ON THE BINDING IN  $A^nA_M^{10}$  PHASES

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#### Summary

In the  $A^nA_M^{10}$  mixture class two types of mixtures are found, mixtures with non-Ekmanian electron count and mixtures with Ekmanian count. The Ekman boundary separating these types is about  $A^7A_M^{10}$ . For  $A^{n<7}A_M^{10}$  the distances of the peripheral d electr. of  $A^n$  are markedly greater than the distances of the peripheral d electrons of the  $A^{10}$  elements, while for  $A^{n>7}A_M^{10}$  these distances are essentially equal. The  $A^3\cdots^7A_M^{10}$  mixtures display a rich variety of interesting structure types permitting to analyse the binding, they may be named pseudo brass-like as the place number ratios  $N_{p^n}^{/p} = 4...16$  occur like as in truly brass-like alloys. An important difference to brass-like phases is caused by the great volume of the  $A^3\cdots^7$  components in pseudo brasses as compared to the  $B^2\cdots^5$  components in brasses; another difference lies in the fact that Hund insertion begins with  $A^6$  here, and with  $B^5$  in truly brass like alloys. The mixtures  $A^7\cdots^{10}A_M^{10}$  on the right of the Ekman boundary must be considered as truly brass like, the b electron concentration is not quite variable and therefore the structural aspect is uniform and poor.

## Introduction.

The mixture class  $A^n A_{\underline{M}}^{10}$  is rich in phases and permits therefore a good test for the electron count assumptions. The d electrons of  $A^{n \cdot 7}$  form the  $\underline{b}$  correlation while  $A^{10}$  contributes essentially no  $\underline{b}$  electrons. This non Ekmanian count causes brass-like bindings (XX2) to occur and the corresponding phases may be considered as pseudo brass-like as shall become clear below. However, it should be kept in mind that, say, the four valued Ti which is also usual in inorganic chemistry is no more four valued when it is alloyed with say Si, as it obeys there the Ekmanian count.

When in the following analysis comparison is made with the binding of a phase which does not belong to the present mixture class then the earlier papers of this series should be consulted. To appreciate the bindings in the table it is very helpful if not indispensable to draw the  $\underline{d}_{\underline{b}}(\underline{N}_{\underline{c}})$  and  $\underline{d}_{\underline{c}}(\underline{N}_{\underline{c}})$  diagram ( $\underline{d}$ =electron distance,  $\underline{N}_{\underline{c}}$ =mole fraction of the second component) and the  $\underline{N}_{\underline{p}}^{PP}(\underline{N}_{\underline{c}})$  diagram ( $\underline{N}_{\underline{p}}^{PP}$ -number of  $\underline{c}$  places per  $\underline{b}$  place).

Chemists sometimes find difficulty in the concept of a correlation. They should appreciate that this concept is only a moderate generalisation of the usual concept of a distribution of covalent bonds. While the latter concept suffers from the serious defect that the interaction of the bonds is neglected, the concept of a correlation avoids this shortcoming. Furthermore the covalent bond concept neglects the correlation of the valence electrons to the core electrons, also this has been taken into account by the two-correlations model. Therefore the model is more appropriate than earlier ones, to rationalize the stability of metallic phases in a first and therefore qualitative manner. The model is a logical continuation of the work of earlier crystallographers who studied the influence of atomic or ionic radius ratios and electric charges on stability. These earlier stability arguments are conserved in the present approach and should always be taken for granted. The new stability arguments add to our understanding of inorganic phases numerous rules which could be formulated with the concepts of the model.

Some readers ask how a classification in a binding represents a stability argument; they should remember that the existence of a lattice like spatial correlation is an indication of a low energy and so are the simple commensurabilities  $\underline{b}^{-1}\underline{a}$ ,  $\underline{c}^{-1}\underline{a}$ ,  $\underline{c}^{-1}\underline{b}$ . The present-time lack of valence rules for A<sup>n</sup>A<sup>10</sup> alloys may be confirmed from 73 Nic e.g.

 $A^1A_{\underline{M}}^{10}$  phases. The homologous mixture class of  $A^1A_{\underline{M}}^{10}$  contains following present knowledge at normal conditions only the phase NaPt<sub>2</sub>(MgCu<sub>2</sub>type) stabilized by a CF2 binding with the place number ratio  $N_{p}^{P_1}=32$ . The reason for this weak alloying tendency lies in the expansion of only one b electron of the  $A^1$  atoms into the direction of the  $A^{10}$  atoms which also may have a  $\underline{b}$  electron contribution of less than one electron per atom. That the phase forms with Pt, corresponds to the additional energy of formation afforded by Pt because of the high density of its core electrons.

 $\frac{A^2A_M^{10}}{P_1}$  phases. In  $A^2A_M^{10}$  mixtures more intermediate phases are formed, as here two belectrons per  $A^2$  tend to expand. Let us begin with the phase  $CaNi_2$  (MgCu<sub>2</sub>) containing a BF2 binding yielding  $N_p^{P_1}=16$ . It is homeodesmic to  $NaPt_2(MgCu_2, CF2)$ , and its equilibrium with Ca.h(Cu) containing CB2 and  $N_p^{P_1}=16$  represents a plateau of  $N_p^{P_1}$ . The phases  $CaNi_3(PuNi_3, R3.9)$ ,  $CaNi_{3.5}(GdCo_{3.5}, R4.14)$ , and  $CaNi_5(CaCu_5)$  are homeotypic to  $CaNi_2(MgCu_2)$  (74Bus,59Cro) by simple substitution of Ni for Ca and shears parallel (001) $CaNi_5$ . It appears that all phases have the same  $CaNi_3(CaCu_5)$  correlation but show different  $CaNi_3(CaCu_5)$  correlations which are in good commensurability to  $CaNi_3(CaCu_5)$  (note  $CaNi_3(CaCu_5)$ ). The assumption that  $CaNi_3(CaCu_5)$  has electrons leads to the great value  $CaNi_3(CaCu_5)$  for  $CaNi_3(CaCu_5)$  the congruent melting of this phase is compatible with the  $CaNi_3(CaCu_5)$  however,  $CaNi_3(CaCu_5)$  requiring  $CaNi_3(CaCu_5)$  contribution by  $CaNi_3(CaCu_5)$  is more probable; clearly these assumptions require corroboration by magnetic measurements.

Just as CaNi $_2$  formed a plateau with Ca.h, it appears that  ${\rm Mg}_2{\rm Ni}$  (H12.6) forms a plateau with Mg(H2). Contrary to CaNi $_2$  it must be assumed that MgNi $_2$  contains a little positive  $\underline{b}$  contribution by Ni, this would solve the old problem of the heterotypism MgNi $_2$ -CaNi $_2$ .

Leaving aside Mg<sub>6</sub>Pd and Mg<sub>4</sub>Pd the simple Mg<sub>3</sub>Pd(Na<sub>3</sub>As) permits HCH/3 with  $N_{p''}^{P'}=12.5$ , and the same binding in different commensurability to <u>a</u> stabilizes Mg<sub>5</sub>Pd<sub>2</sub>(Co<sub>2</sub>Al<sub>5</sub>). MgPd(CsCl) permits UF2 with  $N_{p''}^{P'}=13.0$ , and it is gratifying that Mg<sub>0.9</sub>Pd<sub>1.1</sub>(CuAu) puts the tetragonal binding in evidence. It is very conspicious that MgPd<sub>3</sub>(Cu<sub>3</sub>Au,HIB2) forms only atlower temperatures, probably Pd has there the binding n=n=n(1)=n=n(48;2.8).

The heterotypism CaPd(CsC1)-SrPd(T1I) is interpreted by the remark that the greater Sr causes a greater  $\frac{N}{PP}$ .

The phase MgPt<sub>7</sub>(F1.7), when it exists, might have a CB2 binding, and the distances fit well to the other values. The mixture CaPt<sub>M</sub> is another example with a non-monotonous  $N_{p^n}^{/P}(N_2^r)$  function. While for Ca.h( $\overline{N}$ ,FUU2)  $N_{p^n}^{/P}=14$ , for Ca<sub>5</sub>Pt<sub>3</sub>( $N_5$ Si<sub>3</sub>) is found a UF2 binding with  $N_{p^n}^{/P}=13$ ; it must be assumed that the Pt atoms have a contractive influence on the  $N_p$  electrons of Ca.h.The Er<sub>3</sub>S

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NaNiM(probably nic, see E)
KNiM(prob.nic, see S)
RbNiM
CSNiM
NaPdM(prob.nic, see HA)
KPdM
RbPdM
CsPdM
NaPt.p(see HA)
NaPt2(MgCu2,71Eck)7.48A=bC(2)=cF(4)
KPtM(prob.nic, see HA)
RbPtM
CsPtM
A2A10M
Mq2Ni(H12.6,SR15.95,46.72)H5.216;13.20A=bUH(2;6/2)=cCH(\sqrt{12;21/3}) N=24,156
MgN12(H8.16,SR3.31,46.96)H4.824;15.826A=bUU(\sqrt{3};6.5/2)=cFH(4;16/3) N=16,224 cmp
CaNi2(MgCu2, SR40, 103)7, 256A=bB(2)=cF(4) N=16,224 phdM
CaNi3(PuNi3, SR40.103) H5.030; 24.27A=b\dot{U}H(\sqrt{2.3}; 8/3)=cFH(4; 24/3)
Ca2Ni7(Gd2Co7.SR40.103)H5.009:36.06A=bH(\sqrt{2.3:11})=cFH(4:35/3) N=24.516
CaNi5(CaCu5, SR11.59)H4.960; 3.948A=bBH(1;4/3)=cFH(4;4/3) N=2,58 cmp
SrNi phdM
BaNiM(nic, phdM)
Mg6Pd(F84.14,SR38.120)20.108A→H14.2;34.8A=bCH(√19;26/3)=cH(√171;32) N=672,3248
Mg4Pd( ,SR23.176) phdS
Mg3Pd(Na3 As,SR23.176)H4.613;8.410A=bH(2;3.7)=cCH(√12;16/3) N=12,68
Mg5 Pd2(Co2A15,H20.8,SR33.110)H8.660;8.169A=hH(\sqrt{13};3.4)=cCH(\sqrt{39};14/3) N=40,240
MgPd(CsC1, SR23.175)3.16A=bU(1;1.2)=cF(2)
MgO.9Pd1.1(CuAu, SR24.173)3.03;3.42A=hdmMgPd cmp
MgPd3(Cu3Au?, SR23.175)3.907A=bNT(\sqrt{2};1.6)=cB(\sqrt{8};2.8) cmp
CaPd(CsC1, SR39.109, 46.126)3.522A=idmMgPd
CaPd2(MgCu2, SR22.75)7.665A=idmCaNi2 BF2
SrPd(T1I, JLCM38.1974.1)4.19; 11.31; 4.52A=bC(0.93x/2; 3.5; \sqrt{2})=cB(\sqrt{8}; 7) N=8,72
SrPd2(MgCu2,SR21.137)7.800A=idmCaNi2 BF2
SrPd5(CaCu5, SR21.137) H5.411; 4.416A=idmCaNi5 BF2
BaPd(T11, JLCM38.1974.1)4.35;11.79;4.68A=idmSrPd phdM
BaPd2(MgCu2, SR22.75)7.953A=idmCaNi2
BaPd5(CaCu5,71Eck)H5.494;4.344A=idmCaNi5
Mg6Pt(Mg6Pd, SR24.174)20.11A=idmMg6Pd CHH3
Mg3Pt(Na3As, SR24.174)H4.577;8.322A=idmMg3Pd HCH/3
MgPt(FeSi,SR26.225)4.86A+H6.88;8.42A=bCH(2;6/3)=cFH(6;9/3)
MgPt3(Cu3Au, SR27.322)3.906A=idmMgPd3 HTB2
MgPt7(F1.7, $R27.322)7.824A=bq(%,1)=cB(J3;5.6)
Ca5Pt2(Mn5C2,JLCM78.1981.P49)M97.47<sup>0</sup>16.154;6.627;7.662A
Ca5Pt3(W5Si3,ibid)11.563;5.753A=bU(\sqrt{10};2)=cF(\sqrt{40};6/2)
                                                             N=40,280
Ca3Pt2(Er3Ni2, ibid)H8.786;16.786A=bH(3;6)=cCH(\sqrt{27};24)
CaPt2(MqCu2, SR27.322)7.629A = idm CaNi2 BF2
Ca2Pt7(Ce2Ni7, SR27.324)H5.349; 26.30A=b8M(1;24/3)=cFH(4;24/3) N=16,344
CaPt5(CaCu5, SR27.322) H5.322; 4.368A= idmCaNi5 BF2
Sr9Pt(F
             ,JLCM78.1981.P49)6.091A
SR7Pt3(0
             ,ibid)7.937;24.333;7.109A
Sr3Pt2(Er3Ni2,ibid)H9.337;17.762A=idmCa3Pt2
Sr5Pt4(Pu5Rh4,ibid)7.879;15.606;8.147A
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SrPt2(MgCu2, SR22.75)7.777A=idmCaN12

SrPt3

 $Ni_2(R9.6,SR40.64)$  structure of  $Ca_3Pt_2$  permits a HCH/3 binding with  $N_{p_1}^{P_1}=12.5$ . The phases  $CaPt_2(MgCu_2)$ ,  $Ca_2Pt_7(Ce_2Ni_7)$  and  $CaPt_5(CaCu_5)$  are homeotypic and homeodesmic.

 $\frac{A^3A_M^{10}}{M}$  phases. While in the previous class  $A^2A_M^{10}$  the electron count was not a problem, in  $A^3A_M^{10}$  an Ekmanian or non-Ekmanian count may be chosen (see 83Sch). The observed crystal structures appear to suggest the non-Ekmanian count  $sc^3$ ,  $8Ni_M^{10}$ , but sometimes a little  $\underline{b}$  contribution by Ni might be possible. The  $Ti_2Ni$  type of  $Sc_2Ni$  occurs mainly in  $A_2^4A^{10}$  phases, a HTU/2 binding appears possible here, but in  $Ti_2Ni$  the binding FU2 will be found. For ScNi the HH2 binding of NiAl appears to apply although the BB2 binding of CuZn might be considered too. The phase  $ScNi_2(MgCu_2)$  is not isodesmic to  $CaNi_2(MgCu_2)$ , as binding appears possible HTFU2 with place ratio  $N_p^{(p)}=9.8$ . The radius ratio  $T_{A3}/T_{A10}$  fosteres in  $ScNi_2$  and its homologous isotypes the coalescence of hexagonal atom layers with  $\sqrt{4}$  and  $\sqrt{3}$  commensurability of the atom nets to the crystal mesh, and the large atom in the  $\sqrt{3}$  mesh expels additionally a small atom from the neighbouring  $\sqrt{4}$  mesh so that a double replacement by  $A^3$  occurs (64Sch). The members of this structural family are numerous and in the present example they have , as  $TAB.A^{30}_{M}$  shows, all the same  $\underline{c}$  correlation but differ in the b correlation.

 $Y_3Ni(Fe_3C)$  is a DI-homeotype of CuAu and permits a HH/3 binding.  $Y_3Ni_2C$ (T48.32) yields a HTC2 binding with  $\frac{N}{p_0}=7.0$  and YNi(FeB) permits a HH2 binding with  $N_{pu}^{/P}=8$  . This brass-like binding is expected in brass-like phases near the b electron concentration 1.5 (generalized Hume-Rothery rule). In the present mixture class the occupation ratio of the  $\underline{c}$  correlation is for  $A^3$ rich phases only 0.50 of the ratio in brass-like phases, therefore the XX2 binding may occur at greater b electron concentrations (see Y<sub>2</sub>Pd<sub>2</sub>). The difference in c occupation is the cause of the striking phenomenon that the present pseudo brass-like alloys are structurally quite different from the truly brass-like alloys. The small occupation of the c correlation is caused by the large volume of the  $A^3$  atoms. In the phase with the greatest mole fraction  $N_{Ni}$   $Y_2Ni_{17}(Th_2Ni_{17})$  the <u>c</u> occupation is 0.93 as in many brass-like phases, but the  $\underline{b}$  electron concentration  $\underline{N}_{b}^{/A}$ =0.315 is too small as the place number ratio became  $N_{p\pi}^{/p}=32$  which is equal to the value 32 for the A<sup>1</sup> elements (82aSch). Therefore the stability of YNi<sub>8.5</sub> suggests the ioni-Ni<sup>10</sup> electrons of easily found from the data of A3A10M that  $\underline{d}_b$ =2.6R in YNi $_{8.5}$  while in Y it is near 2.3A. Another feature confirming the binding proposal is the high

SrPt5(CaCu5,SR21.137)H5.397;4.364A=idmCaNi5
BaPt2(MgCu2,SR22.75)7.920A=idmCaNi2 phdM
BaPt5(CaCu5.SR13.31.35.27)H5.505;4.342A=idmCaNi5 cmp

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Sc2Ni(Ti2Ni, SR27.342)12.29A=bHT(\sqrt{32};6.5/2)=cU(8;10) N=192,832
ScNi (CsC1, SR27.342)3.17A=bHT(\sqrt{2}; 1.6/2)=cHTK'(2)
                                                                           N=24,224
ScNi2(MgCu2,SR26.236)6.926A=bHT(\sqrt{8};3.3)=cF(4)
Sc2Ni7(Ce2Ni7, JLCM16.441) H4.74; 22.56A=6H(2; 9)=cFH(4; 24/3)
                                                               N=24.344
ScNi5(CaCu5, JLCM16.441) H4.74; 3.76A=bCH(/1.8; 2.6)=cFH(4; 3.9/3)
                                                                              phdE
Y3Ni(Fe3C,BulSocFrMiCr90.311)6.92;9.49;6.36A=bHO(3;4;1.5)=cHO(3;7;4.8) N=36,136
Y3Ni2(T48,32,SR43.85)7.104;36.597A=bHT(3;16/2)=cC(6;3 1) N=144,703
YNi(FeB, SR24.198)4.124;7.156;5.521A=bHT(2/1;3;2.3)=cHT(4;6;4.6) N=12,72
YNi2 (MgCu2, SR24.198) 7.181A=idmScNi2 HTFU2
                                                 N=24.224
YNi3(PuNi3,R3.9,SR24.198)H5.00;24.30A=b H(2;10 )=cFH(4;24/3) N=27,342
Y2Ni7.h(Gd2Co7,SR34.140,35.122)H4.949;36.23A=bBH(1;36/3)=cFH(4;36/3) N=36,516
Y2Ni7.r(Ce2Ni7, JLCM18.59) H4.928; 24.11A=hdmY2Ni7.h
YNi5(CaCu5, SR24.198)H4.883;3.967A=idmScNi5 CHFH3
Y2Ni17(Th2Ni17, SR24.198)H8.34;8.08A=bCH(γ3355/3)=cFH(γ48; 8/3) N=12,372
La3Ni(Fe3C, BulSocFrMiCr90.311)7.22;10.24;6.60A=idmY3Ni
                                                           HHV3 phdM
La7Ni3(Th7Fe3,SR39.117)H10.140;6.383A=bUH(4;3/2)=cFH(\sqrt{48};5.4/3) N=42,172
LaNi(TìI, SR30.150)3.907;10.810;4.396A=bB(0.9\sqrt{2};3.5;\sqrt{2})=cB(0.9\sqrt{8};7;\sqrt{8}) N=12,72
La2Ni3(Q4.6,SR42.104)5.114;9.732;7.908A
LaNi2(MgCu2, SR11.87)7.262A=idmScNi2 HTFU2
                                                             N=18,168
LaNi3(PuNi3, SR34.140) H5.086; 25.01A=idmYNi3
La2Ni7.h(Gd2Co7,JLCM18.59)H5.056;36.98A=idmY2Ni7.h
La2Ni7.r(Ce2Ni7,SR35.95,39.117)H5.058;24.71A=idmY2Ni7.r
LaNi5(CaCu5, SR11.59) H5.016; 3.982A=idmScNi5 CHFH3
Sc4Pd
Sc2Pd(Ti2Ni,SR27.342)12.427A=idmSc2Ni phdM
ScPd(CsC1,SR27.342)3.283A=idmScNi HTHT2
ScPd2
ScPd3(Cu3Au, SR26.165)3.981A=bFU(\sqrt{2.25;2.12})=cB(3)
                                                             N=3.38
Y3Pd(Fe3C,JLCM72.P17)7.063;9.734;6.453A=idmY3Ni HHV3
                                                          phdM
Y5Pd2(Dy5Pd2,SR40.114)13.625A=bHT(\sqrt{32};6.5)=cU(8;10) N=204,824
Y3Pd2(Er3Ni2,SR43.105)H8.750;16.468A=bH(\sqrt{13};6.5)=cH(\sqrt{52};13) N=81,396
YPd.h
YPd.r
Y3Pd4(Pu3Pd4,SR40.114)H13.147;5.697A=bH(5;2.2)=cUH(10;5/2) N=54,384
Y2Pd3.h
Y2Pd3.r
YPd2
YPd3(Cu3Au, SR26.165)4.074A=idmScPd3 FUB2 cmp
La3Pd
La7Pd3(Th7Fe3,SR39.117)H10.387;6.552A=idmLa7Ni3 UHFH/3
LaPd(T1I, ThermChimAct12.267)3.945;11.032;4.660A=bU(0.81/2;4:1/2)=cUHK'(2)
La3Pd4(Pu3Pd4,SR40.111)H13.860;5.848A=idmY3Pd4 HUH2
LaPd3(Cu3Au, SR26.165)4.235A=idmScPd3 FUB2
SQPt(Ni2Si, SR45.106)6.592;4.491;8.206A=bF(2;1.3;2.5)=cFK'(2)
ScPt(CsC1, SR27.342)3.270A=bHT(\sqrt{2}; 1.6/2)=cHTK'(2)
ScPt2(MgCu2,79Ian)
ScPt3(Cu3Au, SR26.165)3.958A=idmScPd3 FUB2
Y3Pt(Fe3C, SR45.85)7.101;9.584;6.454A=idmYNi3 HH/3
Y7Pt3(Th7Fe3,PhyRevA137.119)H9.864;6.299A=bUH(4;3/2)=cFH(/48;5.5/3) N=42,172
Y2Pt(Ni2Si, SR44120)7.141;4.764;8.753A=bF(2;1.3;2.5)=cC(\sqrt{32};...) N=44,104
Y5Pt3(Mn5Si3,SR44.120)H8.370;6.276A=bUH(\sqrt{12};3/2)=cH(\sqrt{48};5.2) N=30,140
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melting temperature  $T_c(YNi_5)=1490^{O}C$  (see 65E11) which is near to  $T(Y)=1500^{O}C$ ; this temperature is caused by the energetic favourable  $c_{FH}$  correlation of  $YNi_5$ : thoughtis cubic and F1 is cubic the first element of the commensurability matrix 3 yields parallel axes of  $\underline{b}$  and  $\underline{c}$  so that nowhere the correlations need to deform each other as it occurs in bindings which are factorial only in one plane.

The isotypic phases ScPd $_3$ (Cu $_3$ Au),YPd $_3$ ,LaPd $_3$  are quite stable as YPd $_3$  has a very high melting temperature, and this confirms the fUB2 binding. A R-homeotype of Ti $_2$ Ni is Y $_5$ Pd $_2$ (Dy $_5$ Pd $_2$ ,F18.7), a HTU $_7$ 2 binding might apply. The Er $_3$ Ni $_2$ (R9.6,SR40.64) structure of Y $_3$ Pd $_2$  permits a HH2 binding with N $_p^{P_1}$ =8.0. For Y $_3$ Pd $_4$ (Pu $_3$ Pd $_4$ ,R 6.8) a HUH2 binding is possible with N $_p^{P_1}$ =9.2 and LaPd(TII) is with UU2 surprisingly heterodesmic to LaNi(TII,BB2). Furthermore it is astonishing that in A $_3$ Pd $_2$  no MgCu $_2$  type appears to occur.

In  $Sc_2Pt(Ni_2Si,FF2)$  a strong shift of the XX2 binding to  $A^{10}$  poorer compositions is found. ScPt(CsC1) might be isodesmic to ScNi(CsC1), like as  $Y_2Pt(Ni_2Si)$  to  $Sc_2Pt$ . It may be understood from this that the binding in first line steers the stability while the structure depends also on radius ratio etc. A remarkable phenomenon is the heterotypism ScPt -YPt -LaPt; the number of  $\underline{c}$  places per atom  $\underline{N}_{P^n}^{/A}$  is 16, 13.5, 12.5 conforming to the place number rule; it may therefore be said that the place number rule causes the heterotypism.

 $\frac{A^4A_h^{10}}{A^4}$  phases.  $\text{Ti}_2\text{Ni}(\text{F16.8})$  is a RLI-homeotype of W. The difference to the homeotype  $\text{NiSi}_2(\text{CaF}_2)$  lies in the possibility of formation of Ni clusters in  $\text{Ti}_2\text{Ni}$ , which is favourable here as the Ni-Ni core interaction is stronger than the Ti-Ni core interaction (83Sch). The binding cannot be FB2 as the melting point of  $\text{Ti}_2\text{Ni}$  is relatively low and not congruent; it is FU2 and must therefore be twinned in the crystal. For TiNi.h(CsCl) a FF2 binding fits, the famous room temperature structures may have to do with a split of the  $\text{Ti}^4$  electrons into two correlations. In  $\text{TiNi}_3.r(\text{H4.12})$  a hexagonal homeotype of  $\text{Cu}_3\text{Au}$ , four close packed atom layers parallel to the hexagonal basal plane are stacked in the sequence ABAC. The high and congruent melting point of  $\text{TiNi}_3.r$  suggests a favourable binding, and the FHCHH/3 binding of TAB.4 permits a preferred fit of  $\underline{b}$  to the  $\underline{a}$  cell. The dipole assessment of 64Sch favours the shear when  $\underline{c}_{\text{CH}}$  is somewhat deformed.

During a study of  $TiNi_{\underline{M}}Cu_{\underline{M}^1}$  alloys (68Pfe) high temperature homeotypes of  $TiNi_3$  have been found, for increasing  $\underline{b}$  electron concentration the sequence of the phases was L4, L10, L9, L21 where L4 means a structure with 4 layers per cell. Similar sequences of structures have been found in brass-like mixtures

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Ti2Ni(F16.8, SR23.195)11.278A=bF(4)=cU(8;10) N=256,832 phdHA
TiNi.h(CsCl, SR13.91)2.986A=bF(1)=cF(2) N=4,18
TiNi.r(Z6.6, H5.5, Z3.3, SR38.131)
TiNi2.h(homeotype of TiNi3 with 21 layers)
Ti30Ni70.h(9 layers)
Ti27Ni73.h(10 layers)
TiNi3(H4.12,SR7.14)H5.199;8.319A=bFH(2;4/3)=cCH(\(\frac{1}{2}\);15/3) N=16,152
Zr2Ni(CuA12,SR27.297)6.477;5.241A=bFU(3;3.5/2)=cU(\(\frac{1}{2}\);15/3) N=32,104 phdM cmp
ZrNi(TII,SR27.297)3.268;9.937;4.101A=bFU(\(\frac{1}{2}\);1.25\(\frac{1}{2}\);1.25\(\frac{1}{2}\);2-cFUK'(2) N=16,72 cmp
Zr9Ni11.h(U9.11, SR45.97)9.88;6.61A=bB(\sqrt{13};2.4)=cBK'(2) N=72,364
Zr7Ni10(Q14.20,SR27.298)12.386;9.156;9.211A-bHT(4;6)=cHT(8;12) N=112,624
Zr2Ni5(0
               ,SR26.207)6.5;10.1;12.1A
ZrNi3(Ni3Sn,$R45.97)H5.309;4,303A=bH(2;1.6)=cCH(12;7/3) N=8,76 cmp
Zr2Ni7(N4.14,$R38.132)M95.83°4.698;8.235;12.193A=bBH(1;13/3)=cFH(4;13/3)N=32,344
ZrNi5(Be5Pd, SR21.158)6.706A=bB(2)=cF(4) N=16,232
Hf2Ni(CuA12, SR38.6)6.405;5.252A=idmZr2Ni phdM
HfNi.h
HfNi.r(T1I, SR27.232)3.220;9.820;4.120A=idmZrNi
Hf9Ni11(Zr9Ni11,SR26.206)9.79;6.53A=idmZr9Ni11
Hf7Ni10(Zr7Ni10,SR27.232)12.275;9.078;9.126A=idmZr7Ni10
Hf3Ni7.h(Z6.14.SR44.69)
Hf8Ni21.h(Z8.21,SR44.69)
HfNi3.h(BaPb3,R3.9,SR44.69)H5.279;19.232A=hdmTiNi3
HfNi3.r(Ta(Rh,Pd)3,H10.30,$R44.69)H5.282;21.392A=hdmTiNi3
Hf2Ni7(Zr2Ni7,SR39.68)M95.509<sup>0</sup>4.657;8.191;12.102A=idmZr2Ni7
HfNi5(Be5Pd, SR26.207)6.68A=idmZrNi5
Ti4Pd(Cr3Si,71Eck)5.055A=bHT(\sqrt{8};3.2)=cB(4) N=26.68 phdM
Ti2Pd(Zr2Cu, SR27.234)3.090;10.054A=bB(\sqrt{2};4.5)=cFU(\sqrt{8};13) N=16,52
TiPd.h(CsCl,70Don)3.18A=idmTiNi,h FF2
TiPd.r(AuCd, SR30.163)4.56;2.81;4.89A=bH(/1.75;2.1)cHK'(2) N=8,36 cmp
Ti2Pd3(Q4.6,SR33.126)4.61;14.33;4.64A=bFU(2;8/2)=cFU(4;18/2) N=32,184
Ti3Pd5(T3.5,SR33.127)3.263;11.436A=bHT(\sqrt{2};6/2)=cFU(\sqrt{8};7) N=12,74
TiPd1.7(MoSi2,71Eck)3.24;8.48A=bHT(\sqrt{2};4.3/2)=cFU(\sqrt{8};10.5/2) N=9.55
TiPd2(DhtpMoSi2,71Eck)3.41;3.07;8.56A
TiPd2.9(TiNi3,SR22.181)H5.489; 8.964A=idmTiNi3 FHCH/3 cmp
TiPd4(Cu3Au,68Kra)40A=bFU(\sqrt{2};2/2)=cB(\sqrt{8};2.8) N=3.2,39
Zr2Pd(Zr2Cu, SR27.227)3.297;10.92A=idmTi2Pd phdM
ZrPd cmp
Zr4Pd5(tetr
                          )10.25;6.68A=idmZr9Ni11 BB2
ZrPd2(MoSi2,SR27.227)3.407;8.597A=idmTiPd1.7
ZrPd3(TiNi3,SR27.227)H5.623;9.254A=idmTiNi3 FHCH/3 cmp
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(58Weg) and in the mixture TiNi $_3$ (NbNi $_3$ ) $_M$ (66Vuc). Several structure proposals (71Bha) refer to a substructure, they do not correspond to results of (58Weg) and need therefore confirmation. It appears probable that a change of  $\underline{b}$  electron concentration alters the stacking sequence, but a full interpretation is yet to be worked out.

The phase  $\mathrm{Zr}_2\mathrm{Ni}(\mathrm{CuAl}_2)$  has a FU2 binding like  $\mathrm{Ti}_2\mathrm{Ni}(\mathrm{F16.8})$  and the heterotypism  $\mathrm{Ti}_2\mathrm{Ni}\mathrm{-Zr}_2\mathrm{Ni}$  obeys the place number rule:  $\underline{\mathbb{N}}_{p^{\mathrm{H}}}^{/A}(\mathrm{Ti}_2\mathrm{Ni}) = 13.3$ ,  $\underline{\mathbb{N}}_{p^{\mathrm{H}}}^{/A}(\mathrm{Zr}_2\mathrm{Ni}) = 12$ . It becomes clear now why the  $\mathrm{Ti}_2\mathrm{Ni}$  type is stabilized by small amounts of N ( $\mathrm{Zr}_2\mathrm{NiN}_{0.5}$ , see 71Eck) or 0 ( $\mathrm{Hf}_2\mathrm{NiO}_{0.5}$ , etc., SR24.133): the electrons of the atoms occupy  $\underline{\mathbf{c}}$  places (82Sch) and increase therefore the  $\underline{\mathbb{N}}_{p^{\mathrm{H}}}^{/A}$  number so that the  $\mathrm{Ti}_2\mathrm{Ni}$  type becomes more favourable. The phase  $\mathrm{ZrNi}(\mathrm{TII})$  opens the brass plateau with FF2 and it is seen that there are enough  $\underline{\mathbf{c}}$  places for the count  $\mathrm{Zr}^{4,8}\mathrm{Ni}^{0,10}$ . The phases  $\mathrm{Zr}_9\mathrm{Ni}_{11}$ .h(U9.11) and  $\mathrm{Zr}_7\mathrm{Ni}_{10}(\mathrm{Q14.20})$  with BB2 and HH2 binding complete the plateau. The phases  $\mathrm{Zr}_2\mathrm{Ni}_7(\mathrm{N4.14})$  and  $\mathrm{ZrNi}_5(\mathrm{BePd}_5)$  belong to a BF2 plateau. The phases of HfNi<sub>M</sub> are mostly isodesmic to  $\mathrm{ZrNi}_M$  phases.

In TiPd<sub>M</sub> a fairly smooth  $N_{P}^{/P}(N_2)$  "curve follows from the data of TAB.4. The FUB2 binding for TiPd<sub>A</sub>(Cu<sub>3</sub>Au) suggests that Pd contributes some  $\underline{b}$  electrons.

The CB/2 binding of  ${\rm Ti}_3{\rm Pt}({\rm Cr}_3{\rm Si})$  is closely homeotypic to the favourable FB2 binding occurring in  ${\rm V}_3{\rm Ni}({\rm Cr}_3{\rm Si})$ . In TiPt.h(CsCl,FF2) the brass plateau begins which ends in  ${\rm Ti}_3{\rm Pt}_5({\rm P6}.10)$ , a R-homeotype of TiAl $_3$  with a BB2 binding explaining the TiAl $_3$  shear by the electro dipole rule (64Sch). The FHCH/3 binding of TiPt $_2$ .g(TiNi $_3$ ) is probably responsible for the congruent melting point of TiPt $_3$ . The rare structure of TiPt $_8({\rm Ul.8})$  corroborates the assumption that for sufficient small  ${\rm NT}_1$  the  ${\rm \underline{b}}$  contribution of  ${\rm A}^{10}$  becomes positive; the  ${\rm \underline{NN}}_1$  independent value of  ${\rm \underline{d}}_{\rm \underline{b}}({\rm \underline{NN}}_1)$  suggests that the electron concentration becomes constant.

The phase  $\rm Zr_5Pt_3(Mn_5Si_3)$  permits the good HUH/3 binding, the other phases of the mixture are isodesmic to earlier phases, and the same is valid for HfPt<sub>M</sub>.

 $\frac{A^5A_{M}^{10}}{P}$  phases. It is remarkable that  $V_3Ni(Cr_3Si,FB2)$  has not a congruent melting point, but considering that the  $\underline{b}$  correlation is not fully occupied it becomes probable that the  $\underline{b}$  correlation is in fact a little strained and this spoils the high melting point. Compared with this assumption  $V_3Ni_2(U.h,FU2)$  has a better commensurability and reamins stable at higher temperatures.  $VNi_2(MoPt_2,UU2)$  and  $VNi_3(TiAl_3,BB2)$  belong to the XX2 plateau and conforming to a rule the closer UU2 binding is stable at greater  $\underline{b}$  electron concentration.

The phase  $\mathrm{Nb}_5\mathrm{Ni}(\mathrm{F20.4})$ , a homeotype of  $\mathrm{TiNi}_2$ , has not been traced in the phase diagram (see 69Shu). Since the well fitting BC2 binding permits 432  $\underline{\mathrm{b}}$ 

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Hf2Pd(Zr2Cu, SR27.234)3.251;11.061A=idmTi2Pd BFU2 phdM
HfPd
Hf3Pd4
HfPd2.h(MoSi2.
                       cmp
HfPd3(TiNi3, SR23, 258) H5.595; 9.192A=idmTiNi3 FHCH/3
Ti3Pt(Cr3Si, SR16.100) 5.033A=bC(\sqrt{8}; 2.8)=cB(4) N=24,68 phdE
TiPt.h(CsCl,SR38.170)3.19A=idmTiNi.h FF2
                                             cmp
TiPt.r(AuCd, SR29.129)4.59;2.76;4.82A=idmTiPd.r HH2
Ti3Pt5(P6.10, SR33.127)10.953;5.441;8.169A=bB(4;2;3)=cBK'(2) N=48,296
TiPt2.9(TiNi3.SR29.129)H5.52.9.02A=idmTiNi3 FHCHV3
TiPt3(Cu3Au, SR21.164)3.916A=bF(1)=cB(\sqrt{8};2.8) cmp
TiPt8(U1.8, SR30.86)8.312;3.897\hat{A}=\hat{b}FU(3;2/2)=\hat{c}U(6;3.5) N=8,176
Zr2Pt(Zr5Ir3,ZMetKd55.704)
                             phdE
Zr5Pt3(Mn5Si3,ZMetKd58.558)H8.201;5.405A=bH(4;2.5)=cUH(\sqrt{48};5/2) N=40,140
ZrPt.h(CsCl,SR29.130)3.31A=idmTiNi.h FF2
ZrPt.r(T1I, SR30.164)3.409;10.315;4.277A=idmZrNi FF2
                  )10.29;6.88A=idmZr9Nill.h BB2
Zr9Pt11(tetr.
Zr7Pt10(tetr.
                  )6.78;13.03A=idmZr7Ni10 HH2
ZrPt3(TiNi3,SR9.116)H5.644;9.226A=idmTiNi3 FHCH/3
ZrPt4(Cu3Au,
                  )3.99A=idmTiPt3 FB/8
ZrPt8(TiPt8, ZMetKd59.724)8.386; 4.027A=idmTiPt8 FUU2
Hf2Pt(Ti2Ni, SR22.188)12.46A=idmTi2Ni
HfPt(T11, SR30.144)3.345;10.269;4.288A=idmZrNi FF2
HfPt1.1(CsC1,ZMetKd55.704)3.23A=idmTiNi.h FF2
Hf2Pt3(MoSi2,SR29.119)3.43;8.73A=bFU(\sqrt{2};5/2)=cFUK'(2) N=9.6,55
HfPt3(TiNi3, SR23.258) H5.636; 9.208A = idmTiNi3 FHCH/3
A5A10M
V3Ni(Cr3Si, SR18.313)4.711A=bF(2)=cB(4) N=30,68 phdM
V3Ni2(U.hl,T30,SR20.163)8.97;4.64A=bFU(5;3.7/2)=cU(√50;4.5) N=90,264
VNi2(MoPt2,P1.2,SR30.161)2.56;7.64;3.55A=bU(1;3;1.7)=cUK'(2)
VNi3(TiAl3, SR16.124)3.54;7.21A=bB(\(\sigma\)2;3)=cBK'(2)
VNi8(TiPt8, JMatSci6.1971.1425)
Nb5Ni?(F20.4,htpTi2Ni,Kristja12.350)11.642A=bB(6)=cC(12) phdS
NbNi (W6Fe7, SR27.287) H4.893; 26.64A=bH(\sqrt{7}; 14.3)=cUH(\sqrt{21}; 28.6/2
NbNi3(Cu3Sb.h, SR22.173)5.11;4.54;4.25A=bCH(\sqrt{3};1.5;3.5/3)=cCHK'(2)
NbNi8(TiPt8,TransMet1SocAIME245.1969.345)7.6;3.6A=bFU(3;2/2)=cB(6;3.8) N=10,176
Ta5Ni?(Nb5Ni,Kristja12.350)11.635A=idmNb5Ni phdS
Ta2Ni (CuA12, SR27.294)6.216; 4.872A=bHT (\sqrt{13}; 3.2/2)=cB(\sqrt{26}; 4)
TaNi(W6Fe7, SR27.287) H4.921; 26.905A=idmNbNi HUH/3
TaNi2(MoSi2, SR29.69)3.154;7.905A=bF(1;5/2)=cFK'(2)
TaNi3.h(TiAl3,SR29.127)3.627;7,455A=idmVNi3 BB2 cmp
TaNi3.r(M12.36,SR30.160)M90.63°5.11;4.54;25.50A=bCH(√3;1.5;21/3)=cCHK'(2)N=60,456
TaNi8(TiPt8, MetTrans1.1970.485)7.60;3.70A=idmNbNi8
V3Pd(Cr3Si, SR22.182)4.816A=idmV3Ni FB2 phdE
VPd.r(htpCu,71Eck)3.83A
VPd2.r(MoPt2, SR29.129)2.750;8.250;3.751A=idmVNi2 UU2 N=10.56
VPd3.r(TiA13,SR26.165)3.847;7.753A=idmVNi3 BB2
Nb3Pd2.h(U.hl, SR20.75, 29.125)9.89;5.11A=idmV3N2 FU2 phdE
Nb2.9Pd2.r(NbRu, MetKd55.1964.619)4.30;4.23;3.65A=bFU(2;2.5/2)=cC(4;3.5) N=12,36
NbPd.h?(Mn.r,71Eck)9.77A
NbPd2(MoPt2,SR30.156)2.839;8.376;3.886A=idmVNi2 UU2
NbPd3.h(06.18,SR29.70)5.486;4.845;13.602A=bCH(\(\frac{1}{3}\);1.5;10.5/3)=cCHK'(2) N=30,228
NbPd3.r(TiA13,71Eck)3.87;7.96A=idmVNi3 BB2
Ta3Pd(U.h', SR28.48) 9.978; 5.208A=bFU(\sqrt{29}; 4/2)=cU(\sqrt{58}; 4.8) N=112,256 phdM
TaPd.h(Cu, MetTrans 94.1978.643)
```

places while only 400  $\underline{b}$  electrons are offered it might be that the phase is stabilized by atoms like oxygen. NbNi(W<sub>6</sub>F<sub>7</sub>,drawing 64Sch,p.157) is a neat representation of the  $\sqrt{4}$ , $\sqrt{3}$  coalescence; it enjoys a HUH $\sqrt{3}$  binding. NbNi<sub>3</sub> (Cu<sub>3</sub>Sb.h, formerly named after the non existent TiCu<sub>3</sub>, drawing 64Schp.114) is RD-homeotypic to Mg and yields a CC2 binding.FurNbNi<sub>8</sub>(TiPt<sub>8</sub>) a non-vanishing  $\underline{b}$  contribution appears necessary and has in fact been confirmed by magnetic measurements (58Vog). However, the magneton numbers in the ordered state appear not to be known at present.

In  ${\sf TaNi_M}$  following the rule of heavy components more phases occur than in  ${\sf NbNi_M}$ . Interesting is the brass plateau consisting of  ${\sf TaNi_MMoSi_2}$ , FF2),  ${\sf TaNi_3}$ .h (TiAT<sub>2</sub>,BB2) and  ${\sf TaNi_3}$ .r(M12.36,CC2).

The consideration of the phase diagrams of  $A^5 Pd_M$  mixtures shows that the characteristic crystal structures of intermediate phases frequently form in the solid state from a Cu type mixed trystal; this indicates a decrease of the influence of the electron correlation just as in the Ekman gap of  $A^{r1}B_M^1$  alloys. The phase  $V_3Pd(Cr_3Si)$  forms at a relatively low temperature of  $840^{\circ}C$  for reasons mentioned at  $V_3Ni$ ; it must be conjectured that partial substitution of V by Mo increases the maximum stability temperature essentially. The brass plateau phases  $VPd_2(MoPt_2,UU2)$  and  $VPd_3.r(TiAl_3,BB2)$  follow in the expected sequence with respect to the closeness of the binding.

In NbPd $_3$ .h(06.18) a close packed structure is found with 6 layers in the stacking sequence ABCACB; since the  $\underline{c}_{CH}$  correlation has 21 layers, there are 7 electrons on a straight line parallel to  $\underline{a}_3$  and these cause together with 6 atomic layers a system of electrical dipoles which presumably cause the rare stacking sequence. In TaPd.r(TiCu) perhaps a FF2 binding must be assumed.

The  $A^5\text{Pt}_{\underline{M}}$  phase diagrams once more display the weakness of  $\underline{b}$  electron correlation found in  $A^5\text{Ni}_{\underline{M}}$  and  $A^5\text{Pd}_{\underline{M}}$ , it may be conjectured that at high temperatures the Ekman count is valid. From the melting temperature of  $V_3\text{Pt}$  it may be concluded that  $V_4\text{Pt}$  is the most stable composition of  $V_3\text{Pt}(\text{Cr}_3\text{Si})$  and just this composition fills the FB2 binding in the  $\underline{b}$  correlation. The HUH/3 binding of VPt(AuCd) favours the Mg type stacking of VPt(AuCd) as  $K_{33}^*$ 2. The sequence UU2-BB2 for VPt $_2(\text{MoPt}_2)$ , VPt $_3$ .r(TiAl $_3$ ) confirms the above mentioned rule.

The stacking homeotype MoPt $_{3.1}$ (M12.36) of NbPt $_{3}$ (Cu $_{3}$ Sb.h $_{1}$ ) fulfills the rule that the structure tends to make K' $_{33}$  integer.

```
TaPd.r(TiCu, SR28.48)3.279;6.036A=bFU(\sqrt{2}.25;4/2)=cHT(3;6.4) N=10,36
TaPd2(MoPt2, SR30.77)2.896;8.397;3.790A=idmVNi2 UU2 cmp
TaPd3(TiAl3, SR28.48)3.880;7.978A=idmVNi3 BB2
V3Pt(Cr3Si, SR20.76)4.817A=idmV3Ni FB2 phdM
VPt.h(CuAu, SR29.129)3.81;3.88A=bHT(2;2.3)=cU(\sqrt{8};3.5) N=10,36
VPt(AuCd,SR29.130)4.42;2.69;4.76A=bH(2.2;\sqrt{16/9})=cUH(4.4/2;4/\sqrt{3}) N=10,36
VPt2(MoPt2,SR30.77)2.730;8.323;3.800A=idmVNi2
VPt3.h(Cu3Au, SR29.129)3.87A=bFU(\sqrt{2.5};2.2/2)=cFUK'(2) N=5.38
VPt3.r(TiAl3,SR26.165)3.861;7.824A=idmVNi3 BB2
Nb3Pt(Cr3Si,SR19.243)5.147A=idmV3Ni FB2 phdE
Nb2Pt(U.hl, SR20.75)9.89;5.11A=bFU(\sqrt{26};3.8)=cU(\sqrt{52};4.6)
NbPt(AuCd, SR29.70)2.780;4.983;4.611=idmVPt HUH/3
NbPt2(MoPt2,SR29.125)2.801;8.459;3.951A=idmVNi2 UU2
Ta7Pt(Cr3Si.
                               =idmV3Ni FB2 phdM
Ta3Pt(U.h1,SR20.75)9.93;5.16A=idmTa3Pd FU2
TaPt.h
TaPt2.h
TaPt2.r(VAu2,Q2.4,SR29.129)8.403;4.785;4.744A= N=20.112
TaPt3.h(NbPt3.1,SR29.70)M90.54<sup>0</sup>4.869;5.537;27.33A=idmNbPt3.1 HH2
TaPt3.r(Cu3Sb.h1,SR30.163)5.538;4.869;4.560A
TaPt4(TiA13, SR29.129)3.91;7.94A=idmVNi3 BB2
A6A10M
CrNi2(MoPt2,SR20.73,22.96)2.523;7.570;3.568A=bU(1;3;1.7)=cUK'(2) N=12,56 phdS
MoNi (028.28, SR28.29) 911; 911; 8.852A=bB(\sqrt{17}; 4)=cFU(\sqrt{68}; 12/2) N=174,504 phdS
MoNi3(Cu3Sb.h1,SR23.181)5.064;4.224;4.448A=bCH(√3;3.5/3;1.5)=cCHK'(2) N=12,76
MoNi4(U1.4, SR9.110)5.683;3.592A=bB(\sqrt{5};1.4)=cBK'(2) N=12,96
         ,ScriptMet8.1974.1297)10.40;10.80A phdM
W2Ni(U
         ,ScriptMet8.1974.1297)7.76;12.48;7.10A
WNi (Ò
WNi3(Cu3Sb.h1,SR39.118)
WNi4(MoNi4, SR12.115)5.730;3.553A=idmMoNi4
CrPd(CuAu, SR18.115)3.879;3.801A phdHA
CrPd3(Cu3Au,
MoPd.h(Mg, SR29.124)2.777;4.488A
MoPd2(MoPt2,71Eck)2.75;8.25;3.89A=idmCrNi2
WPdM(nic,phdS)
Cr3Pt(Cr3Si,SR20.76)4.706A=bF(2)=cB(4) phdM
CrPt3(Cu3Au, SR19.109)3.874A
Mo4Pt.h(Cr3Si,SR29.124)4.987=idmCr3Pt phdM
Mo3Pt2(Ni3Sn.r, SR29.124)H5.59;4.51A
MoPt.h(Mg,ZMetkd55.1964.619)H2.795;4.48A
MoPt.r(AuCd,71Eck)4.47;2.74;4.89A=hdmVPt
MoPt2(P1.2, SR20.29)2.748;8.238;3.915A=idmCrNi2 UU2
MoPt3(htpTiA13,SR29.124)3.897;3.936A
WPt2(MoPt2, SR34.141)2.762;8.251;3.907A phdHA
WPt3
A7A10M
MnNi.h(CsCl,SR15.99)3.028A+H7.4;5.3A=bH(2;7/3)=cBHK'(2)
MnNi.r(CuAu, SR30.239)2.635;3.527A=bB(1;1.3)=cU(2;3.3)
MnNi3.r(Cu3Au, SR12.65)3.589A=bF(1)=cB(y8;2.8)
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TcNiM(nic,phdM)
ReNiM(nic,phdE)

 $\underline{A^6A_M^{10}}$  phases. As judged from the phase diagram these mixtures belong to the  $\underline{Kkman}$  boundary which devides the phases with non-Ekmanian count from the phases with Ekmanian count.

A courious change of electron count occurs in  $CrNi_2(MoPt_2)$ ; if this phase is to be assumed isodesmic with  $VNi_2(MoPt_2)$  then the electron count should be  $Cr^{5,8}Ni_2^{0,10}$ , one electron of Cr is in another correlation or Hund inserted.

Analogous observations may be made in  $\text{MoNi}_{\underline{M}}$ . The BB2 binding of  $\text{MoNi}_{\underline{4}}(\text{U1.4})$  yields  $\underline{\text{MoNi}}_{\underline{b}}^{/\underline{a}}=14$   $\underline{b}$  places per crystal cell, which may be accounted for by the electron count  $\text{Mo}^{5,8}\text{Ni}_{\underline{4}}^{0.5,9.5}$ . On the other hand it appears that in MoNi(0 28.28) Ni does no more contribute  $\underline{b}$  electrons according to Ekman rule. The variability of the electron count does not facilitate the binding analysis here. For instance  $\text{CrPt}_3(\text{Cu}_3\text{Au})$  is probably heterodesmic to  $\text{MoPt}_3(\text{htpTiAl}_3)$ , a more thorough analysis should be supported by a better knowledge of the structures (MoPt $_3$  e.g.).

 $A^7A_M^{10}$  phases. It appears that the Ekman boundary has been passed, as none of the typical non-Ekmanian structures are stabilized in this mixture class, furthermore mixtures not containing Mn, do not form intermediate phases at all (Ekman gap).

MnNi.h(CsCl) and MnNi.r(CuAu) correspond to NiZn.h(CsCl) and NiZn.r(CuAu) (51Col) so that the electron count may be taken as  $\text{Mn}^2, {}^5\text{Ni}^{0,10}$ . However, it is seen from the heterotypic transformation h-r that the  $\underline{b}$  electron concentration depends on temperature: in MnNi.h it is  $\underline{N}_b^{/A} = 1.5$  while in MnNi.r it is  $\underline{N}_b^{/A} = 1.25$  following the assumed binding. In MnNī $_3$ .r(Cu $_3$ Au) the  $\underline{N}_b^{/A}$  may equal 1 so that the phase is isodesmic to Cu (FUB2).

The phase  $\mathsf{MnPd}_3(\mathsf{ZrAl}_3)$  cannot have the FUB2 binding because of its superstructure; the CFU2 binding assumed favours formally the  $\mathsf{TiAl}_3$  type by  $\underline{\mathsf{b}}$  and the  $\mathsf{ZrAl}_3$  type by  $\underline{\mathsf{c}}$  by the method of electrical dipoles (64Sch); an inspection to the commensurabilites in the tetragonal basal plane reveals that the influence of the c correlation is preponderant in this case.

Summarizing, it may be said that all phases of the  ${\rm A}^7{\rm A}_{\rm M}^{10}$  class may be interpreted using the Ekman count.

 $A^8A_M^{10}$ , $A^9A_M^{10}$ , $A^{10}A_M^{10}$  phases. These mixtures form the so talled mixing class of alloys: the components form uninterrupted series of mixed crystals with Cu structure. From the view of the binding this property is conceivable. The electron count is of the Ekman type, the peripheral d-electrons of both components form the  $\underline{c}$  correlation and in the  $\underline{b}$  correlation there are about 0.5 to 1 b electron per atom. Therefore the binding is BB/8 or CB2 or FB/8.

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MnPd.h(CsCl,SR18.216)3.174A=idmMnNi.h BB2 phdA
MnPd.r(CuAu,SR18.216)2.89;3.61A=idmMnNi.r BU2
Mn3Pd5(Pt5Ga3,SR38.122)8.072;7.279;4.044A
Mn32.1Pd67.9(Ni2Si,SR38.124)5.460;4.029;8.127A
Mn27.4Pd72.6(ZrAl3,SR38.123)3.913;4x3.874A=bC(√2.5;6/2)=cFU(√10;18/2)
TcPdM(nic,phdM)
RePdM(nic,phdS)
Mn3Pt(Cu3Au,SR19.221)3.836A phdHA
MnPt.h(CsCl,SR19.221) = idmMnNi.h BB2
MnPt.r(CuAu,SR19.221)2.827;3.669A=idmMnNi.r BU2
MnPt3(Cu3Au,SR19.220)3.898A=idmMnNi3.r FUB2
TcPtM(nic,phdM)
RaPtM(nic,phdHA)
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#### A8A10M

FeNim.h(Cu,SR2.634) phdS
FeNi3(Cu3Au,SR17.197)3.559A
RuNim(nic,phdS)
0SNim(nic,phdM)
FePdm.h(Cu,SR7.188) phdM
FePd.r(CuAu,SR7.188)3.860;3.731A
FePd3.r(Cu3Au,SR28.46)3.84A
RuPd4.h?(see E)
0SPdM(nic,phdS)
FePtm.h(Cu,SR13.129) phdHA
Fe3Pt(Cu3Au,SR13.131)3.76A
FePt3(Cu3Au,SR13.131)3.846;3.723A
FePt3(Cu3Au,SR27.254)3.87A
RuPtM(nic,phdM)
CsPtM(nic,phdM)

### A9A10M

CoNiM.h(Cu, SR13.88) phdHA CoNi3(Cu3Au?. phdM RhNiM(Cu, SR29.199) IrNiM(Cu, phdM phdHA CoPdM(Cu, SR26.127) RhPdM.h(Cu, SR23.203) phdE IrPdM.h(Cu,SR21.136) phdE CoPtM.h(Cu,SR8.58) phdHA CoPt(CuAu, SR8.57)3.818;3.639A CoPt3(Cu3Au, SR15.53)3.831A RhPtM.h(Cu ,SR23.207) phdM IrPtM.h(Cu, SR20.122)

# A10A10M

NiPdM.h(Cu,SR29.198) phdHA Ni3Pd NiPtM.h(Cu,SR9.112) phdHA Ni3Pt(Cu3Au,SR12.114)3.65A NiPt(CuAu,SR9.112)3.823;3.589A PdPtM.h(Cu,SR23.207) phdM As to be expected the analysis of the spatial correlation of electrons adds to our understanding of the  $\text{A}^n\text{A}_\text{M}^{10}$  alloys.

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