# ON THE BINDING IN $A^n B_{M}^3$ PHASES

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## Summary

The systematic assignment of bonding types (bindings) to two-component alloy phases given previously for  $AB_M^4$  phases is continued for Al, Ga, In, Tl as a second component. The values of temperature and mole fraction dependent valence electron contribution (b contribution) of the  $A^{n}$  components as found in earlier analyses have been confirmed. The rule of decrease of number  $\underline{N}_{pn}^{/p}(\underline{N}_2)$ of peripheral core electron correlation places (c correlation places P") per  $\underline{b}$  correlation place (P'), with increasing mole fraction  $\underline{N_2}$  holds in the present alloy class. In  $A^{10..11}B_M^3$  mixtures the  $\underline{N_P''(N_2)}$  function displays a distinct plateau for the two-factorial isotypic bindings XX2. This plateau is characteristic for the brass-like mixtures. It appears that within the plateau the closer packed binding is stable at the greater valence electron concentration  $\underline{N}_b^{/A}$ . The  $A^{12..13}B_{\underline{M}}^3$  mixtures cannot permit XX2 as this binding is limited to the valence electron concentration  $\underline{N}_b^{/A}$ 1.5 (generalized rule of Hume-Rothery). The rule of Raynor that A<sup>n</sup> Atoms may absorb b electrons in Al rich alloys has been confirmed. This absorption causes suppression of paramagnetic susceptibility and decrease of distance d(A,A1) (rule of W.H.Taylor). For several phases as Fe<sub>3</sub>Al.r or NiAl the assumption must be made that the 3sp electrons are in correlation with the 3d electrons (great count) while in neighbouring phases this is not the case (little count); it appears that the transition temperature of this change is in some alloys nearly equal to the Curie temperature. Also the great count may cause a smaller mean atomic volume than the little count. Further energetic arguments emerge for lacuna homeotypism (L), filling homeotypism (F), deformation homeotypism (D), displacing homeotypism (I), shear homeotypism (S), and chain shear homeotypism(C). An interpretation of new transformations found recently in  $FeAl_M$  alloys is proposed. The model also suggests possible high pressure structural transformations. The binding analysis of the more complicated structures has been postponed in order to finish a first approach for the whole  $A^{\mathsf{D}}_{\mathsf{M}}^{\mathsf{S}}$  alloy class. There is a good probability that future improvement of the analysis method will permit extension of interpretations to the more complicated structures.

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Concordance of symbols used in binding analysis
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Homologous classes (columns of the periodic system of elements):  $A^1$  (alcali metals),  $A^2$  (Be,..),  $A^3$  (Sc,..),  $A^4$ ,  $A^5$ ,...,  $A^{10}$ ,  $B^1$  (Cu,..),  $B^2$  (Zn,..),  $B^3$  (B,..),..,  $B^8$  (nob.g.). This notation is especially appropriate to describe subsets of mixtures or phases. Phase designation by chemical formula with element symbols in the sequence of the above homologous classes; within a homologous class the lighter element first. Affixes separated by a point: p= high pressure phase, h= high temperature-, r= room temperature- (mostly omitted), l= low temperature; i= impurity stabilized; m= metastable phase. The stoichiometric index M (undetermined mole number) serves to designate a whole mixture. Sometimes the mole fraction designates composition, Structural type is noted by formula of prototype i.e. of the first found representative. The prototype itself is described (not exhaustively) by a letter for the Bravais group (Amer.Soc.Test.Mater.Standard E157-77), the number of atoms of the first component in the primitive cell, point, number of atoms of sec.comp. Bravais groups: C,B,F = cubic primitive, body centered, face centered T,U= tetragonal primitive, body centered H,R= hexagonal primitive, rhombohedrally centered 0,P,Q,S= orthorhombic primitive, body centered, one face centered, all faces c. M,N,Z= monoclinic primitive , face centered; triclinic. <u>Homeotypisms</u>: R= replacement of atoms, L= formation of vacancies (lacunae),F= filling of interstices, D= homogeneous deformation, I= inhomogeneous deformation, S= shear of layers, C= shear of chains. The symbols may be placed with the affix htp (homeotypical to) before a prototype formula. <u>Densities</u>:  $\underline{\underline{D}}\underline{X}\underline{X}'$  = density matrix,  $\underline{X}$  = configuration (spin and spatial coordinates)  $\underline{D}_{\chi}$ = diagonal of  $\underline{D}_{\chi\chi'}$ ,  $\underline{D}_{\chi',\chi'}^{SC}$ = spatial correlation,  $\underline{D}^{av}$ = averaged spatial correl.,  $\underline{D}^{ed}$ = electron density,  $\underline{\chi}$ = spatial coordinate. Cells and commensurabilities:  $\underline{a}$  = cell (matrix) of crystal,  $\underline{a}_1$  = edge vector of  $\underline{a}$ , Isometric lattices (containing three linearly independent shortest vectors) are written omitting the 1 for one atom in the cell, as C,B,F,R,U,H. A lattice aspect different from the conventional aspect may be indicated by the (pseudo) symmetry of the aspect and noted behind the Bravais group. Sometimes the lattices are deformed (for instance by spin correlation) this is indicated by  $\sim$ . Sometimes at certain places Hund insertion of spin down electrons into a spin up lattice occurs, this is indicated by a prime behind the isometric lattice symbol .  $\begin{array}{lll} \underline{\text{Particle numbers:}} & \underline{N_A^{/\underline{a}}} & \underline{N_A^{/\underline{a}}} & \underline{\text{number of atoms per cell,}} \\ \underline{N_0^{'\underline{a}}} & \underline{N_C^{'\underline{a}}}, & \underline{N_C^{'\underline{a}}}, & \underline{N_C^{'\underline{a}}} & \underline{\text{number of \underline{b}, \underline{c}}} & \underline{\text{electrons,atom places, \underline{b}-places,per \underline{a}} \\ \underline{N^{'A}} & \underline{\text{number per atom,}} & \underline{N_C^{'\underline{p_1^{'}}}} & \underline{\text{number of \underline{c}}} & \underline{\text{places per \underline{b}}} & \underline{\text{places}} \\ \end{array}$ <u>Matrix notation</u>:  $\underline{a}_{ip} = (\underline{a}_{11}, \underline{a}_{12}, \underline{a}_{13}; \underline{a}_{21}, \dots)$ , i (mostly omitted) refers to an orthonormal spatial coordinate system, P numbers the edge vectors and incidentally designates the phase. An H before a numerical matrix or behind the last index of a symbolic matrix indicates that i refers to a hexanormal i coordinate system, analogously MB for a monoclinknormal system. Following abbreviations are convenient:  $(\underline{a}_{11},0,0;\ldots)=(\underline{a}_{11};\ldots)$ ,  $(\underline{a}_{11};\underline{a}_{11};\underline{a}_{33})=(\underline{a}_{11};\underline{a}_{33})$ ,  $(\underline{a}_{11};\underline{a}_{11})=(\underline{a}_{11})$ . Furthermore  $(2,1,0;-1,2,0;1)=(\sqrt{5};1)R$ , where  $5=\det(2,1;-1,2)$  and R=rotationmatrix which is generally not noted.

#### Alphabethical index of symbols used in binding analysis

A=class of homologous elements left to the Cu class in the periodic system; atom  $\underline{a}$ =elementary cell of crystal,  $\underline{a}_1$ =edge vector of el. cell;  $\underline{a}_1p$ =matrix element

B=class of homologous elements right to the Ni class; body cent.cub. Bravais group

 $\underline{\underline{b}}$ =elementary cell of valence electron correlation;  $\underline{\underline{b}}$ -electrons=valence electrons

C=cubic primitive Bravais group; chain shear homeotypism

 $\underline{c}$ =cell of peripheral core electrons;  $\underline{c}$ -electrons=peripheral core electrons

 $\underline{\textbf{D}} = \texttt{density}, \ \underline{\textbf{D}}_{\textbf{XX}} = \texttt{density} \ \texttt{matrix}; \\ \textbf{\textbf{P}} = \texttt{deformation homeotypism}$ 

 $\underline{\underline{D}}^{\text{SC}}$  = spatial correlation;  $\underline{\underline{D}}^{\text{aV}}$  = averaged spatial correlation;  $\underline{\underline{D}}^{\text{ed}}$  = electron density  $\underline{\underline{d}}_{b}$  = distance of essential maxima in  $\underline{\underline{D}}^{\text{aV},b}$ ;  $\underline{\underline{d}}_{c}$  = the same for  $\underline{\underline{D}}^{\text{aV},c}$ 

 $\underline{\underline{E}}$  electrical dipol vector,  $\underline{\underline{E}}_3$  its third component

F= cubic face centered Bravais group; filling homeotyism

H= hexagonal Bravais group; hexagonal aspect

h= high temperature phase

I= inhomogeneous deformation homeotypism

i= impurity stabilized phase; matrix index referring to orthonOrmal coord.system

K= commensurability matrix,  $\underline{K}=\underline{a}^{-1}\underline{a}'$ ,  $\underline{K}'=\underline{b}^{-1}\underline{a}$ ,  $\underline{K}''=\underline{c}^{-1}\underline{a}$ ,  $\underline{K}'''=\underline{c}^{-1}\underline{b}$ 

k= running index for components

L= vacancy formation (lacuna) homeotypism

1= low temperature phase

M= monoclinic primitive Bravais group; undetermined mole number

m= metastable phase

component

N= monoclinic face centered Bravais group; number;  $N_2$  = mole fraction of the second

n= exponent indicating the homologous class; number index of electron

O= orthorhombic primitive Bravais group; orthorhombic aspect

P= atom place, P'= b-correlation place; P"= c-correlation place; index counting edge v.

P= orthorhombic body centered Bravais group

p= high pressure phase

Q= orthorhombic one face centered Bravais group

R= rhombohedral Bravais group; replacement homeotypism

r= room temperature phase

S= orthorhombic all faces centered Bravais group; layer shear homeotypism

T= tetragonal primitive Bravais group; tetragonal aspect

U= tetragonal body centered Bravais group

W= wolfram type

X= spin spatial configuration

x= local coordinate of an electron

Z= triclinic Bravais group

#### Introduction

In the title tacitly the liberty has been taken to equate  $B^{n}=A^{10+n}$ , where A and B are homologous classes of chemical elements defined by the well known IUPAC convention [1] and n may be taken as column number of the periodic system of elements. The phases considered here may therefore be delimited by  $A^{n = 13} B_M^3$  ( $\underline{M}$ = undetermined mole number). These phases have been reviewed thoroughly [2a...f]. They shall be analysed here with respect to their bonding type (binding) by means of the two-correlations model [3a...i]; the procedure of the analysis and the format of the results is the same as in the previous investigation of the binding in  $AB_M^4$  phases [3c], and for concepts like the different homeotypisms this reference should be consulted. It will be understood that the Structure ReportsA(SR) reference used in the tables is very appropriate because of its brevity, but that the information given there cannot be assumed to be completely free of mistakes, these may be avoided by regression to the original publications cited there. It is an old desideratum of systematic crystallography and of systematic chemostatics to develop a coherent valence classification of the  $\mathsf{AB}^3_\mathsf{M}$  phases. The two-correlations model is the first to enter this problem. Starting points are electron counts. As the electron count is not quite certain in many of these compounds the rule of smoothness of the  $\underline{N}_{P''}^{/P'}(\underline{N}_2)$  function [3c] is very helpful  $(\underline{N}_{P''}^{/P'}$ =number of  $\underline{c}$  places per  $\underline{b}$  place,  $\underline{N}_2$ =mole fraction of the second component). The unexpected result of earlier analyses, that the majority of the phases display whole numbered commensurability between b correlation and c correlation only in two directions is confirmed in the present alloy class. It is apparently a fundamental phenomenon.

In advance it should be mentioned that a complete analysis in the first attempt may not be attained, as the assignment of a binding becomes uncertain in phases with large elementary cells. Therefore it is appropriate at first to try an analysis of the simpler structures of the present alloy class. When the results of this attempt appear promising, the discussion of the more complicated structures may be added. Of course a completenes of the table of the phases stabilized must be aspired in order to indicate where the analysis is to be continued.

Sometimes it happens that isotypic phases are not assumed isodesmic. This may be real when the phases are not homologous, but it may also be erroneous. Since it is sometimes difficult to decide where the error may lie, both proposals are noted to have a first approach at least.

# A<sup>1</sup>B<sub>M</sub> phases

The type  $\mathrm{BaAl}_4(\mathrm{U1.4}\ \mathrm{drawing}\ [3a]\ \mathrm{p.313},\ \mathrm{see}[4])$  of  $\mathrm{NaGa}_4$  (electron count  $\mathrm{Na}^{4,8}\mathrm{Ga}_{\mathrm{M}}^{3,10})$  is a F-homestype of  $\mathrm{Cu}_3\mathrm{Au}$  with the commensurability  $\underline{\mathrm{a}}=\underline{\mathrm{a}}_{\mathrm{Cu}3\mathrm{Au}}(1;2)$ , in a (001) plane together with  $\mathrm{Ba}$  are packed  $\mathrm{Al}_2$  dumbbells with [001] direction. Assuming  $\underline{\mathrm{a}}=\underline{\mathrm{c}}_{\mathrm{B}}(\sqrt{8};7.5)$  leads to a HTB/2 binding. The misfit of the number  $\underline{\mathrm{N}}_{\mathrm{P}}^{/\mathrm{C}}$  of  $\underline{\mathrm{b}}$  electrons per cell to the number  $\underline{\mathrm{N}}_{\mathrm{P}}^{/\mathrm{C}}$  of  $\underline{\mathrm{b}}$  places per cell could be reduced by assuming that the  $\mathrm{Na}^1$  electrons form a correlation of their own.

Another simple phase is NaIn(NaT1,F2.2, drawing [3a] p.127) a R-homeotype of W which obeys Zint1's rule. A FB2 binding does not give enough  $\underline{c}$  places, therefore a FF2 binding may be assumed with  $\underline{N}_{p}^{fC} = 256 \underline{c}$  places per cell. The elements K,Rb,Cs do not form this type as their partial structure of the Si type would require too greata volume.

Other simple structures have been reported for  $\text{Cs}_5\text{In}_8$  and  $\text{CsIn}_4$ , but their analysis must be deferred until the atomic positions are known. The more complicated structures shall be postponed. It must be admitted that the  $\text{A}^1\text{B}_{\underline{M}}^3$  and  $\text{A}^2\text{B}_{\underline{M}}^3$  phases do not have the most convincing binding proposals as the great size of the  $\text{A}^1\cdots^2$  atoms causes a great number of  $\underline{c}$  places per atom and thus makes the approximation of the two correlations less good.

# $A^2B_M^3$ phases

With the electron count  $\mathrm{Mg}^{2,8}\mathrm{Al}_{\mathrm{M}}^{3,8}$  comes for  $\mathrm{Mg}_{17}\mathrm{Al}_{12}(\mathrm{Mn.r,B29},\ \mathrm{drawing}\ [3a]$  p.155) a HTC2 or C'C2 binding and for  $\mathrm{MgAl}_{2}.\mathrm{m}$  (HfGa<sub>2</sub>,drawing [3a] p.92), a RD-homeotype of Cu, a BHT2 binding. This binding has more  $\underline{\mathrm{c}}$  places per  $\underline{\mathrm{b}}$  place,  $\mathrm{Np''}_{\mathrm{p''}}$ =5.6 than the FB2 binding of In with  $\mathrm{Np''}_{\mathrm{p''}}$ =4. This leads to conjecture that the binding of Al is  $\underline{\mathrm{a}}$ =4.05A= $\underline{\mathrm{br}}_{\mathrm{U}}(\sqrt{4.5};2.7/2)=\underline{\mathrm{cg}}_{\mathrm{B}}(3)$  which is a fore-runner of the FB2 binding; the number of  $\underline{\mathrm{c}}$  places per atom,  $\underline{\mathrm{Np''}}_{\mathrm{p''}}$ =13.5, is greater than in Ga and In, in agreement with the place number rule [3b]. Also the frequent BaAl<sub>4</sub> structure which occurred already in NaGa<sub>4</sub> has for CaAl<sub>4</sub> a fully occupied  $\underline{\mathrm{b}}_{\mathrm{F}}$  correlation as part of a FU2 binding and may be easily understood in comparison with Al by decrease of  $\underline{\mathrm{b}}$  electron concentration. See also  $\mathrm{Mg}_{33}\mathrm{Al}_{5}(\mathrm{R}^{38}\mathrm{R}^{38}.7)$ .

SrA1(C32.32,drawing SR42.11) is an I-homeotype of NaCl with  $\underline{a}=\underline{a}_{NaCl}(2)$ , the FUHT2 binding opens a possibility to understand the I-homeotypism. SrAl $_2$  (KHg $_2$ ,drawing [3a] p.218) is an I-homeotype of B $_2$ Al with  $\underline{a}=\underline{a}_{B2Al}(0,:1:0,1,1:2,0,0)$  the UHUH/3 binding is given in the table—for the hexagonal subcell.

 $\rm Ba_4Al_5$  (H8.10,drawing SR41,4) and  $\rm Ba_7Al_{13}(H7.13)$  are homeotypic to MgZn\_2 (H4.8,drawing [3a]p.161) which is composed of layers with  $\rm 1/4$  and  $\rm 1/4$  commensions.

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TABLE 1: A1B3M
NaAlM (nic.phdHA)
KAIM (nic,phdHA)
RbA1M (nic, phdHA)
Na5Ga8 phdHA cmp, Na22Ga39(ActCryst.B38.1101), Na7Ga13(Z Natf 37b.119,127)
NaGa4(BaA14, SR34.140)4.223; 11.19A=bHT(2;6/2)=cB(\sqrt{8};7.5)N=26,96
K5Qa8 phdM,KGa3(U3.9,CRParis294.1982.1083)6.278;14.799A
K3Ga13(Q12.52,SR46.81)6.441;16.143;28.404A
Rb5Ga8 phdM, RbGa3(
                          ,Z anallg Chem 480.1981.181)
RbGa4
RbGa7(N2.14 ,ACB37,1981.2060)M111.85<sup>0</sup>11.432:6.603:10.259A
Cs5Ga8 phdM
CsGa4
Na2In phdM
NaIn(NaT1,SR3.19)7.31A=bF(2)=cF(4) N=32.144
Na5In8 cmp
K5In8 phdM cmp
KIn4(BaA14, SR34.140)4.835; 12.71A=idmNaGa4
Rb5In8 phdM
RbIn4(BaA14, SR34140)4.914;12.82A=idmNaGa4
Cs5In8(08.12,JLCM83.1982.143)6.805;6.965;16.40A phdM
CsIn4(T2.8, JLCM83.1982.143)7.089;6.693A
Na6T1 (F88.14, SR38.146) 24.154A=bU(6;7.3)=cB(18) phdHA N=520,3376
Na2T1(Q16.8, SR32.124)13.935;8.880;11.693A=\frac{6}{10}FU(5;2/1;4)=\frac{6}{10}FU(6.8) N=80.416
NaT1 (F2.2, SR3.19)7.487A=idmNaIn cmp
NaT12
KT1 phdM
K4T15 cmp
K5T18
Rb4T15 phdM cmp
RbT12
RbT13
Cs5T17
        phdM cmp
Cs4T17
CsT13
TABLE 2: A2B3M
Mg17A112(Mn.r,SR3.358, Nawi57.1970.128)10.481A=bHT(5;5.7/2)=cC(10) N=140.464
Mg44A156.m(Mn.rD, SR44.105)10.501;10.185A=idmMg17A112 phdHA
Mg23A130(R23.30,SR33.8)H12.825;21.748A=bUH(6;11.5)=H(12;20)
                                                                      N=408,1272
Mq2A13(F116.176.SR30.5)28.239A=bU(11;13)=cB(22) N=3040,9312
MgA12.m(HfGa2.SR44.105)4.132;26.602A=bB(\sqrt{3}.25;10)=cHT(\sqrt{13};23) N=64,192
CaA12(MgCu2, SR8.6)8.038A=bU(3;3.7)=cB(6) N=64,192 phdHA cmp
CaA14(BaA14, SR8.6)4.362;11.09A=bF(\sqrt{2};3.5)=cU(\sqrt{8};9) N=28,80
Sr_{A17}(\hat{c}_{32.28},SR42.\hat{1}_{1})_{12.753A=bFU(5,7)=cHT(10;\hat{1}_{1}/2)} N=160,512 (Fornas in iMer lo 1983)
SrA12(KHg2, SR41.119)4.793;7.922;7.937A=bùH( 1.3;4/2)=cUH( 13;7/2) N=32,96phdM
SrA14(BaA14,SR7.203)4.46;11.07A=idmBaA14 cmp Ba4A15(H8.10,SR41.3)H6.C92;17.782A=bFH(\sqrt{5.3;9/3})=cH(\sqrt{21;13}) N=46,144 phdM
Ba7A113(H7.13, SR41.3)H6.099; 17.269A=bFH(\sqrt{5.3}; 8/3)=cH(\sqrt{21}; 13) N=53,160
BaA14(U1.4, SR21.3)4.566;11.250A=bF(\sqrt{2};3.5)=cU(\sqrt{8};9) N=28,80 cmp
Mg5Ga2(P10.4,SR28.23)13.708;7.017;6.020A=bFU(6;3;3.6/2)=cFUK'(2) N=64,240
Mg2Ga(\dot{H}12.6, SR35.62)\dot{H}7.794; 6.893A=bUH(\sqrt{12}; 3.5/2)=cH(2\sqrt{12}; 6) \dot{N}=42,156
MgGa(\dot{U}8.8, SR28.23)10.53; 5.53A=bU(4;5/2)=cB(8;4) N=80,288
MgGa2(08.16, SR34.84)6.802; 16.346; 4.111A=bB(2\sqrt{2}; 5\sqrt{2}; 1.7)=cHT(4\sqrt{2}; 10\sqrt{2}; 4/2)
MgGa2.m(CaIn2,SR46.129)H4.343;6.982A=bFH(2;4/3)=cBH(2;16/3)N=16,56 N=64,224
Mq2Ga5(U4.10,SR34.84)8.63;7.11A=bB(\sqrt{13};3)=cCK'(2) N=76,264
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Ca3Ga phdM
Ca5Ga2
Ca5Ga3(Cr5B3,SR44.108)7.954;15.084A=bB(\sqrt{7}.3;5)=cB(\sqrt{2}9;10) N=76,280
CaGa(T11,71Ec)4.382;11.535;4.196A=bC(2;5.3)=cU(\sqrt{8};9) N=20,72
Ca2Ga3
CaGa2(B2A1, SR9.37)H4.323;4.323A=bH(2;2)=cUH(\sqrt{12};4/2) cmp N=8,28
CaGa4(htpBaA14,JLCM63.105)4.34;25.90A=hdmBaA14
Sr8Ga7(Sr8A17,FornasiniMer1G1983)12.484A=idmSr8A17 phdM
SrGa2(B2A1, SR19.61)H4.344;4.732A=idmCaGa2 cmp
SrGa4(BaA14, SR30.140)4.437;10.70A=idmBaA14
Ba10Ga(VA155, SR45.31)20.52 A
Ba8Ga7(Sr8A17, Fornas in iMer101983)12.990=idmSr8A17
BaGa
BaGa2(B2A1, SR19.61)H4.432;5.064A=idmCaGa2
BaGa4(BaA14, SR30.116)4.560;10.81A=idmBaA14 cmp
Mg3 In(R12.4, SR28.23)H6.323;31.060A=bUH(\sqrt{7};15/2)=cH(\sqrt{28};26) N=108,408 phdM
Mg2.9In1.1(Cu3Au, SR11.130)4.49A=bHT(2;2.3/2)=cC(4) N=9.1,34
Mg5In2(Mg5Ga2,SR28.23)14.23;7.36;6.19A=bFU(6;3;3.6/2)=cHT(12;6;6/2) N=64,240
Mg2In(H6.3,SR28.23)H8.27;3.42A=bFH(√12;1.75)=cH(√48;2.8) N=21,78
MgIn(CuAu,SR6.180)3.25;4.39A→4.60;439A=bF(√2;1.35)=cC(4;3.8) N=10,36
MgIn2.5(Cu3Au, SR6.180)4.61A=bF(\sqrt{2};1.4)=cU(\sqrt{8};3.5)
MgIn5(Cu, ZM54.1963.422)4.66A=bF(\sqrt{2};1.4)=cB(\sqrt{8};2.8)
Ca3In(Fe3Si, SR29.108)7.860A=bF(2)=cF(4) N=36,136
                                                                                                                              cmp
CaIn(CsC1, SR29.107)3.856A=bFU(\sqrt{2}.25;2.1/2)=cC(3) N=5,18 cmp
CaIn2(H2.4, SR29.107) H4.895; 7.750A=bFH(2; 4/3)=cUH(\sqrt{12}; 6.5) N=16,56 cmp
Sr3In(Fe3Si,71Ec)8.360A=idmCa3In FF2 phdM cmp
Sr5In3(Cr5B3, SR44.117)8.738;16.442A=idmCa5Ga3 BB2
SrIn(0
                ,71Ec)4.09;5.18;11.10A
Sr2In3
SrIn2(CaIn2, SR29.121) H5.000; 8.021A=idmCaIn2 cmp
Sr2In5
SrIn3(Ni3Sn, JLCM11.1966.249)H6.769; 5.481A=bUH(\sqrt{8.3}; 2.7/2)=cH(5;4) N=22,76
                     ,JLCM11.1966.249)H5.937;4.827A
SrIn5(H
Bal3In phdM
Ba3In
BaIn,BaIn2(CeCu2,RendAccadNazLi48.1970.235)5.225;8.439;8.439A
BaIn2(O ,JLCM11.1966.249)5.94;5.225A cmp
 BaIn4(BaA14, JLCM11.1966.249)4.963;11.905A=idmBaA14
Mg5T12(Mg5Ga2,SR35.63)14.285;7.328;6.197A=idmMg5Ga2
Mg2TL(Fe2P,SR35.62)H8.083;3.680A=bUH(\sqrt{12};1.8/2)=cH(2\sqrt{12};2.8)
 MgT1(CsC1,SR3.271)3.635A=idmCaIn
 Ca3T1(Fe3Si,71Ec)7.85A=idmCa3In,Ca5T12(
                                                                                          ,AnnChim Roma56.1966.1306)
 CaT1(CsC1, SR3.271)3.855A=idmCaIn phdH cmp
Ca3T14
 CaTl3(Cu3Au, SR3.639)4.803A=idmMgIn2.5 N=11,38
 Sr3T1(0
                      ,71Ec)23.72;8.07;5.77A
 Sr5T13(Cr5B3, SR44.122)8.635;16.389A=idmCa5Ga3
SrT12(CaIn2, SR29.133) H5.074; 8.217A=idmCaIn2
SrT13(T1 3.715) 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.882 4.8
 SrT13(T1.3,71Ec)4.882;4.843A
 BaT1, Ba13T1, Ba2T1 (seeSr2T13)
 BaT12(CaIn2, SR29.105) H5.220; 8.437A=idmCaIn2
 BaT13
 BaT14
```

surability to the basal mesh, while in MgZn<sub>2</sub> the stacking sequence is  $\sqrt{3}$ , $\sqrt{4}$ ,  $\sqrt{3}$ , $\sqrt{4}$ , in Ba<sub>4</sub>Al<sub>5</sub> it is  $\sqrt{3}$ , $\sqrt{4}$ , $\sqrt{3}$ , $\sqrt{4}$ , $\sqrt{3}$ , and in Ba<sub>7</sub>Al<sub>13</sub>  $\sqrt{3}$ , $\sqrt{4}$ , $\sqrt{3}$ , $\sqrt{4}$ , $\sqrt{3}$ , the binding might be FHH2 in a  $\sqrt{21}$  commensurability which is greater than the  $\sqrt{4}$  commensurability of many NiAs type phases.

 ${\rm Mg}_5{\rm Ga}_2({\rm P10.4,drawing}$  [5]) obeys the Lewis rule and the Zintl rule, and in the Cu type partial structure of Ga one Mg per Ga is in an octahedral interstice and 1.5Mg per Ga are in tetrahedral interstices, a FF2 binding appears possible.  ${\rm Mg}_2{\rm Ga}({\rm H12.6,drawing}~{\rm SR35.63})~{\rm a}~{\rm RDI-homeotype}~{\rm of}~{\rm W}~{\rm is}~{\rm also}~{\rm homeotypic}~{\rm to}~{\rm Fe}_2{\rm P}~{\rm with}~{\rm a}{\rm =a}_{\rm Fe}{\rm 2P}(1;2)$  and permits a UHH2 or FHUH2 binding.

MgGa(U8.8,drawing [5]) is a DIC-homeotype of NaCl with  $\underline{a}=\underline{a}_{NaCl}(2;1)$ , the electrical dipole vectors generated by the UB2 binding are probably the cause of the row shears as compared to NaCl. MgGa $_2$ (08.16,drawing SR34.85) is an I-homeotype of B $_2$ Al, one of four Ga is shifted into the Mg layer ( $\underline{a}_1\&\underline{a}_2$ )by the BHT2 binding. MgGa $_2$ .m (CaIn $_2$ ) another I-homeotype of B $_2$ Al with  $\underline{a}=\underline{a}_{B2Al}(1;2)$  permits a FB2 binding. Mg $_2$ Ga $_2$ (U4.10,drawing SR34.87) permits a BC2 binding.

 $\text{Ca}_5\text{Ga}_3(\text{Cr}_5\text{B}_3,\text{drawing [3a] p.254})$  is a RDI-homeotype of W, in the quasi homologous  $\text{Ca}_5\text{Si}_3(\text{Cr}_5\text{B}_3)$  the binding was  $\underline{\text{a}}=\underline{\text{b}}_{\mathbb{C}}(\sqrt{13};6.9)=\underline{\text{c}}_{\mathbb{B}}(\sqrt{26};10)$ , it is seen that the  $\underline{\text{c}}$  correlation is closely homeotypic. Also CaGa(TII) is isotypic to CaSi.r but heterodesmic.

 ${\rm Mg_3In}({\rm R}12.4)$  is a S-homeotype of  ${\rm Ni_3Sn.r}$  or  ${\rm Cu_3Au}$  and a RS-homeotype of  ${\rm Mg}$ with  $\underline{a} = \underline{a}_{Mg}(2;6)$ . The distance value  $\underline{d}_{h}(Mg_{3}In) = 2.4A$  leads to  $\underline{a} = \underline{b}_{IIH}(\sqrt{7};15/2)$ and this could be supplemented by  $\underline{a} = \underline{c}_{\mu}(\sqrt{28}; 26)$ . The value  $K_{33}^{\mu} = 26$  might be idealized to  $K_{33}^{"}=25.5$  and this would lead by the method [3a] used for the explanation of the shear law in  $Cu_3AuZn_m$  (m=small mole number) to an explanation of the shears distinguishing  $Mg_3$ In from the Ni<sub>3</sub>Sn.r(H6.2) type. The number of <u>c</u> places per <u>b</u> place is  $N_{p}^{/p} = 7.0$  for UHH2 binding, therefore it is gratifying that for  $Mg_2$   $_{Q}In_1$   $_{1}$  ( $Cu_3Au$ ) a HTC2 binding fits which has also  $\underline{N}_{p}^{/P} = 7.0$ . Extrapolating the  $\underline{N}_{p}^{/P}$  values towards Mg leads for this element to the surprising binding <u>a=H3.21;5.21A=b\_H( $\sqrt{1.75}$ ;2.3)=c\_{IH}( $\sqrt{7}$ ;5), the absence</u> of a CC2 or homeotypic binding apparently has to do with the great atomic volume of Mg. The simple structures  $Ca_3In(Fe_3Si)$ , CaIn(CsCl) and  $CaIn_2(H2.4)$ are all homeotypes of W and permit FF2, FUC2 and FHUH/3; Ca2In gives indication of  $\underline{b}$  electron descent. Plotting the number of  $\underline{c}$  places per atom it is found  $\underline{N}_{p}^{/A}=16,13.5,13.0,12$ ; this strong decrease is caused by the great atomic volume of Ca, and this volume influence accounts for the change of binding when the  $\underline{b}$  electron concentration does not change as in  $\operatorname{CaZn}_{\underline{M}}$  e.g.. This could not be understood before.

The FU2 binding of  $CaT1_3(Cu_3Au)$  is confirmed by the tetragonality of  $SrT1_3$ .

# $A^3B_M^3$ phases

The phase ScAl(CsCl) is apparently not isodesmic to CaIn(CsCl), its BFU2 binding yields  $\underline{N}_{p}^{/C}$ =5.7  $\underline{b}$  places per cell so that the  $\underline{b}$  contribution of Sc is nearly 3; for this reason YAl.h(CsCl) is not stable at lower temperatures as the  $\underline{b}$  electron contribution diminishes with decreasing temperature. Curiously a FUC2 binding fits in ScAl<sub>2</sub>(MgCu<sub>2</sub>), however, using the hexagonal cell probably opens other possibilities. ScAl<sub>3</sub>(Cu<sub>3</sub>Au) is homeotypic and homeodesmic to In and this confirms a  $\underline{b}$  electron contribution below 3.

The ditypism of  $Y_2Al$  is caused by the temperature dependent  $\underline{b}$  contribution of Y; as  $Y_2Al(Ni_2Si)$  is compatible with a FF2 binding it must be assumed that Y contributes here no  $\underline{b}$  electrons.  $Y_3Al_2(Zr_3Al_2)$  is homeotypic to  $U_3Si_2(T6.4)$  with  $\underline{a}=\underline{a}_{U3Si2}(1;2)$  and permits  $CU_2/2$ .  $YAl_3$ .h has a BaPb $_3(R3.9,SR29.30)$  structure a stacking homeotype of  $Cu_3Au$  like  $Mg_3In$ , while  $YAl_3.r(Ni_3Sn)$  has a simple two layer structure. The binding of h has a smaller  $\underline{N}_{p''}^{P'}$  value (4.9) than the binding of r (6.0).

While  ${\rm La_3Al}({\rm Ni_3Sn})$  belongs to the Cu family, in LaAl(CeAl) there are only ribbons of CsCl cells. The binding has not yet been found. Just as  ${\rm LaAl_2(MgCu_2)}$  may be described as a structure in which La replaces two Al atoms [3a] , also  ${\rm LaAl_4}$ .h(BaAl\_4) may be described similarly.  ${\rm La_3Al_{11}(P3.11,drawing~SR32.7)}$  is L-homeotypic to BaAl\_4 with the commensurability  ${\rm \underline{a=a_{BaAl4}(1;3;1)}}$ .

The high melting point of  $LaGa_2(B_2A1)$  is due to the good commensurability of the b correlation to the small crystal cell.

## $A^4B_M^3$ phases

In the mixture  ${\rm TiAl}_{\underline{M}}$  two different phases of the same structure have been reported,  ${\rm Ti}_3{\rm Al}({\rm Ni}_3{\rm Sn.r})$  and  ${\rm Ti}_2{\rm Al}({\rm Ni}_3{\rm Sn.r})$ . Although two different bindings are available, additional confirmation of the empirical facts appears desirable. Also in  ${\rm TiAl}({\rm CuAu})$  the electron count  ${\rm Ti}^{1,3}{\rm Al}^{3,8}$  is probable and leads to a UFU2 binding but in  ${\rm TiAl}_2({\rm HfGa}_2,{\rm drawing}~[3a]~p.92)$  this count appears less acceptable, the Ekman rule (see [3a]) becomes valid.  ${\rm TiAl}_2$  opens a series of S-homeotypes of  ${\rm Cu}_3{\rm Au}$  which displays a remarkable increase of the axial ratio of the Cu type subcell with increasing  $\underline{b}$  concentration:  ${\rm TiAl}_2 |a_3|/6|a_1! = 1.021$ ,  ${\rm Ti}_5{\rm Al}_{11}$  1.055,  ${\rm Ti}_9{\rm Al}_{23}$  1.089,  ${\rm TiAl}_3$  1.116. This D-homeotypism follows easily from the binding. Curiously the binding appears to be the same in all four phases and the electrodipole vectors generated by the  $\underline{c}$  correlation favour

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TABLE 3: A3B3M
Sc2AI (Ni2In, SR41.112)H4.888;6.166 phdM
ScA1(CsC1.SR30.108)3.450A=bB(\sqrt{2};1.4)=cF(2) cmp
ScA12(MgCu2.SR29.100)7.580A=bFU(\sqrt{13};5/2)=cC(\sqrt{52};7)
                                                        N=64.200
ScA13(Cu3Au, SR29.100)4.10A=bF(\sqrt{2};1.4)=cU(\sqrt{8};3.5)
Y3A1(Cu3Au, SR32.16)4.818A=bC(2)=cC(4) N=6,38
Y2A1.h(Er2A1, SR30.110)7.62;9.22;11.14A phdE
Y2A1.r(Ni2Si,SR32.16)6.642;5.084;3.469A=bF(2;1.5;2/2)=cFK'(2) N=20,112
Y3A12(Zr3A12,SR28.43)8.239;7.648A=bC(\sqrt{13};3.3)=cU(\sqrt{26};6) N=36,184 cmp
YA1.h(CsC1,SR32.16)3.75A=idmScA1
YA1.r(TII, SR31.16)3.884;11.522;4.385A=bC(1.75;5;2)=cB(1.7\sqrt{2};7;2\sqrt{2}) N=12,76
YA12(MgCu2, SR28, 43, 24, 35)7, 860A=idmScA12 N=56, 208 cmp
                                                            N=90,306
YA13.h(BaPb3, SR32.15)H6.204;21.184A=bH(3;10)=cBH(3;50)
YA13.r(Ni3Sn.r.SR32.15)H6.276;4.582A=bH(3;2.2)=cUH(\sqrt{27};4.4/2) N=20,68
YA14(BaA14, SR26, 238)
La3A1(Ni3Sn.r,SR30.106)H7.195;5.503A=bH(3;2.3)=cUH(6;5/2) N12,82 phdM
LaAl (CeAl, SR30.106, 30.105) 5.809; 7.734; 9.531A N=24,152
LaA12(MgCu2, SR23.214, 30.105)8.153A=idmScA12 cmp
La3A17.h (B2A1, SR30.105)H4.478;4.347A=bH(2;2)=cH(\sqrt{12};3.5)
LaA13(Ni3Sn.r.30.105.41.9)H6.662;4.609A=idmYA13.r
La3All1.r(0 ,SR32.65)4.431;13.142;10.132A
LaAl4.h(BaAl4,SR9.10,SR30.105)4.48;10.42A=bF(√2;3.3)=cU(√8;4) cmp
Sc5Ga3(Mn5Si3,SR29.53)H8.074;5.951A=bUH(\sqrt{13};3/2)=cUHK'(2) N=38,138 phdM cmp
Sc5Ga4
ScGa(T11, SR45.121)4.022;10.205;3.895A=idmYA1.r
ScGa2 cmp
ScGa3(Cu3Au, SR45.122)4.095A=bHT(2;2.3/2)=cB(1/8;2.8)
                                                         N=9.41
Y5Ga3(Mn5Si3,SR29.53)H8.576;6.479A=idmSc5Ga3 phdM
YGa(T11, SR45, 122)4, 296; 10, 876; 4, 074A=idmYA1, r cmp
YGa2(B2A1, SR26.146) H4.198; 4.095A=idmLa3A17.h cmp
La3Ga(Cu3Au, SR45.121)5.66A=bC(\sqrt{5};2.2)=cFU(\sqrt{20};6/2)
                                                         phdM
La5Ga3(Cr5B3, 71Ec)8.066;14.733A=bC(\sqrt{10};6)=cCK'(2)
                                                         N=56,320
LaGa(TII, SR45.121)4.523;11.588;4.256A=idmYA1.r
LaGa2(B2A1, SR26.146)H4.320;4.416A=idmLaA12.3.h cmp
LaGa6.h
LaGa6.r
Sc3In(Ni3Sn, SR27.245)H6.421;5.183A=idmLa3A1 Sc2In(Ni2In, SR39.116)
YIn(CsC1,71Ec)3.806A=idmScA1
YIn3(Cu3Au, SR29.121)4.597A=ScA13
La3In(Cu3Au,71Ec)5.075A=idmY3A1
LaIn(CsC1,71Ec)3.985=idmScA1
LaIn3(Cu3Au,71Ec)4.732A=idmScA13
ScT1M
YTI(CsCl,71Ec)3.751A=idmScAl
YT13(Cu3Au,71Ec)4.680A=idmScA13
La3T1(Cu3Au,71Ec)5.13A=idmLa3A1
                                    phdM
La2T1
La5T13(W5Si3.
                  JLCM18.93)
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LaT1(CsC1,SR8.51)3.922A=idmScA1 cmp LaT13(Cu3Au,71Ec)4.806A=idmScA13 cmp

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TABLE 4: A4B3M
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Ti3A1(Ni3Sn.SR26.28)H2*5.806;4.655A=bUH(\sqrt{5}.3;2.1)=cH(\sqrt{21};3.6) N=12,34 phdM
Ti2A1(Ni3Sn, SR27.30)H5.789;4.639A=bFH(\sqrt{5}.3;2.1)=cH(\sqrt{21};3.6)
TiAI(CuAu, SR16.15)4.011;4.069A=bU(\sqrt{2};1.75)=cFU(\sqrt{8};4/2)
                                                                  N=8,22
TiA12(HfGa2,U4.8,\$R27.35)3.976;24.360A=bB(/2.5;10)=cC(\sqrt{10};20)
                                                                            N=56,152
Ti5A111(ZrA13,SR30.109)3.917;16.524A=bB(\sqrt{2.5};6.5/2)=c(\sqrt{10};13) N=33,108
                  ,SR30.109)3.84;33.46A=
Ti9Al23/tetr.
TiA13(U1.3,SR7.13)3.85;8.59A=bB(\sqrt{2.5};3.5)=cC(\sqrt{10};7.05) N=18,56
Zr3A1 (Cu3Au, SR19.45, 27.37) 4.37A=bU(\sqrt{2}; 1.75)=cU(\sqrt{8}; 3.5/1) N=6,14
                                                                               phdHA
Zr2A1.h?(CuA12,SR26.1,27.36)6.854;5.501A=bHT(\sqrt{8};2.6/2)=cC(\sqrt{3}2;4.5) N=24,112
Zr2A1(Ni2In, SR26.31, 27.37)H4.882; 5.918A=bH(\sqrt{4.3}; 2.5)=cUH(\sqrt{13}; 5/2) N=10,28
Zr5A13.h(W5Si3,SR24.21)11.049;5.396A=bB(\sqrt{17};2)=cFU(\sqrt{68};5.6/2)
                                                                            N=56,156
Zr3A12(T12.8,SR24.39)7.630;6.998A=bB(\sqrt{8.5};2.6)=cFU(\sqrt{34};7.5/2)
                                                                            N=36.100
                                                                          N=13,68
Zr4A13(H4.3, SR24.39)H5.433; 5.390A=bCH(\sqrt{3}; 4.3/3)=cCH(3; 7.2/3)
Zr5A14.h(Ti5Ga4,H10.8,SR27.37)H8.447;5.810A=bCH(\sqrt{7};4.5/3)=cCH(\sqrt{21};7.8/3) N=34,H0
ZrA1(T11,SR27.37)3.353;10.866;4.266A=bFU(2.3/2;2;5)=cU(27;\sqrt{8};\sqrt{50}) N=14,80 Zr2A13(S4.6,SR26.31,27.37)5.572;9.599;13.879A=bH(\sqrt{7};6.5)=cBH(\sqrt{7};32) N=72,256
ZrA12(MgZn2,H 4.8;SR23.20)H5.282;8.748A=bH(\sqrt{7};4.3)=cBH(\sqrt{7};21/3) N=28,112 cmp
ZrA13(U2.6,SR7.14)4.01;17.32A=bB(\sqrt{2.5};6.8)=cC(\sqrt{10};13.6) N=36,112
Hf3A12(Zr3A12,SR24.20)7.535;6.906A=idmZr3A12
HF4A13(Zr4A13,SR27.16)H5.343;5.422A=idmZr4A13
HfA1(T11,SR26.9)3.253;10.831;4.282A=idmZrA1
Hf2A13(Zr2A13, SR24.20)9.523;13.763;5.522A=idmZr2A13
HfA12(MgZn2, SR24.20) H5.288; 8.739A=idmZrA12
HfA13.h(TiA13,SR27.16)3.893;8.925A=idmTiA13
HfA13.1.r(ZrA13,SR24.20)4.010;17.310A=idmZrA13
Ti3Ga(Ni3Sn, SR22.122)H5.752;4.645A=idmTi3A1 phdS
Ti2Ga(Ni2In, SR22.122)H4.51;5.50A=idmZr2A1 HUH/3
                                                                 cmp
Ti5Ga3(W5Si3,SR27.204)10.22;5.054A=idmZr5AI3.h
Ti2Ga3(T4.6, SR27.204)6.284; 4.010 A=bU(\sqrt{6.25}; 2)=cFU(5; 4.5/2)
                                                                        N=22,72
TiGa2(HfGa2, U4.8, SR27.204)3.929; 24.37A=bB(\sqrt{2}.5; 10)=cC(\sqrt{10}; 20) N=48,112
TiGa3(TiA13, SR9.83, 27.204)3.789;8.734A=idmTiA13 BC2
Zr2Ga(CuA12,SR27.205)6.712;5.443A=bHT(\sqrt{8};2.7/2)=cC(\sqrt{3}2;4.5) N=20,64 phdS Zr5Ga3(Mn5Si3,SR22.124)H8.04;5.71A=bH(\sqrt{12};2.5)=cUH(6;5/2) N=28,90 cmp Zr3Ga2(U3Si2,SR27.205)7.349;3.692A=bB(\sqrt{8};1.4)=cFU(\sqrt{3}2;4/2) N=18,58
Zr5Ga4.h(Ti5Ga4,SR27.205)H8.350;5.757A=idmZr5A14
ZrGa.r(MoB,U4.4,SR27.205)3.865;20.56A=bU(\sqrt{2};9.5)=cFU(\sqrt{8};21/2)
Zr2Ga3(Zr2A13,SR27.205)5.497;9.444;13.755A=idmZr2A13
Zr3Ga5(orth, SR27.205)7.111;8.848;9.084A
ZrGa2(Q2.4,SR27.205)12.89;3.994;4.123A=bB(\sqrt{2.5};5)=cC(\sqrt{10};10) N=24,128
ZrGa3(ZrA13,SR27.205)3.960;17.44A=bB(\sqrt{2.5};7)=cC(\sqrt{10};14)
Hf2Ga(CuAl2,SR27.207)6.686;5.295A=idmZr2Ga phdM
Hf5Ga3(Mn5Si3,SR27.207)H7.970;5.686A=idmZr5Ga3
Hf5Ga4
HfGa
Hf2Ga3(Zr2A13,SR27.207)5.472;9.402;13.63A=idmZr2A13
HfGa2(U4.8,SR27.207)4.046;25.446A=bB(\sqrt{2.5};10)=cC(\sqrt{10};20)
                                                                      N=48,192
HfGa3(TiAl3,SR27.207)3.881;9.032A=bB(\sqrt{2.5};3.7)=cC(\sqrt{10};7.4)

TiMn0.9(Ni3Sn,SR22.123)H5.89;4.76A=idmTi3A1 UHH2 phdE
Ti3In2(CuAu, SR30.149)4.203;4.238A=bU(\sqrt{2};1.75)=cB(\sqrt{8};2.8) N=8,25
TiIn.h(CuAu,
Ti3In4(T6.8,SR30.14)9.98;2.98A=bHT(\sqrt{17};1.43/2)=cB(\sqrt{34};1.75) N=24,104
 Zr3In(Cu3Au, SR27.379)4.46A=bU(\sqrt{2};1.75)=cB(\sqrt{8};2.8) N=6,19
 Zr2In(CuAu, SR30.149)4.419;4.460A=bU(\sqrt{2};1.75)=cB(\sqrt{8};2.8) N=6,23
 ZrIn.h(Cu ,SR30.149)4.418A
 ZrIn3.h(TiA13,SR30.149)4.238;9.786A=bB(½2.5;3.65)=cC(½10;7.3)
ZrIn3.r(ZrA13,SR30.149)4.303;18.94A=bB(½2.5;7)=cC(½10;14)
 Hf3In4(Ti3In4, SR30.14)10.23;3.053A=idmTi3In4
 HfIn2(CuAu, SR30.144)4.36;4.51A
 Ti3.2T10.8(Cr3Si,71Ec)5.256A=bC(2)=cC(4)
 ZrT1M
 HFTIM
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the observed stacking sequences following the method of [3a]. To be sure the average dipole vectors probably disappear, but the  $\underline{c}$  correlation is a function in the six-dimensional space [3] and the three-dimensional sections certainly generate"momentaneous" electrical dipoles. It might be questioned whether the  $\sqrt{10}$  commensurability element might be replaced by a simpler, say whole number commensurability element like 3 e.g., however, a little inspection reveals that the  $\sqrt{10}$  element is better adapted to the atomic sites than the element 3.

While in Ti<sub>3</sub>Al only UHH2 (with  $N_{p''}^{P'}=7$ ) was found, the phase  $Zr_3Al(Cu_3Au)$  permits a UU2 binding (with  $N_{p''}^{P'}=8$ ); this evidently is caused by the greater atomic volume of Zr which favours greater  $N_{p''}^{P'}$  values.  $Zr_2Al(Ni_2In)$ , a RC-homeotype of W falls into the HUH/3 binding  $(N_{p''}^{P'}=6)$  and  $Zr_3Al_3$   $h(W_5Si_3)$  a homeotype of NaCl permits the BFU2  $(N_{p''}^{P'}=5.6)$  binding which reappears with different commensurability in  $Zr_3Al_2(T12.8,drawing~SR24.41)$  an I-homeotype of  $U_2Si_2(T6.4,drawing~[3a]~p.252)$  with  $a=a_{U3Si_2}(1;2)$ .  $Zr_3Al_4(H4.3,drawing~SR24.40)$  represents the coalescence of a  $\sqrt{3}$  and a  $\sqrt{4}$  packing in a small cell, it is a RF-homeotype of  $CaZn_5(H1.5,drawing~[3a]~p.165)$  and belongs therefore to the Laves phase family.  $Zr_5Al_4(Ti_5Ga_4)$  a F-homeotype of  $Mn_5Si_3(H10.6,drawing~[3a]~p.306)$  reveals the CHCH/3 binding but ZrAl(T1I) is stabilized by a FU2 binding which has a slightly different commensurability from that in CaSi(T1I). The quasi hexagonal  $Zr_2Al_3(S8.12,drawing~SR27.38)$  permits FHUH/3 while  $ZrAl_2(MgZn_2)$  is compatible whith HBH1. It is surprising that  $ZrAl_3(U2.6)$  a S-homeotype of  $Cu_3Au$  is not isotypic with  $TiAl_3$  but it suggests a BC2 binding, which affords dipole vectors favouring the stacking sequence.

A fortunate event is the occurrence of  $HfAl_3.h(TiAl_3)$  and  $HfAl_3.1.r(ZrAl_3)$  in one mixture; the great  $\underline{d}_b$  value of  $HfAl_3.h$  is compatible with the stability of that phase only at high temperatures.

In  $\text{TiGa}_{\underline{M}}$  the highest melting point of an intermediary phase occurs for  $\text{Ti}_2\text{Ga}(\text{Ni}_2\text{In})$  which is stabilized by the favourable HUH/3 binding containing simple commensurability in three directions. The rooted commensurability of TiGa(CuAu) is confirmed by  $\text{Ti}_2\text{Ga}_3(\text{T4.6})$  which reveals the rotation connected with the root [3] by the superstructure. The electron count is here  $\text{Ti}_2^{1.5}, 2.5$ -  $\text{Ga}_3^{3}, 10$  and in the next phase  $\text{Ti}_3^{0.4}, \text{Ga}_2^{3.10}$ ; surprisingly this difference appears to cause a distinct irregularity in the  $\underline{d}_b(\underline{N}_2)$  function  $(\underline{d}_b$ = distance in the  $\underline{b}$  correlation,  $\underline{N}_2$ = mole fraction of the second component). It is not clear at the moment why the change in electron count is so abrupt, but it appears to be real.

For  $\operatorname{ZrGa}_{M}$  and  $\operatorname{HfGa}_{M}$  similar irregularities have been found.

In A  $^4$ In $_{\underline{M}}$  and A  $^4$ TI $_{\underline{M}}$  only few compounds are stable, perhaps the d electron distance of In and T1 is too great for the natural d electron distance of the A  $^4$ . The remarkable phase Ti $_3$ In $_4$ (T6.8) a LI-homeotype of CsCl with  $\underline{a}=\underline{a}_{\text{CsCl}}$  ( $\sqrt{8}$ ;1), or R-homeotype of Mn $_2$ Hg $_5$ (T4.10, $\sqrt{8}$ rawing [3 $\alpha$ ] p.289)may be understood by the rooted commensurability which favours the I-homeotypism. Appreciating the homeotypism of U1 and C1 and of C1 and H1 it is found that the  $\sqrt{17}$  commensurability is a successor of the  $\sqrt{16}$  commensurability of Ti $_3$ In $_2$  e.g. The gratifying coalescence of ZrIn $_3$ .h,r(TiAl $_3$ ,ZrAl $_3$ ) clearly shows that the TiAl3 type offers more  $\underline{b}$  and  $\underline{c}$  places than the ZrAl $_3$  type, therefore the homeotypism TiAl $_3$ -ZrAl $_3$  follows the place number rule [3].

## $A^5B_M^3$ phases

Starting with the electron count  $V^{1.5}$ , $I^{1.5}$ Al $_{\rm M}^{3}$ , $^{8}$  permits for  $V_3$ Al( ${\rm Cr}_3$ Si,drawing [3c]p.15o) a BB2 binding. Reminding that  ${\rm Cr}_3$ Si(C6.2) is a RC-homeotype of NaCl, a homeotype of W appears probable for  $V_5$ Al $_8$ (Cu $_5$ Zn $_8$ ), however, this phase should not be considered isodesmic with  ${\rm Cu}_5$ Zn $_8$  as the alloys are very different. With respect to the rhombohedral symmetry of  ${\rm Cr}_5$ Al $_8$  a hexagonal cell with the content  $V_{30}$  Al $_{48}$  may be considered, it permits a FHFH/3 binding or something similar, for coordination polyhedra and drawings see [5]. VAl $_4$ TiAl $_3$ ) has the binding of TiAl $_3$  so that the old problem is solved why both phases with such a different electron count are isotypic: the difference of electron number refers to the c correlation where it has less influence. A cHT correlation could be assumed also in order to have a smoother  $V_{\rm pm}^{P'}$  ( $V_2$ ) curve.

Another old problem emerges here: why are so many and complicated Al-rich phases formed? The binding analysis confirms an earlier suggestion of Raynor [61] that A atoms in these phases absorb belectrons of Al; this has been corroborated by magnetic measurements (see [3a] p.290), and also the abnormally small  $\underline{d}_{AB}$  distances [7] fit into this assumption. Because of this good confirmation we speak of the Raynor rule. In these phases frequently icosahedrally surrounded by 12 (preferredly) B atoms similar as Au in  $\underline{Cu}_3Au$ ; if A atoms are in the icosahedral shell of another A atom then A contacts accur and this has been described as icosahedra-fusion ([3a]p.293).  $\underline{V}_4Al_{23}(H8.46,drawing [3a] p.294)$  is remotely homeotypic to a H1 structure with the commensurability  $\underline{a}=\underline{a}_{H1}(3;6)$  and this confirms the homeotypism to  $\underline{Co}_2Al_5$ ,  $\underline{Mn}_3Al_{10}$  [3a], it permits FHH/3. Postponing  $\underline{V}_7Al_{45}(N7.45)$  the phase  $\underline{VAl}_{10}(F4.40,drawing [3a]p.292)$  may be considered; a part of a F1 structure may be seen [3a] similarly as in  $\underline{VAl}_{12}$  and

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TABLE 5: A5B3M
V3A1(Cr3Si, SR28.43)4.926A=bB(2)=cB(4) N=12.94 phdHA.S
V5A18(Cu5Zn8,SR19.40,43.9)9.234A+H13.02;7.97A=bFH(6;4.5/3)=cFH(√108;8/3)N=96,356
VA13(TiA13, SR19.40)3.778;8.324A=bB(\sqrt{2.5};3.5)=cC(\sqrt{10};7) N=18.58
V4A123(H8.46, SR21.25)H7.693;17.040\hat{A}=bFH(\sqrt{13};10/3)=cH(\sqrt{39};14)
V7A145(N7.45, SR23.15)M128, 9025.604; 7.621; 11.081A
VA110(F4.40, SR21.23)14.49A=bB(6)=cC(12)
Nb3A1(Cr3Si,SR22.24)5.19A=idmV3Á1 phdŚ
Nb2A1(U.h1,SR23.13)9.90;5.19A=bHT(√20;2.7/2)=cC(√80;4.7) N=50,32D
NbA13(TiA13, SR7, 100)3,844;8,605A=idmVA13
Ta3A1
       phdM
Ta2A1(U.h1,SR26.25)9.825;5.232A=idmNb2A1
Ta17A112.h(Mn.r,SR30.109)9.88A=hdmNb2A1
Ta17A112.r( ,$R30.109)19.315A
Ta2A13(H92.138,$R38.157)H12.776;27.04A no atomic pos.
TaA13(TiA13, SR7.100, 30.109)3.842;8.553A=idmVA13
V3Ga.h phdM
V3Ga.r(Cr3Si,SR30.206)4.82A=idmV3A1
V5Ga3.i(Mn5Si3,71Ec)H7.28;4.69A
V6Ga5(Ti6Sn5.h, SR29.117)H8.496;5.176A=bH(4;2.5)=cH(\sqrt{48};4) N=42.244
V6Ga7.h(Cu5Zn8?,SR29.117)9.197A
V2Ga5(Mn2Hq5, T4.10, SR30.140)8.954; 2.689A=bB(\sqrt{13}; 1.1)=cHT(\sqrt{52}; 25/2) N=30,120
V8Ga41(R8.41, SR41.68)H13.938;14.892A=bBH(4;21/3)=cCH(8;21/3) N=369,1350
Nb3Ga(Cr3Si, SR44.115, 22.24)5.171A=idmV3A1
                                               phdM
Nb5Ga3(W5Si3,SR30.139)10.28;5.06A=bB(\sqrt{17};2)=cFU(\sqrt{68};5.7/2)
Nb3Ga2(U3Si2, SR29.116)6.922;3.500A=bFU(\sqrt{10};2.2/2)=cC(\sqrt{40};3.2)
                                                                     N=22, cmp
Nb5Ga4(Ti5Ga4, SR30.139)H7.96;5.45A=bCH(\sqrt{7};4.5/3)=cCH(\sqrt{21};7.7/3)
            ,JLCM58.1978.111)8.381;17.081A
Nb5Ga13(Q5.13, SR30.49)3.778;3.778;40.335A=bB(\sqrt{2.5};17)=cC(10;34)
NbGa3(TiA13, SR27.379)3.789;8.715A=idmVA13
NbGa4.h
Ta5Ga3.h(W5Si3,SR28.46)10.208;5.116A=idmNb5Ga3
Ta5Ga3(Cr5B3, SR29.117)6.588;11.92A
Ta3Ga2(U3Si2, SR28.46)6.817;3.471A=idmNb3Ga2
           ,JLCM52.1977.77)
TaGa2(T
           ,71Ec)
TaGa3(T
V3In(Cr3Si,71Ec)5.28A=idmV3A1
Nb5In.h(W,SR29.121;Z.Metallk.73.1982.169)3.326A phd Z.Metallk.73.169
Nb3In(Cr3Si, SR29.121,71Ec)5.303A=idmV3A1
TaInM(nic,Z.Metallk.93,169)
V3T1(Cr3Si,71Ec)5.21A=idmV3A1
NbTIM(nic,Z.Metallk.73,169)
TaTlM(nic, ibid)
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a BC2 binding fits well.

 $Nb_2Al(U.h_1,T30,drawing [3a]p.152)$  is homeotypic to  $\ell r_3Si$  and displays rotated tetrahedral stars; this corresponds as a rule to a rooted commensurability.

While  $V_3$ Ga.r(Cr $_3$ Si) is a RC-homeotype of NaCl, $V_6$ Ga $_5$ (Ti $_6$ Sn $_5$ .h,H12.10) is a RF-homeotype of NiAs with the commensurability  $\underline{a}=\underline{a}_{NiAS}(2;1)$  and therefore RL-homeotypic to W and so are  $V_6$ Ga $_7$ .h(Cu $_5$ Zn $_8$ ) and  $V_2$ Ga $_5$ (Mn $_2$ Hg $_5$ ,drawing [3a] p.289). If for  $V_2$ Ga $_5$ , wich may be described as a junction of VGa $_{10}$  polyhedra a BHT2 binding is assumed, then for  $V_8$ Ga $_{41}$ (R8.41) a BC2 binding is possible which requires 1.4  $\underline{b}$  electrons absorbed by a V atom. The astonishing fact that NbGa $_{M}$  and TaGa $_{M}$  do not display such phases must be interpreted by a smaller absorbing ability of these A atoms. The cell of Nb $_5$ Ga $_{13}$  is homeotypic to TiAl $_3$  with  $\underline{a}=\underline{a}_{TiA13}(1;4.5)$ . It would be of interest to examine the shear sequence in relation to the binding proposed.

The phases  $V_3In(Cr_3Si)$ ,  $Nb_3In(Cr_3Si)$  and  $V_3TI(Cr_3Si)$  have been observed, but no one richer in B.

# $A^6B_M^3$ phases

The phase  $\mathrm{Cr}_2\mathrm{Al}(\mathrm{MoSi}_2)$  is RD-homeotypic to W and yields a CC'2 binding(for the electron count  $\mathrm{Cr}_2^{0.5}, 13.5\,\mathrm{Al}^{3.8}$ ) where the prime on C indicates Hund insertion, and this binding has a different commensurability to the crystal than the BB2 binding of CuZn. But the Bradley mechanism of vacancy formation (see [3d] ) may apply here too and leads to phases homeotypic to  $\mathrm{Cu}_5\mathrm{Zn}_8$ .  $\mathrm{Cr}_5\mathrm{Al}_8.\mathrm{r}(\gamma_2)$  has a well confirmed structure but the other  $\mathrm{CrAl}_{\underline{M}}$  phases homeotypic to  $\mathrm{Cu}_5\mathrm{Zn}_8$  need further study. With  $\mathrm{CrAl}_4$  the set of phases with Raynor absorption by Cr begins. Well established is  $\mathrm{CrAl}_7(\mathrm{N7.45})$  but the interpretation must be postponed until the interpretation of simpler structures provides a firm basis for the more complicated problems.

In MoAl<sub>M</sub> the structures of MoAl.h and Mo<sub>3</sub>Al<sub>5</sub>.h are not yet known. The structure of Mo<sub>3</sub>Al<sub>8</sub>(N3.8,drawing [3al̄ p.104) is S-homeotypic to TiAl<sub>3</sub> and may be generated by one non normal shear system [3al̄ from TiAl<sub>3</sub>. The calculation of the TiAl<sub>3</sub> subcell of Mo<sub>3</sub>Al<sub>8</sub> (tab.6) reveals a strong orthorhombic split of al̄ and al̄ 2. The electron count for MoAl̄ 3(TiAl̄ 3) gives  $\frac{N^{C}}{b_{,c}}$ =18,60 and this value might be too great for the BC2 binding to that BHT2 might be aspired. If the axis of this binding points into an al̄ (TiAl̄ 3) direction than

an orthorhombic split and also a shear might result. But as Tab.6 shows even the BC2 could cause a shear as the ratio of commensurability elements  $K_{i,j}^{\mu}/K_{j,j}^{\mu} + 1$ .

MoAl<sub>5</sub>.h(WAl<sub>5</sub>,drawing [3a]p.118) is R-homeotypic to Nd with  $\underline{a}=\underline{a}_{Nd}(\sqrt{3};1)$ . The FHH/3 binding yields Raynor descent, and the electro-dipole vectors generated by the  $\underline{c}$  correlation at the minority component favour the observed stacking sequence.

MoAl  $_{12}$  (WAl  $_{12}$ , B1.12, drawing [3a]p.291) may be described as a LI-homeotype of Cu $_3$ Au with the commensurability  $\underline{a}=\underline{a}_{Cu3Au}(2)$ . The lacuna-forming W atoms have in fact the smaller  $\underline{b}$  electron contribution as compared with AI like the Ni in Bradley's prototype example NiAl. The W atoms are not inserted into the Cu type substructure, they are substituted, but they are inserted into the  $\underline{b}$  correlation and therefore a L-homeotypism becomes possible. A  $\underline{c}_{C}$  correlation would fit excellently to the structure but  $\underline{c}_{HT}$  is chosen for its  $N_p^{Pl}$  value 3.8. The  $\underline{b}$  correlation does not give place for all valence electrons so that Raynor descent must be assumed.

The phase  $\mathrm{Cr_3Ga}(\mathrm{Cr_3Si})$  is stabilized by a BB2 binding in which a  $\mathrm{Cr^{1.7,12.3}}$  count is valid. The structure of  $\mathrm{Cr_3Ga_4}(\mathrm{Fe_3Ga_4})$  will be discussed later.  $\mathrm{CrGa_4}$  (NiHg<sub>4</sub>) is a L-homeotype of CsCl, the Ga partial structure may be derived from In(U1) by a change of support number [3a] of (001) layers. It is therefore satisfactory that a  $\underline{c_8}(4)$  correlation is found as in In but the BB2 binding of NiHg<sub>4</sub> [8] would give too great a Raynor descent, therefore a twimed CBV2 binding is probable which gives a smaller Raynor descent.

In the phases  ${\rm Mo}_6{\rm Ga}_{31}$ ,  ${\rm Mo}_8{\rm Ga}_{41}$  the characteristic close coordination of Ga to Mo is observed just as it was found in the earlier phases with Raynor descent, but here the coordination number is 10 [9], similar as in  ${\rm V}_2{\rm Ga}_5$  and several structures to be discussed below. The binding proposal shall be postponed.

# $A^7 B_{\underline{M}}^3$ phases

Several structures of the mixture  $\operatorname{MnAl}_{\underline{M}}$  are not yet solved so that the interpretation must remain tentative or also  $\overline{\operatorname{lacking}}$  when the crystal cells are too great.  $\operatorname{Mn_3Al_2}$ .h(Mg) is compatible with a HH2 binding and  $\operatorname{Mn_1.1Al_{0.9}}$ .h(CuAu) a magnetic phase (SR 22.20,28.7) permits a CU/2 binding.  $\operatorname{Mn_4Al_{11}}(74.11,\operatorname{drawing}[3a]p.296)$  is homeotypic to  $\operatorname{MnAl_6}$ . A simple structure has been found for  $\operatorname{Mn_3Al_{10}}$ .m-(H6.20,drawing [3a]p.294) the metastability of which has been reported [40] on

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TABLE 6: A6B3M
Cr2A1(MoSi2,SR5.35)3.00;8.64A=bC(\sqrt{2};4)=cCK'(2) N=8,70 phdHA,S
Cr5A18.h(see phdS)
Cr5A18.r(R10.16, SR5.5, 43.8) H12.73; 7.95A=bH(\sqrt{39}; 4)=cUH(\sqrt{117}; 8) N=144,564
Cr4A19.h
Cr4A19.r
Cr3A17(CúZn8, SR8.7)9.123A needs confirmation
CrA14
Cr2A111
Cr7A145(V7A145, SR24.9)M128.72°25.196;7.574;10.949A
Mo3A1(Cr3Si, SR22.24)4.950A=bB(2)=cB(4) N=16,88
MoAl.h
Mo3A15.h
Mo3A18(N3.8, SR27.23, 27.377)M100.78<sup>0</sup>9.21;3.64;10.07A N=48,164
TiA13 subcell 3.64;3.95;8.35A=bB(1.5;1.63;3.5)=cC(3;3.26;7)
MoA14.h(WA14,SR29.7)M100.8805.255;17.768;5.225A
MoA15.h(Wa15,H210,SR23.12)H4.89;8.80A=bFH(\sqrt{5.3};5/3)=cH(4;7.2) N=30,92
MoA16(M4.24, SR24.26)M95°5.12;13.0;13.5A sites desired N=72,216
MoA112(WA112,SR18.30)7.582A=bU(3;3.7)=cHT(6;7/2) N=72,204
WA12.h phdHA
W3A17.h, WA13.h
             N3.12, SR22.28)M100.205.272;17.77;5.218A
WA14(
WA15(H2.10, SR19.42)H4.902;8.857A=idmMoA15
WA112(B1.12, SR18.30)7.580A=idmMoA112
Cr3Ga(Cr3Si, SR22.24)4.645A=idmMo3Al N=16,94
CrGa.h(Cr5A18,SR30.125)R89.209.01A=idmCr5A18
Cr3Ga4(Fe3Ga4,N9.12,SR41.45)M105.58010.135;7.845;7.986A
CrGa4(NiHg4.B1.4.SR30.125)5.64A=bC(\sqrt{8}:2.8)=cB(4) N=24.92
Mo3Ga(Cr3Si, SR22.24)4.943A phdM
MoGa~1(
          ,ACB31.117)
MoGa-2(
           ,ACB31.117)
Mo6Ga31 (M24.124, SR40.69)M95.0909.517;16.067;16.995A
Mo8Ga41(V8Ga41, ACB31. 1975. 117) H14. 04; 15. 05A
WGaM(nic,phdHA)
CrIn3(Cu.SR29.111)4.69A=bC(2)=cB(\sqrt{8};2.8)
MoInM(nic,phdS)
WInM
CrTIM
MoT1M
MITW
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the basis of thermal analysis and metallography;  $Mn_9Al_{31}$  and  $MnAl_{3.9}$  too are perhaps metastable. The structure of  $Mn_3Al_{10}$  m which is probably stable in  $Mn_3Al_9Si(SR16.11)$  is RLIC-homeotypic to W and permits a HH/3 binding with Raynor descent. To be sure the descent should be confirmed by magnetic analysis.

While MnAl $_{3.9}$ (H) and MnAl $_4$ (H) are not yet known sufficiently, the phase MnAl $_6$ (Q2.12,drawing  $\{3a\}p.294$ ) has a small cell and a structure characteristic for Raynor descent. All Mn are 10-coordinated by Al and many Al belong to two Mn. The Al polyhedra around a Mn maybe derived from an icosahedron by replacing 4 Al by two Al. The  $\underline{b}_{FH}$  correlation in Q-aspect requires full Raynor descent and may be supplemented to a FHH $\sqrt{3}$  binding. The full descent results in an abnormally great  $\underline{d}_{\underline{b}}$  value, we return to this problem once more below.

The phase  ${\rm Tc_2Al\,(MoSi_2)}$  is doubtless homeodesmic to  ${\rm CrAl\,(MoSi_2)}$  but the commensurability element  ${\rm K}_{33}^+$ =45 is necessary for the <u>c</u> correlation to give sufficient <u>c</u> places in the CC'2 binding. In  ${\rm Tc_2Al_3(Ni_2Al_3)}$  there is a smaller <u>b</u> contribution of Tc, and the electron count must be chosen  ${\rm Tc^{0.5,6.5}}$  instead of  ${\rm Tc^{0.5,14.5}}$ .  ${\rm TcAl_4(M)}$  has the same basal mesh as  ${\rm TcAl_6}$  and is homeotypic to it.

When for  $Re_3Al_2$  (Mn.r,drawing [3a]p.155)a FF2 binding is assumed then the same commensurability comes as for the BB2 binding of Mn.r [44].

The equilibrium of  $\rm Mn_8Ga_5$  and  $\rm Mn_7Ga_6$  hints to the existence of twinned bindings. Two different bindings for two different phases with CuAu structure are available.  $\rm Mn_2Ga_5(Mn_2Hg_5)$  is assumed to be not isodesmic to  $\rm V_2Ga_5(Mn_2Hg_5)$ , further development must show which binding proposal is to be preferred.

## $A^8B_M^3$ phases

If for  ${\rm Fe_3Al.r}({\rm Fe_3Si,drawing~[3a]p.127})$ , a R-homeotype of W, a FF2 binding is chosen just as in  ${\rm Fe_3Si}$  then for FeA1(CsC1,drawing [3a]p.127) a HTU/2 binding appears appropriate which does not require Raynor descent. Besides these well-known phases new phases have been proposed by Köster and Gödecke [12] on the basis of thermoanalytic and dilatometric effects. They assume for instance a  ${\rm Fe_3Al.h}$  and a FeA1.h; the ordering structures of these phases are not yet fully established, but it appears tempting to see a relation between the temperature dependent  $\underline{b}$  electron contribution of Fe assumed in the present analysis and the effects found by these authors. When the  $\underline{b}$  electron contribution of Fe is increased in FeA1(HTU/2) then the possibility arises that the bind-

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TABLE 7: A7B3M
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Mn3A12.h(Mq,SR24.25)H2.68;4.34A=bH(\sqrt{7/2};2)=cHK'(2) phdM
Mn1.1A10.9.h(CuAu, SR28.7)2.77;3.54A=bC(\sqrt{2};1.8)=cU(2;2.5)
MnAl.h
Mn5A18.r(Cr5A18.SR24.120)H12.739;15.871A=idmCr5A18 HUH/3
Mn4A111(Z8.22,SR22,20)Z85,32°100,4°105,33°5,092;8,862;5,047A
MnA13.h
Mn3A110.m(H6.20,SR23.9)H7.543;7.898A=bH(\sqrt{13};3.8)=cH(\sqrt{39};6.5) N=60,20
Mn9A131(036.124, SR26.16)14.79;12.42;12.95A
MnA13.9(H
              ,SR24.25)H19.95;24.52A
            ,SR24.25)H28.41;12.38A
MnA14(H
MnA16(Q2.12,SR17.25)6.498;7.552;8.870A=bFHQ(3;2;5/3)=cHQ(3;6;7) N=72,220
MnA112.m(WA112,71E)7.47A=bU(3;3.7)=cHT(6;7/2)
Tc2A1(MoSi2,SR30.109)2.977; 9.476A=bC(\sqrt{2};4.5)=cC(\sqrt{8};9) N=10,72
Tc2A13(Ni2A13.SR28.43)H4.16;5.13A=bH(2;2.5)=cUH(\sqrt{12};5/2) N=9,54
           ,SR28.42)M100<sup>0</sup>5.1;17.0;5.1A
TcA14(M
TcA16(MnA16, SR27.30)6.58;7.63;9.00A=idmMnA16
TcAll2(WAll2, SR29.9)7.526A=idmMnAll2.m
Re3A12(Mn.r, SR27.29)9.58A=bF(3)=cF(6) N=104,708 phdE
ReAl (CsC1, SR24.29)2.88A=bC(\sqrt{2};1.4)=cU(2;2.5)
ReA12(htpMo3A18,phdE)atomic positions desired Re4A111(Mn4A111,SR28.42)Z85°100°106°4.97;8.80;4.90A ReA14(Z,htpMoA14,SR28.42)Z99.5°94°103.5°9.13;13.8;5.16A
ReA16 (MnA16, SR27.30) 6.59; 7.61; 9.02A=idmMnA16
ReAll2(WAll2.SR29.9)7.527A=idmMnAll2.m
Mn2Ga.h(Mq,SR30.139)2.68;4.34A=idmMn3A12.h phd Z.Metk.56,527
Mn2Ga.r(CuAu.SR30.139)3.89;3.61A=bHT(2;2.1)=cC(4;3.7)
Mn8Ga5(htpCu5Zn8,SR30.139)9.00A
Mn7Ga6.h(Cr5A18,SR30.138)H12.59;8.04A=idmCr5A18
Mn3Ga2.r(CuAu, SR30.138)3.88;3.69A=bC(2;1.9)=cU(\sqrt{8};3.3)
MnGa1.1
Mn5Ga7
Mn3Ga5
Mn2Ga5(Mn2Hg5,SR27.379)8.80;2.69A=bHT(\sqrt{20};1.5/2)=cB(\sqrt{40};2)
MnGa4(NiHg4, SR30.138)5.59A=idmCrGa4
MnGa6(0
           ,SR30.138)8.95;8.81;9.94A
Tc GaM
ReGaM
Mn3In(htpCu5Zn8, SR. 120, 45.81)9.420A=hdmCr5A18
TcInM
ReInM
MnT1M(nic,phdHA)
TcT1M
ReT1M
```

ing goes over to the related FU2 type. Since the  $\underline{b}$  electron contribution by Fe is "soft" it is concievable that the transition happens in a small temperature interval.

With FeAl $_2$ (Z6.12) the phases with Raynor descent begin. Fe $_2$ Al $_5$  has an especially simple substructure which is homeotypic to MnAl $_6$ (SR17.23); a UHH/3 binding fits well. Using a similar binding for FeAl $_6$ (MnAl $_6$ ) would give too great a Raynor descent. However, since the ( $\underline{a}_1,\underline{a}_2$ ) mesh of FeAl $_6$  is very nearly hexagonal ( $\underline{a}_H$ = $\underline{a}_{FeAl}$ 6(-0.5,0.5,0;0.5,0.5,0;0,0,1)) and  $\underline{a}_H$  contains a  $\sqrt{12}$  commensurability with  $\underline{b}_{FH}$  as is easily verified, this commensurability needs only to be changed into a  $\sqrt{13}$  commensurability to get a better  $\underline{d}_{\underline{b}}$  distance value and an admissible Raynor descent.

While RuAl(CsCl) is isodesmic to FeAl,  $Ru_2Al_3(0s_2Al_3)$  is homeodesmic in an interesting manner. In  $\underline{a}=\underline{a}_{CSCl}(1;5)$  it is conspictors that  $|\underline{a}_1|>|\underline{a}_{1RuAl}|$  and this suggests a changed commensurability of the HTU/2 binding to the cell. This binding conservation is continued in  $0sAl_2(MoSi_2)$  which gives with  $K_{33}^{"}=7.2/2$  an additional energy gain by the electron dipole method [3a]. It is seen that the binding of  $Ru_2Al_3$ . h is quite hidden, it could not be found without analysis of the binding in the neighbouring phases.

Similar as in FeAl $_{\underline{M}}$ , in FeGa $_{\underline{M}}$  a new phase Fe $_{2.9}$ Ga $_{1.1}$ . $h_2$  has been found by Köster and Gödecke [13] which is said to have at the stability temperature a CsCl powder diffraction diagram, but is not identical with Fe $_{3}$ Ga $_{2}$ .h(CsCl). Since some disordering of the Fe $_{3}$ Si(F3.1) type of structure may produce a CsCl diagram the phase Fe $_{2.9}$ Ga $_{1.1}$ . $h_2$ ("B2'") is subsumed to Fe $_{3}$ Ga.h(Fe $_{3}$ Si type) in TAB.8 For Fe $_{3}$ Ga.h the electron count Fe $_{3}^{1.7}$ ,14.3Ga $_{3}^{3}$ ,10 may be used. it permits the FF2 binding. Similarly for Fe $_{2.9}$ Ga $_{1.1}$ .r(Cu $_{3}$ Au) a BB2 binding may be assumed, but for Fe $_{2.9}$ Ga $_{1.1}$ .h(Ni $_{3}$ Sn) a HUH/3 has been assumed which implies that in Fe the 3sp electrons fall out of correlation. As the loss of ferromagnetism is very near to the temperatures at which the 3sp electrons fall out of correlation, there may be a causal connection between both phenomena so that the Curie temperature does not only imply a disordering of the magnetic polarisation but also a falling of 3sp electrons out of the 3d electron correlation.

The phase  $\operatorname{FeGa}_3(\operatorname{CoGa}_3,\operatorname{T4.12},\operatorname{drawing}\ [3a]p.301)$  shows the typical high coordination of Fe by  $\operatorname{8Ga+1Fe}$  of a structure with Raynor descent and permits a HTBv/2 binding. The  $\underline{c}_B$  correlation of Ga.p and In is conserved and fits very well to the atom positions, the  $\underline{b}_F$  correlation of Ga.p and In has been strained to a  $\underline{b}_{HT}$  correlation which requests Raynor descent and this is corroborated by the fact that no  $\operatorname{A}^{10}\operatorname{B}^3_3(\operatorname{CoGa3})$  phase has been found so far.

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TABLE 8: A8B3M
Fe13A13(C13.3, SR22.14)5.794A=bHT(\sqrt{8};3.3/2)=cFU(\sqrt{32};8/2)
Fe3A1.r(Fe3Si, SR2.680, 22.14)5.793A=bF(2)=cF(4) N=24.212
FeA1 (CsC1, SR2.680, 22.14) 2.909A=bHT (\sqrt{2}; 1.65/2)=cU(2; 2.5) N=4,15
FeA12(Z6.12,SR39.5)Z91.75<sup>0</sup>73.27<sup>0</sup>96.89<sup>0</sup>4.878;6.461;8.800A
Fe2A15(substr.Q2.5,SR17.23)7.67;6.40;4.20A=bUH&(2;3;2.3/3)=cHQ(6;3;3.3) N=30,112
Fe4A113(N12.39, SR19.22)M107.72015.498;8.083;12.476A
Fe2A17(Edshammar)
FeA16(MnA16, SR30.4)6.464;7.440;8.779A=hdmMnA16
RuA1(CsC1, SR24.29)2.95A=idmFeA1 HTU/2 N=4,15 phdS
Ru2A13.h(0s2A13,71Ec)3.079;14.33A=bHT(\sqrt{2.25};8/2)=cU(\sqrt{4.5};12) N=18,80
RuA12(TiSi2, SR31.16)8.012;4.717;8.735A
Ru2A15
Ru4A113(Fe4A113.SR30.12)M107.77<sup>0</sup>15.862;8.188;12.736A
RuA14
RuA16(MnA16, SR33.16)7.488;6.556;8.961A=idmFeA16
RuA112
OsA1(CsC1, SR21.12)3.005A=idmFeA1
Os2A13(U2.3, SR30.10)3.106;14.184A=idmRu2A13.h
OsA12 (MoSi2, SR30.10)3.162; 8.302A=bHT (1/2.5; 4.8/2)=cU (1/5; 7.2/2) N=12,48
0s4A113(N4.13, SR29.10)M115.15<sup>0</sup>17.64; 4.228; 7.773A
0x2A15
Fe3Ga.h(Fe3Si,71Ec)5.81A=idmFe3A1.r FF2 N=24,220 phdM
Fe2.9Ga1.1.h(Ni3Sn, SR24.120)5.234; 4.213A=bH(\sqrt{7}; 2)=cUH(\sqrt{21}; 4) N=12,62
Fe2.9Ga1.1.r(Cu3Au, SR24.120)3.701A=bB(\sqrt{2.5}; 1.6)=cBK'(2) N=6,55
Fe3Ga2.h(CsCl,71Ec)2.91A=idmFeA1 HTU/2
Fe3Ga2.m(Cr5A18?, Z.Metk. 68.1977.661)
Fe6Ga5.h(Cr5A18,SR24.120)H12.463;15.577A
Fe6Ga5.r(N12.10, SR40.67)M109.33°10.058;7.946;7.747A
Fe3Ga4(N9.12, SR41.45)M106.67°10.091;7.666;7.866A
FeGa3(CoGa3, T4.12, SR23.119)6.25; 6.56A=bHT(3; 3.6/2)=cB(\sqrt{18}; 4.5) N=36,152
RuGa (CsC1, SR28, 46)3,010A
RuGa2(TiSi2, SR28.46)8.184;4.749;8.686A
RuGa3(CoGa3, SR23.119)6.47;6.73A=idmFeGa3
OsGa3(CoGa3, SR23.119)6.488;6.748A=idmFeGa3
FeInM(nic,phdM)
Ru3In(Ni3Sn, SR29.121)H5.942;4.689A=idmFe2.9Ga1.1.h
RuIn3(CoGa3, SR29.121)6.998;7.240=idmFeGa3
0s InM
FeT1M(nic,phdHA)
RuT1M
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OSTIM

## A 9BMphases

A melting temperature of CoAl(CsCl) which is greater that that of Co indicates a great stability of CoAl at high temperatures. Remembering the temperature dependence of the  $\underline{b}$  electron contribution of Co suggests a binding  $\underline{a}=\underline{b}_F(1)=\underline{c}_U(2;2.5)$  which implies a positive  $\underline{b}$  contribution of Co and is energetically favourable. At lower temperatures the  $\underline{b}$  contribution of Co must decrease and a binding  $\underline{a}=\underline{b}_{HT}(\sqrt{2};1.6~5/2)=\underline{c}_U(2;2.5)$  becomes probable. This transition should lead to effects which are similar to the effects found by Köster and Gödecke in FeAl<sub>M</sub> [12] and FeGa<sub>M</sub> [13]. In the phase Co<sub>2</sub>Al<sub>5</sub>(H8.20,drawing[3a] p.294) the Raynor descent begins for CoAl<sub>M</sub>, the structure is remotely homeotypic to Ni<sub>2</sub>In or W and contains one more  $\overline{a}$ tom in the cell than suggested by the homeotypism to W, a BHBH/3 binding appears probable.

Also Co<sub>2</sub>Al<sub>q</sub>(M4.18, drawing [3a]p.302) displays a coordination of 9Al to Co as to be expected in phases with Raynor descent. The a &a mesh is quasi tetragonal and the pure Al layers have a  $\sqrt{5}$  commensurability to it, so that a  $\sqrt{20}$  commensurability of c to a may be conjectured. In fact the electron distances suggest a HTB√2 binding in √20 commensurability and this is reministent of the  $\sqrt{18}$  commensurability of the HTB $\sqrt{2}$  binding in FeGa $_3$  in agreement with the place number rule [3b]. The monoclinic deformation of the  $Co_2Al_q$  cell probably has to do with the value of the commensurability element  $K_{33}^{1}=5/2$ , it should be mentioned here that FeCu2Al7(T4.8.28, drawing [3a]p.302) is tetragonal and homeotypic to Co<sub>2</sub>Al<sub>9</sub>. The structure of CoGa<sub>3</sub>(T4.12, drawing [3a]p.301) is RDIhomeotypic to W with  $\underline{a} = \underline{a}_{\text{M}}(2)$  and yields a HTB/2 binding like FeGa<sub>3</sub>(CoGa<sub>3</sub>). This binding occurs also in the phase  $Co_2Al_q$ , and the  $N_{p''}^{/B}$  value (B=AlorGa) for Co<sub>2</sub>Al<sub>q</sub> is 13.3, but 13.5 for CoGa<sub>3</sub>, so that Ga with 1.25 times more peripheral core electrons has only 1.02 times more core places. This is one more example for the place rumber rule [3b] which destabilizes the CoGa, type for Al alloys. The phase Rh<sub>10</sub>Ga<sub>17</sub>(T40.68) is homeotypic to TiSi<sub>2</sub>(S2.4,drawing [3a]p.313) which is stacked in hexagonal close packed layers with the support number 2. The isometric U1 lattice also has this property and therefore TiSi, is pseudo tetragonal. This fact and the thermodynamic equilibrium of  $Rh_{10}Ga_{17}$  with RhGa(CsC1) suggests to consider the remote homeotypism with W:  $\underline{a}=a_{M}(2;16)$ . This homeotypism makes the isodesmism as described in TAB.9 quite plausible. The TiSi<sub>2</sub>(S2.4) homeotypes obey the Ekman rule [3a] and therefore the  $\underline{b}$  correlation is built up exclusively of the B atom valence electrons and this causes an adaptation of the atom sites to the electron correlation [14].

The phase CoIn<sub>2</sub>(Mg<sub>2</sub>Cu,S8.4,drawing [3a]p.288) displays the coordination

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TABLE 9: A9B3M
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IrTIM

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Co3A1.m(Cu3Au,71Ec)3.658A=bU(\sqrt{2};1.75)=cUK'(2) N=6,56 phdM
CoA1(CsC1, SR7.196)2.86A=bHT(\sqrt{2};1.65/2)=cU(2;2.5) N=3,17 cmp
Co2A15(H8.20,SR6.175)H7.672,7.672,7.609A=bBH(\sqrt{5.3},11/3)=cBH(4;19/3) N=60,232
Co4A113(Fe4A113, SR27.8)15.183,0,-3.793;8.122;11.743A
Co2A19(M4.18,SR11.8)8.527;6.290;-0.710,0,6.213A=bHT(\sqrt{10};5/2)=cB(\sqrt{20};6) N=54,180
RhAI (CsC1, SR21.12)2.99A=idmCoA1
Rh2A15(Co2A15, SR32.12)H7.893;7.854A=idmCo2A15
RhA13
Rh2A19(Co2A19,SR33.15)M94.81<sup>o</sup>6.352;6.428;8.721A=idmCo2A19
IrAl (CsCl, SR21.11)2.983A=idmCoAl
IrAl3(Na3As,71Ec)H4.246;7.756A=bFH(2;4.5/3)=cFH(\sqrt{12};7.8/3) N=18.57
Ir2A19(Co2A19,SR33.15)M94.77°6.378;6.430;8.732A=idmCo2A19
                                   phdM
CoGa (CsC1, SR23.119)2.87A=idmCoA1
CoGa3(T4.12,SR23.119)6.26;6.48A=bHT(3;3.6/2)=cB(\sqrt{18};4.5) N=36,156
RhGa(CsC1, SR23.118)3.01A=idmCoA1 HTUV2 or HTC2
Rh10Ga17 (T40.68, SR32.68) 5.813; 47.46A=bHT (\sqrt{8}; 2.6/2)=cU(4;40)
RhGa3(CoGa3, SR23.119)6.488;6.553A=idmCoGa3 HTBV2
Rh2Ga9(Co2A19,
RhGa6
IrGa(CsC1, SR23.118)2.98A=idmCoA1
Ir3Ga5(T12.20,SR32.69)5.823;14.20A=bHT(\sqrt{8};8)=cU(4;12)
IrGa3.h(CoGa3,SR23.119)6.41;6.61A=idmCoGa3
Ir2Ga9(Co2A19,
                           idmCo2A19
IrGa6
CoIn(Mg2Cu, SR41.52)9.402; 17.846; 5.282A=bH(\sqrt{5.3}; 8/2)=cUH(4; 16/2) N=96,464
CoIn3(CoGa3, SR43.49)6.830;7.094A=idmCoGa3
RhIn(CsCl, SR23.118)=idmCoAl
RhIn3(CoGa3, SR23.119)7.01;7.15A
Ir2In3
IrIn2(Mg2Cu, JLCM79.1981.P1)9.809;18.060;5.349A
IrIn3(CoGa3, SR23.119)6.99;7.20A=idmCoGa3
CoTIM(nic,phdHA)
RhT1M
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(2Co+8In)-Co so that Raynor descent is possible. The HUH $\sqrt{3}$  binding requests in fact a descent of 11 electrons.

A 10 Bmphases. Themphases have been analysed with respect to binding several years ago [3d]. The present TABLE 10 eliminates shortcomings and mistakes of this analysis and uses a more appropriate binding notation. It is found in the present alloys that the stability of several Al rich phases with neighbouring compositions is no more observed, as Raynor descent is no longer possible. For Ni  $_3$ Al the binding of Cu has been proposed [3d] but the N $_{p''}^{/p}$ (N $_2$ ) function suggests a smaller dh value to attain a BU2 binding which is homeotypic to the UU2 binding in  $Ni_3Ge[3c]$ . The phases  $Ni_2Al$  and  $Ni_3Al_2$ .h need further confirmation. NiAl must have a very favourable binding as its melting temperature is comparable to that of Fe and Ti. Probably lower electrons take part in the binding, i.e. the electron count is Ni<sup>1,17</sup>Al<sup>3,8</sup>. The structure is ordered up to the melting temperature [15]. The FF2 binding is valid only for high temperatures, the good internal commensurability of the binding causes the Bradley vacancy formation to extend the binding to more Al rich compositions [see 3a]. At lower temperatures the binding might be as in FeAl and this change should cause weak thermal effects like as in FeAlm. The HUH/3 binding of Ni, Al, (12,6) was found earlier [3c]. The <u>b</u> place number  $N_p/c = 9.6$  explains the fact that isotypes solve B4 but not B2 [3g,h].

The UFU2 binding of NiAl $_3$  is an improvement of the earlier [3d] UC2 binding which violates the place number rule. The  $\underline{d}_c$  values of Ni $_2$ Al $_3$  and NiAl $_3$  are strikingly great, probably as the soft  $\underline{c}(Ni)$  correlation is no more supported by the 3sp electrons and comes under the pressure of the b(Al) correlation.

Pd<sub>2</sub>Al(Ni<sub>2</sub>Si,drawing [3a]p.322), a RDI-homeotype of Cu,permits a UU2 binding for the great count Pd<sub>2</sub><sup>1,17</sup>Al<sup>3,8</sup> where the <u>c</u> correlation is fully occupied, a rare event. For the homeotype Pd<sub>5</sub>Al<sub>3</sub>(Rh<sub>5</sub>Ge<sub>3</sub>, drawing [3a]p.324) a similar binding is acceptable. The non whole number commensurability elements should generate shears, but these have not yet been found. The transformation PdAl.h-r is caused by the temperature dependent <u>b</u> electron contribution. The FF2 binding of PdAl.h(CsCl) requires 1 <u>b</u> electron per Pd while the HH2 binding of the I-homeotype PdAl.r(R13.13) needs only 0.6. The decrease of <u>b</u> concentration favours the transition to <u>b</u><sub>H</sub> and the tendency to attain a whole number element  $(\underline{b}^{-1}\underline{a})_{33}$ =K'<sub>33</sub> leads to the root  $\gamma$ 57 which causes the I-homeotypism PdAl.h-r. The phase PdAl<sub>1.1</sub>(FeSi,drawing [3a]p.308) should be considered in the hexagonal aspect ([3a]p.331) which reveals the LDI-homeotypism to W. Astonishingly the HH2 binding appears to be stable once more. Pd<sub>2</sub>Al<sub>3</sub>(Ni<sub>2</sub>Al<sub>3</sub>) belongs to the

#### TABLE 10: A10B3M

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Ni 3A1 (Cu3Au, SR2.684) 3.568A=bB(\sqrt{2}; 1.4)=cU(\sqrt{8}; 3.5) N=6,59g phdHA
Ni2A1(H4.2, Japp1Cryst9.1976.263)H4.02;4.93A=bCH(\sqrt{1.75};4/3)=cCHK'(2)
                                                                         N=10.52
Ni3A12h(CuAu, SR15.11)3.78;3.24A=bFU(\sqrt{3}.25;2.5/2)=cFU(\sqrt{13};5/2) N=72,54g
NiAl(CsCl, SR5.127)2.873A=bF(1)=cF(2) N=3,26g
Ni2Ai3(H2.3, SR5.67)H4.036;4.901A=bH(2;2.4)=cUH(/12;4.8/2) N=9,441
NiAl3(Fe3C, SR5.60)6.612;7.366;4.812A=bU(3.3/1;3;2)=cFU(7.6/2;6;4) N=36,136
Pd2A1(Ni2Si, SR21.15)7.77;5.41;4.05A=bU(2.9;2;1.8)=cUK'(2) N=20,168g phdS
Pd5A13(Rh5Ge3, SR23, 121)10, 41;5, 35;4, 03A=bU(3, 9;2;1, 8/1)=cUK'(2) N=28, 218g
PdAl.h(CsCl,SR13.23)3.037A=idmNiAl FF2 cmp
PdA1.r(R13.13, SR43.12) H15.659; 5.251A=bH(\sqrt{57}; 2.5)=cHK'(2) N=117,1014
PdA11.1(FeSi, SR29.12)4.859AorH6.86;8.41A=bH(\sqrt{10.7};4)=cH(\sqrt{43};8) N=36,312g
Pd2A13(Ni2A13, SR13.23)H4.22;5.16A=idmNi2A13
              ,SR17.31)
PdA12.70
PdA13.8(PtA14, Japp1Cryst14.1981.212)H13.085;9.633A FHUH/3
                                                                                 phdS
Pt3A1.r(Pt3Ga.r,JLCM41.1975.19)5.459;7.806A=bFU(\sqrt{5};4.5/2)=cB(\sqrt{20};6.5) N=24,236g
Pt2.9A11.1(Cu3Au, SR22.25)3.876A=idmNi3A1 BU2 N=6,58 cmp
Pt2A1.h(Ni2Si, SR41.8)5.401;4.055;7.899A=idmPd2A1
Pt2A1.r(016.8,SR42.10)16.297;3.921;5.439A=bU(6;1.8;2)=cUK'(2) N=40.336
Pt5A13(Rh5Ge3, SR22.25)5.41;10.70;3.95A=idmPd5A13
Pt1.1A10.9.h(CsC1, SR44.105)3.123A=idmNiA1
PtA1(FeSi, SR21.12)4.865AorH6.87;8.42A=idmPdA11.1 cmp
Pt2A13(Ni2A13, JLCM41.1975.19) H4.209; 5.175A=idmNi2A13
PtA12(CaF2, SR5.54)5.922A=bHT(\sqrt{8}; 3.3/2)=cB(4) N=24,104
Pt8A121(U16.42, SR31.10)12.97;10.65A=bU(5;5)=cB(10;8)
                                                          N=252,1248q
PtA14(H18.72,
                    )13.068;9.619A=bFH(\sqrt{39};5.5/3)=cUH(\sqrt{117};9/2) N=16,756
Ni3Ga(Cu3Au, SR21.118)3.532A=idmNi3A1 phdM
Ni5Ga3(Pt5Ga3,SR34.140)7.53;6.72;3.77A=bU(3;2.66;1.8/1)=cUK'(2) N=28,230g
Ni3Ga2.h(NiAs, SR11.122)H4.000; 4.983A=bCH(\sqrt{1.75}; 4/3)=cCHK'(2) N=9,501
Nil3Ga9(Nl3.9, SR34.137)13.822,0,6.869;7.894;4.968A=bCH(/21;/7;4.1)=cCHK'(2)
NiGa(CsC1, SR11.123)2.895A=idmNiA1 FF2 N=4,27g
                                                                        N=54.4401
Ni3Ga4(B24.32, SR34.137)11.411A=bC(\sqrt{32};5.7)=cU(8;10)
                                                         N=192,11201
Ni2Ga3(Ni2A13, SR11.123)H4.060;4.897A=idmNi2A13 HUH/3
NiGa4(htpRu3Sn7, SR13.111)8.42A=bHT(\sqrt{17};4.8)=cB(\sqrt{34};6) N=84.340
Pd13Ga5
         phdE
Pd5Ga2(020.8,SR40.71)18.396;5.485;4.083A=bU(6.7;2;1.8)=cUK'(2) N=44,340m
Pd7Ga3
Pd2Ga(Ni2Si, SR23.120)5.493;4.064;7.814A=idmPa2Al N=20,144m cmp
Pd5Ga3(Rh5Ge3, SR23.121)10.51;5.42;4.03A=idmPd5A13
Pd5Ga4.h(CsC1,SR40.108)3.04A=idmNiA1
PdGa(FeSi, SR11.123)4.89AorH6.92;8.47A=bBH(2;12/3)=cFH(6;9/3) N=16,108g
Pd3Ga7(Ru3Sn7, SR11.123)8.77A=bHT(\sqrt{18};5/2)=cB(6) N=84,400
PdGa5(U2.10, SR23.119)6.448; 10.003A=bHT(\sqrt{10;6/2})=cB(\sqrt{20;7})
                                                               N=60.240
Pt3Ga(T12.4, SR41.8)5.472;7.886A=idmPt3A1.r N=24,244g phdM
Pt2.8Ga1.2(Cu3Au, SR24.115)3.892A=idmNi3A1
                                              BU<sub>2</sub>
Pt.69Ga.31.h(CuAu, SR34.140)3.93;3.79A=bB(\sqrt{2};1.37)=cU(\sqrt{8};3.3) N=6.5,60g
Pt.68Ga.32.h(htpCuAu, Metal 128.1974.1160)3.90;3.92;3.79A
Pt2Ga.r(Pt2A1.r,SR42.83)16.440;3.922;5.488A=idmPt2A1.r
Pt1.95Ga.h(Rh5Ge3,SR42.83)10.860;5.484;3.950A=idmPd5A13
Pt5Ga3(Q5.3,SR24.115)8.031;7.440;3.948A=idmNi5Ga3
PtGa(FeSi,SR11.123)4.91AorH6.94;8.50A=idmPdGa
Pt2Ga3(Ni2Al3,SR11.123)H4.23;5.18A=idmNi2Al3
PtGa2(CaF2,SR5.54)5.923A=bHT(y8;3)=cB(4) N=24,120
Pt3Ga7(Ru3Sn7, SR23.156)8.799A=idmPd3Ga7 HTB1/12
PtGa5
PtGa6(
            ,SR24.116)15.946;12.034;8.866A
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Ni3In(Ni3Sn.r,SR13.121)H5.331;4.251A=bH(\sqrt{5}.3;1.8)=cFH(\sqrt{21};4.5/3) N=12,122g
Ni2In.r
                                                                           phdHA
Ni3In2.h(FhtpNiAs.SR9.91)H4.185;5.135A=idmNi3Ga2.h
Ni12.8In9.2(Ni13Ga9,SR34.137)14.65,0,7.324;8.33;5.195A=idmNi13Ga9
NiIn.h(CsCl,SR11.132)3.099A=idmNiA1
Ni In. r(CoSn, SR11.132)H5.210;4.343Aor5.2;4.3;9.0A=bH(2.4;2;4.8)=cHK'(2)N=9.601
Ni2In3(Ni2A13, SR11.132) H4.396; 5.302A=idmNi2A13
Ni3In7(Ru3Sn7, SR30.61)9.18A=idmPd3Ga7
Pd3In.h(TiAl3,JLCM17.1969.73)4.15;2x3.74A=bU(\sqrt{2};3)=cC(4;7.2) N=12,122g
Pd3In.r(ZrA13,JLCM17.1969.73)4.07;4x3.80A=bB(\sqrt{2};5)=cC(4;15)
Pd2In(Ni2Si, SR21.15)8.24;5.61;4.22A=idmPd2AI
Pd5In3(Rh5Ge3,SR23.121)11.02;5.60;4.24A=idmPd5A13
PdIn(CsCl,SR11.133)3.26A=idmNiAl
Pd2In3(Ni2Al3, SR11.133)H4.53;5.50A=idmNi2Al3
Pd3In7(Ru3Sn7, SR11.133)9.44A=idmPd3Ga7 HTB/2
Pt3In(Cu3Au, SR34.140)3.992A=idmNi3A1 BU2
Pt2In(Pt5Ga3, SR34.140)8.18; 7.81; 4.08A=bU(2\sqrt{2}; 3.3; \sqrt{2})=cUK'(2) N=23,160
Pt3In2.h(FhtpNiAs, SR34.140)H4.35;5.55A=idmNi3Ga2.h
Pt3In2.r(Pt3T12,SR34.140)H5.56;13,65A=bCH(\(\frac{1}{3}\);10/3)=cCHK'(2) N=30,1941
Pt13In9(Ni13Ga9, SR44.72)15.338,0,7.626;8.802;5.563A=idmNi13Ga9
Pt1.1In(CuAl.r, $R44.72)11.007;4.430;7.939,0,7.580A=bCH(8/3;1.75) N=30,200
PtIn.h(CsC1,ZMetk69.1978.333)3.28A=idmNiA1 FF2
Pt2In3(Ni2A13, SR11.133)H4.52;5.50A=idmNi2A13 HUH/3
PtIn2.h(CaF2,SR5.54)6.366A=idmPtA12 HTU/2
Pt3In7(Ru3Sn7, SR13.112)9.435A=idmPd3Ga7 HTB/2
NiT1M(nic,phdHA)
Pd3T1.h(TiAl3,JLCM16.1968.415)4.146;7.497A=idmPd3In.h phdM
Pd3T1.r(ZrA13, SR34.141)4.10;15.32A=idmPdIn.r
Pd2T1.h(FhtpNiAs, SR18.158)H4.53;5.66A=idmNi3Ga2.h
Pd2T1.r(Ni2Si, SR34.141)8.30;5.72;4.21A=idmPd2A1
Pd13T19(H13.9, SR34.137)H8.958;5.623A=bCH(√7;4/3)=cCHK'(2) N=27,220
PdT12(CuA12, SR34.141)6.71;5.74A=bHT(√8;3/2)=cU(4;4) N=24,120
Pt3T12(H12.8, SR33.125) H5.645;13.851A=bUH(√5.2;6.5)=cUHK'(2) N=30,200
PtT1(CoSn, SR3.618)H5.616;4.648A=bH(\sqrt{5}.2;2)=cH(\sqrt{21};4) N=9,60
PtT12(CuA12, SR34.141)6.82;5.56A=idmPdT12
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small electron count  $Pd_2^{0,10}Al_3^{3,8}$  and is isodesmic to  $Ni_2Al_3$ . It is gratifying that the mean atomic volume in the mixture  $PdAl_{\underline{M}}$  [16] clearly shows the difference between great and little count. The great count forces the volume down as the electron distance of the 4sp shell is smallerthan that of the 4d shell [11]. The choice between great and small electron count is another parameter influencing the valence picture of the  $AB_{\underline{M}}^3$  alloys.

The BU2 binding of Pt<sub>2.9</sub>Al<sub>1.1</sub>(Cu<sub>3</sub>Au) appears to have an over-occupied  $\underline{c}_U$  correlation. At lower temperatures and smaller Al content the  $\underline{b}$  electron concentration decreases and the  $\underline{c}$  electron concentration increases. This causes a change to a FUB2 binding with a new commensurability in Pt<sub>3</sub>Al.r-(Pt<sub>3</sub>Ga.r,T12.4), a I-homeotype of Cu<sub>3</sub>Au with  $\underline{a}=\underline{a}_{Cu3}Au(\sqrt{2};2)$ . The phases Pt<sub>2</sub>Al.h(Ni<sub>2</sub>Si) up to PtAl(FeSi)have XX2 bindings (X=U,F,H) which are especially frequent in brass-like alloys [8]. While Pt<sub>2</sub>Al<sub>3</sub>(Ni<sub>2</sub>Al<sub>3</sub>) obeys the small count, the phase Pt<sub>8</sub>Al<sub>21</sub>(Ul6.42,drawing SR31.12) probably returns to the great count. This results in a curious behaviour of the V<sub>At</sub>(N'<sub>2</sub>) curve [17] which even appears to be oscillatory [16b].

Starting from the binding Ni(Cu,SR1.68)3.52Å=b\_( $(\sqrt{2};1.4)$ =c<sub>R</sub>( $(\sqrt{8};2.8)$ ) affords for Ni<sub>3</sub>Ga(Cu<sub>3</sub>Au) a BU2 binding which leads over to the set of phases with XX2 binding. The main phase is NiGa(CsCl) with FF2 binding under great count, but also Ni<sub>3</sub>Ga<sub>2</sub>.h(NiAs) belongs to the set and yields a CC2 binding under little count. The quasi hexagonal  $Ni_{13}Ga_9(N13.9,drawing [18])$  is a RF-homeotype of NiAs with the commensurability  $\underline{a} = \underline{a}_{NiAs}(-2,2,-1;2,2,1;0,0,1)$  and with anomalous substitution. It also yields CC2 under little count and the anomalous substitution serves to fill the b correlation while the lacunae on Ni places serve to not overfill the c correlation under little count and the monoclinicity gives a better commensurability. It may be that the little count is only apparent and that  $\underline{c}_{c}$  is partly filled to  $\underline{c}_{B}$ . Ni<sub>5</sub>Ga<sub>3</sub>(Pt<sub>5</sub>Ga<sub>3</sub>,Q5.3,drawing [3a] p.105) is a RDI-homeotype of CuAu.r and permits a UU2 binding the c correlation of which is fully occupied in great count. NiGa(CsCl) curiously returns to the great count while Ni<sub>3</sub>Ga<sub>4</sub>(B24.32,drawing JLCM19.1969.245) is L-homeotypic to CsCl, its CU/2 binding (little count) having been correctly found earlier [3d]. Ni<sub>2</sub>Ga<sub>3</sub>(Ni<sub>2</sub>Al<sub>3</sub>) confirms the little count and was also correctly found in [3d]. NiGa $_4$ (htpRu $_3$ Sn $_7$ ) is not yet completely known but its remarkable  $\mbox{HTB}/2$  binding appears fairly certain. In summary it is found that the  $N_{pu}^{/P_1}(N_2)$  function implied in the data of TAB.10 is smooth and monotonous but has a plateau for the XX2 bindings, which confirms the energetic favourable property of the XX2 bindings.

The XX2 plateau gives an interpretation for the puzzling phenomenon that in the mixture  $PdGa_M$  five phases not yet all solved are crowded around  $Pd_2Ga$ .

The solved phases are RDI-homeotypes of Cu like  $Pd_2A1$  and yield therefore a UU2 binding. In  $Pd_5Ga_2$  (020.8) the great electron count did not work, therefore a medium count (m) was used which assumes that 4 electrons of the 4sp shell are in Hund insertion and therefore need not be counted. The phases  $Pd_2Ga$  and  $Pd_5Ga_3$  have different commensurability of UU2 to the cell  $\underline{a}$  and therefore are separate phases. The UU2 binding is followed by a FF2 binding in  $Pd_5Ga_4$ .h(CsC1). Following the place number rule [3b] PdGa (FeSi) has less P'' places than NiAl or PdA1 so that other structures are stable. It is curious that in  $PdGa_5$   $\underline{a}$   $\widetilde{H}TB\sqrt{2}$  binding is stable where  $\underline{\sim}$  indicates a little deformation.

As in Pt<sub>2.8</sub>Ga<sub>1.2</sub>(Cu<sub>3</sub>Au) Hund insertion is to be assumed (see Ni<sub>3</sub>Al) the small deformation in Pt<sub>.69</sub>Ga<sub>.31</sub> and Pt<sub>.68</sub>Ga<sub>.32</sub> may be caused by this influence. A new structure appears in PtGa<sub>2</sub>(CaF<sub>2</sub>), the small compression of  $p_{HT}$  is compatible with an increase of  $p_{P''}^{P''}$  as compared with Pt<sub>3</sub>Ga<sub>7</sub>. The knowledge of the structures of PtGa<sub>5</sub> and PtGa<sub>6</sub> would be of interest.

It is an old question why Ni $_3$ In(Ni $_3$ Sn.\*) and Ni $_3$ Al(Cu $_3$ Au) are not isotypic. Now N/C=56 for Ni $_3$ Al and N/C=2x47 for Ni $_3$ In so that the great In atom increases  $\underline{d}_{\underline{C}}$  and Causes another commensurability and another structure. For a greater mole fraction of In the XX2 bindings come and stabilize homeotypes of W. A structure which is not so frequent has NiIn.r(CoSn); it is a FC-homeotype of NiAs [3c] and may have a HH2 binding as the  $\underline{b}$  contribution of Ni decreases.

The phase Pd<sub>3</sub>In.h(TiAl<sub>3</sub>) and also Pd<sub>3</sub>In.r(ZrAl<sub>3</sub>) is homeotypic to Cu as N<sub>p</sub><sup>C</sup>-58 because of the UC $\sqrt{8}$  binding. The  $\underline{b}_U$  and  $\underline{b}_B$  correlations just stabilize the structures found following the energy assessment [3a p.99] by correlation-induced electro-dipoles.

The phase  $\text{Pt}_2\text{In}(\text{Pt}_5\text{Ga}_3)$  is quasi tetragonal with  $\underline{a}_2$  as axis . The BU2 binding of  $\text{Pt}_3\text{In}(\text{Cu}_3\text{Au})$  goes over here into a UU2 binding, but it is surprising that after this phase homeotypes of W become stable which display a CC2 binding, as it is a rule that XX2 bindings increase their density with increasing  $\underline{b}$  concentration.  $\text{Pt}_3\text{In}_2\text{.h}(\text{NiAs})$ ,  $\text{Pt}_3\text{In}_2\text{.r}(\text{Pt}_3\text{Tl}_2)$  and  $\text{Pt}_{13}\text{In}_9(\text{Ni}_{13}\text{Ga}_9)$  show a CC2 binding, it is therefore surprising that  $\text{Pt}_{1.1}\text{In}(\text{CuAl.r},\text{N5.5})$ , a homeotype of NiAs, also is compatible with this binding. Following Bradley's rule [3a] the phase  $\text{Pt}_{13}\text{In}_9$  has 0.5 vacancies per NiAs substructure cell while  $\text{Pt}_{11}\text{In}$  has 1.0; this number is conserved in  $\text{Pt}_2\text{In}_3$  as the binding is here no more of the XX2 type,  $\text{Pt}_3\text{In}_7$  has 1.6 vacancies per three W substructure cells.

The phase  $PdTl_2(CuAl_2, HTU/2)$  is in competition with  $Pd_3In_7(Ru_3Sn_7, HTB/2)$  and

 $PtIn_2$ .h(CaF<sub>2</sub>,HTU $\sqrt{2}$ ), the emergence of the CuAl<sub>2</sub>type conforms to the place number rule [3b] as it requires the smallest number of places.

 $\frac{B^1B_M^3phases}{Mphases}$ . These phases have been discussed previously [3e] but shall be included as the better appreciation of the  $N_{p''}^{P'}$  ( $N_2'$ ) rule allows some improvements. The twinned FUB2 binding of Cu and Cu  $_{3.4}$ Al  $_{0.9}$  has been discussed earlier [3f], the  $\underline{b}$  correlation is compressed tetragonally when the  $\underline{b}$  electron concentration is increased as this is the easiest way. When ideally the compression is continued then the correlation goes over eventually into the BB2 type and this is compatible here by experience with a structure homeotypic to W. The phases NiAl and Cu Al.h are not isodesmic as the  $\underline{b}$  electron concentration of NiAl is really  $N_{\underline{b}}^{/A}$  =2 because of the temperature dependent  $\underline{b}$  contribution of Ni, while of Cu  $_3$ Al.h it is  $N_{\underline{b}}^{/A}$ =1.5. Just as the NiAl type, the Cu  $_3$ Al.h type permits the L-homeotypism of Bradley, i.e. vacancy formation when  $N_{\underline{b}}^{/A}$  increases; different order of the vacancies causes different structure types. The plateau of  $N_{\underline{p''}}^{P'}$  belonging to BB2 phases ends with Cu  $_3$ 2Al  $_1$ 9, and for greater  $N_{\underline{A}}^{/A}$  follow homeotypes of NiAs, one of these with HUH/3 binding. Finally the FU2 binding is found in CuAl  $_2$ , the compression of  $\underline{b}_{\underline{F}}$  is mitigated by a slight shift of stability range to Al richer compositions.

In AgAl $_{\underline{M}}$  three phases correspond to different possibilities of XX2 binding, and the greatest N $_{\underline{b}}^{/A}$  value corresponds to the closest packing of the correlations

In AuAl $_{\underline{M}}$  the BB2 and UU2 binding is shifted to smaller Al mole fractions as Au has a  $\underline{b}$  electron contribution  $N_{\underline{b}}^{/Au}$ =1.15 [3a p.80], however, the FF2 binding belongs to a MoSi $_2$  type of structure, while in AgAl $_{\underline{M}}$  it belonged to a Mg type. The number of  $\underline{b}$  places per atom is  $N_{p}^{/A}$ =1.5 in Ag $_2$ Al and  $N_{p}^{/A}$ =1.75 in Au $_2$ Al because of the greater  $\underline{b}$  electron contribution of Au. At lower temperatures DI-homeotypes of MoSi $_2$  become stable in order to adapt the atom sites to the electrical dipoles induced by the bindings at the atoms. AuAl (M4.4) is another RDI-homeotype of W. A FF2 binding is, following the  $N_{p}^{/P}$  rule, not possible but the FUC2 bindings fits well. The tetragonal binding of AuAl $_2$  responds to the problem of pleochroism of this phase [19,16].

CuGa $_{M}$  is isotypic to CuAl $_{M}$  with the exception of CuGa $_{2}$ (T1.2) which is heterotypic to CuAl $_{2}$ , the HTU $_{2}$ D binding is preferred to FUU $_{2}$ C as Ga has a greater  $\underline{c}$  contribution than Al. Ag $_{3}$ Ga.r(Ag $_{2}$ Zn.r,drawing [3a]p.127) isaRD-homeotype of W, it has also a FF2 binding but the commensurability is improved. Au $_{7}$ Ga(TiNi $_{3}$ ) has a HFH2 binding which favours the stacking sequence of the structure. Au $_{7}$ Ga $_{2}$ .h(H21.6,drawing JLCM23.1971.83) is a RI-homeotype of Fe $_{2}$ P with  $\underline{a}=\underline{a}_{Fe}$ 2P

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TABLE 11: B1B3M
Cu3.1A10.9(ShtpCu3Au,ZMetk60.1969.488,TransJIM18.1977.807)3.668;8x3.677A=hdmCu
Cu3A1.h(W,SR13.5)2.94AorH7.20;5.09A=bBH(2;7/3)=cBHK'(2) phdHA
Cu3A1.m1(Fe35i,SR13.5)5.83A=idmCu3A1.h
Cu3A1.m2(Cu3Sb.h1, SR8.9)4.52;5.21;4.23
Cu7A13.h
Cu2Al.h1=htpCu9Al4
Cu2Al.h2=htpCu9Al4
Cu9A14(C36.16, SR33.72)8.702A=idmCu3A1.h
Cu32A119(M64.38, Natur168.1951.661)
Cu3A12.h2
Cu3A12.h1(H(3.2).(2.2),JLCM29.1972.133)H4.146;5.063A=bFH(\sqrt{3.2};2.7/3)=cUH(\sqrt{13.5}/2)
Cu30A120(JInstMet63.1938.149)
                                                                                                                                                                  N=10.50
Cu4A13.h
Cu4A13.r(M12.9, JInstMet63.1938.149)M90.63<sup>0</sup>7.08;4.09:10.04A
CuAl.h(orth.PhilMag12.1931.980)
CuAl.r(N5.5,SR38.4)9.889;4.105;6.914,0,6.913AorH4.1;5.0A=bH(2;2.5)=cUH(\sqrt{12};5/2)
Cu2A13.m?(Ni2A13,SR40.100)H4.106;5.094A=probablyCu3A12.h1
CuA12(U2.4,SR3.589)6.066;4.874A=bF(2;3.5/2)=cU(4;4) N=28,104
                                                                                                                                                                      N=40.180
Ag3Al.h(W,SR4.233)3.302A+H8.1;5.7A=idmCu3Al.h BB2 phdHA
Ag3A1.r(Mn.h ,SR21.22)6.945A=bU(√5;2.8)=cUK'(2) N=29,190
Ag2A1 (Mg, SR1.558)H2.88; 4.60A-H4.99; 4.60A=bFH(2; 2.25)=cFHK'(2)
Au4A1.h(W,SR15.5)3.24A=idmCu3A1.h BB2
Au4Al r(Mn.h,SR8.13)6.921A=idmAg3Al.r UU2 phdHA
Au8Al3.r(H96.36?, )H7.718;41.99A N=204,1248
Au2Al.h(MoSi2,SR40.100)3.349;8.893A=bF(1;5.39=cFK'(2) N=10,56
Au2Al.r(08.4,SR40.3)6.715;3.219;8.815A=bF(2.1;1;2.75)=cFK'(2)
Aul.97A11.03.r(020.10,SR40.3)16.772;3.219;8.801A=bF(5.25;1;2.75)=cFK'(2)
AuA1(M4.4,SR35.7)M93.04<sup>0</sup>6.415;3.331;6.339=bFU(\(\frac{7}{8}\);2.1/2;\(\frac{7}{8}\))=cC(\(\frac{7}{3}\);3;\(\frac{7}{3}\);32)N=16,72
AuA12(CaF2, SR3.20)6.01A=bHT(\sqrt{8}; 3.5/2)=cB(4) N=28,104
Cu3Ga.h2(W,SR3.600)2.967A=idmCu3A1.h phdHA
Cu3Ga.h1(Mg, SR4.237)H2.598;4.236A=idmAg2A1
Cu3Ga.r(htpMg,
                                             )=hdmCu3Ga.hl
Cu9Ga4.h(Cu9A14,SR40.54)8.749A=idmCu9A14
Cu2Ga (htpCu5Zn8)
Cul.8Ga(htpCu5Zn8)
Cu3Ga2(htpCu5Zn8)
CuGa2(\uparrow1.2,SR38.79)2.830;5.839A=bHT(\checkmark2;3.5/2)=cU(2;5) N=7,30
Ag3Ga.h(Mg, SR26.248) H2.887; 4.675A=idmAg2A1 FF2 phdHA, E
Ag3Ga.r(Ag2Zn.r,SR29.53)H7.768;2.877A=bFH(\sqrt{9}.75;1.5/3)=cFHK'(2) N=13.5,90
Aŭ7Ga(TîNŤ3,71Ec)H2.874;9.426AorH4.96;9.43A=bBH(γ/1.3;11/3)=cFH(4;9/3) N=15,120
Au7Ga2.h(H21.6,SR37.87)H7.724;8.751A=bFH(3;4.2/3)=cFHK'(2) N=39,270
Au7Ga2.r
                                                )7.649;8.766;9.014A
Au2Ga(Pd2As.r, SR40.66)18.023;3.199;6.999A=b\tilde{F}(5;1;2)=cF(10;1.8;4) N=39,240
\begin{array}{lll} \text{AuGa}(\grave{\text{MnP}},\text{SR13}.28) & 6.26 \\ 7; & 3.421 \\ 6.397 \\ 4 & \text{Ga2}(\texttt{CaF2},\text{SR5}.54) \\ 6.075 \\ \text{AuGa2}(\texttt{CaF2},\text{SR5}.54) & 6.075 \\
Cu4In.h(W.SR3.573)3.00A=idmCu3A1.h phdHA
Cu7In3.h(Cu5Zn8,SR16.82)9.250A=idmCu3A1.h BB2
Cu7In3.r(Z28.12,SR46.63)Z90.1°81.8106.81°10.071;9.126;6.724A
Cu2In.h(NiAs, SR9.65)H4.289;5.263A+H7.43;5.26A=bUH(2;2.8/2)=cH(4;5)
Cu2In.r(htpNiAs,ZMetk63.1972.456)
Cu7In4.h(htpNiAs,ZMetk63.456)21.38;7.41;5.22A=bB(6,2,0;6,2,0;0,0,2) N=95,550
Cu7In4.r(htpNiAs,ZMetk63.456)
CullIn9(CuAl.r,ZMetk72.1981.275)M54.49012.814;4.354;7.353AorH4.3;5.2A=idmCuAl
                                                                                                                                                                      N=38,200
Ag3In.h2(W, SR26.172)3.368A=idmCu3A1.h phdHA
Ag3In.h1(Mg,SR26.248)H2.95;4.79A+H5.11;4.79A=idmAg2A1
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Ag3In.r(Ni3Sn.SR15.82)H2.95;4.80A=idmh
Ag9In4.h(Cu9A14,SR43.66)9.922A=idmCu3A1.h
AggIn4.r
AgIn2(CuA12, SR15.82)6.883;5.615A=bFU(3;3.5/2)=cU(18;4) N=28,120
Au7In(Nd, SR^{2}(2.69) H2.901; 9.528A(\sqrt{3}.1)=bBH(\sqrt{1}.33; 1 1/3)=cFH(4; 9/3) N=15,120 phdS
Au6In(Mg, SR22.69)H2.91;4.79A HH2 N=2.57,20
Au10In3.h(Cu4.5Sb,ZM51.1960.327)H2.914;4.775A
Aul0In3.r(Cu10Sb3.h,SR24.119)H10.524;4.759A=bH(√19;2)=cHK'(2) N=38,260
Au3In(Cu3Sb.hr,SR22.69)5.850;5.140;4.733A=bÜ(2; 1.5;2/1)=cÜK'(2) N=12.80
Au7In3(H42.18, SR41.74)H12.215;8.509A=bBH(3;10.3h=cBHK'(2) N=96,600
Au9In4.h(Cu9A14.SR41.73)9.843A=idmCu9A14 BB2
Au3In2.h(Ni2A13, SR23.151)H4.537;5.658Aor a(\sqrt{3};1)=bBH(2;7/3)=cFH(6;5/3)
AuIn, htp:Au5In4Sn1(T1I,ZMetk50.1959.146)4.28;10.50;3.60A=bB(\sqrt{2.5};4;0.84\sqrt{2.5})=
AuIn2(CaF2, SR6.164)6.515A=idmAuA12 HTB/2
                                                      cFU(\sqrt{10;11/2;0.84\sqrt{10}})N=17.80
CuT1M(nic,phdHA)
AgT1M(nic,phdHA)
AuT12(CuA12, SR38.5)7.26;5.60A=bHT(9;3/2)=cU(\sqrt{18};4) N=28,120 phdHA
TABLE 12: B2B3M
Zn3A12(Cu, see Elliott)4.045A=bC(\sqrt{4.5};2.1)=cB(3) phdE
ZnA12.m(R1,SR31.17)H2.852;6.785A
CdAlM(nic,phdHA,M)
HqAlM(nic,phdHA)
ZnGaM(nic,phdHA)
CdGaM(nic,phdE)
HgGaM(nic.phdE)
ZnInM(nic,phdHA)
Cd3In.h(Cu,SR23.74)4.513A=bHT(2;2.3/2)=cB(\sqrt{8};2.8) phdE
Cd0.4In3.6.h(Cu,SR6.179)4.5A=bF(\sqrt{2};1.4)=cB(\sqrt{8};2.8)
Hg6In(T3?, JLCM5.1963.41)3.89;5.21A? phdS
Hg4In(Pu.h2,S2,SR45.82)10.872;4.847;3.522A=bUH(5.2;2;1.7)? N=17.6,80
HgIn.I(PtCu,R1.1,SR38.105)H3.572;13.168A=bUH(\sqrt{2}.3;6.5/2)=cH(\sqrt{7};10/2) N=15,60
HgIn2.1(
              ,JLCM11.1966.186)
HgIn8(Cu, SR18.173)4.69A=idmCdIn9 FB2
ZnT1M(nic,phdHA)
CdT1M(nic,phdE)
Hg3T1(Cu, SR4.136)4.68A=idmCd3In.h HTBv/2
HqT15(W,SR3.645)3.82A=bB(1.5)=cC(3)
TABLE 13: B3B3M
AlGaM(nic.phdE)
AllnM(nic,phdHA)
Ga InM(nic, phdHA)
AlTIM(nic, phdHA)
GaTIM(nic, phdE)
In2T1(Cu, SR13.122)4.76A=bF(1.5;1.5)=cB(3) phdS
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(1;3) and permits FF2.  $Au_2Ga(Pd_2As.r,drawingSR40.67)$  is also homeotypic with  $Fe_2P$  and displays alternating 8- and 9-coordination, the FF2 binding is a degeneration of the FF2 binding.

CuIn<sub>M</sub> has a XX2 plateau extending from Cu<sub>4</sub>In.h(W) to Cu<sub>7</sub>In<sub>3</sub>.h(Cu<sub>5</sub>Zn<sub>8</sub>). Cu<sub>7</sub>In<sub>3</sub>.r(Z28.12) must have a slightly different binding as judged from N<sup>/p'</sup><sub>p'</sub>(N<sub>2</sub>). An investigation of the RF-homeotypes of NiAs would be of interest for the analysis of binding. The homeodesmism of AgIn<sub>2</sub> to CuAl<sub>2</sub> should be noted. AuIn<sub>M</sub> has like AuGa<sub>M</sub> pre-XX2 compounds. While for Au<sub>7</sub>In(Nd) a S-homeotype of M<sub>g</sub> before a FF2 binding appeared probable [20], the consideration of the N<sup>/p'</sup><sub>p''</sub>(N'<sub>2</sub>) function lead to the interesting modified binding BHFH/12 which changed the  $\underline{d}_b$ (N'<sub>2</sub>) fraction slightly and had therefore influence on neighboured proposals. The HH2 binding of Au<sub>10</sub>In<sub>3</sub>(H20.6,drawing [3a]p.114), a R-homeotype of Mg with  $\underline{a}=\underline{a}_{Mg}(\gamma'13;1)$ , is to be preferred to the earlier FF2 binding because of its whole number commensurability element K'<sub>33</sub>=2. Also for Au<sub>6</sub>In(Mg) a HH2 binding must be assumed which displays a small rotation against the  $\gamma'19/\gamma'13$  commensurability of Au<sub>10</sub>In<sub>3</sub>.r.

For  $\operatorname{Au_3In}(\operatorname{Cu_3Sb.h_1}$ , formerly named  $\operatorname{TiCu_3}$  type, drawing [3a]p.114) a deformed  $\widetilde{\operatorname{UU2}}$  binding might be possible which was not found earlier but which has some advantages for the atom sites, it might explain them by the method used for the S-homeotypes of  $\operatorname{Cu_3Au[3a]}$ . Perhaps this  $\widetilde{\operatorname{UU2}}$  binding describes only a twinned HH2 binding but this problem should be postponed here with respect to the good fit of the remaining bindings.

 $\frac{B^2 \cdots 3}{M_{p}} \frac{B_{p}^3}{B_{p}^3}$  in the mixture ZnAl<sub>M</sub> the existence of Zn<sub>3</sub>Al<sub>2</sub>(Cu) was assumed. The binding of Al may be described by  $\underline{a} = \underline{b}_{HT}^* (\sqrt{4.5}; 2.7/2) = \underline{c}_B(3)$ , so that the  $\underline{b}$  correlation is somewhat compressed. Substitution of Zn mitigates the deformation and even permits a CB/2 binding. Since this yields  $\frac{N_{p}^{\prime C}}{P} = 9.5$  places per cell the occupation rule requests the composition  $\text{Zn}_3\text{Al}_2$ , which in fact is observed. Many  $B^2B_M^3$  mixtures do not form intermediary phases as the energy of formation is  $\overline{to}$  small since no expansion of  $B^3$  electrons into the  $B^2$  atoms is possible the  $\underline{b}$  electron density of  $B^2$  being too great. In  $CdIn_M$  two phases are formed, the binding of which confirms neatly the binding of  $\overline{In}$ .

The translation group of  ${\rm Hg}_6{\rm In}$  needs confirmation and the binding problem of  ${\rm Hg}_4{\rm In}$  is not yet solved.  ${\rm HgIn}({\rm PtCu})$  is homeotypic to  ${\rm Hg}({\rm R1})$  with commensurability  ${\rm \underline{a=a}_{Hg}}(1;2)$  and permits a UHH/3 binding. The phase  ${\rm HgIn}_8({\rm Cu,FB2})$  is a confirmation of the binding of In, and also  ${\rm In}_2{\rm Tl}({\rm Cu})$  permits a simple FB2 binding, and the possibility of the change of commensurability of the binding to the crystal answers the old question why  ${\rm In}_2{\rm Tl}$  is cubic and  ${\rm In}_3{\rm Sn}$  not.

## Concluding remarks

With respect to the utility of valence models in chemistry of salt-like compounds for learning and memorizing empirical facts, there can be no doubt that a valence model is desirable also for alloy phases. The strange fact that the two-correlations model is somewhat different from the known valence models of inorganic chemistry may be connected with the other strange fact that the inorganic valence models could not be extended so far to the interpretation of metallic phases. A gain afforded by the new model lies in the emergence of crystal chemical rules which give better insight into what is happening energetically during compound formation.

For instance it was early realized that the isotypes NiAl(CsCl) and CuZn(CsCl) have seemingly the same valence electron concentration  $N_b^{/A}$ , but since they are melting at  $1630^{\circ}$ C and  $900^{\circ}$ C respectively, there must  $\overline{b}e$  a distinct difference in binding between them. In fact the present analysis assumes that NiAl has a FF2 binding with much better commensurability to the crystal than the BB2 binding of CuZn or  $Cu_3Al.h$  has, and therefore causes as a rule a higher melting temperature. Many new questions arise in connection with the new understanding. For instance when the b electron contribution of Ni is dependent on temperature, to what value does it decrease at temperature 20°C in NiAl? May it be confirmed by susceptibility measurements that  $N_h^{N_i}=1$  at  $1500^{\circ}$ C as is assumed here? Is there some change of b correlation at medium temperatures? Has this change a more gradual or a more sudden character? Another example for new questions is the optical anisotropy of AuAl,: at which temperature above 20°C does it go lost? Is it feasible to anneal crystals below that temperature long enough as to get a tetragonally deformed translation group? Is the process of loss of anisotropy more gradual or more sudden? Are there domains of anisotropy in a single crystal?

Another new crystal chemical rule is the monotonous decrease of the  $N_{p_1}^{/P^1}(\underline{N_2'})$  function (see summary) with increasing valence electron concentration  $\underline{N_D^{+}}$ . The validity of this rule is a confirmation for the assumption that the  $\underline{b}$  electron gas may be considered in a first approximation as uniformly distributed in the crystal. Another confirmation is the rule of full occupation of the  $\underline{b}$  gas, for if the distribution were not uniform, there were no reason for full occupation. A phenomenon not to be expected immediately is the distinct plateau (at  $\underline{N_p^{+P}}^{-P} = 8$ ) for the XX2 binding. This plateau is an expression for the energetic advantage of the XX2 binding. An analogous plateau is to be expected for the FB2 binding, but it cannot be found in the present alloys as the marginal elements lie just at the beginning of the FB2 binding as

 $\frac{N_0^{/A}}{c}$  increases. When several  $\frac{N_0^{/P^*}}{c}(N_2^*)$  curves are drawn using the data contained in the tables it becomes apparent that frequently a positive value of the second derivative of  $N_{P^*}^{/P^*}(N_2^*)$  is found, while the first derivative is never positive. Since the  $\underline{c}$  distance may be considered as constant in the first approximation it may be said that an increase of the mole fraction  $N_2^*$  of the second component causes a compression of the  $\underline{b}$  gas against the  $\underline{c}$  gas. In the XX2 plateau the compression is interrupted because of the energetic advantage of the XX2 binding, but at the end of the plateau a stronger compression begins which decreases soon so that a positive second derivative is formed.

A rule of great and little electron count was found for the A elements for which the electron distance  $\underline{d}(nsp) \cdot \underline{s} \underline{d}(nd)$ , where n = main quantum number of atomic arbitals and s, p, d are their different representations. This rule needs further confirmation so that its discussion should be postponed here.

Besides the emergence of new crystal chemical rules many old questions for the incident alloys are answered by the two-correlations model. Only few examples will be given:

Why are in  ${\rm AgAl}_{\rm M}$  just three different phases stable near  ${\rm Ag}_3{\rm Al}$ ? All three phases have the wellknown valence electron concentration  $N_h^{/A}=1.5$ , they obey the extended Hume-Rothery rule. But it was not understood  $\overline{\overline{\mathbf{w}}}\mathbf{h}\mathbf{y}$  three different structures belong to one and the same  $\underline{N}_b^{/A}$ . It is easily seen that any two-factorial isotypic binding leads for brass-Tike phases just to  $\underline{N}_b^{/A}$ =1.5: there are 10 peripheral core electrons per atom, this number suggests TO/0.83=12 c places per atom (0.83= average occupation in c correlation), and since to 8 c-places there belongs 1 b-place in a XX2 binding, to 12 c-places belong 1.5 valence electrons. This suggests that all three phases of  ${\rm AgAl}_{\rm M}$  belong to a XX2 binding and the consequence that different bindings must exist confirms once more the assumption that in the two-correlations model different isometric [3b] correlations are to be expected. The question which of the XX2 bindings belongs to a given phase is a problem for the analysis. For instance the BB2 binding of Ag<sub>2</sub>Al.h was found during a solution of the structure of AuCd.r [3b] which makes apparent the commensurability of the binding by little shifts of the atoms. A similar lucky chance applies to Ag<sub>2</sub>Al which is closely homeotypic to Au<sub>5</sub>Sn.r, revealing the commensurability by the sites of the minority component.

Why are  ${\rm CuGa_2(T1.2)}$  and  ${\rm AuGa_2(CaF_2)}$  not isotypic [2f]? In fact the are closely homeotypic and homeodesmic and the homeotypism obeys the rule of place numbers [3b]:  ${\rm N}_{\rm p}^{/C}({\rm CuGa_2})$ =40> ${\rm N}_{\rm p}^{/C}({\rm AuGa_2})$ /4=32. Why are  ${\rm CuAl_2}$  and  ${\rm CuGa_2}$  not isotypic [2f]? Also these phases are homeodesmic, but  ${\rm CuGa_2}$  offers more

peripheral core electrons than CuAl $_2$ , therefore  $N_{p^{\,\prime\prime}}^{/C}(\text{CuAl}_2)/4=32 < N_{p^{\,\prime\prime}}^{/C}(\text{CuGa}_2)=40$ . Why are CuGa $_2$  and AgIn $_2(\text{CuAl}_2)$  not isotypic? Once more  $N_{p^{\,\prime\prime}}^{/C}(\text{CuGa}_2)=40 > N_{p^{\,\prime\prime}}^{/C}(\text{AgIn}_2)/4=36$  i.e. the place number rule is fulfilled. These remarks suggest an experiment: CuGa $_2$  should under pressure transform to the AgIn $_2$  type.

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