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ON THE BINDING IN $A^nB^4_{\underline{M}}$ AND $B^nB^4_{\underline{M}}$ PHASES

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Summary

The chemo-geometrical analysis of the bonding type (binding) in the above delimited phases shows that the electron count is of prime importance for the energetical interpretation of the phases. It is found that the A^n atoms frequently contribute in B^4-poor phases about one electron to the valence electron correlation; in B^4-rich phases the contribution may disappear (extended Ekman rule). The valence contribution of B^4 is invariably four electrons. This electron count yields by the two-correlations model a valence classification with energetic background of many of the delimited compounds the structures of which have been determined in the last 50 years nearly exhaustively. Numerous new crystal chemical rules emerge which make the stability and structural observations in these alloys energetically very transparent. The energy of formation of these alloys stems mainly from the fact that the valence electron of the A^n atom is pressed back by the valence electrons of the B^4 atoms into the A^n core. A phase is formed when the valence and core electron correlations are in a good commensurability with the crystal. More electrons than in any previous valence theory appear decisive for chemical affinity because of the participation of the peripheral core electrons in the binding. This might be one of the reasons for the surprising fact that the two-correlations model remained hidden so long. Another valence model for these phases has not been advanced previously but such a model is in any case a prerequisite for a phenomenological assessment of the energy of alloy phases.

Introduction

The $A^nB^4_M$ phases (A^n,B^n=homologous classes of chemical elements according to IUPAC [1], $\overline{\underline{M}}$=undetermined mole number) and the $B^nB^4_{\underline{M}}$ phases have been thoroughly reviewed in many helpful works [2a-j]. The phases shall be analysed in the following with respect to their electron spatial correlation by means of the two-correlations model [3a-d]. Carbides are not included here as they have been analysed previously [4b]. The format of the results collected in the tables has been explained earlier [4a-e]. The analysis of the type of spatial correlation of the valence electrons (b correlation) and of the pheripheral core electrons (c correlation), together named a binding, gives a better energetic understanding of the stability of these phases [3]. After having exhaused the stability arguments from electron density, crystal chemistry now enters the search for stability arguments from electron correlation. Just as the atomic radii and atomic charges have been found by the earlier authors using an analysis of structural and chemical knowledge, the correlation types will be found by the trial and error method, using the rules found in previous analyses [3,4] as a criterium for the probability of the assumptions.

In order to have a short description of crystal chemical relations, abbreviated symbols for the kind of a homeotypism are used: R=replacement of an atom by another, L=vacancy formation (lacuna), F=filling of interstices, D=homogeneous deformation, I=inhomogeneous deformation, S=shear of layers, C=shear of chains.

The present analysis in first line tries to find out from the structural data, which types of spatial electron correlations are probable. The problem why no other correlations are stable may be treated later. The probability of the bindings can only be appreciated by considering the whole classification in relation to the whole class of phases. A useful means of analysis found in the present investigation is the smoothness of the function $\underline{N}^{/P'}_{P''}\smile(\underline{N}_2')$, where $\underline{N}^{/P'}_{P''}$ = number of places in the c correlation per number of places in the b correlation, $\underline{N}_2'$= mole fraction of the second component of the phase.

Several authors have complained that the binding analysis be difficult to reproduce. This is a frequent property of inductive reasoning: Inference has to be made from many experimental facts, this leads to a model which has to be examined by additional facts. A simple example for this procedure is a structure determination before the advent of direct methods. The inductive process is the finding of the model. It is more or less rapid and depends on the presence of numerous, sometimes little informations like (in our case) structural facts, rules for bindings, numerical values of lattice lengths, values of commensurability elements etc. Just as structure determination has been learned by many workers, also binding analysis can easily be learned if the papers describing it have been studied carefully.

Analysis

$\underline{A^1B^4_M}$ phases. A surprising phenomenon in the mixture $NaSi_{\underline{M}}$ is the occurrence of "polysilicides" i.e. of phases which have more anions than the Lewis octet completion rule [5]("normal valence") requests. The phase Na_4Si_{23}(C8.46) contains a Cr_3Si type partial structure of Na atoms and these atoms are, corresponding to their great radius, highly coordinated by Si atoms. The high Si content of the phase suggests that the valence electrons of Si are in a certain correlation with the core electrons of Na, so that the electron count [3] becomes $Na_4^{1,8}Si_{23}^{0,4}$ and a CC'3 correlation appears possible (see TABLE 1); the prime on C indicates partial filling of the cubic primitive C type: The $\underline{c}$ correlation is of the B type in the neighbourhood of the Na atoms, and of the C type near the Si. This is a typical case of Hund insertion[3] and it may be verified that the $\underline{c}$ correlation fits well to the Si sites. In this case $\underline{b}$ and $\underline{c}$ correlations are fully occupied. The distance in the $\underline{c}$ correlation, $\underline{d}_c$ is somewhat decreased relative to the value expected by the $\underline{d}$ ($\underline{N}'_{Si}$) diagram [3], conforming to the rule of distances[3]. When the mole fraction N'_{Si} increases then more Si enter the cell and this is compatible with a HH'4 binding in $NaSi_{17}$(F(1..3).34), which must be twinned in the $\underline{a}$ cell. Unfortunately the true Na content appears to be controversial. It may be mentioned that the present alloy phase interpretation sheds new light also on isotypic gas hydrates (SR37.134).

NaSi(N8.8,drawing SR29.60) has a quasi hexagonal $\underline{a}_2$&$\underline{a}_3$ mesh being parallel to four Na layers stacked in $\underline{a}_1$ direction. Between the layers there are Si_4 tetrahedra ("polyanions") which are stabilized as the valence electrons of Si form Si-Si bonds since their correlation probably only weakly extends into the Na cores. The fact that 3 electron holes per Si are free for Si-Si bonds is sometimes attributed to the Zintl supply rule [6a,b] or to the Mooser-Pearson rule [7a,b] (valence electrons or valence holes not used in cation-anion bonding are localized in cation-cation bonds or in anion-anion bonds). To be sure both rules are not genuine valence rules, as they presume the stability of some composition and give a statement on the structure. On the other hand a binding proposal for NaSi is to be understood as a valence argument. It may be seen that the increase of $\underline{b}$ electron concentration as compared with that in Na_4Si_{23} is expressed by the transition from the $\underline{b}_C$ to the closer packed $\underline{b}_B$ correlation. The commensurability of the $\underline{b}$ correlation to the cell $\underline{a}$ is good and $\underline{c}^{-1}\underline{a}$ is fully whole numbered.

KSi(KGe,C32.32,drawing [3a]p.228) contains Si tetrahedra like NaSi, but these tetrahedra are here on the atom positions of a Cr_3Si structure. The

TABLE 1: Binding in $A^1B^4_{\underline{M}}$ phases

Formula, type, reference, cellmatrix , binding, N= number of b,c electrons per cell, phd= phase diagram, HA= Hansen Anderko, E= Elliott, S= Shunk, M= Moffatt (see references), cmp= congruent melting point, idm= isodesmic.

Na4Si(Ang Chem 85(1973)742)
NaSi(N8.8,SR29.58)10.66;6.55;-5.91,0,11.18A=bBHO(8/3;1;1)=cCHO(12/3;3;3) N=16,128
NaSi2(T4.8,ZM38.1947.76)4.98;16.73A needs confirmation N=4,48
Na4Si23(C8.46,SR30.96,37.133)10.19A=bC(2)=cC'(6) N=8,216
Na3Si17(F(1..3).34,SR30.96)14.62A=bHT(2;2.2/2)=cHT(8;9) N=8,576
KSi(KGe,SR26.84)12.62A=bF(2)=cC(8) N=32,256
K4Si23(Na4Si23,SR32.117,34.122)10.30A=idm Na4Si23
KSi6(cubic?,SR26.157)13.4A
RbSi(KGe,SR26.84)13.04A=idm KSi
RbSi6(cubic?,SR26.157)13.4A
RbSi8(AngChem85.742)
CsSi(KGe,SR26.84)13.50A=idm KSi
CsSi8(AngChem85.742)
NaGe(M16;16,SR29.57)11.42;6.70;-6.15,0,10.69A
Na4Ge23(Na4Si23,JSSC2.570)=idm Na4Si23 CC'3
Na3 Ge17(Na3Si17,JSSC 2.570)
KGe(C32.32,SR26.84)12.78A=bF(2)=cC(8)N=32,256
K4Ge23(Na4Si23,SR34.122)10.71A=idm Na4Si23
RbGe(KGe,SR26.84)13.19A=idm KGe
Rb4Ge23(Na4Si23,JSSC 2.570)=idm Na4Si23
CsGe(KGe,SR26.84)13.67A=idm KGe
Cs4Ge23(Na4Si23,JSSC 2.570)=idm Na4Si23
Na15Sn4 (Cu15Si4,SR44.99)13.14A=id m Na15Pb4 CC'2 phdH
Na 3.7Sn(O30.8,SR41.107)9.82;5.57;22.79A
Na15Sn4 (Cu15Si4,SR44.99)13.14A N=36,208
Na9Sn4(Li9Ge4,Q18.8,SR44.99)5.42;9.39;29.62A=bFH(√3;12/3)= cÛH(3;24/2) cmp
Na4Sn3.h
NaSn.h
NaSn.r(NaPb,SR44.99)10.46;17.39A= idm NaPb cmp
NaSn2
NaSn3
NaSn4(complex powder diagr.ACB25.1206)
Na4Sn23
K2Sn
KSn(NaPb,SR29.83)11.42;18.57A= idm NaPb phdH
KSn2 cmp
KSn4.h
KSn4.r
K4Sn23(Na4Si23,SR34.122)12.03A= idm Na4Si23
RbSn(NaPb,SR29.130)11.71;19.09A= idm NaPb
CsSn(NaPb.SR29.111)12.19:19.87A= idm NaPb
Na15Pb4(Cu15Si4,B30.8,SR4.138,21.146)13.32A=bC(4)=cC'(8) phdH N=60,304
Na13Pb5(H26.10,AC10.1957.775)H5.51;40.39A=bCH(√1.33;20/3)=cĈH(√5.3;42/3) N=26,144
Na5Pb2(R5.2,AC10.1957.775)H5.54;23.15A N=15,84
Na9Pb4.h(H18.8,AC10.1957.775)H5.47;30.41A additional superstructure
Na9Pb4.r(AC 10.1957.775)
NaPb(U16.16,SR17.204)10.580;17.746A=bC(√8;4.3)=cFU(√32;13/2) N=32,256
NaPb3(Cu3Au,SR2.735)4.884A=bC(1)=cB(2)=eC(4) N=1,12
K2Pb phdE
KPb(NaPb,SR29.122)11.50;18.76A=idm NaPbCFU2 cmp
K2Pb3 (Russ.J.inorg.Chem.4.1959.728)
KPb2(MgZn2,H4.8,SR20.140)H6.66;10.76A=bCH(1;4/3)=cF'H(3;6/3)
K4Pb9
KPb4(B ,SR20.140)12.31A
RbPb(NaPb,SR29.128)11.84;19.42A=idm NaPb
CsPb(NaPb,SR29.111)12.26;19.99A= idm NaPb

KSi structure is I-homeotypic to NaCl with the commensurability $\underline{a}=\underline{a}\mathrm{NaCl}(2)$. A well fitting FC4 binding is found. The BC3 binding of NaSi had $N_{P''}^{/P'}=13.5$ $\underline{c}$ places per $\underline{b}$ place while in the FC4 binding there are $N_{P''}^{/P'}=16$. Therefore FC4 is preferred to BC3 as the radius of K is greater than the radius of Na. An alternative tempting interpretation $\underline{a}_{KSi}=\underline{b}_F(2)=\underline{c}_F(4)=\underline{e}_F(8)$ would yield $\underline{a}_{K4Si23}=\underline{b}_C(2)=\underline{c}_F(4)=\underline{e}_B(8)$.

NaGe(M16.16,drawing SR29.60) is homeotypic to NaSi, perhaps some influence of the Ge-d electrons is effective. $Na_{15}Sn_4(Cu_{15}Sn_4)$ is isodesmic to $Na_{15}Pb_4$ discussed below. $Na_9Sn_4(Li_9Ge_4$,Q18.8) has a quasi hexagonal mesh $\underline{a}_1$&$\underline{a}_2$, a FHÛH/3 binding might be possible. However, any binding proposal gets confidence from the proposals for neighboured phases, as these are not yet known the above proposal is at present only tentative.

$Na_{15}Pb_4(Cu_{15}Si_4$,B30.8, drawing [3a] p.226) has a B1 partial structure of Pb so that the Pb cannot extend bonds to neighboured Pb, rather they show correlations with the peripheral core electrons of Na, so that the Na atom is compressed and a CC'2 binding comes. The Pb atoms compress the Na atoms by the forces of correlation to the Na core electrons. The partial occupation of the $\underline{b}$ correlation should cause increase of metallic conductivity. Around the composition Na_5Pb_2 three phases have been found, but their structures need more refinement. They have perhaps to do with a CC2 binding in which $\underline{c}_C$ suffers some contraction in the trigonal axis. NaPb(U16.16,drawing [3a] p.227) contains double layers parallel to $\underline{a}_1$&$\underline{a}_2$ containing 8 atoms so that they may be idealized to $\underline{a}=\underline{a}_{F1}(2;4)$, similarly as for KGe the homeotypism to C1 with $\underline{a}=\underline{a}_{C1}$ (4) could be noted; the closer packing of NaPb as compared to KGe fulfills the rule that heavier B^n elements favour closer packed structures (as for instance in the heterotypism Sn-Pb). The strong deviation from this idealized structure comes from the binding between the B^4 atoms. For NaPb a CFU2 binding is found which describes a compression of the $\underline{c}$ correlation against the $\underline{b}$ correlation as compared with the CC'2 binding of $Na_{15}Pb_4$. It is quite satisfactory that $NaPb_3$ yields a CB2C4 binding, as Pb(Cu type) probably has a BHH/7 binding [22].

In $KPb_2(MgZn_2$,H4.8,drawing [3a] p.161) a CHF'H3 binding is found which conveys the ratio of places per cell $\underline{N}_{P''}^{/P'}=12.5$ being smaller than in $NaPb_3(Cu_3Au)$ $\underline{N}_{P''}^{/P'}=16$. It should be reminded here that structural arguments derived from electron density, like atomic radius ratio arguments are taken for granted.

$\underline{A^2B^4_M}$ phases. As the $\underline{b}$ electron distances in Mg are comparable to those in Si [3b], in $MgSi_M$ the electron count $Mg^{2,8}Si^{4,8}_M$ is to be expected. Mg_2Si(CaF_2, F2.1) obeys the rules of Lewis and Zintl and yields the FB2 binding which is also responsible for the great Si structure family [2h,3a]. If in silicon four Si per cell are replaced by eight Mg then the Mg_2Si structure results. This is an example of an extension of the Grimm-Simmerfeld rule (see [3a]p. 31,181,[2h]); since it is also expressed by the binding, the rule is integrated into the two-correlations model. The relation $\underline{d}_{\underline{c}}(Mg_2Si) > \underline{d}_{\underline{c}}(Mg)$ might be caused by $\underline{b}$ electron pressure. However, the binding $\underline{a}_{/\underline{P}\,Mg2Si} = \underline{b}_{\underline{F}}(2) = \underline{c}(\sqrt{32}; 5.6)$, which is to be assumed twinned, gives a better $\underline{N}^{/P'}_{\underline{P}''}$ value, and should therefore be taken into consideration.

It is not a priori clear which electron count is valid for $CaSi_M$, but since the A^1Si_M phases are mostly heterotypic to the A^2Si_M phases, the count $Ca^{2,8}Si^{4,8}_M$ like as in $Mg^{2,8}Si^{4,8}_M$ appears probable. Ca_2Si(Ni_2Si, drawing [3a] p.322) is RDI-homeotypic to Cu, the heterotypism to Mg_2Si fulfills the rule that heavier compounds prefer closer packing. The $\underline{c}_U$ correlation is well fitting and a $CU\sqrt{2}$ binding might apply. This binding is remotely homeotypic to the FB2 binding of Si, it should therefore not surprise that homeotypic bindings are stable also in other $CaSi_M$ phases. Although the $\underline{b}$ electron concentration increases, the $\underline{c}$ concentration is conserved in Ca_5Si_3(Cr_5B_3, drawing [3a]p.254), a RL-homeotype of W, and a $CB\sqrt{2}$ binding is found. The B1 substructure is more loosely packed than in Ca_2Si because of increase of $\underline{b}$ concentration (rule of volume [3a]p.169). CaSi.r(TlI, drawing [3a]p.263) a shear homeotype of CaS(NaCl) is even more loosely packed, and FU2 bound; the shear contained in the cell as compared to CaS is generated by the FU2 binding as may be shown using the method applied in [3a] to the shear homeotypes of Cu_3Au. Also the strong deformation in the quasi tetragonal basal plane is explained by the commensurability rule. Further increase of Si concentration does once more allow the $\underline{b}_{\underline{F}}$ correlation, if a smaller $\underline{b}$ electron contribution of Ca is assumed, in $CaSi_2$(R1.2), a S-homeotype of B_2Al. Pressure stabilizes the $ThSi_2$ type yielding a FB2 binding with smaller $N^{/P'}_{P''}$. It appears remarkable that the two-correlations model gives easily concepts to discuss the bonding in a mixture for which no stability argument was known before. The one or other binding proposal may be erroneous, but the model opens a first understanding for a class of substances which was since without any explanation.

For Sr_4Si_7, a L-homeotype of $ThSi_2$(S2.4, drawing [3a]p.313), the vacancies occur in accordance with the occupation rule [3], the application of pressure

TABLE 2: Binding in $A^2B^4_{\underline{M}}$ phases

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Mg2Si(CaF2,SR8.70)6.351A=bF(2)=cB(4)  N=32,96  phd H  cmp
Mg2Si.p(H,SR29.123)H7.20;8.12A
Ca7Si                                          phd H
Ca2Si(Ni2Si,SR19.84)7.667;4.799;9.002A=bC(2.5√2;2.2;3√2)=cU(5;4/1;6)  N=32,96
Ca5Si3(Cr5B3,SR40.46)7.64;14.62A=bC(√13;6.9)=cB(√26;10)  N=88,256
CaSi.h
CaSi.r(TlI,SR13.48)4.59;10.795;3.91A=bFU(√4.5;7/2;1.8)=cU(3;7;3/1) N=24,64  cmp
Ca3Si4(High-T.Sci 4.1972.192,205)
CaSi2(R1.2,SR33.51)H3.82;15.98A=bFH(√3;9/3)=cH( 3;12.5) N=30,72
CaSi2.p(ThSi2,SR32.139)4.283;13.542A=bFU(2;9/2)=cB(√8;9)  N=40,96
Sr7Si                                            phdS
Sr2Si(Ni2Si,SR42.124)8.110;5.150;9.540A=idm Ca2Si         N=32,96
Sr5Si3(Cr5B3,71Ec)8.05;15.688A=idm Ca5Si3
SrSi(TlI,SR27.348)4.83;11.33;4.04A=idm CaSi.r     N=24,64  cmp
SrSi(P10.10,SR40.77)12.98,4.89;18.03A=bF(4;1.5;5.5)=cU(8;3;13.5/1)N=120,320
Sr4Si7(htpThSi2,SR32.122)4.41;13.93A=idm CaSi2.p N=36,88
SrSi2(C4.8,SR31.63,38.145)6.535A=bFU(3;4.25)=cB(√18;4.25)  cmp N=40,96
SrSi2.p(ThSi2,SR43.42)4.438;13.83A
Ba2Si(Ni2Si,SR42.42,44.3)8.430;5.400;9.880A=idm Ca2Si  phd S
Ba5Si3(htpCr5B3,SR31.25)8.436;16.5 35A=idm Ca5Si3
BaSi(TlI,71Ec)5.028;11.929;4.131A=idm CaSi.r
Ba3Si4(T12.16,ZNaturf24b.1969.457)8.52;11.84A=bFU(√13;7)=cB(√26;7)N=88,224
BaSi2(B2Al,SR23.44)H4.39;4.83A=bFH(2;2.7/3)=cBH(2;11/3)  cmp N=10,24
BaSi2(O8.16,SR28.11)8.92;6.80;11.58A N=80,129
BaSi2.p(EuGe2,SR43.29)H4.047;5.330A
Mg2Ge(CaF2,SR3.20,13.112)6.390A=idm Mg2Si  phdH      cmp
Mg2Ge.p(H  ,SR29.118)H7.20;8.24A
Ca33Ge(F8.(o.5),SR28.14),Ca7Ge(F7.1,SR28.14) do not exist:phdM
Ca2Ge(Ni2Si,SR19.84)7.734;4.834;9.069A=idm Ca2Si  cmp
Ca5Ge3(Cr5B3,SR40.46)7.74;14.66A=idm Ca5Si3
CaGe(TlI,SR19.82)4.575;10.845;4.001A=idm CaSi.r
CaGe2(CaSi2,SR9.37)H3.957;30.776A=hdm CaSi2
Sr2Ge(   ,JLCM20.130)     phdM
Sr4Ge3(SrSi,SR40.77)13.38;4.84;18.52A=idm SrSi
SrGe(TlI,SR32.139)4.86;11,40;4.19A=idm CaSi.r  cmp
Sr3Ge4(Ta3B4,ZNaturf29B.464)
SrGe2(BaSi2,SR33.152)8.74;6.65;11.24A=idm BaSi2
SrGe2.p1(EuGe2,SR45.78)H4.104;5.165A
SrGe2.p2(SrSi2,AngChem 90.1978.562)
Ba2Ge(Ni2Si,SR39.21)8.38;5.48;10.04A=idm Ca2Si  phdM
Ba5Ge3(Cr5B3,Hul.)
BaGe(TlI,JLCM13.603)5.058;11.98;4.300A=idm CaSi.r  cmp
Ba3Ge4(Ba3Si4,Diss. J.Evers)
BaGe2(BaSi2,SR33.152)9.05;6.83;11.65A=idm BaSi2
BaGe2p(ThSi2,SR43.26)4.755;14.73A
Mg2Sn(CaF2,SR1.150,3.20,13.112)6.759A=idm Mg2Si  phd H
Mg2Sn.p(H   ,SR29.123)H13.09;13.44A
Ca3Sn(AngewChem.85.742)  phd H
Ca2Sn(Ni2Si,SR26.87)9.562;7.975;5.044A=idm Ca2Si  cmp
Ca31Sn20(Pu31Pt20,U62.40,SR43.42)12.542;40.00A=bC(√32;18)=cB(8;26) N=568,1792
CaSn(TlI,SR19.82)4.821;11.52;4.349A=idm CaSi.r
CaSn3(Cu3Au,SR3.638,15.25)4.742A=bF(3/2)=cB(3)  cmp
Sr2Sn.h  phd JLCM77.29
Sr2Sn.r(Ni2Si,SR44.3  )8.402;5.378;10.078A=idm Ca2Si  cmp
Sr5Sn3(Cr5B2,SR44.32)8.54;16.06A=idm Ca5Si3  cmp
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SrSn(TlI,71Ec)5.064;12.04;4.494A=idm CaSi.r cmp
SrSn3(R   ,JLCM77.29)H12.00;32.94A cmp
SrSn5(N   ,71Ec)M104.3°12.17;4.06;5.16A cmp
Ba2Sn(Ni2Si.SR44.3)8.648;5.691;18.588A=idm Ca2Si phd H
Ba5Sn3(Cr5B3,SR44.32)9.02;16.78A=idm Ca5Si3
BaSn(TlI,71Ec)5.316;12.55;4.657A=idm CaSi.r
BaSn3
BaSn5
Mg2Pb(CaF2,SR1.150,3.20)6.85A=idm Mg2Si
Ca2Pb(Ni2Si,SR24.84)9.647;8.072;5.100A=idm Ca2Si.r N=32,104
Ca5Pb3(htpMn5Si3,SR42.136)H9.355;7.004A=bH(4;3)=cUH(√48;6) N=44,140
CaPb(CuAu,SR42.136)5.118;4.491A=bFU(√5 ;2.75)=cU(√10;3.4) N=12,36
CaPb3(Cu3Au,SR3.174)4.901A=bFU(√5;3.2/2)=cB(√10;3.2) cmp
Sr2Pb(Ni2Si,SR44.3)8.445;5.378;10.078A=idm Ca2Si
Sr5Pb3(Cr5B3,SR44.120)8.67;15.94A=idm Ca5Si3 N=88.280]Sr5Pb4(Gd5Si4,JLCM81.1981.155)
SrPb(TlI,JLCM13.1967.60)5.018;12.23;4.648A=idm CaSi.r N=24,72
SrPb3(T1.3,SR3.639)4.965;5.035A=bU(√3.25;2.25)=cFU(√13;5.2) N=14,38
Ba2P b(Ni2Si,SR43.102)10.61;5.71;8.64A=idm Ca2Si
Ba5Pb3(Cr5B3,SR29.29)9.038;16.843A=idm Sr5Pb3
BaPb(TlI,SR29.29)5.29;12.60;4.78A=idm CaSi.r
Ba3Pb5.h
BaPb3(R3.9,SR29.30)H7.287;25.77A=bUH(3;12/2)=cBH(3;52/3) 126,342
(Ba3Pb5.r(Pu3Pd5,JLCM52.1977.211)11.148;9.049;11.368A

pushes $\underline{b}$ electrons of $SrSi_2$.p into the $\underline{c}$ correlation so that the vacancies may be filled.

$Ca_{31}Sn_{20}$($Pu_{31}Pt_{20}$,see SR43.92) is a stacking homeotype of W_5Si_3(U10.6, drawing [3a]p.305) with 7 layers; the $\underline{c}_B$ correlation is not commensurable with the subcell and fosteres therefore the supercell. $CaSn_3$(Cu_3Au) as compared with $CaSi_2$ obeys the rule that heavier compounds tend to closer packing. The tetragonal strain in the direction of minimum elastic modulus of $SrPb_3$ corresponds to the rule of Laves (increase of $|\underline{a}_3|/|\underline{a}_1|$ with increasing $\underline{b}$ electron concentration) and permits a better reproduction of the number $N_{\underline{b}}^{/C}$ of $\underline{b}$ electrons per cell. CaPb(CuAu) has a smaller axial ratio and a smaller $\underline{b}$ electron concentration than $SrPb_3$. A binding as in In [3] is not stable here as the great Sr atom requests a greater $N_{P''}^{/P'}$.

Structures which belong in some sense to the above close packings are Mg_3Pb.m(Cu_3Au,ActaMet18.1970.991) $\underline{a}=\underline{b}_{HT}$(2;2.3/2)=cHTK'(2) and also $Mg_2Pb_{1.1}$.h(Ni_2Si?,SR30.152)4.45;7.50;8.82A=idmCa_2Si.

$\underline{A^3B^4_M}$ phases. Using the tentative electron count $Sc^{1,10}Si^{4,8}_{\underline{M}}$, yields for $Sc_5Si_3(Mn_5Si_3)$ a UU2 binding, which may be compared with the BB2 binding found for brass like phases [4f]. The factorial property of the binding accounts [3d] for the fact that isotypes of Mn_5Si_3 frequently have a congruent melting point. Increase of $\underline{b}$ electron concentration leads over to the FU2 and BC2 binding, in ScSi(TlI) $\underline{c}$ must be twinned, therefore the last commensurability element has been left undetermined.

Y_5Si_4(Sm_5Ge_4,020.16,seeSR32.87) is a S-homeotype of $Ca_5Si_3(Cr_5B_3)$ with few more Si atoms in the cell; it must therefore be assumed that these phases are homeodesmic and that perhaps electron counts differing in the A components Ca and Y cause the homeodesmism. The displacive homeotypism between $\underline{a}_1\&\underline{a}_2(Y_5Si_4)$ and $\underline{a}_1\&\underline{a}_3$(YSi) is caused by the increase of the $\underline{b}$ electron concentration. Very conspicious are the structures of $YSi_{1.4}$. At temperatures above 450°C the electron count is $Y^{3,8}Si^{4,8}_{1,4}$ and a FB2 binding stabilizes the structure with randomly distributed vacancies (as compared with $ThSi_2$). At temperatures below 450°C it is reported that the Si distribution remains random, but presumably the electron count changes, i.e. several $\underline{b}$ electrons of Y enter the $\underline{c}$ correlation and cause the D-homeotypism of $YSi_{1.4}$.r as compared with $YSi_{1.4}$.h.

For the count $La^{2,9}Si^{4,8}_{\underline{M}}$ come in $La_5Si_3(Cr_5B_3)$ the electron numbers per cell $N^{/C}_{\underline{b},\underline{c}}$=88,276 being compatible with a CU$\sqrt{2}$ binding. In $La_3Si_2(U_3Si_2)$ which is homeotypic to La_5Si_3 the binding is conserved.

$ScGe_2$($ZrSi_2$,drawing [3a]p.92) is homeotypic to Cu, not to B_2Al like Sc_3Si_5 etc., as the radius ratio is nearer to 1. The UHT2 binding is homeotypic to FB2. La_4Ge_3(Th_3P_4,B6.8,drawing [3a]p.326) is homeotypic to $Na_{15}Sn_4(Cu_{15}Si_4)$ and also permits a CC2 binding. Another two-factorial isotypic binding, the BB2 binding, comes in La_5Sn_3.r(W_5Si_3,drawing [3a]p.305) which is remotely homeotypic to a NaCl structure by $\underline{a}=\underline{a}_{NaCl}(2;1)$, while La_5Sn_3.h(Mn_5Si_3) is RL-homeotypic to a W structure. Just as NaCl is less close packed than W, the BB2 binding is less close packed than the UU2 binding.

TABLE 3: A3B4M

Sc5Si3(Mn5Si3,H1o.6,SR27.341)H7.861;5.812A=bUH(√12;3/2)=cUHK'(2) N=34,148
ScSi(TlI,SR30.167)3.988;9.882;3.659A=bFU(2;7/2;1.8)=cU(√8;7;x) N=24,40
Sc3Si5(LhtpB2Al,SR28.49)H3.66;3.87A=bBH(√1.3;6/3)=cCH(2√1.3;6/3) N=75,24
Y5Si3(Mn5Si3, (SR24.147)H8.403;6.303A=idmSc5Si3
Y5Si4(Sm5Ge4,O20.16,71Ec)7.39;14.52;7.64A=bFU(√10;8.8/2)=cHT(√40;14/2) N=84,328
YSi(TlI,SR23.146)4.251;10.526;3.826A=idmScSi
YSi1.4h(ThSi2,SR23.220)4.04;13.42A=bFU(2;9.5/2)=cB(√8;9.5) N=35,77
YSi1.4r(GdSi2.r,SR23.220)4.04;3.95;13.33A=hdm h
Y3Si5.h(LhtpB2Al,SR32.140)H3.83;4.14A=idmSc3Si5
La5Si3.h(H ,71Ec)H9.75;7.06A
La5Si3.r(Cr5B3,SR30.150)7.95;14.04A=bC(√13;6.4)=cU(√26;11) N=88,276
La3Si2(U3Si2,T64,SR30.150)7.87;4.50A=bC(√13;2)=cU(√26;3.5) N=22,92
La5Si4(Zr5Si4,71Ec)8.04;15.43A=bHT(√13;8)=cU(√26;12) N=84,328
LaSi(FeB,SR30.151)8.404;4.010;6.059A=bFU(3.5;2.3/2;2.5)=cC(7;3.3;5) N=20,72
LaSi2.h(ThSi2,SR30.151)4.332;13.86A=bFU(2;9/2)=cU(√8;11) N=36,104
LaSi2.r(GdSi2.r,SR30.151)4.272;4.184;14.02A=hdm h
Sc5Ge3(Mn5Si3,SR27.341)H7.939;5.883A=idmSc5Si3
ScGe(TlI,71Ec)4.007;10.06;3.762A=idmScSi
ScGe2(ZrSi2,SR29.119)3.88;14.87;3.79A=bU(√2.5;7)=cHT(√10;14/2) N=36,120
Y5Ge3(Mn5Si3,SR24.147)H8.471;6.350A=idmSc5Si3 phdM
Y5Ge4(Sm5Ge4,71Ec)7.63;14.68;7.68A=idmY5Si4
Y11Ge10(Ho11Ge10, JLCM 26.1972.53
YGe(TlI,SR30.144)4.262;10.694;3.941A=idmScSi
Y2Ge3(B2Al,SR29.119)H3.93;4.13A=idmSc3Si5
YGe1.7
YGe2.h(ThSi2.r,SR29.119)4.060;13.683A=hdmYSi1.4.h
YGe3.5
La3Ge phdM
La5Ge3(Mn5Si3,SR27.341)H8.958;6.795A=idmSc5Si3
La4Ge3(Th3P4,71Ec)9.356A=bC(4)=cC(8)
La5Ge4(Sm5Si4,71Ec)8.06;15.47;8.17=idmY5Si4
LaGe(FeB,SR30.143)8.4 7 4;4.118;6.097A=idmLaSi
La3Ge5.h(ThSi2,SR29.118)4.33;14.23A=idmYSi1.4.h
La3Ge5.r(GdSi2,SR29.118)4.41;4.30;14.19A=hdm h
Sc5Sn3(Mn5Si3,SR30.167)H8.408;6.081A=idmSc5Si3
Y5Sn3(Mn5Si3,71Ec)H8.878;6.516A=idmSc5Si3 phdM
Y5Sn4(Sm5Ge4, JLCM 15.1968 1)
Y11Sn10(Ho11Ge10, JLCM 15.1968.1)
YSn2(ZrSi2,71Ec)4.394;16.340;4.305A=idmScGe2
YSn3
La5Sn3.h(Mn5Si3,71Ec)H.9.435;6.961A=idmSc5Si3 phdHA
La5Sn3.r(W5Si3,SR45.92)12.749;6.343A=bB(√17;2)=cBK'(2) N=68,320
La2Sn3
LaSn3(Cu3Cu,SR3.646)4.782A=bF(3/2)=cU(3;3.6)
Sc5Pb3(Mn5Si3,SR30.161)H8.467;6.158A=bFH(√12;3/3)=cFHK'(2) N=34,160
Y5Pb3(Mn5Si3,SR30.162)H8.971;6.614A=idmSc5Si3 phdM
Y5Pb4(Sm5Ge4, MonhChem 101.1971.1499
YPb2(, ibid)
YPb3(Cu3Au,SR29.129)4.814A=idmLaSn3
La5Pb3(Mn5Si3,SR30.150)H9.528;6.993A=idmSc5Si3 phdM
La5Pb4(Sm5Ge4, MonhChem 101.1971.1499)
La11Pb10.h(Ho11Ge10, ibid.)
La3Pb4.h
La3Pb4.r
LaPb2(MoSi2? ibid.)
LaPb3(Cu3Cu,SR3.646)4.903A=idmLaSn3

$A^4B^4_M$ phases. The simplest assumption on electron count is the continuation of the previous count: $Ti^{1,11}Si^{4,8}_M$. The assumption Ti^1 is compatible with the shell occupation found by atomic spectroscopy and it must generally be assumed to be somewhat dependent on $\underline{M}$ and on temperature. Ti_3Si(Ti_3P,T24,8, drawing [8b]) is closely homeotypic [8a,c] to Fe_3P(U12.4,drawing [3a]p.319) and RI-homeotypic to NaCl by $\underline{a}=\underline{a}_{NaCl}$(2;1). It permits a BB2 binding but has not a congruent melting point, this property is found for Ti_5Si_3(Mn_5Si_3) stabilized by a FF2 binding. Ti_5Si_4(Zr_5Si_4,drawing SR31.66) is homeotypic to U_3Si_3(T6.4) and homeodesmic to Ti_5Si_3 by FUHT2. TiSi(FeB,04.4,drawing[3a]p. 265) has quite different axial ratios than LaSi(FeB) and is therefore only homeodesmic to it. Also $TiSi_{1.8}$($ZrSi_2$) is not isodesmic to $ScGe_2$ as may be inferred from the Si vacancy. A quite important phenomenon emerges here: The binding FUC2 which was found by metric comparison permits only $N^{/C}_{p'}$=31 $\underline{b}$-places per cell, therefore it is probable that Ti contributes here only 0.5 $\underline{b}$ electrons per atom. Therefore with increasing $\underline{b}$ electron concentration because of increasing Si content the Ti contribution decreases, and it may also occur that for $TiSi_2$ the $\underline{b}$ electron contribution of Ti disappears (generalized Ekman rule, see [3a]) and the peripheral nobel gas shell of Ti falls perhaps out of correlation. The ÛHH$\sqrt{3}$ binding of TAB.4 is written for the hexagonal cell. This binding has been discussed earlier [9].

In $ZrSi_M$ three phases display different commensurabilites of the FF2 binding. ZrSi consists of two phases, the h(TlI) phase affords more $\underline{c}$ places than the r(FeB) phase. While the A^4Ge_M phases are mostly isotypic to A^4Si_M phases, in A^4Sn_M several new structures are found. In equilibrium with Ti_3Sn(Ni_3Sn) having a congruent melting point (HUH2 binding) is a NiAs homeotype Ti_2Sn(Ni_2In) with a FF2 binding preparing the FHUH2 binding of Ti_5Sn_3(Mn_5Si_3). Ti_6Sn_5.h(H12.10,drawing ZMetk56.483) is a RL-homeotype of Ni_2In with Sn on Ni places, a FHH2 binding finds an improved commensurability in the $\underline{a}_3$ direction as compared with Ti_5Sn_3(Mn_5Si_3). The Cr_3Si type of $Zr_{3.2}Sn$ and Zr_5Pb will be considered below.

TABLE 4: A4B4M

Ti3Si(Ti3P,T24.8,SR30.169)10.196;5.097A=bB(4;2)=cB(8;4) phdM N=56,328
Ti5Si3(Mn5Si3,SR23.238)H7.448;5.115A=bFH(√12;3/3)=cFHK'(2) N=34,158 cmp
Ti5Si4(Zr5Si4,T20.16,SR32.140)6.71;12.17A=bFU(√10;8/2)=cHT(√40;13/2) N=84,348
TiSi(FeB,SR21.172)6.544;3.638;4.997A=bFH(3;√3;3/3)=cH(6;√12;4.5) N=20,76
TiSi1.8(ZrSi2,SR20.116)3.620;13.76;3.605A=bFU(√3.2;9.6)=cC(√13;14) N=31,112
TiSi2(S2.4,SR7.12)8.253;4.783;8.540A=bÛH(√5.3;6)=cH(4;7) N=64,216
Zr3Si(Ti3P,SR30.169)11.10;5.45A=idmTi3Si phdM
Zr2Si(CuAl2,SR18.281)6.612;5.294A=bF(2;1.6)=cFK'(2) N=24,120
Zr5Si3.i(Mn5Si3,SR17.262)H7.886;5.558A=idmTi5Si3
Zr3Si2(U3Si2,SR26.11)7.082;3.715A=bFU(√10;2.3/2)=cFUK'(2) N=22,98 cmp
Zr5Si4(T20.16,SR31.65)7.122;13.000A=bFU(√10;8/2)=cHT(√40;12/2)
ZrSi.h(TlI,71Ec)3.762;9.91;3.754A=bU(√2;4.5)=cB(√8;7.5) N=18,78
ZrSi.r(FeB,SR18.280)6.982;3.786;5.302A=idmTiSi N=18,78
ZrSi2(Q2.4,SR18.280)3.721;14.68;3.683A=bFU(√3.25;10/2)=cC(√13;14) N=32,80
Hf2Si(CuAl2,SR22.135)6.48;5.21A=idmZr2Si phdM
Hf5Si3.i(Mn5Si3,SR22.135)H7.890;5.558A=idmZr5Si3.i
Hf3Si2(U3Si2,SR22.11)7.000;3.671A=idmZr3Si2
Hf5Si4(Zr5Si4,SR31.65)7.039;12.826A=idmZr5Si4
HfSi(FeB,SR22.135)6.855;3.753;5.191A=idmZrSi.r
HfSi2(ZrSi2,SR20.116)3.677;14.550;3.649A=idmZrSi2
Ti3Ge(Fe3P,SR30.144)10.29;5.14A=idmTi3Si
Ti5Ge3(Mn5Si3,SR15.72)H7.537;5.223A=idmTi5Si3
Ti6Ge5(Nb6Sn5,P ,71Ec)16.915;7.954;5.233A
TiGe(FeB,SR23.256)3.809;6.834;5.235A=idmTiSi
TiGe2(TiSi2,SR9.85)8.864;5.030;8.594A=idmTiSi2
Zr3Ge(Ti3P,SR29.119)11.08;5.48A=idmTi3Si
Zr5Ge3(Mn5Si3,SR22.95)H7.993;5.597A=idmTi5Si3
Zr3Ge2
Zr5Ge4(Zr5Si4,SR31.65)7.243;13.162A=idmTi5Si4
ZrGe(FeB,SR29.119)7.07;3.90;5.39A=idmTiSi
ZrGe2(ZrSi2,SR20.112)3.789;14.975;3.761A=idmTiSi1.8
Hf3Ge(Ti3P,SR29.119)10.92;5.42A=idmTi3Si phdE
Hf2Ge(CuAl2,SR24.143)6.587;5.372A=idmZr2Si
Hf5Ge3(Mn5Si3,SR23.146)H7.871;5.557A=idmTi5Si3 cmp
Hf3Ge2(U3Si2,SR29.118)7.08;3.59A=idmZr3Si2
Hf6Ge5
HfGe(FeB,71Ec)
HfGe2(ZrSi2,SR21.124)3.815;15.004;3.780A=idmTiSi1.8
Ti3Sn(Ni3Sn,SR16.141)H5.916;4.764A=bH(√6.75;2)=cUH(√2 7;4.7) N=14,86 phdHA
Ti2Sn(Ni2In,SR21.180)4.653;5.700A=bFH(2;3/3)=cFH(4;6/3) N=12,64
Ti5Sn3(Mn5Si3,SR15.72,13.238)H8.05;5.45A=bFH(√12;2.9/3)=cUH(√48;4.7) N=34,170
Ti6Sn5.h(H12.10,SR30.169)H9.248;5.690A=bFH(4;3/3)=cH(8;5) N=52,232
Ti6Sn5.r(P12.10,SR29.54)16.930;9.144;5.735A
Zr4Sn(T ,SR17.276)7.645;12.461A phdHA
Zr3.2Sn(Cr3Si,SR24.239)5.634A=bB(2)=cB(4) N=14,38
Zr5Sn3(Mn5Si3,SR24.239)H8.46;5.78A=idmTi5Sn3 cmp
Zr5Sn4(Ti5Ga4,H10.8,SR30.169)H8.759;5.916A=bFH(√13;3/3)=cH(√52;5) N=32,200
ZrSn2(TiSi2,SR17.277)9.573;5.644;9.927A=idmTiSi2
Hf5Sn3(Mn5Si3,SR26.164)H8.391;5.823A=idmTi5Sn3 phdM cmp
Hf5Sn4(Ti5Ga4,SR30.145)H8.695;5.875A=idmZr5Sn4
HfSn2(CrSi2,SR24.21)H5.487;7.625A=bFH(√5.3;4/3)=cH(4;5.6)
Ti4Pb(Ni3Sn,SR15.91)H5.985;4.846A=idmTi3Sn
Ti5Pb3(Mn5Si3,71Ec)
Zr5Pb(Cr3Si,71Ec)
Zr5Pb3(Mn5Si3,SR23.238)H8.528;5.862A=idmTi5Sn3

$\underline{A^5B^4_M}$ phases. The electron count $V^{1,4}Si^{4,8}_{\underline{M}}$ would yield BC2 for $V_3Si(Cr_3Si)$, a RC-homeotype of NaCl, but it should be noted that with the count $V^{1,12}Si^{4,8}_{\underline{M}}$ this binding could also be described as BB2 binding. A temperature dependent $\underline{b}$ electron contribution of the V atoms may cause a change in $\underline{b}$ and therefore the D-homeotypism of V_3Si.l. Perhaps the superconductivity is here not in the $\underline{b}$ correlation but in the $\underline{c}$ correlation, the reported charge transfer from Si to V ([2f]p.337) is compatible with the present interpretation. Increase in $\underline{b}$ electron concentration leads to a changed commensurability of the $\underline{b}_B$ correlation in V_5Si_3.h(W_5Si_3); the phase La_5Sn_3.r(W_5Si_3) had a BB2 binding in the same commensurability. V_6Si_5($Nb_2Cr_4Si_4$,P4.8.10,SR33.64) is hometypic to W_5Si_3 and Mn_5Si_3 but shall be postponed. The phase VSi_2($CrSi_2$,H3.6,drawing [3a]p.313) is S-homeotypic to $TiSi_2$ and therefore homeodesmic to it, the electron count is here $V^{0,13}Si_2^{4,8}$ so that it obeys the Ekman rule [see 3a].

Nb_3Si.h(Ti_3P) is RI-homeotypic to NaCl like $V_3Si(Cr_3Si)$ and it permits the same BB2 binding in a different commensurability (see TABLE 5). It is easy to see that the root indicates that a rotation in the commensurability has been dropped [3d], this rotation is pictured in the rotation of atom groups relative to the cell $\underline{a}$ (see for instance [3a]p.319). An increase of $\underline{b}$ electron concentration, which is the cause for a root containing commensurability, is therefore also the cause for the rotation of atom groups. However, rotation of atom groups as in $CuAl_2$ may also be a mechanism for decrease of $\underline{a}_3$ without the support of a commensurability containing a root. The FHUH2 binding of V_5Ge_3.r(Mn_5Si_3) gives the number of $\underline{b}$ places per cell $N^{/C}_{P'}=39$ which permits a count near $V_5^{1,12}Ge_3^{4,10}$. The fact that $Nb_{10}Ge_7$ is a F-homeotype of Mn_5Si_3, appears to confirm this $\underline{b}$ correlation. In $V_{17}Ge_{31}$(T68.124) a phase with defect dicilicide type of structure appears which has been discussed earlier [9]. The binding is no more of the two-factorial FB2 type which has been found in Ge, but the simple commensurability is lost in one direction only. As the $\underline{b}$ electron concentration is increased from V_5Ge_3.r to $V_{17}Ge_{31}$, the number of $\underline{c}$ electron places per $\underline{b}$ electron place $N^{/P'}_{P''}$ must decrease. In fact for V_5Ge_3.r $N^{/P'}_{P''}=7.5$ while for $V_{17}Ge_{31}$ $N^{/P'}_{P''}=4.9$ and for VSi_2 $N^{/P'}_{P''}=4.3$. The T68.124 structure is preferred in $V_{17}Ge_{31}$ to the $CrSi_2$ structure, as it affords more $\underline{c}$ places per cell. In $NbGe_2(CrSi_2)$ and $TaGe_2(CrSi_2)$ the hexagonal type reappears as the heavier compounds endure higher occupation. The phase $NbSn_2$(Mg_2Cu,S4.8,drawing [3a]p.288) is quasi hexagonal and homeotypic to $CuAl_2$, the interpretation HH$\sqrt{3}$ could also be HBH1.

TABLE 5: A5B4M

V3Si(Cr3Si,SR16.137,30.231)4.725A=bB(2)=cB(4) N=14,88 phdM
V3Si.1(DhtpCr3Si,SR31.64)4.715;4.275A
V5Si3.h(W5Si3,U10.6,SR19.278)9.429;4.757A=bB(√17;2)=cFU(√68;6/ 2) N=68,336
V5Si3.r(Cr5B3,DoklAN 209.1973.1347)
V6Si5(Nb2Cr4Si5,SR38.101)15.966;7.501;4.858A
VSi2(CrSi2,H3.6,SR8.102)H4.571;6.372A=bFH(√5.3;4/3)=cH(4;5.7) N=24,87
Nb3Si(Cr3Si,JLCM61.1978.213)
Nb3Si.h(Ti3P,T24.8,SR30.157)10.23;5.19A=bB(√17;2)=cBK'(2) N=56,152 phdM
Nb5Si3.h(W5Si3,SR19.278)10.018;5.072A=idmV5Si3.h
Nb5Si3.r(Cr5B3,SR19.279)6.570;11.884A=bHT(√10;6.6)=cU(√20;10) N=68,336
NbSi2(CrSi2,SR8.102,38.98)H4.819;6.592=idmVSi2
Ta4Si(Ti3P,SR30.168)10.193;5.175A=idmNb3Si.h phdHA
Ta2Si(CuAl2,SR17.259)6.157;5.039A=bC(3;2.5)=cU(√18;4) N=24,128
Ta5Si3.h(W5Si3,SR19.278)9.88;5.06A=idmV5Si3.h
Ta5Si3.r(Cr5B3,SR19.279)6.516;11.873A=idmNb5Si3.r
TaSi2(CrSi2,SR23.236)H4.782;6.569A=idmVSi2
V3Ge(Cr3Si,SR9.47)4.623A=idmV3Si phdM
V3Ge.1(DhtpCr3Si,71Ec)seeV3Si.1
V5Ge3.h(W5Si3,71Ec)9.57;4.84A=idmV5Si3.h N=68,360 cmp
V5Ge3.r(Mn5Si3,SR22.129)H7.294;4.970A=bFH(√13;3/3)=cUH(√52;5.6/2) N=34,180
V11Ge8(Cr11Ge8,SR29.119)13.41;16.09;5.02A
V17Ge31(T68.124,SR32.74)5.91;83.65A=bF(2;56.5/2)=cU(4;68) N=496,2124
Nb4Ge(Cr3Si,SR20.108)5.168A=idmV3Si phdM
Nb3Ge(Ti3P,SR46.130)
Nb5Ge3(W5Si3,SR20.109)10.148;5.152A=idm V5Si3.h
Nb10Ge7(FhtpMn5Si3,SR37.91)7.783;5.390A=bFH(√13;3/3)=cFH(√39;4) N=38,110
NbGe2(CrSi2,SR9.85)H4.967;6.784A=idm VSi2
Ta3Ge.h(Fe3P,SR30.144)10.36;5.16A=hdm Nb3Si.h
Ta3Ge.r(Ti3P,SR30.143)10.28;5.22A=idm Nb3Si.h
Ta3Ge.i(Cr3Si,JapplPhys41.1970.4958)
Ta5Ge3.h(W5Si3,SR20.109)10.010;5.150A=idm V5Si3.h
Ta5Ge3.r(Cr5B3,SR20.110)6.599;12.010A=idm Nb5Si3.r
TaGe2(CrSi2,SR9.85)H4.958;6.751A=idm VSi2
V3Sn(Cr3Si,SR19.243)4.94A=idm V3Si phdM
V3Sn(Ni3Sn,SR38.150)H5.694;4.555A=bH(√7;2.1)=cHK'(2) N=14,92
V2Sn3.h
Nb3Sn.h(Cr3Si,SR29.126)5.289A=idm V3Si phdS
Nb3Sn.m(DhtpCr3Si,71Ec)5.298;5.252A=idm V3Si.1
Nb6Sn5.h(P12.10,SR30.157)16.814;9.206;5.655A
Nb6Sn5.r(Ti6Sn5.r,SR30.157)H9.38;5.65A
NbSn2(Mg2Cu,S4.8,SR30.157)9.860;5.648;19.127A=bH(√7;9)=cH(√21;16) N=128,528
Ta3Sn(Cr3Si,SR19.243)5.276A=idm V3Si
Ta2Sn3(Mg2Cu,SR38.149)5.628;9.801;19.177A=idm NbSn2
V3Pb(Cr3Si,SR28.48)4.937A=idm V3Si
Nb3Pb(Cr3Si,SR28.48)5.270A=idm V3Si

TABLE 6: A6B4$\underline{M}$

Cr3Si(C6.2,SR3.628)4.57A=bB(2)=cB(4) N=14,94 phdM cmp
Cr5Si3.h(W5Si3,SR20.78)9.170;4.636A=bB(√17;2)=cFU(√17;6/2) N=68,356 cmp
Cr5Si3.r N=16,88
CrSi(FeSi,SR3.628)4.629A=bB(2)=cFU(4;5.6/2)orH6.55;8.02A=bH(√12;4.2)=cH(6;7.4)
CrSi2(H3.6,SR3.628)H4.43;6.37A=bFH(√5.3;4/3)=cH(4;5.7) N=24,66 cmp
Mo3Si(Cr3Si,SR16.117)4.890A=idm Cr3Si phdHA
Mo5Si3.h(W5Si3,SR19.278)9.62;4.90A=idm Cr5Si3.h
Mo5Si3.r(Cr5B3,ChemAbstr 73.1970.92056)
MoSi2.h(U1.2,SR1.783)3.203;7.855A→H4.53;4.53A=bFH(√5.3;2.8)=cH(4;4) N=8,40
MoSi2.r(CrSi2,SR30.154)H4.605;6.559A=idm CrSi2
W3Si(Cr3Si,SR23.239)4.910A=idm Cr3Si phdE
W5Si3(U10.6,SR20.155)9.605;4.964A=idm Cr5Si3.h
WSi2(MoSi2.h,SR1.219)3.212;7.835A=idm MoSi2
Cr3Ge(Cr3Si,SR9.47)4.768A=idm Cr3Si N=14,98 phdM
Cr5Ge3(W5Si3,SR22.95)9.413;4.780A=bB(4;2)=cFU(8;5.6/2)
Cr11Ge8(044.32,SR29.111)13.15;15.75;4.94A
CrGe(FeSi,SR9.48,39.45)4.790A=idm CrSi
Cr11Ge19(Mn11Si19,SR32.70)5.80;52.34A=bF(2;36/2)=cU(4;44) N=304,1024
Mo3Ge(Cr3Si,SR16.94)4.933A=idm Cr3Si phdS
Mo5Ge3(W5Si3,71Ec)9.84;4.97A=idm Cr5Si3
Mo13Ge23(T52.92,SR32.72)5.987;63.54A=bF(2;42/2)=cU(4;52)
Mo9Ge16(U18.32,71Ec)5.994;43.995A=bF(2;29/2)=cU(4;36)
MoGe2.h(MoSi2,SR17.173)3.313;8.195=idm MoSi2
MoGe2.r(Ni2Si,SR30.21)6.343;8.582;3.451A=bFU(3;4;2.7/2)=cU(3√2;4√2;2.8)
W5Ge3(W5Si3,Hul.) phdM
W5Ge3.p(Cr5B3,Inorg Mat 14.1978.533)
WGe2.p(MoSi2,Hul.)
CrSnM nic phdM
Mo3Sn.p(Cr3Si,SR29.124)5.094A=idm Cr3Si
WSnM nic phdHA
CrPbM nic phdHA
MoPbM nic phdS
WPbM nic phdHA

$\underline{A^6B^4_M}$ phases. CrSi(FeSi,C4.4,drawing [3a]p.308) is a I-homeotype of NaCl like Cr_3Si(C6.2). The $\underline{b}$ correlation was found first [10a], the approximate $\underline{c}$ correlation later [10b], and that these correlations coexist somehow was assumed last [10c], however, a somewhat different $\underline{c}$ correlation must be assumed to account for a curious neighboured phase of PdGa[11], see TABLE 6. This example illustrates the difficulty to find the correct binding. The change of electron count in $CrSi_{\underline{M}}$ should be appreciated. In the mixture $MoSi_{\underline{M}}$ the simple $MoSi_2$(U1.2,drawing [3a]p.313) emerges, the $\underline{b}$ correlation is perhaps somewhat compressed in its trigonal axis, for the $Mn_{11}Si_{19}$ homeotypes see [9], these structures are very elucidating examples for the fact of partial incommensurability of $\underline{b}$ and $\underline{c}$ correlation.

$A^7B^4_{\underline{M}}$ phases. Although in Cr Hund insertion is possible, structural consequences of this phenomenon, except for Cr.r(SR23.113) were not visible in $CrB^4_{\underline{M}}$ phases, also in Mn.r(B29) the clustering of atoms is an indication for Hund insertion [3]. In $MnSi_{\underline{M}}$ because of the electron count $Mn^{1,14}Si^{4,8}_{\underline{M}}$ Hund insertion is to be expected and the first two phases Mn_6Si and $Mn_{76}Si_{17}$ would be good examples to investigate the phenomenon. However, in the present analysis these phases shall be postponed as the great cells cause a less certain analysis. The FF2 binding of $Mn_3Si(Fe_3Si$ type) continues the BB2 binding of Cr_3Si and its homologues. This latter type and its homeotypes are no more stable probably as there are too many $\underline{c}$ electrons ($Mn^{1,14}$) to occupy a $\underline{c}_B$ correlation. $Tc_3Si(Cu_5Zn_8)$ appears to display Bradley partial occupation (see [3a]), the explanation is the same as for NiAl. For $Mn_{3.25}Ge(Ni_3Sn$,drawing [3a] p.114) the homeotypism to $Mn_3Si(Fe_3Si)$ should be appreciated (compare $(110)_{Mn_3Si}$ with $(001)_{Mn_3Ge}$). A satisfactory commensurability of a HH2 or UU2 binding is found with more $\underline{c}$ places per atom than in Mn_3Si, the shift of the homogeneity range to smaller Ge contents may be understood as an improvement of the $\underline{c}$ occupation. The magnetic properties of $MnGe_{\underline{M}}$ phases (SR26.151) signalize Hund insertion and the more complicated strucutres of that mixture may serve to enter this interesting problem.

In $Mn_2Sn(Ni_2In)$ a F-homeotype of NiAs emerges, it permits a FHUH2 binding. It should be noted that Mn_5Si_3 is also a homeotype of NiAs or Ni_2In, but it has not a $\underline{c}_{UH}$ correlation, probably the $\underline{c}_H$ correlation in Mn_5Si_3 favours the specific ordering of vacancies. With respect to the FB2 binding in Sn it is satisfactory that also $MnSn_2(CuAl_2$,U2.4,drawing [3a]p.299) aRLDI-homeotype of W, permits a FU2 binding. As compared with $CoSi_2(CaF_2)$ the phase $MnSn_2$ is closer packed, conforming to the closer packing of heavier compounds. The homeotypism of $Mn_{11}Si_{19}$ to $MnSn_2$ is enlighteningly explained by the different commensurability of the FU2 binding.

TABLE 7: A7B4M

Mn6Si(R15.3,SR29.124)H10.874;19.177A phdM
Mn81.5Si 18.5(P152.34,SR39.111)16.992;28.634;4.656A
Mn3Si(Fe3Si,SR24.78)5.722A=bF(2)=cF(4) N=32,200
Mn5Si2(T40.16,SR29.124)8.910;8.716A=bHT(√20;5/2)=cHTK'(2) N=104,688
Mn5Si3(H10.6,SR4.24)H6.91;4.81A=bFH(√12;3/3)=cH(√48;5) N=34,188
MnSi(FeSi,SR3.628)4.558A→H6.45;7.89A=bBH(2;12/3)=cBH(√12;20/3) N=16,60
Mn11Si19(T44.76,SR29.64)5.52;48.2A=bF(2;√38/2)=cU(4;44) N=304,916
Mn26Si45(T104.180,SR)5.515;113.36A=hdm Mn11Si19
Mn15Si26(U30.52,SR32.99)5.525;65.55A=hdm Mn11Si19
Mn27Si47(T108.188,SR39.83)5.530;117.94A=hdm Mn11Si19
Mn4Si7(T16.28,SR34.101)5.506;17.522A=hdm Mn11Si19
Tc4Si(W,SR30.168)3.009A=hdm Mn3Si
Tc3Si(Cu5Zn8,SR30.168)9.014A=hdm Mn3Si
Tc5Si3(W5Si3,SR30.168)9.403;4.849A=idm Cr5Si3
TcSi(FeSi,SR30.168)4.755A=idm MnSi
Tc4Si7(htpMn11Si19,71Ec)5.737;18.099A=hdm Mn11Si19
Re5Si3(M15.9,SR45.107)M94.203°6.451;9.601;5.394A phdE
ReSi(FeSi,SR23.224)4.774A=idm MnSi
ReSi1.8(DhtpMoSi2,SR23.224,7.Eur.Cryst.Meet1982)3.131;7.676A=idm MoSi2
Mn3.25Ge.h(Ni3Sn,SR12.95)H5.347;4.374A=bH(√6.75;2.1/3)=cHK'(2) N=14,104
Mn3.25Ge.r(In,SR26.150)3.803;3.618A
Mn5Ge2.h(,SR26.150)H7.186;13.08A
Mn5Ge2.r
Mn5Ge3(Mn5Si3,SR17.171)H7.185;5.053A=idm Mn5Si3
Mn11Ge8(Cr11Ge8,SR29.118)13.22;15.83;5.09A
TcGeM
Re4Ge7.p(Tc4Si7,JLCM84.1982.87)5.895;18.86A
ReGe2(Hul.,7.Eur.Cryst.Meet1982) phdM
Mn7Sn.m(In,Moffatt) phdM
Mn3.5Sn(Ni3Sn,SR10.72)H5.661;4.515A=idm Mn3.25Ge
Mn2Sn(Ni2In,SR10.72,26.193)H4.39;5.52A=bFH(2;3.1/3)=cUH(4;6) N=12,76
Mn1.8Sn.r(htpNi2In,SR26.193)H13.194;5.516A
MnSn2(CuAl2,SR10.73)6.660;5.445A=bFU(3;3.5/2)=cU(√18;4.3) N=32,140
TcSnM
ReSnM nic phdM
MnPbM nic phdE
TcPbM
RePbM

$A^8B^4_M$ phases. In Fe_3Si(F3.1,drawing [3a] p.127,229), the Si atoms substitute in a most uniform distribution some Fe atoms of Fe.r. The strong increase of b-or valence-electron concentration $N_b^{/A}$ causes the BB2 binding of Fe.r 22 to be changed into a FF2 binding. It should be noted that Fe_3Si is not isodesmic to CuZn which has a BB2 binding [4f]. With respect to the favourable b_F correlation of Fe_3Si it appears reasonable that the Si do not disorder with increasing temperature. The reported transformation of Fe_3Si may be caused by the transition FF2-HTFU2, which does not introduce a structural change.

. If in Fe_3Si the Si mole fraction N'_{Si} is increased the b electron concentration is increased and the c electron concentration decreased so that in Fe_2Si.h a FHUH2 binding becomes stable. Considering the b electron contribution by Fe to be temperature dependent, it is gratifying that this phase decomposes eutectoidally and that a quenched phase Fe_2Si.m exists which is cubic and fits to HTFU2. A favourable binding can be conserved when the Bradley mechanism [see 3] of vacancy formation in the partial structure of the component with small b electron contribution is used. The ordering of the Mn_5Si_3 type is preferred to the ordering of the partly filled NiAs phases (Fe_2Ge e.g.) because of the occupation of the FHH2 binding. FeSi(C4.4) is homeotypic to NiAs [3a,p.331] or Ni_2In and it has 0.66 vacancies per Ni_2In cell, as compared to the filled Ni_2In, like Fe_5Si_3. It appears that Fe has here the b contribution 0 (extended Ekman rule, see [3a]) the number of b electrons per Ni_2In cell is therefore 5.3x2=10.6 while Fe_5Si_3 had 12 as judged from the binding. This permits the b_B binding of FeSi with $N_{P'}^{/Si}=4$ b places per Si atom. In the case $Fe^{0,16}$, vacancy formation of the atoms is easy for increasing $N_b^{/A}$ so that the L-homeotype $FeSi_2$.h of CsCl with FU2 binding becomes favourable, the little contraction in the a_3 direction decreases $N_{P''}^{/C}$ somewhat ($N_{P''}^{/C}$= number of c places per cell). The phase $FeSi_2$.r (Q8.16,drawing SR35.85) has also the FU2 binding. The c commensurability element $K''_{33}=4.7$ of h falls into 4.5 and this requires $K''_{11}=\sqrt{34}$ instead of $\sqrt{32}$. It may be that electron absorption at Fe has also some influence on the structure. While Fe_3Si is a R-homeotype of W, and Fe_5Si_3 a RL-homeotype of W, the phases Ru_2Si(Ni_2Si) and Ru_5Si_3(Rh_5Ge_3) and Ru_4Si_3(O16.12) are homeotypic to Cu, thus conforming to the rule that heavier phases belong to closer packing. The Cu substructure is in Ru_2Si markedly strained in the a_2(Ru_2Si) direction in order to give place to the b_U correlation which is part of a UB2 binding. An important feature is here the great difference in b electron

TABLE 8: A8B4M

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Fe3Si(F3.1,SR10.61)5.655A=bF(2)=cF(4)  N=28,212
Fe2Si.h(Ni2In,SR44.76)H4.052;5.085A=bFH(2;3.05/3)=cUH(4;58/2)  N=12,76
Fe2Si.m(C1.1,SR40.82)2.81A=bHT(√2;1.6)=cF(2)
Fe5Si3(Mn5Si3,SR10.63)H6.755;4.717A=bFH(√12;3/3)=cH(√48;4.8)  N=34,198
FeSi(C4.4,SR8.89)4.488A→H6.35;7.77A=bBH(2;12/3)=cH(6;7.3)  N=16,92
FeSi2.h(T1.2,SR23.169)2.69;5.14A=bF(1;2)=cU(2;4.7)  N=8,32
FeSi2.r(Q8.16,SR37.101)7.8,7.83;9.86A=bFU(√17;7.5/2)=cU(√34;9)  N=28,512        phdM
Ru2Si(Ni2Si,O8.4,SR26.243)5.279;4.005;7.418A=bU(2;2/1;3)=cB(4;3.2;5.6) N=24,152
Ru5Si3(Rh5Ge3,O10.6,SR35.123)5.246;9.815;4.023A=bU(2;4;2/1)=cB(4;8;3)  N=34,118
Ru4Si3(O16.12,SR34.125)5.194;4.022;17.134A=bU(2;2/1;7)=cB(4;3;14)
Ru1.1Si(CsCl,SR21.169)2.909A=bF(1)=cC(√8;2.8)
Ru0.9Si(FeSi,SR21.169)4.703A=idm FeSi
Ru2Si3(O16.24,SR40.75)11.06;8.94;5.53A
RuSi2(OsGe2?,Hul.)
OsSi(FeSi,SR21.161)4.729A=idm FeSi
OsSi.i(CsCl,SR27.372)2.960A=idm RuSi(CsCl)
Os2Si3(Ru2Si3,SR27.372)11.158;8.962;5.58A
OsSi2(FeSi2.r,Q8.16,SR35.84)10.150;8.117;8.223A=idm FeSi2.r
OsSi3(    ,SR27.372,not found 35.84)
Fe13Ge3(C13.3,SR27.209)5.763A=bF(2)=cF(4)  N=32,225
Fe3Ge.h2(Ni3Sn,SR27.210)H5.17;4.22A=bFH(√6.75;2.5)=cUH(√27;5/2)  N=14,110
Fe3Ge.h1(Cu3Au,SR28.46)3.665A=bU(√2;1.75)=cB(√8;2.8)
Fe1.7Ge(FhtpNiAs,SR27.210)H3.985;4.984A=bFH(2;3/3)=cH(4;5)  N=12,80
Fe12Ge9(H13.8,JLCM75.155)H7.976;4.993A=bH(4;2.5)=cFH(√48;5.3/3)  N=48,270
Fe6Ge5(N12.10,SR39.64)M109.66°9.965;7.826;7.801A
FeGe.h2(CoGe,SR32.82)11.51;3.94;-2.76,0,4.93A=bFHO(6.6/2;2;3/3),FHFH/3  N=40,136
FeGe.h1(CoSn,SR28.46)H5.000;4.054A→4.05;8.66;5.00A=bUHO(2;5/2;2.9/2)  N=15,51
FeGe.r(FeSi,SR32.82)4.700=idm FeSi BHH3
FeGe2(CuAl2,SR27.210)5.908;4.955A=bFU(3;3.5)=cU(√18;4.4)
RuGe(FeSi,SR27.214)4.846A=idm FeSi  phdS
Ru2Ge3.h(Ru2Sn3,JLCM40 1975.139)
Ru2Ge3.r(Ru2Si3,SR40.75)11.44;9.24;5.72A
RuGe2(OsGe2?,Hul.)
Os2Ge3(Ru2Si3,SR40.109)
OsGe2(N2.4,SR24.144)M119.17°8.995;3.094;7.685A
Fe3Sn.h(Ni3Sn.SR11.147)H5.458;4.361A=idm Fe3Ge.h2 HBH1  phdHA
Fe3.3Sn2.h(FhtpNiAs,SR11.148)H4.231;5.208A=idm Fe2Ge
Fe3Sn2.h(R6.4,SR42.103)H5.344;19.845A
FeSn(CoSn,SR11.149)H5.298;4.446A→5.30;4.45;9.19A=bH(2.5/1;√4.3)=cUH(5/2;√13)
FeSn2(CuAl2,SR24.168)6.502;5.315A=idm FeGe2
Ru2Sn3(T8.12,SR29.85)6.172;9.915A=bF(2;3.2)=cU(4;8)
RuSn2(CuAl2,SR29.130)6.389;5.693A=bFU(√8.5;3.6/2)=cU(√17;4.4)
Ru3Sn7(B6.14,SR11.136)9.360A=bF(3)=cU(6;7)
OsSnM nic   phdHA
FePbM nic   phdE
RuPbM nic   phdHA
OsPbM
```

contribution of A^8 and B^4 atoms, one and four, it results in the curious fact that the B-B distance is strongly increased relative to the A-B distance, and this imposes a heavy inhomogeneous deformation on the cell making it not obvious to recognize the homeotypism to Cu. The $\underline{b}$ electron concentration $N_{\underline{b}}^{/A}=2$ could be correlated in the form $\underline{a}_{Cu}=\underline{b}_C(2)$, however, the $\underline{b}_U$ correlation chosen here is closer packed than the $\underline{b}_C$ correlation. The phase Ru_2Si_3 is closely homeotypic to Ru_2Sn_3(T8.12,$Mn_{11}Si_{19}$ family) to be discussed below.

$Fe_{13}Ge_3$(C13.3) is homeotypic to Fe_3Si and also isodesmic, the FF2 binding is reached here for lower B^4 content than in Fe_3Si, probably as the $\underline{c}$ electron contribution of Ge causes a greater $\underline{b}$ electron contribution of Fe. In $Fe_3Ge.h_2(Ni_3Sn)$ the number of $\underline{c}$ places per $\underline{b}$ place $N_{P''}^{/P'}$ is decreased by a FHUH2 binding. Also the UB2 binding of $Fe_3Ge.h_1(Cu_3Au)$ has a smaller $N_{P''}^{/P'}$ value. It is probably caused by thermal agitation that the value $N_{P''}^{/P'}=6.5$ of h_1 is smaller than that of h_2 which amounts to 7.5. The good fit of the FHH2 binding in $Fe_{1.7}Ge$(NiAs) is rewarded by a congruent melting point. $Fe_{1.7}Ge$ has its vacancies as compared with Ni_2In not in the FeFe chains along $\underline{a}_3$ like $Fe_5Si_3(Mn_5Si_3)$ but in the FeGe chains. $Fe_{11.5}Ge_{8.9}$(LhtpFe_2Ge), briefly named $Fe_{12}Ge_9$, has [12] two fixed vacancies in FeGe chains and one distributed vacancy in the remaining FeGe chains, it has four Fe less and one Ge more than "Fe_2Ge" has in the comparable cell $\underline{a}=\underline{a}_{"Fe2Ge"}(2;1)$, it is not isodesmic to $Fe_{1.7}Ge$. The phases Fe_6Ge_5,$FeGe.h_2$ and $FeGe.h_1$ are RLC-homeotypic to "Fe_2Ge". In $FeGe.h_2$(CoGe,drawing [3a]p.311) the chains are along $\underline{a}_3$. When the homeotypism from "Fe_2Ge" to $FeGe.h_2$ consisted in pure Fe-vacancy formation, then a NiAs type would be formed. But as already may be seen in $Fe_{12}Ge_9$ besides Fe vacancy formation there is also Ge substitution for Fe (anomalous substitution), i.e. there are to be expected FeFe-, FeGe- and GeL-chains (L=lacuna). Considering the cell $\underline{a}_Q=\underline{a}_{Fe2Ge}(1,-1,0;1,1,0;0,0,1)$ along $\underline{a}_{Q=1}$ we find in "Fe_2Ge" just 6 chains $(FeFe,FeGe,FeGe)^2$. In $FeGe.h_2$(CoGe) viewing along $\underline{a}_2$ ($FeGe.h_2$) we find $(FeFe,GeL,FeGe,FeGe,GeL)^2$. Several homeotypes of this structure family have been drawn in [13]. In $FeGe.h_1$(CoSn,drawing [3a]p.310) the viewing direction is $\underline{a}_3$ and the chain direction may be taken as $\underline{a}_1+\underline{a}_2$, then the sequence of chains is $(FeGe,GeL,FeFe,GeL)^2$, so that the number of FeGe chains has decreased by one as compared with h_2. In TABLE 8 the $\underline{b}$ correlations for $FeGe.h_2$ and $FeGe.h_1$ are given, they may be supplemented to a XHFH$\sqrt{3}$ binding. It is therefore seen that these phases permit the same commensurability in the basal plane. As the chain shear is the outstanding homeotypism within the above structure family the structures may be named RFC-homeotypes of NiAs.

$OsGe_2$(N2.4,drawing SR30.16) is homeotypic to $NbAs_2$(SR30.14). It may be postponed here.

The $FeSn_{\underline{M}}$ phases are mostly isotypic to $FeGe_{\underline{M}}$ phases, and the frequency of the $\underline{b}_F$ correlation indicates how favourable it is. The phase Fe_3Sn_2(R6.4) is a S-homeotype of FeSn(CoSn) and therefore also a RFC-homeotype of NiAs. Another S-homeotype of the CoSn type is Pt_3Tl_2(SR33.127).

Ru_2Sn_3(T8.12) is homeotypic to $Mn_{11}Si_{19}$ and has therefore a FU2 binding. In $RuSn_2(CuAl_2)$ the $\underline{c}_U$ correlation of Ru_2Sn_3 has a slightly different commensuralibity. The high axial ratio as compared with FeSn has probably to do with the advantage of the commensurability element $K''_{33} \approx 4.5$. In Ru_3Sn_7 (B6.14,drawing [3a] p.318) a RL-homeotype of W, the Ekman rule is nearly obeyed. See for these mixtures also [14].

$A^9B^4_{\underline{M}}$ phases. For the phase Co_3Si.h a Fe_3Si structure might be possible as to be inferred from measurements on quenched $CoSi_{\underline{M}}Sn_M$ alloys [15], the phase therefore is isodesmic to Fe_3Si. Like as in Ru_2Si a RDI-homeotype of Cu becomes stable in Co_2Si.r and the phases are isodesmic or homeodesmic. In CoSi(FeSi) a $\underline{c}_F$ or $\underline{c}_{UH}$ correlation must be assumed which is the cause that NiSi is heterotypic to CoSi. $CoSi_2(CaF_2)$ is L-homeotypic to CsCl, Ekmans rule is fulfilled and the phase is isodesmic to $FeSi_2$, the greater $\underline{c}$ electron offer of $CoSi_2$ as compared with $FeSi_2$ causes the cubic symmetry by binding twinning.

The UU2 binding of $Rh_2Si(Ni_2Si)$ and $Rh_5Si_3(Rh_5Ge_3)$ has a quite simple coomensurability to the substructure and this has a stabilizing effect. The phase $Rh_{20}Si_{13}$(H20.13,drawingSR30.90) may be considered as a S-homeotype of Mg or of CsCl (which has in (110) a quasi hexagonal plane) and further homeotypes are Fe_2P and Th_7S_{12} and also $Pd_{12}Ga_2Ge_5$ [16]. The assumed FHUH2 binding is a follower of the UU2 binding; the good commensurability of the $\underline{c}$ correlation stabilizes the Mg related stacking by the commensurability rule. The FHH2 binding of $Rh_{2.8}Si_2$(NiAs) is in good commensurability with the cell $\underline{a}$ so that it serves a starting point for the exploration of the MnP type of RhSi.h which occurs according to the diagram [3a] p.328 in $AB^4_{\underline{M}}$ alloys here for the first time. It is a DI-homeotype of NiAs and the set of representatives is composed of a long and a short subtype [3a,p.330]. The comparison of $\underline{a}_1(Rh_{2.8}Si_2)$ with $\underline{a}_2$(RhSi.h) and of $\underline{a}_3(Rh_{2.8}Si_2)$ with $\underline{a}_1$ (RhSi.h) indicates that a serious change in the commensurability of the FHH2 binding to the crystal must have taken place. The very small $\underline{d}_t = 0.98$Å indicates that the basal commensurability of FHH2 is exhausted. The next commensurability is $\sqrt{3}$ and this decrease will loosen the stacking density of $\underline{b}$,

TABLE 9: A9B4M

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Co3Si.h(W   ,Z.Metk71.456)2.8A=bF(1)=cF(2)  phdHA
Co2Si.h
Co2Si.r(Ni2Si,SR22.94)4.908;3.730;7.095A=bU(2.1;2/1;3)=cU(4.2;4/1;6)  N=24,160
CoSi(FeSi,SR3.14)4.445A→H6.29;7.69A=bBH(2;12/3)=cFH(6;9/3)  N=16,100
Co2Si3.p(Ru2Sn3,JLCM84.1982.87)5.234;8.543A=idm Ru2Sn3
CoSi2(CaF2,SR13.90)5.367A=bF(2)=cU(4.5)  N=32,132
Rh2Si(Ni2Si,SR23.57)5.408;3.930;7.383A=bU(2.2;2/1;3)=cU(4.4;4;6)  N=24,160
Rh5Si3(Rh5Ge3,SR23.113)5.317;10.131;3.895A=bU(2.1;4;2/1)=cU(4.2;8;4)
Rh20Si13(H20.13,SR30.88)H11.851;3.623A=bFH(6;2.2)=cUH(12;4/2)  N=72,424
Rh2.8Si2(FhtpNiAs,SR24.113)H3.949;5.047A=bFH(2;3/3)=c H(4;5)  N=11,61
RhSi.h(MnP.1,SR24.113)5.531;3.068;6.362A=bH(3;√3;3.5)=cUH(6/2;3;7)  N=16,100
RhSi.r(FeSi,SR18.271)4.675A=idm CoSi
Rh4Si5(M8.10,SR33.137)M100.18°12.335;3.508;5.924A                  N=64,332
Rh3Si4(012.16,SR33.136)18.810;3.614;5.813A=bBH(30/3;√1.33;1.85)=cH(18/1;√12;5.5)
Ir3Si(U6.2,SR24.113)5.222;7.954A=bU(√4.25;3.8)=cU(√17;7.7)  N=28,224
Ir2Si(Ni2Si(Ni2Si,SR24.114)5.284;3.989;7.615A=bU(2;2/1;3)=cB(4;3;6)
Ir3Si2.h(FhtpNiAs,SR24.114)H3.968;5.126A=idm Rh2.8Si2
IrSi(MnP.1,SR21.136)5.558;3.211;6.273A=idm RhSi.h  N=16,
Ir4Si5(Rh4Si5,SR35.120)M
Ir3Si4(Rh3Si4,SR35.70)18.870;3.697;5.774A=idm Rh3Si4
Ir2Si3(M   ,SR35.120)M
IrSi2(     ,ZM51.1960.327)
IrSi3(H2.6,SR37.100)H4.351;6.622A=bFH(√5.3;4.3/3)=cH(4;6)  N=24,82
Co2Ge.r(Ni2Si,JLCM18.1969.175)7.26;5.02;3.82A=idm Co2Si.r  N=24,168
Co3.3Ge2.h(FhtpNiAs,SR12.64)H3.92;5.03A=bFH(2;3.1/3)=cUH(4;6/2)  N=11,47
Co5Ge3.r(JLCM75.1980.155)
Co12Ge9.h(Fe12Ge9,JLCM75.1980.155)H7.854;4.999A=bFH(4;3/3)=cH(8;5)
CoGe(FhtpNi3Sn4,SR24.112)M101.10°11.648;3.807;4.945A
Co5Ge7(Ir5Sn7,SR27.161)7.64;5.81A=bF(√7.25;2)=cC(√58;5.8)  N=56,310
CoGe2(Q4.8,SR11.96)5.68;5.68;10.82A=bF(2;3.75)=cU(4;9.3)  N=64,296
Rh2Ge(Ni2Si,SR19.177)5.44;7.57;4.00A=idmCo2Si.r  phdE
Rh5Ge3(010.6,SR19.177)5.42;10.32;3.96A=idm Rh5Si3
RhGe(MnP.1,SR19.179)5.70;6.48;3.25A=idm RhSi.h
Rh11Ge22(U34.44,SR32.83)5.604;78.45A=bHT(√8;44/2)=cU(4;68)  N=352,1492
Rh3Ge4(T9.12,SR20.111)5.7;10.0A=hdm Rh17Ge22
IrGe(MnP.1,SR13.28)6.281;5.611;3.490A=idm RhSi.h
Ir4Ge5(T16.20,SR33.84)5.615;18.308A=bHT(√8;10.5)=cU(4;16)  N=80,344
Ir3Ge7(Ru3Sn7,SR13.112)8.753A=bF(3)=cU(6;7.3)  N=112,388
IrGe4(H3.12,SR34.89)H6.215;7.784A=bÛH(3;5.3/2)=cFH(√27;8/3)  N=18,147
Co3Sn2.h(FhtpNiAs,SR6.178)H4.12;5.19A=idm Rh2.8Si2  phdHA
Co3Sn2.r(Ni3Sn2.r,ZMetk63.1972.258)8.20;7.09;5.22A=idm h
CoSn(H3.3,SR6.4)H5.279;4.259A→4.26;9.13;5.28A=bHO(√4.3;5/2;2.5)=cUH(√13;5/2)
CoSn2(CuAl2,SR6.178)6.361;5.452A=bFU(3;3.6/2)=cU(√18;4.5)  N=32,148
Rh3Sn(     ,SR23.123)
Rh2Sn(Ni2Si,SR23.120)8.209;5.52o;4.220A=idm Co2Si.r  phdHA
Rh3Sn2(FhtpNiAs,SR11.148)H4.340;5.555A=idm Rh2.8Si2
RhSn(FeSi,SR11.179)5.131A=idm CoSi
RhSn2.h(CuAl2,SR11.149)6.412;5.656A=idm CoSn2
RhSn2.r(U6.12,SR20.177)6.346;17.717A=bFU(3;12/2)=cU(4;14)  N=108,432
RhSn4(PtSn4,SR11.180)Hul.
Ir1.1Sn(NiAs,SR11.136)H3.988;5.567A=bFH(√3;3)=cH(√12;5)  N=8,54
Ir5Sn7(U5.7,SR44.74)8.537;6.470A=idm Co5Ge7
IrSn2(CaF2,SR11.136)6.338A=idm CoSi2
Ir3Sn7(Ru3Sn7,SR11.136)9.360A=idm Ir3Ge7
CoPbM nic   phdE
Rh3Pb2(FhtpNiAs,SR38.170)H4.33;5.64A=idm Rh3Si2  phdM
RhPb(CoSn,SR38.170)H5.678;4.428A=bH(2;2.5/1)=cUH(√12;5/2)
Rh4Pb5(S8.10,SR39.79)9.84;5.71;26.51A=bH(√7;12)=cUH(√21;25)  N=176,144
RhPb2(CuAl2,SR9.84)6.664;5.865A=bFU(√10;4/2)=cU(√20.4.8)
RhPb4
IrPb(NiAs,SR13.27) H3.993;5.566A=idm Ir1.1Sn
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therefore HUH$\sqrt{3}$ becomes probable. The number of $\underline{b}$ places per cell is $\underline{N}^{/C}_{P'}=21$ while in $Rh_{2.8}Si_2$ it was $\underline{N}^{/C}_{P'}=24$ in a comparable cell; this must be interpreted by a reduction of valence electron contribution of Rh by the increased $\underline{N}'_{Si}$ mole fraction. The $\underline{c}_{UH}$ correlation distorts the cell probably somewhat. Rh_4Si_5 and Rh_3Si_4(drawings SR33.139,140) are homeotypes of MnP. For Rh_3Si_4 displaying a short basis, the commensurability to RhSi.h is $\underline{a}=\underline{a}_{RhSi.h}(4;1;1)$ in each subcell there is one Rh lacuna. The metrical comparison yields $\underline{a}=\underline{c}_H(18/1;\sqrt{12};5.5)$ with $N^{/C}_{P''}=400$. This $\underline{c}$ correlation may be supplemented to a BHH3 binding with $\underline{a}=\underline{b}_{BH}(30/3;\sqrt{1.33};1.85)$. Since K'_{11} and K''_{11} may not be devided by 4 the supercell is required by the commensurability rule.

Ir_3Si(U6.2,drawing [3a] p.105;U_3Si is heterotypic, SR41.106) is a DI-homeotype of Cu_3Au, since the phase is heavier than Co_3Si.h a closer packed structure appears for the simple composition A_3B. Surprisingly a $\underline{c}_U$ correlation emerges which is supplemented to a UU2 binding. Inferring from the $\underline{d}_b$ value, the binding proposal for IrSi(MnP) must perhaps be improved.

The phase Co_2Ge.r(Ni_2Si,drawing [3a] p.322) is isodesmic to Co_2Si.r. Increase of mole fraction $\underline{N}'_{Ge}$ causes Co vacancies which permit the hexagonal symmetry in $Co_{3.3}Ge_2$(FhtpNiAs), which belongs to the FHUH2 binding yielding more $\underline{c}$ places than FHH2. Further increase of $\underline{N}'_{Ge}$ not only causes further vacancies but also partial substitution of Co by Ge. This remarkable phenomenon has been carefully confirmed [17] and finds its clear expression in the structure of $Co_{12}Ge_9$.h [12] displaying ordered Co vacancies and probably disordered substitution for its FHH2 binding. The Co by Ge substitution mitigates the decrease of $\underline{b}$ electron contribution of Co caused by the vacancies and by the increase of $\underline{N}'_{Ge}$. The ordering of the Co by Ge replacement results in the RFC-homeotypes of NiAs, already mentioned in the mixture $FeGe_{\overline{M}}$; one of the earliest found examples was CoGe(FhtpNi_3Sn_4). Additional examples of RFC-homeotypes of NiAs will be met in $NiSn_M$. The reversed process of Ge by Co replacement is found in Co_5Ge_7(Ir_5Sn_7,SR$\overline{4}$4.74) as compared to $CoSi_2$(CaF_2), a L-homeotype of CsCl. The homeotypism from $CoSi_2$ to Co_5Ge_7 is not by filling in of Co atoms but by replacing B^4 by Co. This process decreases the $\underline{b}$ electron concentration and causes by this a finite rotation of the FUC2 binding around $[001]_{CoSi2}$. Since the $\underline{b}$ correlation is formed nearly exclusively by valence electrons of Ge, the distances $\underline{d}_{GeGe}$ are essentially greater than $\underline{d}_{CoGe}$, for reasons of $\underline{b}$ correlation. The phase $CoGe_2$(Q8.8) is a DI-homeotype of $CoSi_2$-(CaF_2) with the commensurability $\underline{a}_{CoGe2}=\underline{a}_{CoSi2}(1;2)$. Although $CoGe_2$ contains more $\underline{c}$ electrons than $CoSi_2$ the ratio $|\underline{a}_2|/2|\underline{a}_1|$ of $CoGe_2$ is smaller than 1 contrary to simple expectation. This contradicition is solved by the assumption of twinning of the binding in $CoSi_2$ and by the rule that heavier components are more closely packed.

A remarkable finding of the binding analysis in $CoGe_M$ is the very high occupation ratio of the $\underline{c}$ correlation. It is caused by the small $\underline{b}$ electron concentration $\underline{N}_b^{/A}$ and the high filling of the d shells of the components.

The following A^9Ge_M phases are isotypic or homeotypic to earlier phases. A new structure emerges in $IrGe_4$(H3.12). The binding follows the rule that Ir, if it is diluted sufficiently, tends to a $\underline{c}_F$ correlation wich allows the participation of lower electrons in the correlation.

A notable phenomenon in A^9Sn_M phases is the transformation in $RhSn_2$ which evidently is caused by the commensurability rule. Another fact not understood so long is the shift of the stability concentration between Rh_3Sn_2 and $Ir_{1.1}Sn$; it is easily interpreted by a change in commensurability of the FHH2 binding.

$\underline{A^{10}B^4_M}$ phases. These phases have been considered previously [18], however, since the concentration dependent $\underline{b}$ electron contribution of the A^{10} atoms was not yet taken into account appropriately, several of the proposals [18] must be improved; also the nomenclature of the binding has been improved recently so that the table of phases shall be included here anew.

The phases $Ni_{3.1}Si$.r(Cu_3Au) and Ni_3Si.h(Fe_3Si) have UU2 and FF2 binding respectively but further increase of $\underline{b}$ electron concentration generates a UHH2 binding in $Ni_{31}Si_{12}$(H31.12). The electron count $Ni^{1,17}$ can no more be assumed in $Ni_{3.1}Si$.r but for $Ni^{1,9}$ the occupation is near 0.50 which indicates perhaps a count $Ni^{1,9,8}$. In Ni_3Si_2.r the count $Ni^{0,10}$ is probable while for Ni_3Si_2.h $Ni^{1,17}$ may be assumed. As the phases Rh_3Sn_2 and $Ir_{1.1}Sn$ showed there are two subtypes of the NiAs type which display different commensuralibites $\sqrt{4}$ and $\sqrt{3}$ of $\underline{b}_{FH}$ in the basal plane. Ni_3Si_2.h belongs to the $\sqrt{4}$ subtype while NiSi(MnP) belongs to the $\sqrt{3}$ subtype. The $\underline{c}_{UH}$ correlation causes the short subtypes of the MnP type to be stable while the long homeotype RhSi.h has additionally a greater commensurability element in the longest axis. A great jump of the distance $\underline{d}_c$ as compared with the value for Ni_3Si_2.h indicates the precipitation of the correlation of the lowest electrons out of the $\underline{c}$ correlation.

The phase Pd_3Si(Fe_3C,drawing [3a] p.253) is DI-homeotypic to Ni_3Si(Cu_3Au) with the commensurability $\underline{a}_{Pd3Si}=\underline{a}_{Cu3Au}(1,0,-1;1,0,1;0,2,0)$; a CC2 binding appears possible which leaves a UHH2 binding for Pd_2Si(Fe_2P,drawing [3a] p.324). It should be appreciated that the HUH$\sqrt{3}$ binding of PdSi is especially favourable because of its good $(\underline{c}^{-1}\underline{b})_{33}$ commensurability.

In Pt_3Si.h(Fe_3C) the integrated count $Pt^{1,17}$ is possible but not in Pt_3Si.r(Pt_3Ge); here $Pt^{1,9}$ must be assumed, the correlation of the 8 lowest electrons must have been precipitated out of the correlation of the d electrons. The result is an increase of $\underline{d}_{\underline{b}}$ and a decrease of the number $N^{/P'}_{P''}$ of $\underline{c}$ places per $\underline{b}$ place.

The monoclinic deformation of Pt_3Si.r is caused by the $\underline{c}$ correlation [17]. The CB/2 binding is confirmed in Pt_2Si.r(U1.2) a LD-homeotype of CsCl.

Pt_2Ge(Fe_2P) surprisingly is reported to have a lower melting temperature than PtGe. The phase Pt_3Ge_2(O24.16,drawing JLCM45.125) is formed from Pt_2Ge by a LC-homeotypism, where the chains are along $\underline{a}_1$(Pt_3Ge_2) or $\underline{a}_3$(Pt_2Ge). In the cell $\underline{a}_{Pt3Ge2}$ four Pt chains are missing, and three neighboured Pt chains move somewhat against the missing chain. A UB2 binding is probable as it gives a good $N^{/P'}_{P''}$ value and a good commensurability. The MnP type of PtGe may best be understood from the A^n-B^m coordinate system into which the types of $A_1^nB_1^m$ compounds are plotted (see [3a] p.328). There are as has been said short and long representatives. Keeping m constant the long type comes for small n. PtGe is short, therefore by a L-homeotypism of Pt atoms the long type may be stabilized in Pt_2Ge_3; the lacunae order and the cell becomes $\underline{a}_{Pt2Ge3}=\underline{a}_{PtGe}$ (1;3;1) as the commensurability element K'_{22} differs appreciably from a whole number. The short type is caused by the orientation of the $\underline{c}_{UH}$ correlation against the $\underline{a}$ cell. If in the quasi hexagonal basal plane of UH the straight line with support number two lies parallel to the shortest axis $\underline{a}_1$ then a short type results, if an additional strain arrives in the longest axis the long type results. The phase $PtGe_2$(FeS_2.r,drawing [3a] p.343) is homeotypic to $NiSi_2$(CaF_2) and is also isodesmic, the FU2 binding is here not twinned as it is in $NiSi_2$.

It should be appreciated that Ni_3Sn.h like Fe_3Si is heterodesmic to CuZu and that Ni_3Sn.r has a HH2 binding. Ni_3Sn_2.h(FhtpNiAs,drawing [3a] p.331) has with its FHH2 binding the highest melting point in the mixture $NiSn_M$. The RLC-homeotype NiSn(O16.16,drawing [13]) is commensurable by $\underline{a}_{NiSn}=\underline{a}^{orth.asp.}_{Ni3Sn2.h}$ (4;1;1) but because of L-homeotypism there is a strong contraction in $\underline{a}_1$(NiSn) which influences the binding. A second RLC-homeotype of Ni_3Sn_2 is Ni_3Sn_4(N3.4, drawing [13]), the non whole number commensurability element K'_{11} probably has to do with the monoclinic symmetry of the cell.

The surprising tetragonality of $Pd_{3.1}Sn$(DhtpCu_3Au) is quite natural from the point of view of UU2 binding. The increase of $\underline{b}$ electron concentration leads in Pd_2Sn to a $\underline{c}$ correlation poorer in $\underline{c}$ places per $\underline{b}$ place than in the UU2 binding. In $Pd_{3.3}Sn_2$.h(FhtpNiAs) the FHH2 binding emerges and causes a congru-

TABLE 10: A10B4M

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Ni3.1Si.r(Cu3Au,SR15.108)3.504A=bU(√2;1.73)=cU(√8;3.5)  N=7,35(59)  phdHA
Ni3Si.h(Fe3Si,SR44.119)2.808A=bF(1)=cF(2)  N=28,140(236)
Ni25Si9.h(R25.9,JLCM66.1979.163)H6.698;28.855A=hdmNi31Si12
Ni31Si12(H31.12,SR37.114)H6.671;12.288A=bUH(√12;7/2)cH(√4 8;13)  N=79,(623)
Ni2Si(08.4,SR16.123)4.99;3.72;7.06A=bU(2.1;2/1;3)=cB(4.2;3.2;6)  N=24,(168)
Ni3Si2.h(FhtpNiAs,SR26.211)H3.805;4.800A=bFH(2;3.1/3)=cH(4;5)  N=11,43(67)
Ni3Si2.r(Q24.16,SR26.211)12.229;10.805;6.924A=bC(6.4;4√2;2.5√2)=cB(9;8;5.1) N=128,1120
NiSi(MnP.s,SR15.107,35.86)5.18;3.34;5.62A=bH(2.7;√3;3/1)=cUH(5.3;3;6)  N=16,72(104)
NiSi2.h
NiSi2.r(CaF2,SR13.90)5.406A=bF(2)=cU(4;5)  N=32,104(136)
Pd5.2Si.h   phdM
Pd36Si8(O   ,SR31.57)7.418;9.396;9.048A
Pd3Si(Fe3C,SR24.205)5.753;7.555;5.260A=bC(3;4;2.7)=cCK'(2)  N=28,140(236)
Pd2Si(Fe2P,SR16.95,31.56)H6.496;3.433A=bUH(√12;2.1/2)=cH(√48;3.6)  N=18,78(126)
Pd1.9Si(htpFe2P,SR31.57)H13.05;27.49A=idm Pd2Si
PdSi.h(MnP.l,SR13.28,35.86)5.599;3.381;6.133A=idm NiSi
Pt3Si.h(Fe3C,SR44.120)5.581;5.524;7.702A=bC(√8;4)=cCK'(2)  phdS      N=56,296(472)
Pt3Si.r(Pt3Ge.r,SR29.129)7.697;7.758;-0.25,0,7.758A=bHT(√13;4.2/2)=cHTK'(2)
Pt12Si5.h(Ni12P5,SR44.120)9.607;5.542A=bC(5;2.9)=cB(√50;4)
Pt12Si5.r(T48.20,SR30.163)13.40;5.45A=bC(7;2.8)=cB(√98;4)  N=128,592
Pt2Si.h(Fe2P,SR29.129)H6.44;3.57A=bUH(√10.7;2/2)=cH(√43;3.6)
Pt2Si.r(U1.2,SR29.129)3.92;5.91A=bC(2;3)=cB(√8;5.2)  N=12,52
Pt6Si5(M12.10,SR29.79)M86.32°15.462;3.499;6.169A
PtSi(MnP.s,SR13.28)5.932;5.595;3.603A=idm NiSi
Pt2Si3(Pt2Sn3,Ottaviani)
Ni3Ge(Cu3Au,SR13.113)3.567A=idm Ni3Si.r  phdHA
Ni2.8Ge.h(Fe3Si,SR44.116)5.747A=idm Ni3Si.h
Ni5Ge2.h(Pd5Sb2,SR39.158)H6.827;12.395A=idm Ni31Si12
Ni2Ge.r(Ni2Si,SR37.88)5.113;3.830;7.264A=idm Ni2Si
Ni1.9Ge.h(FhtpNiAs,SR37.88)H3.937;5.078A=idm Ni3Si2.h
Ni5Ge3.r(N10.6,SR37.89)M52.11°11.682;6.737;6.264A=hdm Ni1.9Ge.h
Ni19Ge12(N19.12,SR37.90)M90°11.631;6.715;10.048A
Ni3Ge2.h(FhtpNiAs,SR37.158)H3.863;4.998A=idm Ni1.9Ge.h
NiGe(MnP,SR13.28)5.811;5.381;3.428A=idm NiSi
Pd5Ge.h(W,Natw.50.1963.41)3.137A=bF(1)=cF(2)  phdM
Pd5Ge.r(Pd5As,SR44.116)M98.09°5.509;7.725;8.375A  N=36,220
Pd3Ge
Pd25Ge9(H25.9,SR41.71)H7.351;10.605A=bUH(√12;5.7/2)=cH(√48;10)  N=61,315
Pd21Ge8(Pt8Al21,U42.16,SR43.64)13.067;10.033A=bC(√40;4.9)=cU(√80;8.5)  N=212,1076
Pd2Ge(Fe2P,SR17.174)H6.67;3.39A=bFH(√10.7;2/3)=cH(√43;3.3)  N=18,66  cmp
PdGe(MnP.l,SR13.28)6.259;5.782;3.481A=idm NiSi
Pt3Ge.h(Ir3Si,JLCM76.1980.181)5.499;7.933A=bU(√4.5;3.7)=cUK'(2)  phdM
Pt3Ge.r(N6.2,SR24.116)7.924;7.768;-0.087,0,7.768A=bHT(√13;4.3/2)=cHTK'(2) N=56,320
Pt2Ge(Fe2P,SR17.174)H6.68;3.53A=idm Pt2Si.h                                 (488)
Pt3Ge2(O24.16,SR42.90)6.854;12.240;7.549A=bU(2.75;6/1;3)=cB(5.5;10;6)  N=88,376
PtGe(MnP.s,SR13.28)6.088;5.733;3.701A=idm NiSi  cmp
Pt2Ge3(O8.12,SR33.87)16.441;3.377;6.202A=bBH(24/3;1;2/2)=cH(15/1;3;6/2) N=48,200
PtGe2(FeS2.r,SR24.118)6.185;5.767;2.908A=bF(2.1;2;1)=cU(5/1;4;2)  N=16,60
Ni3Sn.h(Fe3Si,SR20.29)5.98A=idm Ni3Si.h  N=28,148  phdHA
Ni3Sn.r(H6.2,SR5.7)H5.29;4.24A=bH(√6.25;2)=cH(5;4)  N=14,74(122)
Ni3Sn2.h(FhtpNiAs,SR1.765)H4.11;5.19A=bFH(2;3/3)=cH(4;5)  N=11,47
Ni3Sn2.r(O12.8,SR32.107)7.11;8.23;5.21A=hdm Ni3Sn2.h
NiSn(O16.16,SR39.88)24.452;5.200;4.091A=bH(14/2;2.5/1;2)=cUH(21;5/2;√12) N=72,304
Ni3Sn4(N3.4,SR10.77)11.871;4.061;-2.911,0,5.187A=bHO(3.3;2;2.5/1)=cHO(10;√12;4.5/1)
                                                                            N=35,137
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Pd3.1Sn(DhtpCu3Au,SR23.123)4.07;3.73A=bU(√2;1.6)=cU(√8;3.2)  N=7,37  phdE
Pd3Sn(Cu3Au,SR23.123)3.97A=idm Ni3Si.r
Pd2Sn(Ni2Si,SR23.120)8.12;5.65;4.31A=idm Ni2Si
Pd3.3Sn2.h(FhtpNiAs,SR11.173)H4.388;5.645A=bFH(2;3.1/3)=cH(4;5)
Pd20Sn13(H40.26,ZMetk72.1981.517)H8.799;16.984A
Pd3Sn2.h
Pd3Sn2.r
Pd59Sn41
PdSn(MnP.s,SR11.174)3.87;6.13;6.32A=idm NiSi
PdSn2(U8.16,SR20.168)6.490;24.378A=bFU(3;16/2)=cU(√18;20)  N=144,464
PdSn3(Q4.12,SR23.123)17.20;6.47;6.50A=bFU(3;11.3/2)=cU(√18;14)  N=104,312
PdSn4(PtSn4,SR13.116)6.395;6.426;11.595A=bFU(3;7.7/2)=cB(√18;7.7)  N=68,196
Pt3Sn(Cu3Au,SR11.177)3.993A=idm Ni3Si.r  phdHA
PtSn(NiAs,SR2.720)H4.11;5.44A=bUH(2;3/2)=cUH(√12;5/2)
Pt2Sn3(H4.6,SR11.177)H4.337;12.960A=bUH(√4.3;7/2)=cH(√13;11)  N=28,96
PtSn2(CaF2,SR9.120)6.426A=bFU(3;42/2)=cU(√18;5.2)
PtSn4(Q2.8,SR13.116)6.388;6.418;11.357A=idm PdSn4
NiPbM nic,NiPb.m(NiAs,SR33.152)H4.15;5.28A=idmNi3Si?.phdHA
Pd3Pb(Cu3Au,SR10.65)4.022A=idm Ni3Si.r  phdHA
Pd3.3Pb2.h2(FhtpNiAs,SR10.65)H4.465;5.704A=bFH(2;3.1/3)=cH(4;5)  N=11,50
Pd3.3Pb2.h1
Pd5Pb3(Ni5Ge3,SR39.119)
Pd13Pb9.h2(FhtpNiAs,JLCM71.1980.P29)H4.49;5.76A=bFH(√4.3;3.2/3)=cFH(√13;5.5)
Pd13Pb9.h1(disordered r)
Pd13Pb9.r(N26.18,SR46.96)M55.875°15.603;9.060;13.911A=hdm h2
PdPb.h2,h1 disordering homeotypes                               N=320,1216
PdPb.r(Z16.16,JLCM72.1980.P1)a≈7.15;8.52;42.38A=bHO(2;4;2 0)=cBHO(2;4;97/3)
PdPb2(CuAl2,SR9.84)6.849;5.833A=bFU(√10;3.8/2)=cB(√20;3.8)  N=36,116
Pt3Pb(Cu3Au,SR10.66)4.053A=idm Ni3Si.r
PtPb(NiAs,SR10.66)H4.259;5.467A=idm PtSn
PtPb4(T2.8,SR15.90)6.665;5.978A=bFU(√10;4/2)=cB(√20;4)  N=34,98
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ent melting point. As is known from preceding mixtures the FHH2 binding leads to several homeotypes of NiAs. $Pd_{20}Sn_{13}$(H40.26) for instance has the commensurability $\underline{a}_{Pd20Sn13}=a_{Pd3.3Sn2\ .h}(2;3)$, it displays besides ordering of vacancies (relative to Ni_2In) also replacement of Pd by Sn (anomalous substitution) which limits the rule [3a] that the NiAs subcell contains only two B^n atoms, and which was found also in the RFC-homeotypes of NiAs like NiSn. The decrease of $\underline{b}$ electron contribution of Pd causes the $HUH\sqrt{3}$ binding in PdSn with the orthogonal distortion of the NiAs type cell. The series $PdSn_2$(U8.16), $PdSn_3$(Q4.12), $PdSn_4$(Q2.8) are LDI-homeotypes of CaF_2, and should be compared with Sn.1 $\underline{a}$= 6.49Å; the different commensurability of the FU2 binding is caused by a positive $\underline{b}$ electron contribution of Pd.

In PtSn(NiAs) a $UHUH\sqrt{3}$ binding is found which is closely homeotypic to the NiSi $HUH\sqrt{3}$ binding. It causes the homeotypism to Pt_2Sn_3(H4.6,$UHH\sqrt{3}$). In $PtSn_2(CaF_2)$ the FU2 binding is stable and in $PtSn_4$ perhaps a FB2 binding.

In $Pd_{3.3}Pb_2.h_2$(FhtpNiAs) metrical reasons suggest a FHH2 binding which is homeotypic to the UU2 binding. A slightly changed commensurability causes the compound $Pd_{13}Pb_9$; only for h_2 the binding is given as the transformations h_2-h_1 and h_1-r give so weak changes that the binding remains closely homeodesmic. In PdPb.r (Z16.16,drawing [19]) a I-homeotype of TlI(Q2.2,drawing [3a] p.191) occurs which may be described for the present purpose in a S16.16 cell $\underline{a}_S$= (7.15;8.52;42.38)Å so that $\underline{a}_S=\underline{a}_{TlI}(2;2;4)$. A HBH1 binding appears possible; the reason why this proposal was not found in earlier work is, that the positive electron contribution of Pd was not realized.

The binding of $PtPb_4$ is somewhat enigmatic, it fits quite well from the distance point of view, but the correlations are not very well occupied.

$\underline{B^1B^4_M}$ phases. The mixture $CuSi_M$ opens the class of brass like phases in which XX2 bindings like HH2,BB2,FF2 etc. are found. It has been shown [20] that for homeotypes of CuZn(CsCl) a twinned BB2 binding must be assumed for which $\underline{a}_{CuZn}3/4=\underline{d}_b$. This binding favours the Cu_5Zu_8 homeotypes and it is also satisfactory that for $Cu_5Si.r(Mn.h_1)$ a FF2 binding is possible. It is surprising that for $Cu_{15}Si_4$(B30.8,drawing [3a]p.226) once more BB2 comes. The structures of Cu_3Si appear to be complicated.

The electron rich atoms Ag and Au do not permit expansion of $\underline{b}$(Si) electrons and also forbid expansion of d electrons of B^1 so that no intermediary phases are formed.

The phase $Cu_5Ge(Mg)$ has a fairly broad range of homogeneity. The FF2 binding is commensurable with the cell $\underline{a}_{Cu5Ge}(\sqrt{3};1)$. The bindings of the other phases are also of the XX2 type.

The phases Cu_6Sn.h, Cu_4Sn.h, $Cu_{41}Sn_{11}$.h, and $Cu_{10}Sn_3$.h are iso- or homeotypic to W and have the BB2 binding. The mechanism generating the Cu_5Zn_8 homeotype $Cu_{41}Sn_{11}$.h has been discussed earlier [21]. $Cu_{10}Sn_3$(H20.6) is separated from Cu_4Sn as it has 9 atomic layers parallel ($\underline{a}_1$,$\underline{a}_2$) per $\underline{a}_3$ length and therefore also slightly more $\underline{b}$ layers per atom layer (namely 1.22) than Cu_4Sn.h which has 1.17 [20].

In Cu_3Sn.r(Q30.10, drawing [3a] p.114) the UU2 binding of Cu_3Ge.r(06.2) is nearly whole numbered; if the system of electrostatic dipole vectors generated at the minority component by the $\underline{b}$ correlation is inserted in the cell then it is seen that the cell part $\underline{a}$(1;0...1/2;1) is with respect to the dipole direction mirror-symmetric to the cell $\underline{a}$(1;1/2...1;1), perhaps this is sufficient to generate the shear; however, a more elaborate investigation of the dipole system remains necessary. Since the binding in Cu_3Ge.r and Cu_3Sn.r is practically the same it may be expected that Cu_3Ge.r Cu_3Sn.r and also Ag_3Sn are isotypic; this expectation might be examined by neutron diffraction. This is an example of an experiment suggested by the binding analysis.

While the $AgSn_M$ phases are isotypic to $CuGe_M$ phases, the mixture $AuSn_M$ displays interesting new phases. Au_5Sn.r(H15.3) is R-homeotypic to Au_6Sn(Mg) with the commensurability $\underline{a}_{Au5Sn}=\underline{a}_{Au6Sn}(\sqrt{3};3)$, it may be said that the phase is stabilized, as the mole fraction permits a Sn array which is favourably adapted to the FF2 binding of Tab.11. In Au_6Sn(Mg) the binding appears to be of the UU2 type and this possibility of smooth binding change in a phase might be the cause for the long known irregularities in the $|\underline{a}_3| / |a_1| (N_b^{/A})$ function, $N_b^{/A}$ average number of valence electrons per atom, see for instance [3a] p.109. In $Au_{10}Sn$.h($TiNi_3$,H4.12, drawing [3a] p.118) even a HH2 or HFH2 binding appears possible. The $\underline{d}_b$ value is a little smaller than in Au_6Sn, this might be caused by the smaller coordination number in the $\underline{b}$ correlation. The good fit of the three bindings confirms the assumption for the brass like homeotypes of Mg. Even Au_4Sn.m(Cu_5Zu_8) fits excellently to Hume-Rothery's rule and therefore to the BB2 binding. AuSn(NiAs) comes with $N_b^{/A}$=2.5 near to the FB2 binding, the HUH$\sqrt{3}$ binding is a fore-runner of it. Also the BC2 binding of $AuSn_2$(O 8.16, drawing [3a] p.347) is a fore-runner of FB2, and in $AuSn_4$ this binding is in fact obtained.

The occurence of the $MgCu_2$(F2.4) type in Au_2Pb.h is surprising as it did not become stable in $CuGe_M$ or $CuSn_M$, the BHT2 binding is related to the BC2 binding of $AuSn_2$, but it may also be compared with the BB2 binding. For $AuPb_2$ ($CuAl_2$) a BC2 binding is possible but the phase could also be isodesmic to $PdPb_2$($CuAl_2$) for which a FB2 binding could be assumed. $AuPb_3$(U4.12) permits

TABLE 11: B1..4B4M

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Cu7Si.h(Mg,SR24.132)H2.56;4.18A→H4.43;4.18A=bH(2;2)=cH(4;4)  N=2.75,19.5 phdHA
Cu6Si.h(W,SR8.66)2.854A→H6.991;4.943A=bBH(2;7/3)=cBHK'(2)
Cu5Si.h
Cu5Si.r(Mn.h1,SR3.332,8.66)6.223A=bF(2)=cF(4)  N=30,194
Cu31Si8.h(∼Cu5Zn8,SR8.66)8.506A=hdmCu6Si.h
Cu15Si4(B30.8,SR3.336)9.714A=bB(4)=cB(8)  N=124,728
Cu3Si.h2(R   ,SR30.129)  phdE
Cu3Si.h1
Cu3Si.r
AgSiM nic  phdS
AuSiM nic  phdM
Cu5Ge(Mg,SR16.77)2.61;4.23A=bFH(√1.3;2.3/3)=cFHK'(2)  N=3,20  phdHA
Cu3Ge.h(Na3AS,SR37.155)H4.169;7.499A=bH(2;3.6)=cHK'(2)  N=14,80
Cu3Ge.r(O6.2,SR16.77)2.645;4.553;4.202A=bU(1;1.75;2/1)=cUK'(2)  N=7,40
Cu5Ge2.h(LhtpFe3Si,SR37.71)5.906A=bHT(√8;3.25)=cHTK'(2)
AgGeM nic  phdHA
AuGeM nic  phdHA
Cu6Sn.h(W,SR1.545)2.98A=idm Cu6Si.h
Cu6Sn.m(Ag2Zn.r,71Ec)H7.30;2.59A
Cu4Sn.h(Fe3Si,SR31.41,20.103)6.118A=idm Cu6Si.h
Cu41Sn11.h(F82.22,SR43.53)17.980A=hdm Cu6Si.h
Cu10Sn3(H20.6,SR39.54)H7.33;7.87A=bBH(2;11/3)=cBH(4;22/3)  N=44,260
Cu3Sn.r(Q30.10,SR19.164)2x2.77;47.8;4.34A=bU(2;17;2/1)=cUK'(2)  N=140,800
Cu3Sn.m(Cu3Sb,SR31.41)4.760;5.523;4.338A
Cu6Sn5(htpNiAs,SR2.716)
Cu6Sn5.1(htpNiAs,    )
Ag5Sn(Mg,SR2.717,26.249)H2.95;4.78A=idm Cu5Ge
Ag3Sn(D htpMg,SR2.717)2.99;5.16;4.78A=idm Cu3Ge.r
Au10Sn.h(TiNi3,SR23.151)H2.904;9.536A=bH(√1.3;3.8)=cHK'(2)  N=20,160
Au6Sn  (Mg,SR2.719)H2.91;4.79A=bUH(√1.3;2.2/2)=cUHK'(2)  N=2.86,20
Au5Sn.r(H15.3,TransJIM15.1974.256)H5.09;14.34A=bFH(2;7/3)=cFHK'(2)  N=27,180
Au4Sn.m(Cu5Zn8,71Ec)9.80A=idm Cu5Zn8
AuSn(NiAs,SR2.719)H4.32;5.52A=bH(2;2.5)=cUH(√12;5/2)  N=10,40  cmp
AuSn2(O8.16,SR23.151)6.909;7.037;11.789A=bB(√8;4.5)=cC(√32;10)  N=72,240
AuSn4(PtSn4,SR13.116)6.446;6.487;11.599A=idm PdSn4 FB2
AuSn10(HgSn12,71Ec)H3.177;2.957A
CuPbM nic mixture gap in liquid  phdHA
AgPbM nic entectic mixture phdHAAg4Pb.m(Mg,SR19.210)H2.92;4.76A=hdm Au6Sn
Au2Pb.h(MgCu2,SR3.612)7.927A=bB(3)=cHT(6,7)  N=48,240  phdM
AuPb2(CuAl2,SR9.84)7.325;5.655A=bB(√8;2.2)=cC(√32;4.4)  N=36,120
AuPb3(U4.12,SR37.94)11.959;5.877A=bFU(√29;3.7)=cB(√58;3.7)  N=104,320
ZnSiM nic  phdE
CdSiM nic
HgSiM nic
ZnGeM nic  phd HA
CdGeM nic  phd E
HgGeM nic
ZnSnM nic
CdSn10.h(HgSn12,SR18.180)H3.233;3.002A=idm HgSn12  phdHA
HgSn3 ?
HgSn10(DhtpHgSn12,SR3.645)5.559;3.202;2.987A
HgSn12(H1,SR18.180)3.213;2.992A=bFU(√2;1.75/2)=cB(2;1.75)
ZnPbM nic
CdPbM nic
HgPb2(SrPb3,SR18.55)4.982;4.512A=bFU(√5;3/2)=cB(√10;3)  N=13.3,40
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AlSiM nic phdHA
GaSiM nic phdHA
InSiM nic phdHA
TlSiM nic
AlGeM nic phdHA
GaGeM nic phdE
InGeM nic phdHA
TlGeM nic phdE
AlSnM nic phdHA
GaSnM nic phdS
In3Sn(SrPb3,SR10.59)4.86;4.40A=bFU(√5;2.8/2)=cB(√10;28) N=13,40 phdS
InSn5(HgSn12,SR10.59)H3.22;3.00A=bFU(√2;1.75/2)=cB(2;1.75) N=3.8,10
Tl4Sn(Cu,SR2.738,24.53)4.84A=bF(1.5)=cB(3) phdM
TlSn.h(CuAu,Ellner)5.108;4.401A=bF(√2.5;1.35)=cB(√10;2.7)
AlPbM nic miscibility gap in liquid phdHA
GaPbM nic miscibility gap in liquid phdE
In3Pb(SrPb3,SR22.139)4.88;4.54A=idm In3Sn phdM
Tl3Pb(Cu,SR16.106)4.870A=idm Tl4Sn
SiGeM(Si,SR7.212)a=bF(2)=cB(4) phdHA
SiSnM nic phdHA
GeSnM nic phdHA
SiPbM nic miscibility gap in liquid phdE
GePbM nic phdHA
SnPbM nic phdHA

TABLE 12: Bindings in $A^nB^4_{\underline{M}}$ alloys in dependence of $\underline{N}^{/P'}_{P''}$

27.0	CC3	HH3	BB3	UU3	FF3
22.1				UB3	
16.0	CB2				FC4
13.5			BC3		
12.5	CHFH3				
11.3	CFU2				FUB2
9.8		HTFU2			
9.2		HUH2			
8.0	CC2	HH2	BB2	UU2	FF2
7.5					FHUH2
7.0		HTC2		UHH2	
6.9	CU√2		BHFH3		
6.6					FHH2
6.5				UB2	FUHT2
6.3		HFH√3	BHUH3		
6.0		HUH√3			
6.0		HTU√2			
5.6	CB√2		BFU2		FUC2
5.5			BHH3	UHFH√3	
5.2	CHCH√3	HH√3	BHBH√3	UHUH√3	FHFH√3
5.0		HTB√2			
4.9		HBH1			FU2
4.9					FHUH√3
4.6			BHT2	UFU2	UHFH√3
4.5				UHH√3	
4.3				UHBH1	FHH√3
4.0	CF1		BC2		FB2
3.8				UHT2	

also a FB2 binding. This shows a somewhat rotated commensurability, since in such a case the atom groups are frequently also a little rotated , it appears possible that this has been overlooked, so that the reliability of the determination stopped at 0.25.

Plotting the $\underline{d}_{\underline{b},\underline{c}}{}^{\circ}(N'_{Pb})$ curves of the mixture $AuPb_{\underline{M}}$ which follows from the binding assumptions shows that the expansion of the $\underline{b}_{Pb}$ electrons is not very great. Extrapolating this behaviour to $CuPb_{\underline{M}}$ could perhaps give a compression of the $\underline{b}_{Pb}$ electrons, and this would mean that no energy of formation of such phases is available so that no intermediary compounds are formed. The possibility of such arguments supports the relevance of a valence model.

$\underline{B^{2..4}B^{4}_{M}\text{ phases.}}$ As the first component has no more essentially less $\underline{b}$ electrons than the B^4 component, a great energy of formation cannot be expected, but Mg has a great atomic radius so that the $\underline{b}$ electron density is low and some expansion of $\underline{b}(B^4)$ electrons is possible, the $Mg_2B^4(CaF_2)$ phases fulfill the octet rule, Zintl's rule and display a FB2 binding. $HgSn_{12}$(H1) has $\underline{N}_{b}^{/A}=3.85$, the quasi tetragonal mesh of $\underline{a}$ may be compared with the tetragonal mesh of $\underline{a}_1$, $\underline{a}_2$(In), which finds in In a slightly strained FU stacking while in $HgSn_{12}$ it finds the HT stacking yielding a greater volume than the FU stacking. The H1 structure is therefore appropriate for $\underline{N}_{b}^{/A}>3$, in fact the FB2 binding yields here $\underline{N}_{P'}^{/A}=3.5$ $\underline{b}$ places per atom. This seems to contradict to the above $\underline{N}_{b}^{/A}=3.85$, but it was found earlier [22] that Sn permits considerable Hund insertion, so that $\underline{N}_{b}^{/A}$ may be greater than $\underline{N}_{P'}^{/A}$. It is quite characteristic that the H1 structure has not been formed with Ge or Pb as main component, as these atoms do not allow so much Hund insertion, corresponding to their diamagnetism, Sn being param.

The $\sqrt{2.5}$ commensurability of the FB2 binding is to be assumed for $HgPb_2$ ($SrPb_3$), this commensurability is confirmed in $InSn_{\underline{M}}$.

The $InSn_{0...0.1}$ marginal phase displays an increasing axial ratio $|\underline{a}_3|\ /|\underline{a}_1|$ with increasing Sn mole fraction (SR10.59). With respect to the binding $\underline{a}_{In}=(4.59;4.94)Å=\underline{b}_{FU}(2;3/2)=\underline{c}_{B}(\sqrt{8};3)$ it may be assumed that in a $\underline{a}_3$ direction the whole number commensurability is lost. Since this is energetically costly, the good commensurability in the $(\underline{a}_1,\underline{a}_3)$ plane is given up by choosing a somewhat greater commensurability element in this plane. This is the begin of the In_3Sn phase. Further increase of the valence electron concentration $N_{b}^{/A}$ will tend to improve the commensurability in the basal plane, therefore $|a_3|\ /|\underline{a}_1|$ decreases by increase of $\underline{N}_{b}^{/A}$(SR10.59). Further increase of $\underline{N}_{b}^{/A}$ attacks the stacking of the $(001)_{In}$ planes. In In and In_3Sn these planes are stacked with support number 4, but the support number 2 is a more volumous possibility. This change is so great that the binding in the plane falls back into the commensurability it had in In. The commensurability in TAB.11 is written for the tetragonal aspect of $InSn_5$, it gives only $\underline{N}_{P'}^{/A}=3.5$ $\underline{b}$ places per atom, while the $\underline{b}$ electron offer is 3.8. This is a new proof for the Hund insertion which had to be assumed in Sn.r ($\underline{a}=(5.83;3.18)$Å$=\underline{b}_{F'}(\sqrt{3.25};1)=\underline{c}_{B}(\sqrt{13};2)$). In $TlSn_{\underline{M}}$ too the binding analysis is instructive. The Tl structures suggest that Tl contributes about 3.2 $\underline{b}$ electrons per atom: Tl.1(W,SR8.114)3.88Å$=\underline{b}_B(1.5)=\underline{c}_C(3)$ offers $\underline{N}_{P'}^{/A}=3.4$ $\underline{b}$ places per atom and Tl.r(Mg,SR1.45,22.198)H3.46;5.53Å$=\underline{b}_{FH}(\sqrt{2.33};3/3)=\underline{c}_{BH}(\sqrt{2.33};12/3)$ offers even $N_{P'}^{/A}=3.5$. The binding in Tl_4Sn offers $N_{P'}^{/A}=3.4$. From this becomes TlSn.h immediately clear, the FB2 binding chooses in the tetragonal basal plane a neighboured commensurability.

Also the puzzling Tl_3Pb(Cu) becomes now comprehensible. There is no two-phase region between Tl_3Pb and Pb, but breaks in $\underline{a}(\underline{N}'_{Pb})$ have been found (SR16.107). Because of different valence electron concentration the binding in Tl_3Pb and Pb must be different.

Concluding remarks

The present chemo-geometrical analysis reveals an interesting distribution of occurring bonding types listed in TAB.12 over the $\underline{N}_{P''}^{/P'}$ values. For instance the $A^1B^4_{\underline{M}}$ alloys are quite foreign to the remaining alloys with respect to bonding as there are no common bindings. Also the brass like alloys with XX2 binding like HH2 or BB2 display an alloy class of their own. The $B^{2\cdots4}B^4_{\underline{M}}$ alloys have the property to permit only the FB2 binding. The table of bindings in $A^nB^4_{\underline{M}}$ alloys is very helpful for finding the correct binding: $\underline{N}_{P''}^{/P'}$ ($\underline{N}'_2$) is, as a rule, a smooth function. A phase not only chooses one of the bindings but also the commensurability of the binding to the crystal. Thus a simple classification arises which has an energetical meaning. As has been said the problem remains often why a certain binding (for instance BB2 instead of FF2) is stable. But this problem is well separated from the question, which binding is compatible with the requirements and rules; it may therefore be postponed. Indications for the correctness of a binding proposal are the main rules [3] especially the distance mole fraction diagram, and also additional rules, named minor rules, which have no broad validity. For instance a favourable binding of Sn.r can only be given when it is assumed that Sn.r permits a little amount of Hund insertion [22]; on the other side TlSn.h(CuAu) has the $\underline{b}$ electron contribution $N_{\underline{b}}^{/A}=3.5$ while the place number is $N_{P'}^{/A}=3.4$; both numbers come into agreement when it is assumed that Sn has also in TlSn.h a little amount of Hund insertion. The minor rules cannot be formulated all, but they may be taken from the tables.

Earlier it was assumed that the lower potential energy of the valence electrons of B^4 caused by the A^n atoms is the main source of energy of formation, but the present analysis shows that the distance $\underline{d}_{\underline{b}}(B^4)$ is not as strongly increased as was assumed earlier. Therefore an additional source of energy of formation is the descent of the $\underline{b}(A^n)$ electrons caused by the great $\underline{b}$ electron density of B^4. Every loss in potential energy corresponds to a loss in internal energy because of the virial theorem. The earlier assumption corresponded to an incorrectly extrapolated Ekman rule, while the present assumption corresponds to a better extrapolation. The phenomen of mole fraction dependent $\underline{b}(A^n)$ electron contribution may therefore be named the generalized Ekman rule. The problem why $\underline{d}_{\underline{b}}(B^4)$ is less strongly increased than $\underline{d}_{\underline{b}}(A^n)$ is decreased is explained by the stronger core forces in B^4 and by the variable $\underline{b}$ contribution of the A^n atoms.

The above binding proposals afford explanations for many crystal chemical phenomena:

(1) Why is $CoGe_2$(Q4.8) not isotypic to $CoSi_2(CaF_2)$? $CoGe_2$ is heavier than $CoSi_2$, therefore it aspires a closer packed structure, one means for this is the reduction of number of $\underline{c}$ places.

(2) Why has Ni_3Si_2.h a congruent melting point and is F-homeotypic to NiAs? The F-homeotypism is necessary to fill the $\underline{c}$ correlation sufficiently and make possible the FHH2 binding; since this is energetically favourable the structure is stabilized and permits a congruent melting point.

(3) Why do in $PdPb_M$ the NiAs homeotypes split into two compounds? There are two favourable commensurabilities for the $\underline{c}$ correlation available.

(4) Why are the $A^{n>3}B^4_M$ structures relatively uniform from mixture to mixture? The uniform $\underline{b}$ electron contribution of the $A^{n>3}$ atoms is the cause for this. It is a gratifying confirmation of the model that the logic of the binding analysis leads to this new and successful electron count.

Manymore explanations of crystal chemical phenomena are contained in the bindings of the tables, and may be formulated by the concepts of the model. However, at the present state of the model a further extension of the interpretation on other alloy and compound classes is necessary (three component alloys[2d]

When it is suspected that a binding proposal should be improved, at any case the distance- molefraction diagram and the $N^{/P'}_{P''}(N^{-}_{2})$ diagram should be drawn, also the homologous and quasihomologous alloys must be compared, finally the main and minor rules should be fulfilled.

It is fascinating how the two-correlations model connects many structural phenomena and generates a unified picture. The system of atomic and ionic radii had this property too, especially in the class of ionic compounds, but for the present alloy phases this system was not sufficient, some chemical influence had to be searched which works together with the radius influences and which affords enough parameters to classify the characteristic manifold of structures in AB_M^4 alloys. Chemists had early exploited the covalent bond concept interpreting many facts of molecular chemistry, but for the metallic phases like the present ones, this concept did not yet yield much understanding. However, the two-correlations model has some similarity with the covalent bond model, for instance both give "satisfactory" explanations for the Si structure and both have to do with electron counts. But while the covalent bond model was taylored for molecules, the two-correlations model makes mainly sense in crystals. As the two-correlations model is a conceptual model starting from the density matrix it avoids the convergence difficulties connected with the application of covalent bond to crystals because of bond interaction. The two-correlations model therefore found the essential influence of the core electrons on compound formation clearer than covalent bond theory and it could incorporate this influence easier into the model than any earlier valence model. Since just in the present alloy phases the influence of the core electrons is very strong, the two-correlations model is the first model to give a rational valence classification for them.

It should not be found fault in the fact that the present analysis is difficult to read. Any new model has this unkind property since we are not used in it. The formulae of the tables should in fact be studied phase for phase in order to recognize and appreciate the crystal chemical rules which are contained in them. Also somewhat involved is the access to learing the binding analysis. For instance the electron count is a prerequisite to find the correct binding, but the correct electron count may only be found when already many bindings have been found. This typical difficulty of inductive reasoning must be overcome by trial and error; therefore it cannot be expected that all trials are a solution, many trials will be killed by some observation or other. This is the reason why, the greater the set of phases is, for which the binding is sought, the more opportunities occur to examine a proposal. Finally then statements remain which interpret so many facts that in them some truth must be contained.

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