVFe.h FF2 phdS
Nb57Ru43(CuAu,SR29.195)3.15;3.22A=idmVRu HH2
NbRu(DhtpRuAu,71Eck)4.35;4.23;3.39A=hdmVRu cmp
NbRu3(Mg,SR29.195)H2.755;4.396A
Ta62Ru38(CsCl,SR26.254)3.18A=idmVFe.h phdE
Ta58Ru42(CuAu,SR26.254)3.11,3.27A=idmVRu
TaRu(DhtpCuAu,71Eck)4.35;4.12;3.39A=idmNbRu
Ta3Ru5
V20s(CsCl,SR23.77)3.010A=idmVFe.h FF2 phdM
V0s.h(Cr3Si,71Eck)4.807A=bU(2;2.5)=cB(4) N=20,64
Nb30s(Cr3Si,SR19.243)5.121A=bF(2)=cB(4) N=30,64 phdM
Nb30s2(U.h1,SR29.86)9.858;5.063A=bHT($\sqrt{25}$;3/2)=cU($\sqrt{50}$;4.5) N=90,240
Nb20s3(Mn.r,SR23.233)9.778A=bHT($\sqrt{20}$;5/2)=cHT($\sqrt{80}$;10/2) N=115,464
Ta~30s(U.h1,SR21.137)9.88;5.14A=idmNb30s2 N=112,240
Ta20s3(Mn.r,SR23.233)9.69A=idmNb20s3

A6A8M

CrFeM.h(W) phdE N=90,240
CrFe.h(U.h1,SR18.104)8.790;4.559A=bHT($\sqrt{6.2}$;1.5/2)=bHT($\sqrt{25}$;3/2)=cU($\sqrt{50}$;4.5)
MoFe.h(U.h1,SR15.44)9.218;4.813A=idmCrFe.h phdM
Mo6Fe7(W6Fe7,SR3.324)H4.751;25.68A=bH($\sqrt{7}$;~15)=cUH($\sqrt{21}$;~30/2) N=108,312
Mo3Fe5.h
MoFe2(MgZn2,JIronSteelInst205.191)H4.745;7.734A=bFH($\sqrt{5.2}$;4.5)=cFHK'(2) N=24,96
WFe.h(U.h1,doubtedSR23.232) phdHA
W6Fe7(R6.7,SR3.364)H4.76;25.90A=idmMo6Fe7
WFe2(MgZn2,SR18.124)H4.745;7.722A=idmMoFe2
Cr4Ru phdS
Cr3Ru(Cr3Si,SR19.113)4.68A=bF(1)=bF(2)=cB(4) N=36,64 N=113,240
Cr5Ru3(U.h1,SR21.95)9.068;4.704A=bFU($\sqrt{6.2}$;8/2)=bFU($\sqrt{25}$;3.7/2)=cU($\sqrt{50}$;4.5)
Mo5Ru3(U.h1,SR24.188)9.557;4.935A=idmCr5Ru3 phdE
W3Ru2(U.h1,SR21.169)9.554;4.972A=idmCr5Ru3 phdE
Cr30s(Cr3Si,SR21.94)4.688A=idmCr3Ru FB2 phdS
Cr20s.h(U.h1,SR21.94)9.105;4.70A=idmCr5Ru3 FUU/2
Mo30s(Cr3Si,SR18.228)4.971A=idmCr3Ru phdS
Mo20s(U.h1,SR29.124)9.615;4.941A=idmCr5Ru3
W30s(U.h1,SR26.223)9.659;5.001A=idmCr5Ru3

A_M^{6,8} phases. Similarly as in A_M^{5,8} the Cr₃Si family prevails. For Cr₃^{6,8}Ru^{0,8} (Cr₃Si) the FB2 binding used for Nb₃O₅(Cr₃Si) appears probable, although there are N_D^a=36 b electrons in one a cell while the number of places is only 32. It might be assumed that the 4 "surplus" electrons descend to the core of Ru, (improbable with respect to the small number of Ru in the cell); or they could make Hund insertion at the Cr atoms, (questionable in view of the strong perturbation of Cr by the Ru atoms); or they could enter a spatial correlation of their own, for, what was valid for Cr(a=b_D¹(1)=b_C(2)=c_F(2)) may be possible for Cr₃Ru. The tendency to superconductivity might be caused by the very free and distant b' electrons. The generally accepted validity of electronic rules for the Cr₃Si and MgCu₂ families (see 39Lav, 53Kuo, 60Das, 64Sho) is here expressed by a numerical model, so that it appears possible to consider the dependence of superconducting transformation temperature in connection with the non-Ekmanian electron count. More completely the binding in Cr₃Ru is therefore FF2B4.

As the FF2 part of the binding is very favourable, it appears suggestive that Cr₃Ru₃(U.h₁) has a FF2U4 binding (see TABLE A_M^{6,8}), in which the c_U correlation has replaced the c_B correlation of Cr₃Ru, as the number of c electrons as compared with the number of b electrons has increased by increase of the mole fraction N_{Ru}. The homeotypism Cr₃Si-U.h₁ (see 64Sch p.150 and 152) may easily be understood when the chains of 14 coordinated atoms parallel to the a₃ axis of U.h₁ are considered. These chains intersect the basal plane (a₁, a₂) in a pointnet which has been named "secondary net" by 58Fra as it contains essentially less atoms than the primary net. The secondary net is of the Schläfli-type 4⁴ in Cr₃Si, and of 4343² in U.h₁. As is well known the net 4343² is closer than the net 4⁴, and just such a shrinking homeotypism is to be expected from the volume rule (64Sch p.169) which asserts that the volume of a structure becomes greater in a homeotypism when the b electron concentration is increased. As is well known (see 69Sho) the W₆Fe₇ type (see 64Sch p.157) belongs to the secondary net 3⁶ which is yet closer than 4343² and in fact the W₆Fe₇ type occurs in WFe_M for mole fractions N_{Fe}'(W₆Fe₇) greater than N_{Fe}'(WFe.h(U.h₁)). A HUH³ binding appears appropriate.

The application of a chain shear to the secondary chains in W₆Fe₇ reveals that this structure represents a coalescence of hexagonal layers (parallel to the basal plane) containing 4 atoms per (a₁,a₂) mesh, with layers containing 3 atoms. The Friauf-Laves structures too, are such layer coalescence structures but contain some more vacancies in the layers with 4 atoms, and this once more permits a closer packing, which is to be expected by decrease of b elec-

A7A8M

MnFeM.h(Cu) phdS
MnFe4.m(Mg,SR2.642)H2.54;4.08A
TcFe(U.h1,SR27.361)9.077;4.756A phdM
Re2Fe3(U.h1,SR20.75)9.08;4.72A phdHA
ReFe3.h(Mn.r,SR27.255)8.918A
MnRuM(nic,broad marg.ph.) phdHA
TcRuM(Mg) phdS
ReRuM(Mg) phdS
MnOsM
TcOsm(Mg) phdS
ReOsM(Mg) phdS

A8A8M

FeRuM(nic,bmp)phdE FeOsM(nic,bmp)phdM RuOsM(Mg)phdS

tron concentration.

At this point it becomes clear that the Cr_3Si structure is not very close packed. A chain shear in three directions, which does not alter the distance in the chain permits to transform the Cr_3Si structure into a replacement homeotype of NaCl which is not a very close packed structure. It becomes apparent that the close packing should be considered relative to the number of \underline{c} places per atom and it is found $\underline{N}_{\text{pr}}^{\text{A}}(\text{Cu})=11.3$ and $\underline{N}_{\text{pr}}^{\text{A}}(\text{Cr}_3\text{Ru})=16$. The above arguments reveal that the A_M^6A_M^8 phases are compatible with the assumption that the \underline{b} electron concentration decreases with increasing $\underline{N}_{\text{pr}}^{\text{A}}$. It is not known as yet whether all \underline{b} electrons are contributed by the A^6 atoms, but it is a working approximation to assume it. The structures of Mn.r and U.h₁ underline the limitation of the assumption as here the structure is built by one component only.

The U.h₁ structure has the homeotypic commensurability $\underline{a}_{\text{U.h}_1} = \underline{a}_{\text{Cr}_3\text{Si}}(2;1)$ so that a \underline{b} correlation $\underline{a} = \underline{b}_{\text{FU}}(\sqrt{32};4/2)$ might be expected. However, because of the decrease of \underline{b} electron concentration it is found $\underline{a} = \underline{b}_{\text{HT}}(\sqrt{25};3/2)$, the good commensurability in the \underline{a}_3 direction has been lost. The reason why the commensurability elements $\sqrt{26}$ and $\sqrt{29}$ have not been used is perhaps connected with the good commensurability of $\underline{b}_{\text{HT}}$ to \underline{c}_{U} having the favourable value $\underline{a} = \underline{c}_{\text{U}}(\sqrt{50};4.5)$. The \underline{b}' correlation which might be assumed because of superconductivity has not much influence on the structure, it adapts to the \underline{b} correlation.

$\text{A}^7 \dots \text{A}_M^8$ phases. The mixtures A_M^7A_M^8 are on the brass side of the Ekman boundary as the extended marginal phases and the completely miscible mixtures show. The occurrence of pseudo brass structures like U.h₁ and Mn.r does not contradict this as the phase Mn.r(B29) shows that both components (for instance in Re_2Fe_3) may contribute to the \underline{b} correlation, so that the typical non-Ekmanian count is no more valid. In the homologous mixtures A_M^8A_M^8 no pseudo-brass structure is found.

It appears remarkable that Ru(Mg) and Os(Mg) have the structure of Fe.p(Mg); this is a special case of the place number rule.

A1A9M

NaCoM(probabl.nic,seeE)KCoM(prob.nic,seeHA) RbCoM CsCoM
 NaRhM Khm RbRhM CsRhM
 NaIrM KIrM RbIrM CsIrM

A2A9M

MgCo2(MgZn2,SR26.219)H4.86;7.92A=bH(2;3.3)=cCH($\sqrt{12}$;14/3) N=8,104 phdS
 CaCo5(CaCu5,SR11.59) phdHA
 SrCoM
 BaCoM
 Mg44Rh7(F88.14,SR37.109)20.148A→H14.2;34.9A=bH(6;15)=cCH($\sqrt{108}$;60/3)N=704,3320
 Mg5Rh2(Co2A15,71Eck)H8.515;8.016A=bH($\sqrt{12}$;3.3)=cCH(6;14/3) N=40,232
 MgRh(CsCl,SR22.161)3.099A=bU(1;1.2)=cF(2)
 CaRh2(MgCu2,SR22.75)7.525A=bB(2)=cF(4)
 SrRh2(MgCu2,SR22.75)7.706A=idmCaRh2
 BaRh2(MgCu2,SR22.75)7.852A=idmCaRh2
 Mg44Ir7(Mg6Rh,SR38.110)20.097A
 Mg3Ir(Na3As,SR27.249)H4.549;8.229A=bFH($\sqrt{3}$;4/3)=cCH(3;13/3) N=12,66
 CaIr2(MgCu2,SR22.75)7.545A=idmCaRh2
 SrIr2(MgCu2,SR22.75)7.849A=idmCaRh2
 BaIrM

A3A9M

Sc3Co(024.8,SR44.53)13.102;8.624;5.829A=bHT(6;4;3/2)=cU($\sqrt{72}$;32;4.7)N=72,264
 Sc2Co(CuAl2,SR27.342)6.374;5.616A=bC(9;2.6)=cU($\sqrt{18}$;4.5) N=24,100
 ScCo(CsCl,SR27.342)3.145A=bF(1)-cF(2)
 ScCo2(MgCu2,SR26.236)6.921A=bHT($\sqrt{8}$;3.2/2)=cF(4) N=24,208 phdM
 Y3Co(Fe3C,71Eck)7.026;9.454;6.290A=bHO(3;4/1;1.5)=cUHO($\sqrt{27}$;8/2;4.6)N=36,132
 Y8Co5(M32.20,SR42.69)M102.117.058;7.286;24.077A
 Y3Co2(012.8,SR41.54)12.248;9.389;3.975A
 Y4Co3(Ho4Co3,H12.9,SR34.72)H11.53;4.04A=bCH($\sqrt{12}$;3/3)=cCHK'(2) N=36,177
 Y2Co3
 YCo2(MgCu2,SR24.36)7.216A=idmScCo2 HTFU2
 YCo3(NbBe3,R3.9,SR30.78)H5.013;24.371A=bBH($\sqrt{1.33}$;27/3)=cFH(4;24/3) N=27,315
 Y2Co7(Gd2Co7,R4.14,SR30.124)H5.002;36.21A=bBH($\sqrt{1.33}$;40/3)=cFH(4;36/3) N=36,474
 YCo5(CaCu5,SR23.222)H4.948;3.975A=bCH($\sqrt{1.78}$;2.6/3)=cFH(4;4/3) N=3,53 cmp,
 Y2Co17.h(Th2Ni17,H4.34,SR29.110)H8.36;8.16A=bBH($\sqrt{3}$;8/3)=cFH($\sqrt{48}$;8/3)N=12.338
 Y2Co17.r(Th2Zn17,R2.17,71Eck)H8.344;12.19A
 La3Co(Fe3C,SR26.127)7.279;10.088;6.578A=idmY3Co HUH/3 phdM
 La1.2Co(C ,71Eck)5.98A
 La2Co3(0 ,71Eck)10.34;4.886;7.811A
 La2Co7.h(Er2Co7,R4.14,SR32.60)H5.11;36.69A=idmY2Co7 BHFH/12
 La2Co7.r(Ce2Ni7,H8.28,71Eck)H5.101;24.511A
 LaCo5(CaCu5,SR26.239)H5.108;3.976A=idmYCo5 CHFH3
 LaCo13(NaZn13,SR32.139)11.33A=bC(4)=cB(8) N=24,1000
 ScRh(CsCl,SR22.186)3.206A=bU($\sqrt{1.25}$;1.4)=cU($\sqrt{5}$;2.75)
 ScRh3(Cu3Au,SR26.165)3.900A=bFU($\sqrt{225}$;2.1)=cB(3)
 Y3Rh(Fe3C,Z.Metk.64.197)7.138;9.438;6.139A=idmY3Co HUH/3
 Y7Rh3(Th7Fe3,71Eck)H9.775;6.190A=bFH(4;3/3)=cH(8;5) N=42,166
 Y5Rh3(Er5RH3,Z.Metk.64.197)
 Y3Rh2(U42.28,SR42.121)11.232;25.15A=bHT($\sqrt{20}$;12.5/2)=cHT($\sqrt{80}$;23/2) N=252,1180
 YRh(CsCl,SR30.165)3.409A=idmScRh UU2
 YRh2(MgCu2,SR23.215)7.488A=idmScCo2 HTFU2
 YRh3(CeNi3,Z.Metk.64.197)H5.230;17.38A=bBH($\sqrt{1.33}$;19/3)=cFH(4;16/3)N=18,210
 YRh5.h(CaCu5,Z.Metk.64.197)H5.141;4.294A=idmYCo5 CHFH3
 La3Rh(0 ,TransAIME245.1561)15.01;10.50;13.34A phdM cmp

A¹A_M⁹ phases. Information on these mixtures is poor but probably no intermediate phases are formed as one A¹ electron does not offer much expansion energy and from the A⁹ component b electron expansion cannot be expected either.

A²A_M⁹ phases. MgCo₂(MgZn₂) and CaRh₂(MgCu₂) are Friauf-Laves phases. As the atomic volume of CaRh₂ is greater than that of MgCo₂ the place number ratio $N_{P''}^{P'}$ is 16 for CaRh₂ and only 12.5 for MgCo₂. The binding of Mg₄₄Rh₇ is difficultly to be found as the cell is so large; a HCH/3 binding with $N_{P''}^{P'}=12$ might apply which has a good commensurability to the a cell in three directions. Curiously a quite homeotypic binding is valid for Mg₅Rh₂(Co₂Al₅) and this might point to a structural homeotypism.

A³A_M⁹ phases. The wealth of phases in this mixture class suggests a great $N_{P''}^{P'}$ interval in each mixture and therefore the non-Ekmanian electron count Sc^{3,8}Co_M^{0,9} e.g. The binding interpretations depend on the b electron contribution of Co; they must be considered as tentative as long as the magnetic measurements are missing. For Aⁿ rich phases b electron descent into the A⁹ core of 1 to 0.5 electrons per A⁹ atom may be assumed. If for ScCo(CsCl) the FF2 binding is accepted then for ScCo₂(MgCu₂) the binding HIFU2 with the place number ratio $N_{P''}^{P'}=9.8$ extrapolates well to the CB2 binding of Co and to the binding of Sc $a=b_{FH}(\sqrt{2.3;3/3})=c_{FH}(\sqrt{7;5/3})$. The bindings of Sc₃Co(024.8) and Sc₂Co(CuAl₂) fit well to these data. The d_b(N₂) function may have for mole fractions greater than N₂=0.66 an inflection to the horizontal; this suggests that the decrease of b electron concentration with increasing N₂ is stopped by a positive b electron contribution of Co; clearly this suggestion must be confirmed by d_b values in other related mixtures.

One such mixture is YCo_M. The phases between YCo₂(MgCu₂) and Co(Mg) are hexagonal and are composed of partly studded close packed layers parallel to the hexagonal basal plane. The layers may contain lacunae but the average elementary mesh a_p of the atom packing in the layers may be proposed as hexagonal and the commensurabilities of these meshes to the crystal basal mesh a_c are $\frac{a_p^{-1}}{a_c}=2=1/4$ when no great atom is contained in the layer; and $\frac{a_p^{-1}}{a_c}=1/3$ when one or two great atoms per crystal mesh are contained. The great atom may expel from a neighbouring layer with commensurability 2 one atom to fit its great volume into the structure. Formerly (64Sch) it was believed that the fact, that A³ replaces two A⁹, is the decisive phenomenon, but the occurrence of phases with MgCu₂ type and CaCu₅ type in one and the same mixture (in YCo_Meg.) shows that two-atom replacement and three-atom replacement may be caused by one and the same component. The fundamental phenomenon is therefore the

La7Rh3(Th7Fe3,79Ia)
La5Rh3
La4Rh3(Th3P4,SR35.77)8.922A=bU($\sqrt{8}$;35)=cUK'(2) N=48,236
La5Rh4
LaRh(TlI,SR30.150)3.986;11.144;4.245A=bB(0.94 $\sqrt{2}$;3.5; $\sqrt{2}$)=cBK'(2) N=12,68
LaRh2(MgCu2,SR23.215)7.647A=idmScCo2
LaRh3.h(PuNi3,SR34.140)H5.326;26.46A=idmYCo3
LaRh3.r(CeNi3,SR34.140)H5.305;17.59AidmYRh3 BHFH/12
La2Rh7.h2(Gd2Co7,R4.14,SR34.140)H5.333;39.46A=idmY2Co7 cmp
La2Rh7.h1(Ce2Ni7,SR34.140)H5.296;26.13A
Sc11Ir4(F22.8,SR46.89)13.350A=bFU($\sqrt{32}$.8)=cHT($\sqrt{128}$;13/2) N=264,992
ScIr(CsCl,SR27.342)3.206A=idmScRh UU2
ScIr2(MgCu2,SR23.215)7.348A=idmScCo2 HTFU2
Y3Ir(Fe3C,SR45.123)7.237;9.297;6.400A=idmY3Co HUH/3
YIr2(MgCu2,SR23.215)7.51A=idmScCo2 HTFU2
La4Ir phdM
La3Ir(Fe3C,SR45.123)7.453;10.103;6.650A=idmY3Co HUH/3
La7Ir3(Th7Fe3,71Eck)H10.235;6.473A=idmY7Rh3 FHH2
La5Ir3(Nd5Ir3,T20.12,SR45.123)11.459;6.629A=bHT($\sqrt{20}$;3)=cC($\sqrt{80}$;5) N=60,268
LaIr
LaIr2(MgCu2,SR23.215)7.688A=idmScCo2 HTFU2 cmp
LaIr3(PuNi3,79Ia)H5.370;26.34A=idmYCo3 BHFH/12
La2Ir7(Ce2Ni7,79Ia)
LaIr5(CaCu5,79Ia)
La2Ir17

A4A9M

Ti2Co(Ti2Ni,SR19.125)11.30A=bF(4)=cU(8;10) phdE
TiCo(CsCl,SR21.145)2.991A=bF(1)=cF(2) cmp
TiCo2(MgCu2,SR7.211)6.706A=bF(2)=cF(4)
TiCo2.1(MgNi2,SR23.129)H4.725;15.40A=bUH(2;7,5,2)=cFH(4;16/3)
TiCo3.2(Cu3Au,SR23.129)3.603A=bF(1)=cB($\sqrt{8}$;2.8)
Zr3Co(Re3B,SR35.53)3.27;10.84;8.95A phdE
Zr3Co(Ni3Sn,SR30.125)H5.996;4.660A=bFH(3;2.7/3)=cFH($\sqrt{27}$;5/3) N=24,66
Zr2Co(CuAl2,SR26.128)6.363;5.469A=bFU(3;3.6/2)=cC(6;5.2) N=32,100 cmp
ZrCo(CsCl,SR23.77)3.196A=idmTiCo FF2 cmp
ZrCo2(MgCu2,SR18.124)6.954A=idmTiCo2 FF2 cmp
Zr6Co23(Th6Mn23,SR30.125)11.53A \rightarrow H8.15;19.97A=bBH(2;24/3)=cFH($\sqrt{48}$;21)N=96,1020
Zr2Co11
Hf2Co(Ti2Ni,SR24.133)12.104A=idmTi2Co phdM
HfCo(CsCl,SR23.77)3.165A=idmTiCo FF2 cmp
HfCo2(MgCu2,SR22.204)6.922A=idmTiCo2 cmp
Hf6Co23(Th6Mn23,SR34.139)11.48A=idmZr6Co23
Ti7ORh30(Zr2Cu,SR29.130)3.06;9.81A=bB($\sqrt{2}$;4.5)=cC($\sqrt{8}$;9) N=17,50 phdM
Ti65Rh35(CsCl,SR29.130)3.11A=bB($\sqrt{2}$;1.4)=cHT($\sqrt{8}$;3.3/2) N=5.2,17 cmp
TiRh.r(CuAu,SR29.130)4.17;3.354A=bFU(2;2.3/2)=cHT(4;3.7/2) N=8,34
Ti45Rh55(NbRu,SR29.130)4.15;4.11;3.40A=bHT(2;2;2/2)=cHT(4;4;4/2)
Ti43Rh57(CuAu,SR29.130)4.11;3.36A=bC(2;1.7)=cCK'(2) N=7,34
Ti3Rh5(Rh5Ge3,SR34.124)5.36;10.42;4.08A=bB(2;4;1.5)=cU(4;8;3.7) N=24,138
TiRh3(Cu3Au,SR23.257)3.822A=idmTiCo3 FUB2 N=4,35
Zr2Rh(CuAl2,SR30.165)6.494;5.606A=idmZr2Co FUC2 phdM
ZrRh0.9(ZrIr,Z.Metk.55.1964.704) cmp
ZrRh1.1(CsCl,Z.Metk.55.1964.704,SR44.121)=idmTiCo FF2
Zr45Rh55(,Z.Metk.55.1964.704)
Zr3Rh5(,Z.Metk.55.1964.704,does not exist:TransAIME245.1207)
ZrRh3(Cu3Au,SR23.257)3.927A=idmTiCo3 cmp

(4,3)-coalescence, it is possible over a broad range of composition and the content of A^3 decides how many $MgCu^2$ type layers and how many $CaCu_5$ type layers are formed.

In $YCo_3(NbBe_3R3.9, drawing 64Sch p.168)$ there is a double layer $A^3A_5^9$ followed by a double layer $A_2^3A_4^9$ and these pairs of double layers are rhombohedrally stacked. From the TABLES it may be concluded that sometimes a \underline{b} contribution comes from Co. It is clear that this assumption needs confirmation by magnetic data. Furthermore it must be admitted that there is some contradiction of the present interpretation with the interpretation of $A_M^{nA}10$ phases. Only one of them can be correct; further analyses must show which one holds better.

It is somewhat surprising that the $NaZn_{13}$ type occurs in $LaCo_{13}$. The extrapolation of $\underline{d}_B(N_2)$ permits a \underline{b}_C correlation which would require a contribution of 0.4 \underline{b} electrons per Co but needs confirmation by magnetic measurements; the \underline{c}_B correlation completes a CB2 binding which yields $\underline{N}_P/P' = 16$ and thus interpolates well the \underline{N}_P/P' values of the neighbouring phases.

The A^3Rh_M phases fulfil the rule that the mixture with heavier A^3 component has more phases. The UU2 binding of $ScRh$ is tentative, it had been preferred to the FF2 binding as it makes the $\underline{d}_B(N_2)$ curve somewhat smoother; Y_3Rh_2 (U42.28) is homeotypic to W_5Si_3 and to $La_5Ir_3(Nd_5Ir_3)$, the HH2 binding is homeotypic to FF2, which has not been assumed as it yields a somewhat great number of \underline{b} electrons per cell. In $LaRh_M$ the phase $LaRh(TII)$ is heterotypic to YRh (CsCl). The values of \underline{N}_P/A are 13.3 and 13.8 in agreement with the place number rule; the heterotypism may therefore be said to be caused by the place number rule.

The heterotypism $Sc_{11}Ir_4(F22.8) - La_3Ir(Fe_3C)$ only weakly conforms to the place number rule: \underline{N}_C/A has the values 13.9 and 13.8 respectively.

$A_M^{4A}9$ phases. In $TiCo_M$ the CF1 binding of Ti_h transforms to the FU2 binding of $Ti_2Co(Ti_2Ni)$. In $TiCo(CsCl)$ the FF2 binding is attained which is repeated in $TiCo_2(MgCu_2)$ and transforms to $FB/8$ in $TiCo_3(Cu_3Au)$. The sensible deviation of the distance \underline{d}_C in $TiCo$ (negative) and $TiCo_3$ (positive) may come from the 2-factorial commensurability at least in a plane. The congruent melting of $TiCo$ (CsCl) fulfills the commensurability rule.

Starting from $ZrCo(CsCl, FF2)$ it appears natural that $Zr_2Co(CuAl_2)$ has a FUC2 binding: the two-factoriality in the tetragonal basal plane is conserved from $ZrCo(FF2)$ but the stacking of the \underline{c} correlation in the direction perpendicular to the basal plane is less close as the \underline{b} concentration has increased relative

Hf2Rh(Ti2Ni,SR22.188)12.326A=idmTi2Co FU2
HfRh(ZrIr,Z.Metk.55.1964.704)
HfRh1.1(CsCl,SR29.119)3.227A=idmTiCo FF2
Hf46Rh54(CsCl distorted,SR29.119)3.268;3.150A=hdTiCo FF2
Hf45Rh55(CuAu,SR29.119)4.41;3.41A=bB($\sqrt{2.5;1.2}$)=B($\sqrt{10;2.5}$),
Hf42Rh58.h(NbRu,SR29.119)4.392;4.306;3.470A=bHT($\sqrt{3.25;1.7}$)=cHTK'(2) N=6.6,34
Hf42Rh58.r
Hf2Rh3(CuAu,SR29.119)4.35;3.451A
Hf3Rh5(Rh5Ge3,SR34.124)5.58;10.73;4.25A=idmTi3Rh5 BU2
HfRh3(Cu3Au,SR23.257)3.912A=idmTiCo3 FUB2
Ti3Ir(Cr3Si,SR29.121)5.01A=bHT($\sqrt{8;3.3/2}$)=cB(4) N=24,57 phdM
Ti65Ir35(CsCl,SR29.121)3.125A=bB($\sqrt{2;1.4}$)=cFU($\sqrt{8;4/2}$) N=5.2,17
Ti55Ir45(CuAu,SR29.121)4.20;3.39A=idmTiRh FUHT2 N=88,34
TiIr(NbRu,SR29.121)4.174;4.107;3.460A=idmTi45Rh55 HH2 cmp
Ti45Ir55.h(CuAu,SR29.121)4.09;3.51A=bHT($\sqrt{3.25;1.8}$)=cHTK'(2)
Ti3Ir7(CuAu,Z.Metk.55.704)3.90;3.78A=bHT($\sqrt{2.5;1.8}$)=cFU($\sqrt{10;4.3/2}$)
TiIr3(Cu3Au,SR23.257)3.845A=idmTiCo3 FB/8
Zr3Ir(U.h,SR29.122)10.78;5.618A=bHT(5;3/2)=cU($\sqrt{50;4.5}$) N=83,248 phdM
Zr2.1Ir(Ti2Ni,SR29.121)12.48A=idmTi2Co FU2
Zr2Ir(Zr2Rh,Z.Metk.55.704)
Zr2Ir1.1(Z.Metk.55.704)
Zr5Ir3(Mn5Si3,71Eck)H8.025;5.488A=bFH($\sqrt{13;3/3}$)=cFH($\sqrt{39;5.4/3}$) N=40,139
ZrIr.h(CsCl,SR44.117)
ZrIr.r(Z.Metk.55.704)
ZrIr2(MgCu2,SR26.237)7.359A=idmTiCo2 FF2
ZrIr3(Cu3Au,SR23.257)3.943A=idmTiCo3 FB/8
Hf2Ir(Ti2Ni,SR22.188)12.352A=idmTi2Co FU2 phdM
Hf5Ir3(htpMn5Si3,71Eck)H7.866;16.92A
Hf5Ir3.1(Mn5Si3,71Eck)H7.943;5.454A=idmZr5Ir3 FHFH/3
HfIr(ZrIr,Z.Metk.55.704) cmp
Hf47Ir53(NbRu,SR29.119)4.740;4.680;3.045A
Hf46Ir54(NbRu,SR29.119)4.21;4.16;3.68A
HfIr3(Cu3Au,SR23.257)3.935A=idmTiCo3 FB/8 cmp

A5A9M

V3Co(Cr3Si,SR15.56)4.675A=bF(2)=cB(4) phdHA
V-1Co~1(U.h,SR23.231)8.817;4.576A=bHT(5;3/2)=cU($\sqrt{50;4.5}$) N=75,255
VCo3(H6.18,SR23.130)H5.032;12.27A=bFH(2;6/3)=cCH($\sqrt{12;21/3}$) N=30,210
VCo3.h(Cu3Au,SR30.124)3.55A=bF(1)=cB($\sqrt{8;2.8}$)
Nb6Co7(W6Fe7,SR30.200)H4.92;26.28A=bH($\sqrt{53;13}$)=cFH(4;27/3) N=90,333 phdM
Nb1.1Co1.9(MgZn2,71Eck)H4.835;7.860A=bFH($\sqrt{4.75;5/3}$)=cFH($\sqrt{19;10/3}$) N=22,104
Nb0.9Co2.1(MgCu2,SR24.127)6.728A=bF(2)=cF(4)
NbCo3(MgNi2,SR24.126)H4.740;;5.45A=bH(2;6.5)=cFH(4;18/3) N=30,210
Ta2Co(CuA12,SR32.139)6.094;4.966A=bFU($\sqrt{10;3.6}$)=cU($\sqrt{20;4.5}$) N=40,100 phdM
Ta6Co7(W6Fe7,SR32.139)H4.905;26.33A=idmNb6Co7 HFH/3 cmp
TaCo2.h(MgCu2,SR27.172)6.778A=idmNb0.9Co2.1 FF2
TaCo2.r(MgZn2,SR27.172)H4.797;7.827A=idmNb1.1Co1.9 FF2
Ta0.8Co2.2(MgNi2,SR27.172)H4.700;15.42A
TaCo3.m(Cu3Au,SR27.172)3.647A=idmVCo3.h
TaCo3(htpMgNi2,SR27.172)H9.411;15.50A
TaCo5(seephd)
V3Rh(Cr3Si,SR20.76)4.786A=idmV3Co FB2 phdM
V4Rh3.h
VRh(VIr,Q2.2,SR44.120)5.78;6.65;2.78A=bF(2;2.5;1)=cF(4;4.5;2) N=20,68
V0.9Rh1.1(CuAu,JLCS2.293)3.89;3.60A=bFU($\sqrt{3.25;2.4/2}$)=cFU($\sqrt{13;4.7/2}$)N=9,34
V3Rh5(Q3.5,SR39.120)5.420;9.276;4.320A=bHT(2.5;5/2;2)=cHTK'(2) N=30,138
VRh3(Cu3Au,SR23.257)3.795A=idmVCo3.h FUB2
Nb3Rh(Cr3Si,SR29.125)5.120A=idmV3Co FB2 phdS

to ZrCo. In $Zr_3Co(Ni_3Sn)$ the two-factoriality is finished and therefore the stacking of \underline{c} may become close.

The phase $Ti_{70}Rh_{30}(Zr_2Cu)$ permits a BC2 binding with $\frac{N/A}{P_n} = 12$ \underline{c} places per atom while the homeotypic $Zr_2Co(CuAl_2)$ had $\frac{N/A}{P_n} = 15$; here an influence of the large atomic volume of Zr must be seen. The decrease of \underline{b} electron concentration for increasing N_{Rh} conserves the \underline{b} correlation type and must therefore compress the \underline{c} correlation. The structure of $Ti_{65}Rh_{35}$ is cubic by twinning of the BHT2 binding. Further decrease of \underline{b} electron concentration permits the FUHT2 binding in $TiRh(CuAu)$. The value $\frac{N/A}{P_n} = 15$ is a little smaller than the value $\frac{N/A}{P_n} = 16$ of $TiCo(CsCl, FF2)$. After FUHT2 appears a HH2 binding in $Ti_{45}Rh_{55}(NbRu)$ which makes the structure orthorhombic. The phase $Ti_3Rh_5(Rh_5Ge_3)$ is a RDI-homeotype of Cu and permits a BU2 binding which has $\frac{N/P}{P_n} > 8$. $TiRh_3(Cu_3Au)$ is isodemic to Cu.

The phase $HfRh_{1,1}(CsCl, FF2)$ is followed by $Hf_{46}Rh_{54}(DhtpCsCl)$ and as the deformation is a tetragonal compression the cause for it must be seen in the decrease of \underline{b} electron concentration. In $Hf_{45}Rh_{55}(CuAu)$ a BB2 binding might be possible and in $Hf_{42}Rh_{58}.h(NbRu)$ a twinned HH2 binding. From the point of view of this interpretation the knowledge of the $Hf_{42}Rh_{58}.r$ structure would be of interest. The phase $Hf_3Rh_5(Rh_5Ge_3)$ illustrates the close relation between brass like and pseudo-brass like alloys.

The phase $Ti_3Ir(Cr_3Si, HTB)$ suggests a contribution of \underline{b} electrons from the Ir core, and this is confirmed by $Ti_{65}Ir_{35}(CsCl, BFU2)$. The brass plateau appears to be concluded at $Ti_{45}Ir_{55}.h(CuAu)$. Contrary to this in $ZrIr_M$ the brass plateau appears to extend up to $ZrIr_2(MgCu_2)$. Therefore a series of \underline{M} phases is stable with $4 < \frac{N/P}{P_n} < 8$. The shift of the brass plateau of $ZrIr_M$ relative to $TiIr_M$ conforms to the place number rule.

$A_M^{5,9}$ phases. The phase $V_3Co(Cr_3Si, FB2)$ is isodesmic to $V_3Ni(Cr_3Si, FB2)$ but in $VCo(U.h_1)$ instead of $FU2 = FUU/2$ as in $V_3Ni_2(U.h_1)$ a $HTU/2$ binding might be stable. The fact that at the Co poor side of V_1Co_1 the $FU2$ binding fits quite well suggests that the VCo phase might be composed of phases with different binding; it seems that this phenomenon has not yet been studied experimentally. $VCo_3.h(Cu_3Au, FB/8)$ is isodesmic to Cu and $VCo_3.r(H6.18)$ is a stacking homeotype of Cu_3Au with 6 layers per cell parallel to the hexagonal basal plane and permits a $FHCH/3$ binding with $\sim 7 \times 3$ layers of the \underline{c} correlation parallel to the basal plane. This may be a cause of the observed stacking sequence $\{ \delta \delta \delta \delta \delta \}$.

In $NbCo_M$ the $\frac{N/P}{P_n}$ curve is shifted to greater mole fractions $\frac{N}{Co}$, conforming once more to the place number rule.

$VRh(VIr)$ a DI-homeotype of CsCl with the commensurability $\underline{a} = a_{CsCl}(2;2;1)$ is

Nb2Rh(U.h1,SR29.125)9.810;5.068A=bFU(5;3.7/2)=cU($\sqrt{50}$;4.5)
NbRh.h
Nb48Rh52(CuAu,SR29.125)4.019;3.809A=idmVO.9Rh1.1 FUHT2 N=9.5,34 27,102
NbO.9Rh1.1(TaRh.r,SR29.125)2.827;4.770;13.587A=bUH(\approx 1.5;2;8/2)=cUHK'(2) N=
Nb40Rh60.h(AuSd,SR29.125)2.813;4.808;4.518A=bUH(1.4;2.2)=cUHK'(2) N=8,34
Nb3Rh5(DhtpSm,SR29.70)M30.52%;7.2.8;20.25A=bUH(2; \approx 1.5;10.5/2)=cUH(4;3;21/2)N=
Nb3Rh7(VCo3,SR29.125)H5.483;13.405A=idmVCo3 FHCH/3 N=36,221 34,155
NbRh3(Cu3Au,SR29.126)3.857A=idmVCo3.h FUB2
Ta2Rh(U.h1,SR29.130)9.822;5.102A=bFU($\sqrt{25}$;3.7/2)=cU($\sqrt{50}$;4.5) phdS
TaRh.h
TaO.8Rh1.2(O6.6,SR29.70)13.551;2.822;4.742A=idmNbO.9Rh1.1 FF2 N=24,100
TaRh2(Ni2Si,SR29.70)8.179;5.453;4.027A=bFU(3;2;2/2)=cB(6;4;3) N=20,105
TaRh3(Cu3Au,SR23.257)3.860A=idmVCo3.h FUB2
V3Ir(Cr3Si,SR23.233)4.786A=idmV3Co FB2 phdM
VIr(Q2.2,SR30.64)5.791;6.756;2.796A=idmVRh FF2
VO.9Ir1.1(CuAu,SR30.150)3.887;3.651A=idmVO.9Rh1.1 FF2
VIr3(Cu3Au,SR23.257)3.812A=idmVCo3.h FB/8
Nb3Ir(Cr3Si,SR29.121)5.134A=idmV3Co FB2 phdS
Nb2Ir(U.h1,SR29.121)9.86;5.05A=idmTa2RhFU2
NbIr(CuAu,SR29.121)4.027;3.863A=idmVO.9Rh1.1 FF2
Nb42Ir58(TaRh,SR29.121)2.823;4.818;13.619A=idmNbO.9Rh1.1 FF2 N=25,100
NbIr3(Cu3Au,SR29.121)3.890A=idmVCo3.h FB/8
Ta3Ir(U.h1,SR21.137)9.928;5.159A=idmTa2Rh FU2 phdS
Ta43Ir57(TaRh,SR28.47)2.830;4.803;13.661A=idmNb42Ir58
Ta41Ir59(CuAu,SR28.47)3.988;3.859A=bFU($\sqrt{2.5}$;2.2/2)=cFU($\sqrt{10}$.4.5/2) N=8,34
TaIr3(Cu3Au,SR28.47)3.907A=idmV3Co.h FB/8

A6A9M

Cr3Co2(U.h1,SR15.43)8.75;4.54A=bFU(5;3.7/2)=cU($\sqrt{50}$;4.5) phdM
Cr2Co3
CrCo2
CrCo3(Ni3Sn.r,SR34.139)H5.028;4.034A=bFH(2;2/3)=cCH($\sqrt{12}$;6.7/3) N=12,70
Mo3Co2.h(U.h1,SR28.17)9.229;4.827A=idmCr3Co2 FU2 phdS
Mo6Co7(W6Fe7,SR12.68)H4.767;25.65A=bH($\sqrt{5}$.3;12)=cFH(4;27/3)
MoCo3(Ni3Sn.r,SR28.44)H5.125;4.113A=idmCrCo3 FHCH/3
Mo2Co9.h
W3Co2(U.h1, ? see HA) phdHA
W6Co7(W6Fe7,SR6.176)H4.76;25.72A=idmMo6Co7 HFH/3
WCo3(Ni3Sn.r,SR6.176)H5.130;4.128A=idmCrCo3 FHCH/3
Cr78Rh22(Cr3Si,SR20.76)4.656A=bF(2)=cB(4) phdM
CrRh~2(Mg,SR19.111)H2.69;4.31A=bCH($\sqrt{3}$ /2;3.5/3)=cCH($\sqrt{3}$;7/3)
MoRh(AuCd,71Eck)2.745;4.785;4.413A phdE
MoRh~2(Mg,SR24.187)H2.76;4.43A=idmCrRh~2 CC2
WRh~3(NiSn.r,SR30.165)H5.453;4.350A=idmCrCo3 FHCH/3 phdS
Cr3Ir(Cr3Si,SR19.111)4.668A=idmCr3Rh FB2 phdM
CrIr(Mg,SR19.110)H2.69;4.296A=CrRh~2 CC2
CrIr3(Cu3Au,SR19.110)3.801A=bF(1)=cB($\sqrt{8}$;2.8)
Mo3Ir(Cr3Si,SR18.229)4.965A=idmCr3Rh FB2 phdM
MoIr.h(Mg,SR18.229)H2.78;4.48A=idmCrRh~2 CC2
MoIr.r(AuCd,SR30.150)2.752;4.804;4.429A
MoIr3(Ni3Sn.r,SR30.150)H5.487;4.385A=idmCrCo3 FHCH/3
W3Ir.h(U.h1,SR22.145)9.70;4.99A=idmCr3Co2 FU2 phdS
WIr(AuCd,SR30.150)4.452;2.760;4.811A
WIr~2(Mg,SR15.83)H2.742;4.387A=idmCrRh~2 CC2
WIr3(Ni3Sn.r,71Eck)H5.496;4.390A=idmCrCo3 FHCH/3

homeodesmic to $\text{TiCo}(\text{CsCl}, \text{FF2})$; as the FF2 binding stabilizes $\text{V}_{0.9}\text{Rh}_{1.1}$, in the outstanding composition VRh a $\check{\text{F}}\text{F}2$ binding is stable with $N_{\text{p}}^{\text{Rh}}=7.2$; the c_{F} correlation causes the I-homeotypism. The FF2 binding of $\text{V}_{0.9}\text{Rh}_{1.1}(\text{CuAu})$ has only in the basal plane a good fit to the a cell, and correspondingly a non-congruent melting. The two-factorial binding may be conserved when the mole fraction N_{Rh}^{r} grows. $\text{V}_3\text{Rh}_5(\text{Q3.5})$, a four layer close packing, contains a HH2 binding with 5 layers parallel to the quasi hexagonal basal plane; in agreement with the shear rule 64Sch. Furthermore the d_{b} distance is contracted as compared with the expectation in agreement with the distance rule (80Sch). The descent of \underline{b} electrons into the \underline{c} correlation is yet to be confirmed by measurements of magnetic susceptibility. In $\text{VRh}_3(\text{Cu}_3\text{Au}, \text{FB}\sqrt{8})$ at least the \underline{b} correlation has a full fit and therefore the highest decomposition temperature.

In $\text{Nb}_{0.9}\text{Rh}_{1.1}(\text{TaRh.r}, \text{O6.6}\check{\text{U}}\check{\text{H}}\check{\text{H}}2)$, a 6 layered close packing with stacking sequence ABCACB, a descent of 0.5 electrons per Rh must be assumed, furthermore there are 8 \underline{b} electron layers parallel to the basal plane. It may be shown (83Sch) that this binding proposal in fact favours the ABCACB stacking. Similar bindings are possible in the other homeotypes. The $d_{\text{b}}(N_{\text{Rh}}^{\text{r}})$ curve runs from NbRh_3 to Rh in a horizontal branch which is caused by a positive \underline{b} electron contribution of Rh.

$A_6^6 A_M^9$ phases. The Cr_3Si type is not stabilized with Co, as Hund insertion or descent would be necessary which increases the energy; for $\text{Cr}_3\text{Rh}(\text{Cr}_3\text{Si})$ and $\text{Cr}_3\text{Ir}(\text{Cr}_3\text{Si})$ the expansion of Rh and Ir compensates for that energy. In $\text{Cr}_3\text{Co}_2(\text{U.h}_1, \text{FU2})$ descent of 1 electron per Co appears necessary, and this forbids for instance " $\text{Cr}_3\text{Ni}_2(\text{U.h}_1)$ " contrary to $\text{V}_3\text{Ni}_2(\text{U.h}_1)$. The phase Cr_2Co_3 having presumably a XX2 binding is not yet determined structurally. $\text{CrCo}_3(\text{Ni}_3\text{Sn.r})$ is favoured by a FHCH $\sqrt{3}$ binding which yields less \underline{c} places than $\text{Cu}_3\text{Au}(\text{FB}\sqrt{8})$ being found in $\text{VCo}_3.\text{h}(\text{Cu}_3\text{Au})$, also perhaps 2 \underline{b} electrons per Cr are in Hund insertion.

The phase $\text{Mo}_6\text{Co}_7(\text{W}_6\text{Fe}_7)$, a 3,4-coalescence phase, is stabilized by a FHFW $\sqrt{3}$ binding with $N_{\text{p}}^{\text{Co}}=6.3$, but a phase stabilized by a XX2 binding is missing surprisingly, at the concentration " $\text{Mo}_{38}\text{Co}_{62}$ " which is favourable for XX2 a structure of the 3,4-coalescence type has not been found.

Inspection of the phase diagrams $A_6^6\text{Rh}_M$ and $A_6^6\text{Ir}_M$ shows that the Ekman boundary is approached: phases with very broad range of homogeneity crystallizing in simple close packed structures are found at elevated temperatures and few typical pseudo brass structures form in the solid state.

For $\text{Cr}_3\text{Rh}(\text{Cr}_3\text{Si})$ a certain amount of Hund insertion at Cr must be assumed to account for the electron numbers; the range of homogeneity somewhat shifted

A7A9M

MnCoM(broad marginal phases) phdS
TcCoM(bmp) see S
ReCoM(bmp) phdE
MnRhM.h(Cu) phdE
Mn3Rh(Cu3Au,SR19.225)3.814A
MnRh(CsCl,SR19.225)3.046A
TcRhM(bmp of Tc) phdM
ReRhM(bmp) phdS
Mn3Ir(Cu3Au,SR19.225)3.78A phdHA
MnIr.h(CsCl,SR19.224)?
MnIr(CuAu,SR19.223)2.73;3.70A
TcIrM(bmp of Tc) phdM
ReIrM(bmp) phdS

A8A9M

Fe3Co phdE
FeCo(CsCl,SR8.54)2.859A
FeCo3
RuCoM(Mg) phdHA
OsCoM(Mg) phdHA
FeRhM(Cu) phdE
FeRh.r(CsCl,SR26.178)2.987A
RuRhM(bmp) phdM
OsRhM(bmp) phdM
FeIrM.h(Cu)
Fe2Ir.r(Mg,SR29.177)H2.61;4.27A
RuIr.M(bmp) phdS
OsIrM(bmp) phdS

A9A9M

CoRhM(Cu) phdHA
CoIrM.h(Cu) phdHA
RhIrM.h(Cu) phdM

towards smaller N_{Rh} is perhaps caused by the leading phase $CrRh_{\sim 2}(Mg)$, which is compatible with a CC2 binding. The homeotypism $CrIr_3(Cu_3Au)$ - $MoIr_3(Ni_3Sn.r)$ obeys the place number rule.

$A^7 \dots A_M^9$ phases. The phase diagrams show that the Ekman boardary is reached. Broad marginal ranges of homogeneity show that the binding of an element endures high content of the other component. When the components are sufficiently similar the mixture consists at an appropriate temperature of one crystalline phase only. Few ordering phases are isodesmic to the disordered structures stable at elevated temperatures. No pseudo brass structures are found.

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