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ON THE BINDINGS IN $A^{1...15}B^{5}_{\underline{M}}$ PHASES

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Summary

The analysis of probable spatial correlations of electrons provides bonding types for many, especially metallic, $A^{n}B^{5}_{\underline{M}}$ phases (M=undetermined mole number), which were not classified with respect to bonding type before, i.e. which could not be interpreted by the earlier valence models. The structural systematics of the $A^{n}B^{5}_{\underline{M}}$ phases (n=homologous class number of element) reveals that here not only two correlations determine stability and structure of intermediate phases but even three. The $A^{4...10}$ atoms contribute only one or less than one valence electron into the b correlation and the remaining d electrons form an extra spatial correlation e which distinctly influences stability and structure of the compounds (plural-correlations model). This specific electron count is a reason for the remarkably high number of compounds in $A^{4...10}B^{5}_{\underline{M}}$ mixtures and also for the challenging complexity of their crystal structures. Furthermore the frequently noted uniformity of structures for variing n finds an easy explanation by the assumption that not all d electrons of the A^{n} atoms take part in the valence electron correlation. It is found that the intermediate phases of $A^{n}B^{5}_{\underline{M}}$ alloys may be collected into different classes according to their site number ratios. The main classes are the brass-like phases, the NiAs-like phases and the Si-like phases. Various structural phenomena are explained by the plural correlations model in a simple manner and numerous new experimental and theoretical problems arise from the analysis of the types of spatial correlation of electrons. The indications for a lattice-like binding are now quite numerous, a search for more direct consequences of spatial correlation of electrons appears rewarding.

Introduction

The crystal chemistry of $A^{n}B^{5}_{\underline{M}}$ mixtures has been reviewed for instance by 62 Run, 64 Sch, 65 Aro, 68 Hūl, 69 Lun, 72 War, 74 Cor, 77vSc, 78 Fra, 80 Cor, 81 Hul. The present review intends to contribute to the valence problem of these mixtures by assigning a bonding type (binding) to many crystalline phases. Reference to a phase is made by a Structure Reports citation (SR) and by citation of a source for the phase diagram (phd). From the SR reference the workers are readily found who own the merit of having solved the structure. The binding is analysed by means of the plural correlations model, a valence model for metallic phases (83aSch, this reference should be known in order to avoid misunderstandings, also the abbreviations and brief notations used below are collected and explained there). The spatial correlations of electrons are formed by rearrangement of the electron pair density in the peripheral parts of the atoms during the process of compound formation. Since this rearrangement is the only which happens during compound formation, spatial correlation is a reliable fundament of any valence model. It is clear that a first analysis like the present one can neither be complete nor free from mistakes, but it may be a first step on the way to analyse the electron spatial correlations in the stable compounds. Generally the proposals for the bindings in a mixture should be considered as a whole. It is helpful to plot for a considered mixture four simple functions of the mole fraction $\underline{N}_2'$ of the second component: the electron distances $\underline{d}$ in $\underline{b}$, $\underline{e}$, and in $\underline{c}$ correlation, and the site number ratio $\underline{N}_{S''}^{/S'}$ of the number of sites per cell in the $\underline{c}$ correlation (S") and in the $\underline{b}$ correlation (S').

When a series of wrong proposals has been assumed then probably the proper electron count has been missed. It is generally a difficulty of inference that a model parameter like the electron count finds its justification only by a considerable number of proposals, or ultimately by the whole interpretation. An example of an electron count which is presumably not the most favourable one is $Ni^{0,10}As^{5,10}_{\underline{M}}$. The d electrons of Ni are assumed to be in correlation with the d electrons of As although they are quite different in their behaviour. Franzen (1978) has stipulated an influencial d band in $AB_{\underline{M}}$ alloys and therefore the electron count should perhaps be $Ni^{0,10,8}As^{5,0,10}_{\underline{M}}$, i.e. besides the $\underline{b}$ correlation of the valence electrons there is an extra $\underline{e}$ correlation occupied only by d electrons of Ni and below both a $\underline{c}$ correlation is the quasi composition independent background of $\underline{b}$ and $\underline{e}$.

$\underline{A^1B^5_M \text{ phases.}}$ The investigation of this class of phases is still in progress. Conforming to the present understanding of the $A^1B^5_M$ phases (65Aro,77vSch) the electron count should be chosen for instance as $Na^{1,8}P^{5,8}_M$ where the first number in the exponent of an element is the $\underline{b}$ electron contribution (valence electrons) and the second number is the $\underline{c}$ electron contribution (peripheral core electrons).

The phases with smallest B^5 content in $A^1B^5_M$ mixtures are $A^1_3B^5$, and they obey the octet rule of Lewis. The structures of these Lewis phases (normal valence compounds) are mainly Li_3Bi(Fe_3Si type, F3.1, replacement homeotype of W, isotypes: Li_3Sb.r,Cs_3Sb,K_3Bi.h,Rb_3Bi,Cs_3Bi) and Na_3As(H6.2,RLS-homeotype of W, R=replacement, L= lacuna, S=shear; isotypes: Na_3P,K_3P,Rb_3As,htpCs_3As,Na_3Sb, K_3Sb,Rb_3Sb,Na_3Bi,K_3Bi.r). The phase K_3Bi.h(Fe_3Si) for instance obeys the supply rule of Zintl (as Bi forms a partial structure of Cu type of the frozen noble gases), it is R-homeotypic to W, has a valence electron concentration $\underline{N}^{/A}_{b}=2$ and permits the correlation $\underline{a}_W=\underline{b}_F(1)$ which may be completed by $\underline{a}_W=\underline{c}_B(\sqrt{8},2.8)$ for reasons of electron distances. The phase Na_3As(H6.2) only approximately obeys the supply rule of Zintl as the As form a partial structure of the Mg type.The correlation $\underline{a}=\underline{b}_{UH}(2;4/2)$ is homeotypic to $\underline{b}_F$ of K_3Bi.h and the reason for the heterotypism K_3Bi.h-Na_3As must lie therefore in the $\underline{c}$ correlation which cannot retain the commensurability found in the element Na because of the strong volume decrease caused by the relatively small $\underline{b}$ electron distance of B^5. If the $\underline{c}_C$ correlation of Na conserves its type and choses only a new commensurability then $U_HC_H\sqrt{3}$ is possible (see Table A1B5M) which might give a reason for the S-homeotypism Na-Na_3As by the commensurability rule (77Sch). It appears remarkable that K_3Bi.h(Fe_3Si) and K_3Bi.r(Na_3As) have approximately the same site number ratio $\underline{N}^{/S'}_{S''}=11$, and also a similar number of $\underline{c}$ sites per atom $\underline{N}^{/A}_{S''}(K_3Bi.h)=23$, $\underline{N}^{/A}_{S''}(Na_3As)=22.5$.

In the equi-atomic region mainly the phases NaSb(LiAs,M8.8,drawing 64Sch p.242,isotypes:NaSb,KSb) and NaP(O8.8,drawing SR45.103,isotypes:KP,NaAs,KAs, RbAs,RbSb,CsSb) are found. The LiAs type is in its projection on (010) homeotypic to NaCl but it does not fulfill the Lewis completion rule; the Zintl supply rule is obeyed as the As atoms form spiral chains in $\underline{a}_2$ direction. Instead of $\underline{b}_F$ as in NaCl a $\underline{b}_C$ correlation is found which may be completed to a $CU\sqrt{2}$ correlation (seeNaSb). The $\underline{d}_b$ value is somewhat small in the $\underline{d}(\underline{N}^{\prime}_2)$ plot, this corresponds to the distance rule which permits a smaller distance in a correlation with small coordination number. The structure of NaP is homeotypic to LiAs, the cell contains in both cases two B^5 spirals and the central lines of the spirals are ordered according to the Schläfli type $\hat{S}=4^4$

in NaSb and $\hat{S}=3^6$ in NaP. The $\mathrm{CU}\sqrt{2}$ binding of NaSb has 320 $\underline{c}$ sites per cell while the H_TC2 binding of NaP has 330; for the two phases NaSb and NaP this relation does fulfill the site number rule (81Sch), but for the heterotypism KSb(LiAs) - RbSb(NaP) it does not; perhaps here the greater volume difference between the components favours the greater site number. The site number ratios of NaSb and NaP are 6.9 and 7.0, and this fact accounts for the stability of phases lying between $A^1_3B^5$ and A^1B^5 using the favourable site number ratio 8. With respect to the catenation of B^5 atoms it may be noted that for instance NiAs does not show catenation, the phenomenon depends therefore not alone on the B^5 component, the A^1 component too contributes to it. Since the A^1 component strongly increases the $\underline{d}_{\underline{b}}$ distance of B^5 there is a $\underline{d}$-stress around these atoms which may be released by catenation.

A simple phase at greater mole fractions $\underline{N}'_{B}$ is KBi_2($MgCu_2$,F2.4, isotypes $RbBi_2$, $CsBi_2$). The binding analysis yields a twinned FB2 binding which is in the same commensurability to the structure as in In and this fits well to the valence electron concentration $\underline{N}_{\underline{b}}^{/A}=3.7$ of this phase.

In Na_3P_7 the P_7 form clusters which have in Na_3P_7.h(F3.7) statistical orientation so that the structure is of the Fe_3Si type with P_7 at the Si sites. In Na_3P_7.r the clusters are ordered. The binding interpretation of these structures must be postponed, perhaps Hund insertion comes into play here.

$\underline{A^2B^5_M\ \text{phases.}}$ Mg_3P_2(Mn_2O_3, B24.16,drawing64Schp.231) is a L-homeotype of $K_3B\bar{i}$.h(Fe_3Si) and Mg_2Si(CaF_2) (L=lacuna) with commensurability $\underline{a}=\underline{a}_{Mg2Si}(2)$. There are 16 lacunae on Mg places of Mg_2Si in the cell and the space group Ia3 permits a point set which allows a closer distance of some of them than the B1 set originally assumed (SR2.40). The phase obeys Lewis' rule, the structure follows Zintl's rule and the homeotypism Mg_2Si-Mg_3P_2 fulfills Bradley's rule that for increasing valence electron concentration lacunae may form in a structure (80Sch). The $\underline{b}_{\underline{F}}$ correlation is well-known (50Sch) but the $\underline{c}_{\underline{F}}$ correlation was only found with the help of the site number rule (82aSch). The binding does not request the commensurability $\underline{a}^{-1}_{Mg2Si}\underline{a}_{Mg3P2}=(2)$ but the closer distance of two lacunae may be energetically favourable. The introduction of lacunae into a structure while the $\underline{b}$ electron concentration increases is a means to conserve a favourable commensurability $\underline{b}^{-1}\underline{a}$, it is furthermore a mechanism for fulfilment of the volume rule (64Sch p.169) that increase of $\underline{b}$ concentration increases the atomic volume. The vacancies enter into the partial structure of the $\underline{b}$ electron poor component as this component is easier to be removed. The interference of L-homeotypism with increase

TABLE 1: A1B5M

Na3P(Na3As,H6.2,SR5.60)H4.99;8.81A=bUH(2;4/2)=cCH(√12;15/3)   N=16,64
NaP(08.8,SR45.102)6.038;5.643;10.142A=bHT(3;5;3.2/2)=cC(6;10;5.5)   N=48,128
Na3P7.h(F3.7;83Met.p.766)10.105A
Na3P7.r(024.56,83Met.p.766)13.740;10.391;13.446A   N=304,640
Na3P11.h(tetr,83Met.p.766)10.21;7.31A
Na3P11.r(012.44,SR39.92)10.410;12.466;9.828A=bC(√32;7)=cB(8;10)   N=232,448
NaP7(LiP7,81Hul)
NaP15(N   ,81Hul)
K3P(Na3As,SR26.53)H5.691;10.05A=idmNa3P UHCH√3
K5P4(,77vSch)
KP(NaP,SR45.102)6.500;6.016;11.288A=idmNaP HTC2
K2P3(Rb4P6,77vSch)
K3P7.h(Na3P7.h,83Met)10.603A
K3P7.r(,83Met)
K3P11.r(0   ,83Met)10.315;13.940;10.450A
KP10.3(,77vSch)
Kp15(Z4.60,71Eck)Z116.7^{o}97.5^{o}90.0^{o}23.74;9.69;7.21A
Rb2P3(S4.6,htpB2Al,AngCh86.1974.379)9.641;14.629;9.009A
Rb3P7.r(Na3P7.h,83Met)10.818A
Rb3P11.r(F3.11,83Met)11.592A
RbP7(CsP7,77vSch)
RbP10.3(,77vSch)
RbP11(M   ,77vSch)
RbP15(KP15,77vSch)
Cs2P3(Rb2P3,77vSch)
Cs3P7.r(Na3P7.h,83Met)11.167A
Cs3P11(F3.11,83Met)11.95A
CsP7(,77vSch)
CsP11(RbP11,77vSch)
CsP15(,77vSch)
Na3As(H6.2,SR5.59)H5.10;8.99A=bUH(2;4/2)=cCH(√12;15/3)seeHA   N=16,68
NaAs(NaP,77vSch)
Na3As7(,77vSch)
NaAs5
K3As(Na3As,SR5.7)H5.79;10.24A=idmNa3AS   phdE   cmp
K5As4
KAs(NaP,77vSch)   cmp
KAs2.h   cmp
KAs2.r
Rb3As(Na3As,SR26.54)H6.05;10.73A=idmNa3As
RbAs(NaP,77vSch)
Rb3As7.h(Na3P7.h,83Met)11.36A
Rb3As7.r(,83Met)
Cs3As(htpNa3As,SR26.54)
CsAs?
Cs2As3(Rb2P3)
Na3Sb(Na3As,SR5.7)H5.37;9.52A=idmNa3As UHCH√3   phdHA
NaSb(LiAs,SR23.29)6.03;6.34;-3.15,0,12.48A=bC(√8;3;2√8)=cU(4;5;8)
K3Sb(Na3As,SR5.7)H6.04;10.71A=idmNa3As   phdE   cmp
K5Sb4
KSb(LiAs,SR26.44)M115.1^{o}7.18;6.97;13.40A=idmNaSb CU√2   cmp
KSb2
Rb3Sb(Na3As,SR26.54)H6.28;11.18A=idmNa3As   phdE   cmp
Rb5Sb2.h
Rb5Sb2.r

of the $\underline{b}$ electron concentration causes that the number of electrons per $\underline{b}$ electron rich component remains constant. This is the octet completion rule of Lewis, and this rule is therefore also a consequence of the present valence model. The structural rule leading to the octet completion has been named the rule of <u>anion packings</u> (64Sch): the anion is in a closest packing and the cations are inserted into this packing to an extent that the valence rule is fulfilled.

MgP_4(CdP_4,M2.8,drawingSR42.108) does not follow Lewis' rule, but the structure follows Zintl's rule as 3-bonding and 2-bonding P atoms are present in equal number. The $\underline{a}_1$ and $\underline{a}_2$ axes form a quasi tetragonal mesh which fits to $\underline{b}_F$ just as in Mg_3P_2. The correlation $\underline{a}=\underline{b}_F(2;3)$ would give too many $\underline{b}$ places,therefore, following the occupation rule the $\underline{b}_F$ correlation must be strained: $\underline{a}=\underline{b}_F(2;5.5/2)$. Assuming the $\underline{c}$ correlation $\underline{a}=\underline{c}_B(4;6)$ would give the site number ratio $\underline{N}_{S''}^{/S'}=4.4$, while $\underline{a}=\underline{c}_U(4;7)$ would give $\underline{N}_{S''}^{/S'}=5.1$. The first may be preferred because of $\underline{d}_{\bar{c}}$. For simplicity here and in Table A2B5M the binding has been written as for an orthorhombic $\underline{a}$, the closer consideration shows that the binding excellently fits to the M2.8 cell. The (001) [0,1/2,0] shear of the Mg sites follows the rule for shearing to be derived from the model for the shear homeotypes of Cu3Au (64Sch p.99), also the monoclinic deformation of the cell may be favoured by the binding. For comparison to polyanion partial structures of other phases see SR42.109.

CaP(NaO,H6.6,isotypesSrP,CaAs,SrAs,EuAs) can be described as a compressed Mg type of Ca with octahedrally inserted P associating to pairs; the commensurability to NiAs is $\underline{a}=\underline{a}_{NiAs}(\sqrt{3};1)$, and Zintl's rule is fulfilled. Since Ca_3P_2(T) appears to be heterodesmic to Mg_3P_2 it might be that a FF2 binding stabilizes CaP, the commensurability may be chosen as to require ($K_{11}=\sqrt{12}$), or not require ($K_{11}=\sqrt{13}$), Hund insertion in $\underline{b}_F$; from the point of view of electron distances the binding with Hund insertion appears somewhat more probable. In CaP_3(Z2.6) there are infinite puckered (010) layers of P containing (in accordance with Zintl's rule) one three-bonding and two two-bonding atoms (73Dah). The phase is perhaps homeodesmic with MgP_4.

$Ba_4P_{2.7}$(Ce_2S_3,Lhtp anti-Th_3P_4,drawing64Sch p.326) follows Lewis' rule. The Ba atoms form an inhomogeneous deformation homeotype of W with $\underline{a}=a_W(2)$, into which the P are inserted. A twinned FF2 binding is possible and therefore a phase "BaP" has not been found. BaP_3(N2.6) follows Zintl's rule as for one three-bonding P two two-bonding P occur. The phase is a R-homeotype of P.m (black phosphorus), in which all atoms are three-bonding, the commensurability is $\underline{a}=\underline{a}_{P.m}(1;2;-1,0,1)$ where $\underline{a}_{P.m}(10.5;3.3;4.4)$Å. The $H_TB\sqrt{2}$ binding

Rb5Sb4
RbSb(NaP,SR45.13)7.315;7.197;12.815A=idm NaP cmp
RbSb2
Rb3Sb7.h
Rb3Sb7.r
Cs3Sb(htpNaTl,SR26.54)9.18A=idmK3Bi.h phdE cmp
Cs5Sb2.h
Cs5Sb2.r
Cs2Sb
Cs3Sb2
Cs5Sb4
CsSb(NaP,SR45.13)7.576;7.345;13.273A=idmNaP cmp
CsSb2
Cs2Sb7 cmp
Na3Bi(Na3As,SR5.7)H5.46;9.67A=idmNa3As phdHA cmp
NaBi(CuAu,SR2.237)3.47;4.81A=bFU(√2;3/2)=cC(√8;4) N=6,18
K3Bi.h(Fe3Si,SR28.44)8.805A=bF(2)=cB(√32;5.7) phdE cmp
K3Bi.r(Na3As,SR5.7)H6.19;10.95A=idmNa3As
K3Bi2
K9Bi7?
KBi2(MgCu2,SR2.271)9.520A=bFU(4;5.5/2)=cB(√32;5.5) N=88,224 cmp
Rb3Bi(Fe3Si,SR26.54)8.98A=idmK3Bi.h phdE cmp
Rb3Bi2
Rb5Bi4
RbBi2(MgCu2,SR26.54)9.60A=idmKBi2 cmp
Cs3Bi(Fe3Si,SR26.54)9.31A=idmK3Bi.h phdE cmp
Cs3Bi2
Cs5Bi4
CsBi2(MgCu2,SR26.54)9.76A=idmKBi2 FB2 cmp

TABLE 2: A2B5M

Mg3P2(Mn2O3,B24.16,SR3.353)12.03A=bF(4)=cF(8) N=256,692
MgP4(CdP4,M2.8,SR41.92)5.131,0,1.148;5.090;7.387A=bF(2;5.5/2)=cB(4;6) N=44,80
Ca3P2(T,65E11)
CaP(NaO,SR39.21)H7.632;5.731A=bF'H(√12;3.2/3)=cFHK'(2) N=42,96
Ca3P5
CaP3(Z2.6,SR39.42)Z69.96°79.49°74.78°5.590;5.618;5.665A
CaP5
Sr3P2
SrP(NaO,SR39.21)H8.040;6.031A=idmCaP FF2
Sr3P4(Sr3As4,   )
SrP2(BaAs2)
SrP3(N4.12,SR45.33)M103.45°11.432;7.387;8.561A
SrP14(M6.28,SR38.136)M123°11.642;12.759;6.352A
Ba3P2(Ce2S3,SR35.28)9.775A=bFU(4;5.5)=cFUK'(2) N=86,213
BaP2(BaAs2,   ) N=68,128
BaP3(N2.6,SR37.22)10.773;7.664;-4.507,0,4.765A=bHT(6.5/2;4;2.5)=cB(8;√32;√12)
Ba3P14(Sr3P14;SR45.33)M123.38°11.994;12.985;6.515A
BaP10(~TlP5,   )
Mg3As2(Mn2O3,SR3.353)12.355A=idmMg3P2 FF2
MgAs4(T4.16,SR43.21)5.385;15.798A=bF(2;5.5)=cU(4;14) N=88,192
Ca2As(La2Sb,U4.2,SR40.16)4.63;15.56A=bHT(2;8/2)=cFU(4;19/2) N=36,104
Ca5As3(Mn5Si3,SR44.106)H8.43;6.75A=bUH(√13;3.4/2)=cUH(√52;7/2)N=50,128
CaAs(NaO,SR39.21)H7.858;5.921A=idmCaP FF2
Ca2As3(M16.24,SR42.26)M131.63°11.985;5.806;18.314A

in Table A2B5M is written for simplicity for the orthorhombic cell which is formed by dropping the vector component $\underline{a}_{13}$=-4.507Å. As is easily verified the $H_TB/2$ binding is a forerunner of the frequent FB2 binding.

SrP_3(N4.12) may be understood as a shear homeotype of BaP_3.

$MgAs_4$(T4.16,drawingSR43.22) is homeotypic to MgP_4(M2.8) the Mg are octahedrally surrounded by As, but the stacking of the units is somewhat different. The binding comes as FU2 which affords more $\underline{c}$ places, as As contributes more $\underline{c}$ electrons than P.

Ca_2As(La_2Sb,U4.2,drawing64Schp.320) is homeotypic to Cu_2Sb with $\underline{a}=\underline{a}_{Cu2Sb}$ (1;2), the structure was first described for Ti_2Bi with a different space group (58Aue). The phase does not follow Lewis' rule, and Zintl's rule is poorely obeyed. If for CaAs(NaO) the F'F2 binding is accepted then for Ca_2As a H_TF_U2 binding comes, a forerunner of FF2. From the electron count Hund insertion of 1 $\underline{b}$ electron at As has to be inferred. For the closely neighbouring Ca_5As_3(Mn_5Si_3,drawing64Schp.306) a LF-homeotype of NiAs, a UU2 binding appears probable, another forerunner of FF2; also for this binding a Hund insertion with $\underline{N}_{\underline{b}}^{/As}$=4 is necessary.

$MgSb_M$ has the only compound Mg_3Sb_2 which has a melting temperature lying 600K above the melting temperatures of the components. The phase Mg_3Sb_2.h is isotypic to Mg_3As_2(Mn_2O_3) but Mg_3Sb_2.r(La_2O_3,H3.2,drawing64Schp.229) has a Mg type site set for Sb. The binding is of the FF2 type but at decreasing temperature Hund insertion sets in, generating an average electric dipole vector of $\underline{a}_3$ direction at every Sb; this factor favours the H3.2 type and confirms the Hund insertion. The La_2O_3 type does not appear for small B^5. Furthermore for $A^2_5B^5_3$ a radius ratio rule holds (78Bru), a great B^5 favours the Y_5Sb_3(O20.12) type against the Mn_5Si_3 type.

The phase diagram $CaSb_M$ shows a congruent melting point for $Ca_{11}Sb_{10}$ ($Ho_{11}Ge_{10}$,U22.20) a cell with 84 atoms. A UU2 binding might be possible, but since for such great cells the binding analysis is not yet certain, the full discussion should be postponed.

$CaSb_2$(M2.4) is a RDI-homeotype of Cu, the influence of the Hund insertion causes the formation of Sb chains (76Del). Since the Hund insertion strongly deforms the $\underline{b}$ correlation the analysis becomes somewhat less certain, but it appears acceptable that the binding is of the F'F2 type, i.e. a FF2 binding with Hund insertion (prime). Since Hund insertion (or lone pair) causes van der Waals distances the condensation of the Sb sites to chains becomes conceivable. If the valence electron concentration is calculated after subtracting the inserted electrons the value $\underline{N}_{\underline{b}}^{/A}$=3.3 is found which confirms the homeotypism of $CaSb_2$ to In.

CaAs3(CaP3)
Sr2As(La2Sb,SR42.23)4.83;16.13A=idmCa2As
Sr5As3(Mn5Si3,SR44.106)H8.94;7.35A=idmCa5As3
SrAs(NaO,SR39.21)H8.269;6.201A=idmCaP
Sr3As4(Eu4As3,SR43.23)14.84;17.89;5.97A
Sr2As3(Ca2As3,   )
SrAs3(EuAs3,SR43.100)Z.120.4°92.4°105.0°5.950;5.723;6.526A
Ba2As(La2Sb,SR42.23)5.13;17.36A=idmCa2As
Ba5As3(Mn5Si3,SR42.23)H9.49;7.90A=idmCa5As2
Ba3As4(Sr3As4,81Hul)
BaAs2(M,   )
Ba3As14(Sr3P14,   )
Mg3Sb2.h(Mn2O3,71Ec)=idmMg3P2 phdHA cmp
Mg3Sb2.r(La2O3,SR3.48,40.12)H4.568;7.229A=bF'H(2;4/3)=cFHK'(2) N=16,44
Ca2Sb(La2Sb,SR40.8)4.67;16.28A=idmCa2As phdM
Ca5Sb3.h(Mn5Si3,SR44.108)H9.824;7.057A=idmCa5As3
Ca5Sb3.r(Yb5,Sb3.r,SR40.8)12.502;9.512;8.284A
Ca11Sb10(Ho11Ge10,SR42.13)11.940;17.400A=bU(√18;7.5)=cUK'(2) N=288,752 cmp
CaSb2(M2.4,SR42.12)4.746,0,-2.549;4.177;8.719A=bFU(2;2;5/2)=cFUK'(2)
Sr2Sb(La2Sb,SR39.7)5.002;17.405A=idmCa2As phdM
Sr5Sb3(Mn5Si3,SR39.7)H9.496;7.422A=idmCa5As3
Sr11Sb10(Ho11Ge10,81Hul) cmp
Sr2Sb3(Eu2Sb3,SR49.19)M90.2°6.69;12.97;15.29A N=152,368
SrSb2(CaSb2,SR42.21)M101.68°4.887;4.280;9.177A
SrSb3
Ba2Sb(La2Sb,SR43.3)5.22;18.46A
Ba5Sb3(Mn5Si3,SR43.3)9.97;7.73A
Ba11Sb10(Ho11Ge10)
BaSb3(EuAs3,SR44.10)M112.66°10.807;8.519;6.471A
Mg3Bi2.h phdHA
Mg3Bi2.r(La2O3,SR3.356)H4.68;7.40A=idmMg3SB2.r
Ca2Bi(La2Sb,SR40.8)4.72;16.54A=idmCa2As phdS
Ca5Bi3.h
Ca5Bi3.r(Yb5Sb3,SR40.36)12.722;9.666;8.432A cmp
Ca11Bi10(Ho11Ge10,SR42.13)12.220;17.790A=idmCa11Sb2
CaBi3
Sr2Bi(La2Sb,SR43.3)5.01;17.68A=idmCa2As phdE
Sr5Bi3(Yb5Sb3,SR44.108)13.370;10.233;8.890A
Sr5Bi3(Mn5Si3,SR43.3)H9.63;7.63A=idmCa5As3
Sr11Bi10(Ho11Ge10,   )
SrBi3(Cu3Au,SR26.62)5.04A=bB(2)=cFU(4;5.6/2)

Ba2Bi(La2Sb,SR40.30)5.263;18.700A=idmCa2As
Ba5Bi3(Mn5Si3,SR44.108)H10.10;7.78A
Ba11Bi10(Ho11Ge10)
BaBi3(SrPb3,SR26.62)5.188;5.157A=idmSrBi3

$SrBi_3(Cu_3Au)$ is homeotypic to $SrSb_2(CaSb_2)$ and permits a BF_U2 binding. Since this binding must be twinned it is gratifying that $BaBi_3(SrPb_3)$ has been found.

$A^3B^5_{\underline{M}}$ phases. Beginning with ScP(NaCl,itpYP,LaP) the electron count $Sc^{3,8}P^{5,8}$ used in inorganic chemistry remains probable. The phase obeys Lewis' and Zintl's rules and the binding may be of the FF2 type, in analogy with Mg_3P_2 $(Mn_2O_3$,FF2). In relation with ScP a curious property should be noted. There is with respect to the b contribution of Sc Hund insertion at P possible but the structure is of a kind to give room for a b correlation without Hund insertion. Therefore, when Hund insertion occurs, then in the b correlation Frenkel detects are formed. This property is not general, but when it is present it may be said that the structure has the Frenkel property in the b correlation. The phases A^3P have the Frenkel property. It should be mentioned that $\underline{d}_c$=0.95Å falls far below the value to be respected from interpolation of the marginal values. This has a destabilizing influence and causes that in A^4P the NaCl type comes only with $ZrP_{0.9}$.h.

The polyphosphides LaP_2,LaP_5,LaP_7 occur similarly as the $A^1P_{\underline{M}}$ polyphosphides, their binding analysis shall be postponed here.

Also in $A^3As_{\underline{M}}$ several interesting structures must be postponed.

$Sc_2Sb(Cu_2Sb$, drawing 64Sch p.320) is RS-homeotypic to Cu with the commensurability $\underline{a}=\underline{a}_{Cu}$(1;1.5). If a CC2 binding is assumed then the electron count should be $Sc_2^{1,2,8}Sb^{5,0,10}$ so that energetically in between b and c there enters an e correlation $\underline{a}=\underline{e}_F$(1;3.7/2). Because of the very good commensurability of e to c the e correlation might be added to the c correlation, but it appears that the e correlation has a meaning of its own. $Sc_5Sb_3(Yb_5Sb_3$.h, 020.12,see SR37.8) is homeotypic to Rh_5Ge_3 and permits a HH2 binding with the count $Sc_5^{1,10}Sb_3^{5,10}$. These assumptions lead to a $\underline{N}_{S''}^{/S'}$=8 plateau with the sequence CC2, HH2, FF2 for increasing b electron concentration, the correlations become as a rule closer packed with increasing b electron concentration. In order to analyse the binding in $YSb_{\underline{M}}$ it is helpful to start from YSb(NaCl, FF2) which has a congruent melting point in agreement with the commensurability rule. However, in $LaSb_{\underline{M}}$ the melting maximum lies at $La_4Sb_3(Th_3P_4$,B6.8) which fortunately also permits a FF2 binding. The number of c sites per atom is $\underline{N}_{S''}^{/A}$=30.9 in La_4Sb_3 and $\underline{N}_{S''}^{/A}$=32 in LaSb(NaCl), the increase of b electron concentration for the heterotypism $La_4Sb_3 \rightarrow LaSb$ causes an increase of the $\underline{N}_{S''}^{/A}$ value and therewith a destabilizing decrease of the $\underline{d}_c$ distance. In $YSb_{\underline{M}}$ the phase $Y_4Sb_3(Th_3P_4)$ is a high temperature phase, probably the Frenkel

TABLE 3: A3B5M

ScP(NaCl,SR28.48)5.312A=bF(2)=cF(4)
YP(NaCl,SR28.48)5.662A=idmScP
YP5(NdP5,   )
LaP(NaCl,SR40.111)6.025A=idmScP
LaP2(LaAs2.h,SR41.84)M90.15°8.883;13.942;8.825A
LaP5(M4.20   ,SR42.105)M105.25°9.768;9.679;5.576A
LaP7(M4.28,SR41.85)M93.24°7.923;11.656;6.989A
Sc2.3As(U   ,SR44.106)14.374;8.026A
Sc3As2(Hf3P2,012.8,SR44.106)10.375;3.806;10.375A
ScAs(NaCl,SR44.106)5.487A=idmScP FF2
YAs(NaCl,SR29.101)5.805A=idmScP FF2
LaAs(NaCl,SR5.44)6.14A=idmScP FF2
LaAs2.h(LaAs2,N8.16,SR35.117)M135.16°12.89;14.45;9.14A
LaAs2.r(NdAs2,M4.8,SR35.117)M106.60°4.212;6.935;10.647A
Sc2Sb(Cu2Sb,SR44.121)4.205;7.790A=bC(2;3.7)=cCK'(2) N=22,52   N=100,280
Sc5Sb3(Yb5Sb3.h,020.12,SR44.121)11.079;8.713;7.627A=bHT(5;4;4/2)=cHTK'(2)
ScSb(NaCl,SR24.43)5.859A=idmScP
Y3Sb(Ti3P,T24.8,JLCM21.415)12.361;6.180A=bC(√26;2.5)=cCK'(2) N=112,272 phdM
Y5Sb3(Mn5Si3,ibid)H8.911;6.296A=bH(4;3)=cH(8;6) N=60,140
Y4Sb3.h(Th3P4,ibid)9.139A=bF(3)=cF(6) N=108,248
YSb(NaCl,SR24.43)6.163A=idmScP FF2 cmp
YSb2(ZrSi2,SR31.20)4.536;16.63;4.271A=bFU(2;11/2)=cHT(4;18/2) N= 52,112
La2Sb(U4.2,SR35.12)4.626;18.06A=bHT(2;9/2)=cHT(4;1.8/2) N=44,104 phdHA
La5Sb3(Mn5Si3,   )
La4Sb3(Th3P4,SR46.13)9.649A=idmY4Sb3.h N=108,248 cmp
LaSb(NaCl,SR5.44)6.48A=idmScP
LaSb2(Q4.8   ,SR32.19)6.314;6.175;18.56A=bFU(√8;12/2)=cC(√32;17) N=104,224
ScBi(NaCl,SR27.88)5.954A=idmScP
Y5Bi3(020.12,SR42.50)8.179;9.401;11.957A=idmSc5Sb3 phdM
YBi(NaCl,SR27.92)6.233A=idmScP cmp
La2Bi(La2Sb,SR43.102)4.674;18.390A=idmLa2SB phdM
La5Bi3(Mn5Si3,SR43.102)H9.614;6.694A=idmY5SB3
La4Bi3(Th3P4,SR43.102)9.759A=idmY4Sb3.h cmp
LaBi(NaCl,SR5.45)6.578A=idmScP
LaBi2(04.8,JLCM52.259)4.737;17.51;4.564A=idmYSb2

TABLE 4: A4B5M

Ti3P(T24.8,SR32.111)9.959;4.987A=bC(√26;2.5)=cCK'(2) N=64,328 phdM
Ti2P(H18.9,SR32.111)H11.531;3.458A=bH(6;1.8)=cHK'(2) N=63,216
Ti5P3(Mn5Si3,SR32.111)H7.223;5.094A=bUH(4;3.2/2)=cUHK'(2) N=40,128 cmp
Ti3P2(T?,SR33.129,30.161)7.483;10.495A
Ti4P3(Th3P4,SR33.10,30.161)7.425A=bF(3)=cF(6) N=124,224
TiP(H4.4,SR18.262)H3.499;11.65A=bH(2;7)=cUH(√12;14/2) N=36,64
TiP2(PbCl2,SR32.111)6.181;3.346;8.259A=bU(3;2/1;4)=cFU(6;5;8) N=56,96
Zr3P(Ti3P,SR31.53)10.799;5.355A=idmTi3P
Zr~2P(0   ,71Eck)16.715;27.572;3.674A
ZrP0.9.h(NaCl,SR18.262)5.27A=bF(2)=cF(4)
ZrP(TiP,SR18.262)H3.684;12.554A=idmTiP
ZrP2(PbCl2,SR33.128)6.494;3.513;8.744A=idmTiP2
Hf3P(Ti3P,71Eck)10.89;5.34A=idmTi3P
Hf2P(Ta2P,SR33.92)15.031;12.258;3.574A
Hf3P2(012.8,SR33.92)10.138;3.578;9.881A
HfP(TiP,SR27.233)H3.650;12.38A=idmTiP

property of the binding in Y_4Sb_3 yields a stabilisation when Hund insertion is reduced at elevated temperatures. $Y_5Sb_3(Mn_5Si_3)$ may have a HH2 binding which yields only $\underline{N}_{S'}^{/a}=48$ sites in the $\underline{b}$ correlation; this cannot be explained by Hund insertion at Sb alone, probably $\underline{b}$ electrons of Y descend. It is tempting to assume for $Y_3Sb(Ti_3P)$ a CC2 binding as for Y also a CC2 binding is not impossible. To be sure the correlation $\underline{a}=\underline{b}_C(\sqrt{26};2.5)$ gives only $\underline{N}_{S'}^{/a}=65$ sites in the cell which confirms the electron count $Y_3^{1,10}Sb^{5,10}$ or $Y_3^{1,2,8}Sb^{5,0,10}$.

For La_2Sb(U4.2), a homeotype of Cu_2Sb with commensurability $\underline{a}=\underline{a}_{Cu2Sb}(1;2)$, a HH2 binding could apply which would explain the homeotypic commensurability by the commensurability rule. $LaSb_2$(Q4.8,drawing SR32.21) is RS-homeotypic to Cu with $\underline{a}=\underline{a}_{Cu}(\sqrt{2};3)$; a F_UC2 binding is probable which incidentally explains the shear of the substructure, i.e. the shear which is sensible without reference to the super structure.

$\underline{A^4B_M^5}$ phases. The phase Ti_3P(T24.8,drawing 65Ros)is RDIC-homeotypic to NaCl (D=homogeneous deformation, I=inhomogeneous deformation, C=chain shear) with the commensurability $\underline{a}=\underline{a}_{NaCl}(2;1)$. From the bindings in $A^3B_M^5$ phases it may be inferred that the electron count is $Ti_3^{1,11}P^{5,8}$ and this leads to a CC2 binding. Unfortunately the present proposal is at variance with the proposal for the hometypic mixture $TiSi_M$; further analysis is necessary to remove this discrepancy. If the BC2F2 binding of Ti.h is described as BF2 binding then the site number ratio $\underline{N}_{S''}^{/S'}$ decreases in the heterotypism Ti.h→Ti_3P from the value 16 to the value 8. This decrease is caused by the P^5 electrons which contract strongly the $\underline{d}_b$ distance. The CC2 binding of Ti_3P opens a series of XX2 bindings (X=C,H,B,U,F), but it seems that the $\underline{b}$ electron contribution of Ti increases somewhat, for instance the UU2 binding of Ti_5P_3 tolerates the count $Ti_5^{2,10}P_3^{5,8}$ and the FF2 binding of Ti_4P_3 tolerates even $Ti_4^{3,9}P_3^{5,8}$. The vacancies in $ZrP_{0.9}$.h(NaCl) indicate that in the ideal "$Zr^{4,8}P^{5,8}$(NaCl)" there are too many $\underline{b}$ electrons. In the real $ZrP_{0.9}$ there are 34 $\underline{b}$ electrons, therefore perhaps some Hund insertion is at P.

The phase TiP(H4.4,drawing 64Sch p.267) is a S-homeotype of NaCl or NiAs with the commensurability $\underline{a}=\underline{a}_{NiAs}(1;2)$. It appears remarkable that for Ti_5P_3 holds $\underline{a}=\underline{a}_{TiP}(2;0.5)$, while from the point of view of atomic positions $\underline{a}=\underline{a}_{TiP}(\sqrt{3};0.5)$ should be expected; this is a good example for the influence of spatial correlation of electrons. The absence of lacunae in TiP suggests that the $\underline{b}$ correlation is no more of the F type but is strained to H because of a change in $\underline{c}^{-1}\underline{b}$ commensurability in the basal plane. It appears conspicious that $Hf_3As(Ta_3As)$ is only homeotypic and not isotypic to Ti_3P; the $d(A^4)$

HfP2(PbCl2,SR29.119)6.467;8.464;3.497A=idmTiP2
Ti3As(Ti3P,SR44.106)10.162;5.110A=idmTi3P CC2 phdE
Ti5As3(Yb5Sb3,O20.12,SR44.106)9.852;7.736;6.723A=bHT(5;4;4/2)=cHTK'(2)
Ti4As3(Th3P4,SR44.106)7.680A=idmTi4P3 FF2
TiAs(TiP,SR44.106)H3.642;12.055A=idmTiP
TiAs.h(NiAs,SR19.59)impurity stabilizedActChemSandA31.1977.514
TiAs2(O8.16,SR29.27)13.27;8.96;3.50A=bUH(9/2;6/2;2)=cFH(13.5;11/3;4) N=96,240
Zr3As(Ti3P,71Eck)10.973;5.450A=idmTi3P
Zr8As5(Nb8P5,O32.20,SR42.35)28.334;10.205;3.774A
ZrAs(TiP,SR22.46)H3.804;12.87A=idmTiP
ZrAs2(PbCl2,SR22.46)6.801;9.027;3.689A=idmTiP2
Hf3As(Ta3As,SR46.18)M90.291°15.390;5.380;15.333A=hdmTi3P
Hf2As(Ta2P,ACSc22.1968.2395)15.360;12.489;3.650A
Hf5As3(Nb5P3,ACSc22.1968.2395)27.388;3.611;12.305A
Hf3As2(Hf3P2,ACSc22.1968.2395)10.436;3.652;10.147A
HfAs(TiP,SR27.55)H3.765;12.681A=idmTiP
HfAs2(PbCl2,SR27.54)6.771;8.941;3.673A=idmTiP2
Ti4Sb(Ni3Sn.r,SR15.17)H5.958;4.808A=bCH($\sqrt{3}$;3.5/3)=cCHK'(2) phdHA
Ti3Sb(Cr3Si,SR27.43)5.219A=bB(2)=eC($\sqrt{8}$;2.8)=cB(4) N=16,18,68 cmp
Ti2.5Sb(U12.4,SR27.44)10.476;5.269A
Ti5Sb3(Yb5Sb3,SR44.121)10.217;8.328;7.146A=bFU(5;4;5/2)=cFUK'(2)
Ti1.2Sb(O   ,SR27.44)14.55;16.34;5.31A
TiSb(NiAs?,SR15.17)H4.115;6.264A=bH(2;3)=cUH($\sqrt{12}$;6/2) N=12,40 cmp
TiSb2(CuAl2,SR15.17)6.666;5.817A=bFU($\sqrt{10}$;4/2)=cU($\sqrt{20}$;5) N= 48,112
Zr3Sb(Fe3P,SR30.166)11.32;5.66A=bB($\sqrt{17}$;2)=cBK'(2) N=64,388
Zr2Sb.h
Zr2Sb.r(tetr.,SR30.166)6.52;7.90A
Zr5Sb3(Mn5Si3,SR27.379)H8.53;5.84A
ZrSb
ZrSb2(TiAs2,SR33.24)14.98;9.94;3.86A=idmTiAs2
Hf3Sb(Fe3P,SR30.144)11.23;5.65A=idmZr3Sb
HfSb(FeSi,SR30.145)5.59A=bB($\sqrt{5}$;2.2)=cFU($\sqrt{20}$;6.3)
HfSb~1(orth,SR30.145)13.87;10.36;3.78A
HfSb2.h(Cu2Sb,SR30.145)3.92;8.68A=bB($\sqrt{2.5}$;3.5)=cC($\sqrt{10}$;7)
HfSb2.r(TiAs2,SR33.24)14.96;9.86;3.85A=idmTiAs2
Ti3Bi(tetr.,SR24.67)6.020;8.204A phdE
Ti2Bi(U4.2,71Eck)4.05;14.50A=bB($\sqrt{2}$;5)=cBK'(2) N=28,24,104
Zr3Bi(Fe3P,71Eck)11.52;5.72A=idmZr3Sb phdS
Zr2Bi
Zr3Bi2 cmp
ZrBi
ZrBi2(TiAs2,SR33.24)15.49;10.18;3.97A
HfBi2(TiAs2,SR29.105)15.7;10.1;3.93A

electrons not involved in the b correlation evidently make a correlation of their own causing the deformation homeotypism. The discussion (80Wil) of the homeotypism Ti_3P-Fe_3P-Hf_3As appears quite helpful. The specific electron count explains the close homeotypism of $A^3B^5_M$ and $A^4B^5_M$.

$TiAs_2$(08.16) is homeotypic to $PbCl_2$ with the commensurability $\underline{a}=\underline{a}_{PbCl2}$ (2;1;1). It must be assumed that $TiAs_2$ is homeodesmic with TiP_2($PbCl_2$) and that a e correlation is responsible for the heterotypism. Numerous arsenides postponed in Tab. $A^4B^5_M$ owe their complicated structures to the interaction of a e correlation. As the e correlation is not as important as the b correlation, it is left out sometimes.

In Ti_3Sb(Cr_3Si) a homeotype of Ti_3P emerges which is here compatible with a count $Ti_3^{1,3,8}Sb^{5,0,10}$ and with the binding BB2. The CC2 binding of Ti_3P might stabilize Ti_4Sb(Ni_3Sn.r). It is satisfactory that $Ti_{2.5}Sb$(DhtpCr_3Si) is stable at greater b electron concentration. The TiSb(NiAs) phase is perhaps more complicated than assumed since, as its atomic volume does not fit to the volumes of the neighbouring phases; it does no more belong to the XX2 plateau and permits a $HU_H\sqrt{3}$ binding. The FU2 binding of $TiSb_2$($CuAl_2$) shows that this phase has the count $Ti^{0,12}Sb_2^{5,10}$ so that it obeys Ekman's rule (64Sch) which allots a b contribution $\underline{N}_b^{/A}=0$ to the A^n atoms.

Zr_3Sb(Fe_3P) and Hf_3Sb(Fe_3P) permit a BB2 binding. HfSb(FeSi) is perhaps of the Cr_3Si type this is yet to be confirmed; a twinned BF_U2 binding might apply. $HfSb_2$.h(Cu_2Sb) with a BC2 binding suggests that $HfSb_2$.r($TiAs_2$) contains Hund insertion.

$A^5B^5_M$ phases. The phase of V_3P(Ti_3P) confirms that the V^5 electrons are distributed on two different correlations and do not form a common band. With the count $V_3^{1,4,8}P^{5,0,8}$ the phase becomes isodesmic to Ti_3P(CC2). The same count yields in V_2P(Ni_2Si) a UU2 binding. The phase $V_{12}P_7$(Th_7S_{12},drawing 64Sch p.354) is shear-homeotypic to WC and is compatible with a UU2 binding; the b correlation has $\underline{N}_{ST}^{/a}=50$ sites per a-cell so that 45 d electrons are in a e correlation (for instance $\underline{a}=\underline{e}_H$(5;1.75)). The influence of three different correlations is a good expression for the obvious complication of the $A^5B^5_M$ mixtures but the analysis becomes more difficult as the third correlation may have a deforming influence on the other two. In V_4P_3(Nb_4As_3,drawing SR37.18) most P atoms are trigonal prismatically surrounded by V atoms, just as in V_2P,$V_{12}P_7$ and VP(NiAs); a FF2 binding appears possible but the analysis of the e correlation must be postponed. For VP(NiAs) a $HU_H\sqrt{3}$ binding is probable, the non-integral property of the commensurability element $K'_{33}=3.4$ might cause a weak superstructure but this has not yet been sought. V_4P_7.p(T8.14)

TABLE 5: A5B5M

V3P(Ti3P,SR37.125)9.387;4.756A=bC(√26;2.5)=eBK'=cCK'(2) N=64,256
V2P(Ni2Si,SR42.119)6.205;3.305;7.544A=bHQ(3.3;2/2;4)=cHQK'(2) N=20,128
V12P7(Th7S12,SR35.89)H9.299;3.279A=bUH(5;2/2)=cUHK'(2) N=35,212
V4P3(Nb4As3,Q16.12,SR39.119)3.261;13.23;17.30A=bFH(2/2;7;11/3)=cFHK'(2)
VP(NiAs,SR18.262)H3.18;6.22A=bH(√3;3.4)=cUH(3;6.8/2)
V4P7.p(T8.14,SR42.118)6.324;7.267A=bU(√8;4)=cFU(√32;9/2) N=70,216
VP2(OsGe2,N2.4,SR41.102)8.46,0,-3.51;3.405;6.255A=bB(4;1.5;3)=cCK'(2) N=40,116
VP4.p(CrP4,N2.8,CA95.1981.143239g)M110.88°5.263;10.98;5.87A FB2
Nb3P(Ti3P,SR31.53)10.128;5.089A=idmV3P CC2
Nb7P4(N14.8,SR31.53)M104,743°14.950;3.440;13.848A
Nb5P3(Hf5As3,SR37.118)25.384;3.433;11.483A
Nb8P5(O32.20,SR39.89)26.200;9.465;3.464A
NbP(NbAs,U2.2,SR28.9)3.325;11.38A=bU(√2;6)=eB(√2;5)=cB(√8;10) N=20,72
Nb4P7.p(V4P7.p,SR42.144)=idmV4P7.p UFU2 ACB32·1499
NbP2(OsGe2,SR29.125)M119.133°8.878;3.266;7.529A=idmVP2
Nb2P5(O8.20,SR46.106)16.742;3.350;7.912A
Ta3P.h(V3S.r,SR44.91)10.154;5.014A=idmV3P CC2
Ta3P.r(Ti3P,SR44.90)10.155;5.013A=idmV3P CC2
Ta2P(O24.12,SR31.58)14.419;11.552;3.399A
Ta5P3(Hf5As3,SR46.110)25.321;3.401;11.461A
TaP(NbAs,SR18.262,28.9)3.330;11.39A=idmNbP UB2
TaP2(OsGe2,SR29.128)M119.40°8.870;3.267;7.497A=idmVP2 BC2
V3As(Cr3Si,SR19.60)4.75A=bB(2)=eF(2)=cB(4) N=16,24,68
V5As3.h(Y5Bi3,SR42.33)6.440;7.677;9.285A
V5As3.r(W5Si3,SR43.25)9.503;4.826A=bB(√17;2)=cU(√17;2.5)=cBK'(2) N=70,90
V3As2(T12.8,SR43.25)9.413;3.336A=bFU(√22.5;2.4/2)=cFU(√90;2.4) N=40,60,176
V4As3.h(Cr4As3,N8.6,SR40.26)M100.521°13.725;3.393;9.230A
V4As3.r(Nb4As3,Q16.12,SR38.31)3.420;13.73;18.12A
VAs(MnP,SR38.32)5.850;6.292;3.362A=bH(3;3.2/1;2/2)=cUH(6/2;6.3/2;3)
VAs2(OsGe2,SR29.102)M119.784°9.059;3.272;7.481A=idmVP2 BC2
Nb3As(Ti3P,SR41.23)10.294;5.199A=idmV3P CBC2
Nb7As4(Nb7P4,SR34.138)M104.742°15.372;3.524;14.192A
Nb5As3(Hf5As3,SR34.138)26.070;3.520;11.787A
Nb4As3(Q16.12,SR34.15)3.516;14.661;18.830A
NbAs(U2.2,SR29.18)3.452;11.677A=idmNbP UBB2
NbAs2(OsGe2,SR29.19)M119.46°9.357;3.382;7.792A=idmVP2
Ta3As(N24.8,SR45.25)M90.572°14.677;14.551;5.095A=idmV3P
Ta2As(Ta2P,SR34.138)14.768;11.837;3.470A   N=40,50,16o
Ta5As4(Ti5Te4,U5.4,SR34.138)9.804;3.434A=bFU(√20;2.2/2)=eFUK'=cHT(√80;3.6/2)
TaAs(NbAs,SR42.32)3.437;11.644A=idmNbP UBB2
TaAs2(OsGe2,SR29.19)M119.75°9.350;3.388;7.760A=idmVP2 BC2
V3Sb(Cr3Si,SR22.24)4.934A=idmV3As BFB2
V3Sb2(Fe3Sn2,R6.4,SR43.18)H5.551;20.35A=bFH(√7;12/3)=eFHK'=cFHK'(2)N=78,72,264
V5Sb4(Ti5Te4,SR33.24)19.81;3.50A=idmTa5As4 FUFUHT2 N=50,40,160
VSb(NiAs,SR30.166)H4.28;5.44A=bH(2;2.5)=cUH(√12;5/2)
VSb2(CuAl2,SR15.18)6.555;5.635A=bFU(√10;4/2)=eU(√5;2.4)=cB(√20;4)
Nb3Sb(Cr3Si,SR29.126)5.264A=idmV3As BFB2 phdM
Nb3Sb2
Nb5Sb4(Ti5Te4,SR29.20)10.314;3.557=idmTa5As4 FUFUHT2
NbSb
NbSb2(OsGe2,SR30.14)M120.07°10.239;3.632;8.333A=idm VP2 BC2
Ta3Sb(Cr3Si,SR30.166)5.265A=idm V3As BFB2
Ta5Sb4(Ti5Te4,SR30.166)10.248;3.546A=idmTa5As4 FUFUHT2
TaSb2(OsGe2,SR30.166)M120.39°10.222;3.645;8.292A=idmVP2 BC2
VBiM(nic,phdM)contradicts to V3Bi(Cr3Si,71Eck)4.72A
NbBiM(nic,phdM)contradicts to Nb3Bi(W,71Eck),Nb3Bi.p(Cr3Si,71Eck)
TaBiM(nic, phdM)

is L-homeotypic to Cu_2Sb with commensurability $\underline{a}=\underline{a}_{Cu2Sb}(2;1)$ and is stabilized by UF_U2. The binding presents only 64 $\underline{b}$ sites so that 46 electrons per cell must be in the $\underline{e}$ correlation or in Hund insertion at P; a simple assumption is $\underline{a}=\underline{e}_F(2;4.5/2)$, it would require 8 electrons in Hund insertion at P confirming an assumption (76Jei) that lone pairs play a role in V_4P_7.p. The phase VP_2($OsGe_2$,drawing SR30.16,73Jei,68Hul p.122) displays CsCl related double layers parallel to $\underline{a}_1,\underline{a}_2$ alternating with a monolayer of P_2 dumbbells. The P_2 suggest that Hund insertion is present, in fact the $\underline{b}_B$ correlation of the BC2 binding yields only $\underline{N}_{PT}^{/a}=36$ sites while 8 P contribute $\underline{N}_{\bar{b}}^{/a}=40$ valence electrons when Ekman's rule (64Sch) is fulfilled, i.e. V contributes no $\underline{b}$ electrons. There are 20 d electrons for a $\underline{e}$ correlation which might satisfy $\underline{a}=\underline{e}_{HT}(4;1.7/2;3)$ using the cell described by the diagonal elements alone, alternatively a $\underline{e}_C$ correlation could be assumed together with a somewhat increased Hund insertion. In a review of AB_2^5 phases (73Jei) the diphosphides of V,Nb,Ta,Cr,W, the diarsenides of V,Nb,Ta,Cr,Mo,W and the diantimonides of Nb,Ta are listed as isotypes of $OsGe_2$; since $OsGe_2$ needs no Hund insertion this phenomenon is not necessary for the stability.

In VP_4.p(CrP_4,N2.8) the V are symmetrical to one another by space group; the V is octahedrally coordinated by P and the octahedra form by edge sharing zigzag chains along $\underline{a}_3$. Different chains have no common P but closely neighbouring P. All P together form a DI-homeotype of Cu. With the electron count $V^{0,5,8}P_4^{5,0,8}$ follow 80 $\underline{b}$ electrons per cell and these may be accounted for by a FB2 binding which may be formulated here for CrP_4.p:$\underline{a}$=5.19,0,-2.04;10.76; 5.40A$=\underline{b}_{FU}(3;6;4.5/2)=\underline{c}_B(\sqrt{18};2\sqrt{18};4.5)$; the 20 d electrons may be in $\underline{a}=\underline{e}_C(\sqrt{4.5};2\sqrt{4.5};2.25)$. The sequence of BC2 binding in VP_2 and FB2 binding in VP_4 obeys the rule for XX2 bindings that at greater $\underline{b}$ electron concentration a closer packed binding becomes stable.

Several NbP_M phases must be postponed as they have a somewhat large cell yielding a less-certain binding analysis. NbP(NbAs,U2.2,drawing SR28.10) is a homeotype of WC. Contrary to VP(NiAs) the Nb atom contributes one $\underline{b}$ electron as to be concluded from the UB2 binding. Therefore 16 $\underline{e}$ electrons might be in $\underline{a}=\underline{e}_B(\sqrt{2};5)$ and enforce the $\underline{c}$ correlation. The commensurability elements $\underline{K}_{33}^{c}=10$ and $\underline{K}_{33}^{e}=5$ probably cause the 4_1 axis.

V_3As(Cr_3Si) is homeotypic to V_3P(Ti_3P), instead of CBC2 a BB2 binding is found, but the d electrons of V are in a $\underline{e}_F$ correlation so that the binding must be named BFB2. The $\underline{e}$ electrons have an astonishingly increasing distance with increasing mole fraction $\underline{N}_B'$. Perhaps the As^{10} electrons tend to prefer a $\underline{c}_B$ correlation. In V_5As_3.r(W_5Si_3) a BUB2 binding emerges in a new commensurability yielding more $\underline{b}$ sites. V_3As_2(T12.8,drawing SR43.26) a filling homeotype of Ti_5Te_4 is compatible with FF2 and concludes probably the XX2 plateau of the mixture. The remarkable fit of the $\underline{c}$ correlation to the atomic sites should be noted. VAs(MnP) is heterotypic to VP(NiAs) and has the same binding in another commensurability. This special commensurability yields only $\underline{N}_{\underline{b}}^{/\underline{a}}$=19 electron sites per cell, perhaps one $\underline{b}$ electron of As has descended into a $\underline{e}$ correlation.

The phase Ta_5As_4(Ti_5Te_4,U5.4,drawing 64Sch p.344) may be described as consisting of B1 chains of Ti and F1 chains of Te. The $F_UF_UH_T2$ binding has an excellent fit to the atomic sites which was already found earlier (64Sch). The value $\underline{N}_{S''}^{/S'}$=6.5 occurred before in NbAs(U2.2,UBB2); this may be understood as a special case of the site number rule (80Sch), the heavier phase has the smaller $\underline{N}_{S''}^{/S'}$. A binding $F_UF_UF_U2$ appears improbable as Nb_5Sb_4(Ti_5Te_4) does not have a congruent melting point.

In V_3Sb(Cr_3Si,BFB2) the CBC2 of V_3P(Ti_3P) is not stable, the bindings are shifted to smaller $\underline{N}_B'$ mole fraction. The same is found for V_3Sb_2(Fe_3Sn_2,FFF2) as compared to V_4P_3(Nb_4As_3,FF2). Although the valence electron concentration does not exclusively depend on the B^5 Element it may be loosely said that in a heavier compound for a given binding a smaller valence electron concentration $\underline{N}_{\underline{b}}^{/A}$ is required. This may be subsumed to the site number rule: for increasing weight of a structure the number of sites per atom decreases. For VSb_2($CuAl_2$) the FB2 binding occurs which was found in VP_4.p(CrP_4). Curiously in $TaSb_{\underline{M}}$ as compared to $VSb_{\underline{M}}$ the increase in weight has consequences for the structures only in $TaSb_2$.

$A^6B^5_M$phases. The homeotypism $CrP_{\underline{M}}$-$VP_{\underline{M}}$ corroborates the electron count $Cr^{1,5,8}$ $P_M^{5,0,8}$. The phase Cr_3P(Fe_3P,U12.4,drawing 64Sch p.319) is homeotypic to V_3P (Ti_3P,T24.8) and both phases permit a CC2 binding, the difference lies probably in the $\underline{e}$ correlation. $Cr_{12}P_7$(Th_7S_{12}) is isotypic to $V_{12}P_7$ and both phases are interpreted by a UU2 binding. The FF2 binding appears not to occur in CrP_M. The phase CrP(MnP) permits the $HU_H\sqrt{3}$ binding of VAs(MnP); and CrP_2 ($OsGe_2$),CrP_4.p(N2.8) belong to the plateau $\underline{N}_{S''}^{/S'}$=4.

Mo_3P(V_3S.h,U12.4) is isodesmic to Cr_3P(Fe_3P), and the phases Mo_8P_5(M8.5) and Mo_4P_3(O32.24) are postponed as the binding analysis is not easy enough. MoP(WC,H1.1) has a $HU_H\sqrt{3}$ or more fully a $HU_HU_H\sqrt{3}$ binding with especially good $\underline{e}^{-1}\underline{a}$ commensurability. MoP_2(Q2.4) is homeotypic to $ZrSi_2$ and permits a $F_HH\sqrt{3}$ binding.

In $CrAs_M$ the phases Cr_3As(Cr_3Si),Cr_2As.h(Fe_2P),Cr_2As.r(Cu_2Sb) and perhaps Cr_3As_2 belong to XX2 bindings. CrAs(MnP) belongs to $HU_H\sqrt{3}$ and $CrAs_2$($OsGe_2$)

TABLE 6: A6B5M

Cr3P(Fe3P,U12.4,SR39.47)9.189;4.559A=bC(√26;2.5)=eBK'=cCK'(2)N=64,120 phdHA
Cr12P7(Th7S12,SR45.54)H8.981;3.313A=bUH(5;2.1/2)=eUHK'=cUHK'(2) N=47,60,152
CrP(MnP,SR30.98)5.362;3.113;6.018A=bH(3;2/2;3.4)=eFH(3;2/2;4/3)=cUH(6/2;3;6.8)
N=20,24,64 N=40,24,96
CrP2(OsGe2,SR39.8)8.213,0,-3.492;3.034;6.180A=bB(4;1.5;3)=eFU(4;2;3)=cCK'(2)
CrP4.p(N2.8,SR38.74)5.191,0,-2.035;10.760;5.400A=bFU(3;6;4.5/2)=eC(√4.5;...)
Mo3P(V3S.h,SR30.69)9.794;4.827A=idmCr3P CBC2 =cB(√18;...)
Mo8P5(M8.5,SR38.126)M109.592°9.399;3.209;6.537A
Mo4P3(O32.24,SR30.67)12.428;3.158;20.440A
MoP(WC,SR18.263)H3.23;3.20A=bH(√3;1.7)=eUH(√3;2/2)=cUH(3;3.4/2) N=5,6,16
MoP2(Q2.4,SR28.33)3.145;11.184;4.983A=bFH(2/2;6;3.3/3)=e=cH(3;12/2;4/7)N=40,24,96
MoP4(CrP4,SR38.74)M110.64°5.313;11.139;5.820A=idmCrP4 FB2
W3P.h(V3S.h,71Eck)9.858;4.800A=idmCr3P CBC2
WP(MnP,SR28.48)5.734;3.249;6.222A=idmCrP HFHUH2
WP2.h(MoP2,SR28.33)3.145;11.184;4.984A=idmMoP2
WP2.r(OsGe2,SR29.128)M119.33°8.501;3.167;7.471A=idmCrP2
Cr≈5As(T ,SR24.44)2.90;6.25A
Cr3.1As0.9(Cr3Si,SR30.110)4.616A=bB(2)=eF(2)=cB(4)
Cr2As.h(Fe2P,SR33.151)H6.307;3.445A=bFH(3;2/3)=eH(√12;2)=cFHK'(2)
Cr2As.r(Cu2Sb,SR33.110)3.595;6.344A=bU(√2;3)=eFU(2;5/2)=cUK'(2)
Cr3As2(T18.12?,SR24.44)7.05;9.05A=bU(√8;4.5)=eUK'=cUK'(2)
Cr4As3(N8.6,SR37.13)M102.19°13.168;3.542;9.302A
CrAs(MnP,SR37.12)5.649;3.461;6.208A=idmCrP HUH/3
CrAs2(OsGe2,SR39.8)M119.88°;8.893;3.273;7.389A=idmCrP2
Mo5As4(Ti5Te4,SR31.24)9.601;3.278A=bFU(√20;2.2/2)=eFUK'=cHT(√80;3.5/2)
MoAs(MnP,SR31.24)5.978;3.360;6.415A=idmCrP
Mo2As3(N4.6,SR31.22)M136.74°16.061;3.235;9.643A
MoAs2(OsGe2,SR30.21)M119.35°9.067;3.300;7.781A=idmCrP2 BC2
MoAs5(LhtpFeS2.r,SR30.21)5.299;5.983;2.884A
W4As5(M ,71Eck)M99.2°7.99;3.28;6.88A
W2As3(Mo2As3,SR31.22)M139.648°15.966;3.279;9.599A
WAs2(OsGe2,SR29.102)M119.50°9.079;3.318;7.692A=idmCrP2
CrSb(NiAs,SR9.22)H4.135;5.462A=bH(2;2.6)=cUH(√12;5.2/2) phdHA cmp
CrSb2(FeS2.r,SR9.22)3.275;6.020;6.877A
Mo3Sb7(Ru3Sn7,SR31.18)9.571A=bF'(3)=eF'K'=cU(6;7)
WSbM(nic,phdM)
CrBiM(nic,phdHA)
MoBiM(nic,phdM)
WBiM(nic,phdM)

TABLE 7: A7B5M

Mn3P(Fe3P,SR27.275)9.181;4.568A=bC(√26;2.5)=eBK' =cCK'(2) N=64,144,256 phdHA
Mn2P(Fe2P,SR23.68)H6.074;3.454A=bH(√12;2)=eF'H(√12;2.5/3)=cHK'(2) N=21,36,72 cmp
Mn3P2.h
MnP(O4.4,SR3.17)5.258;3.172;5.918A=bH(3;2/2;3.3)=cUH(6/2;3;6.6/2) N=20,28,64
MnP4.p(Z2.8,SR46.98)
MnP4.p(Z6.24,81Rüh)
MnP4.p(N8.32,SR41.94) Tc3P(Fe3P,82Rüh)9.568;4.736A
TcP2
TcP3(O4.12,82Rüh)15.359;3.092;5.142A
TcP4 (ReP4,82Rüh)6.238;9.215;10.837A
Re2P(Ni2Si,SR26.227)5.540;2.939;10.040A
Re3P4(Cr3S4,N3.4,SR31.57)M114.073°12.179;3.012;6.042A
Re6P13(R12.26,SR45.103)H15.679;8.320A

to BC2. In $MoAs_{\underline{M}}$ no XX2 bindings are found but $Mo_5As_4(Ti_5Te_4)$ has a $F_UF_UH_T2$ binding.

In CrSb(NiAs) the MnP type is not stable as the big Sb does not tolerate $K''_{11}=3$ but requires $K''_{11}=\sqrt{12}$, the next integer commensurability possibility.

$Mo_3Sb_7(Ru_3Sn_7$,B6.14) a LI-homeotype of CsCl permits a FFU2 binding. It is interesting that earlier (53Sch) the binding $\underline{a}=b_C(6)$ for the count $Ru_3^8Sn_7^4$ was given which is closely related to the present binding.

$\underline{A^7B^5_M}$ phases. From phase diagrams like $MnZn_{\underline{M}}$ it is known that $Mn.h_1$ is stabilized by small mole fractions $\underline{N}'_{Zn}$ at room temperature. This means (84bSch) that Mn presents for $B^{n>2}$ components a $\underline{b}$ electron contribution of $\underline{N}'^{/Mn}_{b} \approx 1$. At higher valence electron concentrations Mn will follow Ekman's rule (see 64Sch) and contribute no $\underline{b}$ electron. Therefore for $Mn_3^{1,6,8}P^{5,0,8}(Fe_3P)$ a CC2 binding may be expected with $\underline{e}$ electrons in a B or U correlation. In $Mn_2P(Fe_2P)$ a $H\breve{F}_HH2$ binding provides a congruent melting point. For the phase $Mn_3P_2.h$ a XX2 binding with X=B,U or F will be open. In MnP(04.4) the $HU_H\sqrt{3}$ binding applies, the commensurability of $\underline{c}_{UH}$ to the cell is as in VP(NiAs), but for $\underline{b}_H$ two possibilities are open either $\underline{b}_3 \| \underline{a}_1$ or $b_3 \| a_3$, The first possibility would stabilize the NiAs type while the second possibility stabilizes the MnP type. The $\underline{b}_H$ correlation reveals that MnP follows the Ekman rule so that the $\underline{b}$ electron contribution of Mn is zero. The $MnP_4.p$ phases are homeotypic and homeodesmic to $CrP_4.p$, which allows for a FB2 binding, the structural difference must be caused by the $\underline{e}$ correlation. The remaining $A^7P_{\underline{M}}$ phases are less simple structured so that they must be postponed.

Mn_3As(012.4,drawing 64Sch p.320) is homeotypic to Cu_2Sb and therefore remotely homeotypic to NaCl just as $Mn_3P(Fe_3P)$ is remotely homeotypic to NaCl. Both Mn_3P and Mn_3As are compatible with a CC2 binding, but while in Mn_3P there are $\underline{N}'^{/A}_{S'}=65/32=2.03$ $\underline{b}$ sites per atom site in the basal plane in Mn_3As there are $\underline{N}'^{/A}_{S'}=8.5/4=2.11$, probably the larger As atom does not tolerate the smaller site number in the basal plane. The atom layers parallel (001) display the sequence of support numbers (coordination of an atom into the underlying plane) 4,4,4,1 in Mn_3As and 4,4,1 in Mn_2As, the phase richer in valence electrons (Mn_2As) has the less close packed structure, a special case of the general volume rule (64Sch p.169). While Mn_3As has a CC2 binding, Mn_2As has a HH2 binding in H_T aspect. A curious effect is that $Mn_2As.p$ has more valence electrons per atom than Mn_2As; perhaps the pressure promotes $\underline{e}$ electrons into the $\underline{b}$ correlation. Another curiosity occurs in MnAs, the $\underline{c}$ correlation of $MnAs.h_1$ is exactly in phase with the $\underline{b}$ correlation so that the structure becomes orthorhombic as the $\underline{c}$ correlation is only pseudo hexagonal; because of the temperature dependent $\underline{b}$ contribution of Mn in MnAs.r and MnAs.h_2 the $\underline{c}$ correlation is not exactly in phase with $\underline{b}$ correlation so that the stacking of $\underline{c}$ staggers and the structure becomes hexagonal.

MnBi(NiAs) undergoes a transformation without change of structural type at 600K. The fact that the axial ratio $|\underline{a}_3|/|\underline{a}_1|$ decreases with increasing temperature confirms that the $\underline{b}$ electron contribution of Mn decreases with increasing temperature.

$\underline{A^8B^5_{M}}$ $\underline{\text{phases.}}$ The homeotypism of $FeP_{\underline{M}}$ to $MnP_{\underline{M}}$ confirms the electron count $Fe^{\bar{1},7,8}P^{5,0,8}_{\underline{M}}$. The elevated $\underline{e}$ contribution 7 suggests an increased influence of the $\underline{e}$ correlation. For Fe_3P(U12.4) the CC2 binding is probable and it is supplemented by a $\underline{e}_U$ correlation which is fully occupied; this finding fits to the fact that $CoP_{\underline{M}}$ does not contain a "Co_3P" phase. Fe_2P(H6.3) allows a BB2 binding which is supplemented by $\underline{e}_{FH}$. In FeP(MnP) the $\underline{e}_{FH}$ correlation requires Hund insertion to accept all $\underline{e}$ electrons; the little off integral commensurability in the $\underline{a}_2$ direction must be considered as a means to allow for the better commensurability of $\underline{e}_{FH}$. $FeP_2(FeS_2.r)$ is lacuna-homeotypic to FeP(MnP) so that the P partial structure is conserved in the Mg type. A FU2 binding fits well. An $\underline{e}$ correlation might exist with $\underline{a}=\underline{e}_{HT}(2\sqrt{2};2.25\sqrt{2};1.8/2)$. In FeP_4.p(Q2.8) a FB2 binding appears possible. The $\underline{e}$ correlation cannot yet be given as it will degenerate from a spatial correlation to a layer or beam or cluster correlation.

$Fe_2As(Cu_2Sb)$ yields a HH2 binding and Fe_3As_2.h probably also belongs to the brass plateau ($\underline{N}^{/S'}_{S''}=8$). The $A^8Sb_{\underline{M}}$ phases are isotypic to earlier phases and in $A^8Bi_{\underline{M}}$ few phases occur because of the large Bi.

$\underline{A^9B^5_{M}}$ $\underline{\text{phases.}}$ $Co_2P(PbCl_2)$ is RDI-homeotypic to Cu and it allows a UU2 binding which is supplemented by a $\underline{e}_B$ correlation; the phase $Ni_2Si(PbCl_2)$ proves that there is some communication between $\underline{b}$ and $\underline{e}$ correlation, i.e. $\underline{e}$ electrons may ascend into the $\underline{b}$ correlation and vice versa. CoP(MnP) is the last member of the isotypic series CrP, MnP, FeP, CoP and it is distiguished from the predecessor by its short axial ratio (see 64Sch p.331). The $HU_H\sqrt{3}$ binding shows why the axial ratio changes: the commensurability in direction of the short $\underline{a}_2$ axis surmounts somewhat the integral value, this may happen at the end of an isotypic series. In the MnP type the A atom is coordinated octahedrally by B atoms, this type of coordination is conserved in $CoP_3(CoAs_3$, drawing 64Sch p.348), a I-homeotype of ReO_3(C1.3) with commensurability $\underline{a}=\underline{a}_{ReO3}(2)$. The binding is not of the FB2 type but of the neighbouring BC2

Re2P5(Z8.20,82aRüh)
ReP3(TcP3,82Rüh)15.354;3.122;5.130A
ReP4(O8.32,SR45.104)6.227;9.231;10.854A
Mn3As(O12.4,SR15.19)3.788;3.788;16.29A=bC(2;8.5)=eBK'=cCK'(2) N=32,60,136phdE
Mn2As(Cu2Sb,SR22.57)3.769;6.278A=bHT(2;3.8/2)=eB(2;3.3)=cHTK'(2)N=14,24,52cmp
Mn2As.p(Fe2P,SR38.27)H6.363;3.678A=bH(√12;2)=cHK'(2)
Mn3As2.h
Mn3As2.r(T ,71Eck)6.85;7.12A
Mn4As3(T ,71Eck)6.10;7.29A
MnAs.h2(NiAs,SR29.25)
MnAs.h1(MnP,SR29.25)5.72;3.676;6.379A=bH(3/1;2;4/2)=eHK'=cUH(6/2;√12;6)
MnAs.r(NiAs,SR11.39)H3.718;5.702A=bH(2;3)=cUH(√12;6/2)
Tc3As7(Ru3Sn7,71Eck)8.702A=bF'(3)=eFK'=cU(6;7) N=140,84,376
Re3As7(Ru3Sn7,SR34.27)8.716A=idmTc3As7
Mn2Sb(Cu2Sb,SR19.53)4.078;6.557A=idmMn2As phdHA
MnSb(NiAs,SR18.46)H4.128;5.789A=idmMnAs.r
TcSbM
ReSbM(nic,phdM)
Mn1.08Bi.h(NiAs,SR18.46)H4.380;5.991A phdM
MnBi(NiAs,SR18.46)H4.286;6.116A=idmMnAs.r
TcBiM
ReBiM(nic,phdM)

TABLE 8: A8B5m

Fe4P(O4.1,SR26.178)3.95;4.01;4.32A metastable? phdHA
Fe3P(U12.4,SR27.97)9.107;4.460A=bC(√26;2.5)=eU(√26;3.2)=cCK'(2) N=64,168,256
Fe2P(H6.3,SR23.68)H5.865;3.456A=bH(√12;2)=eF'H(√12;2.5/3)=cHK'(2)N=21,42,72cmp
FeP(MnP,SR27.319)5.191;3.099;5.792A=bH(3;2.1/2;3.3/1)=eFH(3;2/2;4/3)=cUH(6/2;3;6.6/2) N=20,32,64
FeP2(FeS2.r,SR1.495)4.973;5.657;2.723A=bF(2;2.3;2.2/2)=cU(4;4.5;2.7)N=20,16,48
FeP4(M6.24,SR44.75)M101. 48°4.619;13.670;7.002A
FeP4.p(Q2.8,SR4.475)5.005;10.212;5.530A=bF(2;4;2.2)=cB(4;8;4.5) N=80,32,160
Ru2P(Ni2Si,SR24.130)5.902;3.859;6.896A=bFU(3;2;5/2)=eU(3;2;4.5)=cFUK'(2)N=28,
RuP(MnP,SR27.319)5.520;3.168;6.120A=idmFeP cmp 56,96 phdM cmp ↗
RuP2(FeS2.r,SR33.63)5.117;5.893;2.871A=idmFeP2
RuP4.h(Z3.12,SR44.88)Z RuP4.r(CdP4,82Flö)
OsP(68Hul)
OsP2(FeS2.r,SR33.63)5.100;5.901;2.918A=idmFeP2
OsP4.h(RuP4,SR44.119)Z OsP4.r(CdP4,82Flö)
Fe2As(Cu2Sb,SR3.34,21.43)3.627;5.981A=bHT(2;3.8/2)=eU(2;4)=cHTK'(2)phdM cmp
Fe3As2.h
FeAs(MnP,SR2.7,21.43)5.432;3.372;6.023A=idm FeP cmp
FeAs2(FeS2.r,SR33.63)5.300;5.983;2.882A=idmFeP2
RuAs(MnP,SR26.25)5.70;3.25;6.27A=idmFeP
RuAs2(FeS2.r,SR26.55)5.41;6.17;2.96A=idmFeP2
OsAs2(FeS2.r,SR26.55)5.40;6.16;3.00A=idmFeP2
Fe3Sb2(NiAs,SR1.765)H4.132;5.175A=bH(2;2.5)=e...=cUH(√12;5/2) phdHA
FeSb2(FeS2.r,SR1.597)5.831;6.533;3.195A=idmFeP2
RuSb(MnP,71Eck)
RuSb2(FeS2.r,SR24.45)5.942;6.650;3.174A=idmFeP2
OsSb2(FeS2.r,SR24.45)5.937;6.684;3.210A=idmFeP2
FeBiM(nic,phdM)
Ru2Bi?
RuBi?(see68Hul)
RuBi3(NiBi3?)
OsBiM

type (or BCC2 type) with very high occupation.

A hexahedral coordination of B by A is stable in $Rh_2P(CaF_2)$ which allows a CUC2 binding. The trigonal prismatic coordination of B by A is recovered in Rh_4P_3(016.12,drawing 64Sch p.326) a homeotype of Co_2P. A UU2 binding appears possible but the $\underline{e}$ correlation is not yet known. $RhP_2(CoSb_2$,M4.8) is a homeotype of $FeP_2(FeS_2$.r,02.4,64Sch p.343). FeP_2 may be memorized as a L-homeotype of NiAs with the commensurability $\underline{a}=2.7;5.7;4.7\text{Å}=\underline{a}_{NiAs}(1,-1,0;1,1,0;0,0,1)$. Analogously $\underline{a}_{CoSb2}=\text{M}117.7^{\circ}6.5;6.4;6.6\text{Å}=\underline{a}_{NiAs}(1,1,1;1,-1,1;1,0,-1)$. It may be conjectured that a FU2 binding applies as in FeP_2 and that the heterotypism is caused by the $\underline{e}$ correlation.

Co_2As.h(Fe_2P) is isodesmic to Fe_2P, evidently Co contributes more than one electron to the $\underline{b}$ correlation. The temperature dependence of the $\underline{b}$ contribution causes a phase transformation. The same phenomenon is found in CoAs.h(NiAs). The $HU_H\sqrt{3}$ binding presents $\underline{N}^{/a}_{S^T}=12$ sites per cell in the $\underline{b}$ correlation and the NiAs structure is only stable as long as Co contributes 1 $\underline{b}$ electron per atom. At lower temperatures the contribution is presumably smaller than 1, as it was found in $NiZn_{\underline{M}}$ (see e.g. 64Sch p.62).

$\underline{A^{10}B^{5}_{\underline{M}}\text{phases.}}$ $Ni_3P(Fe_3P)$ has an isotype in $FeP_{\underline{M}}$ but not in $CoP_{\underline{M}}$. The reason is that in between the CUC2 binding of Fe_3P and the $CH_T\sqrt{2}C2$ binding of Ni_3P there is no favourable binding for "Co_3P" available. In Ni_5P_2(H120.48?), a homeotype of Pd_5Sb_2, a C_HH2C_H2 binding is found. The site number ratio $\underline{N}^{/S'}_{S''}(C_HH2)=8/\sqrt{6}$ of Ni_5P_2 is not smaller than $\underline{N}^{/S'}_{S''}(CH_T\sqrt{2})=8/\sqrt{6}$ of Ni_3P but the easy compressibility of C_H in $\underline{b}_3$ direction attributes to the slightly compressed C_HH2 a smaller $\underline{N}^{/S'}_{S''}$ value so that it stabilizes the Ni_5P_2 phase. $Ni_{12}P_5$(U12.5, drawing 64Sch p.319) is FDI-homeotypic to Ni_3P. The CC2 binding has a commensurability different from that in Ni_3P and it is supplemented to $CC\sqrt{2}C2$ with $\underline{N}^{/S(b)}_{S(e)}=2.8$ (84aSch). In $Ni_2P(Fe_2P)$ a HH2 binding is found which concludes here the $\underline{N}^{/S(b)}_{S(c)}=8$ plateau. Ni_5P_4(H20.16) is a F-homeotype of NiAs with the commensurability $\underline{a}=\underline{a}_{NiAs}(2)$. Apparently the $\underline{b}$ contribution of Ni is greater in the presence of P than in the presence of As, therefore the axial ratio of Ni_5P_4 is quite high as compared with NiAs. In order to conserve the favourable $HU_H\sqrt{3}$ binding of NiAs Ni atoms are filled in. NiP(08.8,drawing SR30.73,74) is homeotypic to CoP(MnP,$\underline{a}_{CoP}=(5.6;5.1;3.3)\text{Å}$) with the commensurability $\underline{a}=(6.1;4.9;6.9)\text{Å}=a_{CoP}(1;1;2)$. The $\underline{e}$ correlation appears to be the cause for the heterotypism CoP-NiP. The phase NiP_2.p(FeS_2.h) a I-homeotype of CaF_2, is isotypic and FFB2-isodesmic to PtP_2 in agreement with the site number rule (80Sch) which allots less $\underline{c}$ sites to heavy phases and to phases under pressure. It is

TABLE 9: A9B5M

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Co2P.h(Fe2P,Ellner1984)H5.723;3.476A
Co2P(PbCl2,SR11.98,24.128)5.646;3.513;6.608A=bU(23;2/1;3)=eB(2.5√2;2.2;3√2)=
 cUK'(2)  N=28,64,96  phdHA  cmp                     (6/2;3.3;6.6/2)N=24,32,64
CoP(MnP,SR27.319)5.077;3.281;5.587A=bH(3;2.2/2;3.3/1)=eF'H(3;2.2/2;4/3)=cUH
CoP3(CoAs3,B4.12,SR34.117)7.707A=bB(4)=eC(4)=cC(8)  N=120,72,256
Rh2P(CaF2,SR8.106,24.48)5.498A=bC(3)=eU(3;3.7)=cC(6)  N=28,64,96  phdHA
Rh3P2(LhtpCu2Sb,83Gha)3.327;6.151A=bU(√2;3.2)=eB(2;3.6)=cB(√8;5) N=13,24,40
Rh4P3(O16.12,SR24.207)11.662;3.317;9.994A=bUH(6;2/2;6/2)  N=76,128,224
RhP(MnP,83Gha)
RhP2(CoSb2,SR37.67)M112.911°5.742;5.795;5.839A
RhP3(CoAs3,SR34.117)7.995A=idmCoP3
Ir2P(CaF2,SR8.136,24.48)5.543A=idmRh2P
IrP2(CoSb2,SR37.67)M111.575°5.745;5.792;5.849A
IrP3(CoAs3,SR34.117)8.015A=idmCoP3
Co3As(C?   ,SR21.38)  phdHA
Co3As(H?   ,SR21.38)
Co2As(T?   ,SR21.39)
Co2As.h(Fe2P,SR21.39)H6.06;3.56A=bBH(2;6/3)=eFH(4;3/3)=cBHK'(2)  N=24,45,72
Co2As.r(H?   ,SR21.39)
CoAs.h(NiAs,SR21.39)H3.56;5.22A=bH(2;3)=eŨH(2;4/2)=cUH(√12;6)  N=10,18,36
CoAs.r(MnP,SR21.39)3.458;5.869;5.292A=idmCoP
Co2As3(H   ,68Hul)
CoAs2(CoSb2,SR37.67)M116.432°5.911;5.868;5.959A=idmRhP2
CoAs3(B4.12,SR37.14)8.195A=idmCoP3
Rh2As.h(PbCl2,SR27.61)5.89;3.89;7.32A=idmCo2P
Rh2As.r(CaF2,SR27.61)5.678A=idmRh2P
Rh3As2(H   ,71Eck)H9.15;3.53A
RhAs(MnP,SR26.55)5.62;3.58;6.00A=idmCoP
RhAs2(CoSb2,SR27.61)M114.33°6.041 ;6.082;6.126A=idmRhP2
RhAs3(CoAs3,SR26.55)8.453A=idmCoP3
Ir2As
IrAs2(CoSb2,SR27.61)M113.27°6.060;6.071;6.158A=idmRhP2
IrAs3(CoAs3,SR26.176)8.469A=idmCoP3
CoSb(NiAs,SR1.87,9.23)H3.896;5.181A=idmCoAs.h  phdHA  cmp
CoSb2(M4.8,SR37.67)M117.66°6.508;6.388;6.543A=idmRhP2
CoSb3(CoAs3,SR17.40)9.036A=idmCoP3
Rh2Sb  phdS  cmp
Rh3Sb2.h
RhSb(MnP,SR13.28)5.955;3.876;6.340A=idmCoP
RhSb2(CoSb2,SR37.67)M116.9°6.57;6.52;6.66A=idmRhP2
RhSb3(CoAs3,SR20.27)9.230A=idmCoP3
IrSb(NiAs,SR22.33)H3.978;5.521A=idmCoAs.h  phdE
IrSb2(CoSb2,SR26.35)M115.5°6.58;6.53;6.68A=idmRhP2
IrSb3(CoAs3,SR26.48,26.176)9.250A=idmCoP3
CoBiM(nic,phdHA)
RhBi(NiAs,SR27.87)H4.094;5.663A=idm CoAs.h
RhBi2.h2
RhBi2.h1(CoSb2,SR26.35)M118.2°6.96;6.83;7.01A
RhBi2.r(N8.16,SR26.65)M97.2°15.93;7.04;10.52A
RhBi3(NiBi3,SR24.65)9.027;4.24;11.522A seeSR27.87
RhBi4.h2(H   ,SR20.53) seeSR27.87
RhBi4.h1(SR26.65,  20.53)11.4;4.25;9.0A seeSR27.87
RhBi4.r(B12.48,SR23.54)14.924            A seeSR27.87
Ir2Bi(68Hul)
IrBi
IrBi2(CoSb2,SR30.117)M117°7.0;6.9;7.1A
IrBi3(NiBi3,SR30.117)
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probable that the I-homeotypism is caused by the commensurability of the binding to the $\underline{a}$ cell. In $\mathrm{NiP_3(CoAs_3}$,BC'C2) the $\underline{d}_{\underline{e}}$ distance becomes larger than the $\underline{d}_{\underline{b}}$ distance, this wide variability of $\underline{d}_{\underline{e}}$ in dependence of the mole fraction $\overline{\underline{N}}_P$ probably has to do with the slow decrease of the 3d orbitals for increasing distance from the atomic core.

In the mixture $\mathrm{NiP}_{\underline{M}}$ three sets of phases may be distinguished, the brass-like phases $\mathrm{Ni_3P}$...$\mathrm{Ni_2P}$, (XX2 set), the NiAs like phases $\mathrm{Ni_5P_4}$...NiP, ($\mathrm{HU_H}\sqrt{3}$ set) and the Si like phases $\mathrm{NiP_2}$...$\mathrm{NiP_3}$, (FB2 set). In $\mathrm{PdP}_{\underline{M}}$ a Cu-like set of phases $\mathrm{Pd_{15}P_2}$...$\mathrm{Pd_{4.8}P}$.h is added,the XX2 set is represented by $\mathrm{Pd_3P}$...$\mathrm{Pd_7P_3}$, a NiAs-like set is missing in the two component mixture, and the Si-like set has the only member $\mathrm{PdP_2}$. The phase $\mathrm{Pd_{15}P_2}$(R15.2), a LDC-homeotype of W, permits the binding $\mathrm{HB_HF_H2}$, and between $\mathrm{B_H}$ and $\mathrm{F_H}$ a good commensurability is found. The phase $\mathrm{Pd_6P}$(N6.1,drawing SR40.90) has a simple commensurability to Pd: $\underline{a}$=2.8;9.4;7.7Å=$\underline{a}_{\mathrm{Pd}}$(0.5,1.5,0;0.5,-1.5,0;0,0,2) which yields 12 Pd per $\underline{a}$; by the insertion of 2 P strong displacements of the Pd are caused. A $\mathrm{CH_T2}$ binding might be possible. $\mathrm{Pd_{4.8}P}$(M18.4,drawing SR31.56) is homeotypic to $\mathrm{Pd_3P(Fe_3C)}$. The elementary cell is nearly isotypic to that of $\mathrm{Pd_5As}$, however, the latter is centered. The phases $\mathrm{Pd_3P}$ and $\mathrm{Pd_7P_3}$ both contain a CC2 binding, the difference between the structures comes from the $\underline{e}$ correlation. The heterotypism $\mathrm{PdP_2}$-$\mathrm{PtP_2}$ is compatible with the site number rule, the lighter phase has the greater electron site number ratio. The favourable FF1 binding of the $\underline{b}$ and $\underline{e}$ correlations certainly contributes to the stability of the phases. Because of the high electron density of Pt the b electrons of P cannot establish a $\underline{b}$ correlation leading to P poor phases.

Of the brass-like phases in $\mathrm{NiAs}_{\underline{M}}$ the structure of $\mathrm{Ni_5As_2(Pd_5Sb_2)}$ is analysed, it allows a $\mathrm{HC_HH2}$ binding. $\mathrm{Ni_{11}As_8}$(T44.32) does no more belong to the XX2 binding, the phase is stabilized by the BF part of the $\mathrm{BFF_U2}$ binding. The phase NiAs(H2.2) gives its name to the $\mathrm{HU_H}\sqrt{3}$ binding which is supplemented by $\underline{e}_{\underline{C}}$. The $\mathrm{HU_H}\sqrt{3}$ binding has the favourable commensurability $\underline{c}^{-1}\underline{b}$=($\sqrt{3}$;2) while $\mathrm{BF_U2}$ is not so favourable; this finds an immediate expression in the melting points of the phases $T_m(\mathrm{Ni_{11}As_8})=830^{\circ}\mathrm{C}$, $T_m(\mathrm{NiAs})=962^{\circ}\mathrm{C}$. The phase $\mathrm{NiAs_2}$.h($\mathrm{FeS_2}$.r) is LD-homeotypic to NiAs and allows $\mathrm{HB_H1}$ which is homeotypic to $\mathrm{HU_H}\sqrt{3}$. The old problem why $\mathrm{NiAs_2}$.h does not crystallize in the $\mathrm{CdI_2}$ type is answered by the $\underline{e}$ correlation which requests a more uniform distribution of the minority component than it is found in $\mathrm{CdI_2}$. The more uniform distribution makes the structure orthorhombic and the bindings seeks the most favourable commensurability. $\mathrm{NiAs_2}$.r($\mathrm{AuSn_2}$) is isodesmic to $\mathrm{PdP_2}$, the reason for the heterotypism $\mathrm{NiAs_2}$.r-$\mathrm{PdP_2}$ is not fully understood.

TABLE 10: A10B5M

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Ni3P(Fe3P,SR27.290)8.954;4.386A=bC(√26;2.5)=eHT(√52;4/2)=cCK'(2)N=64,216,256phdHA
Ni5P2(H120.48?,SR30.159)H6.61;49.26A=bCH(√7;51/3)=eH(√28;3 9)=cCHK'(2)N=360,1080
Ni12P5(U12.5,SR23.192)8.646;5.070A=bC(5;3)=eC(√50;4.3)=cCK'(2) N=74,216,      cmp
Ni2P(Fe2P,SR23.192)H5.864;3.385A=bH(√12;2)=eCH(√12;4.9/3)=cHK'(2) N=21,54,72
Ni5P4(H20.16,SR30.70)H6.789;10.986A=bH(4;6.5/1)=cĈH(4;13/3)=cUH(√48;13/2)N=100,180,
NiP(08.8,SR30.72)6.050;4.881;6.890A=bH(4/2;2.9;4)=eCH(4/2;2.9;10/3)=cUH(6;      ,288'
 5.5/2;8/2)  N=48,128                                              N=40,40,96
NiP2(PdP2,SR30.73)5.537;5.615;3.140,0,5.63A=bF(√5;2.25)=eFK'=cU(√20;5.5) ↓
NiP2.p(FeS2.h,Struct Bond4.206)5.5A=idmPtP2  FFB2
NiP3(CoAs3,SR34.117)7.819A=bB(4)=eC'(4)=cC(8)  N=120,80,256          N=75,405,408
Pd15P2(R15.2,SR43.89)H7.108;17.087A=bH(√12;8)=eBH(√12;42/3)=cFH(√48;2 1/3)phdM ↓
Pd6P(N6.1,SR40.90)2.83;9.44;-0.01,0,7.69A=bC(√2;3/2;4)=eFU(2;7;8/2)=cHT(√8;3√8;9)
Pd4.8P.h(M18.4,SR31.54)4.9;7.6;-0.5,0,8.4A   N=38,162,176          N=22,108,112
Pd3P(Fe3C,SR26.225)5.65;7.57;5.08A=bC(3;4;2.7)=eFK'=cCK'(2) N=32.108,128 cmp
Pd5P2
Pd7P3(R14.6,SR43.90)H11.98;7.06A=bCH(√21;6.3/3)=eFH(√63;6/3)=cCHK'(2)N=132,480
PdP2(N2.4,SR28.35)5.763;5.857;-2.305,0,5.874A=bF(√5;2.2)=eFK'=cU(√20;5.5)N=40,40,
PdP3(CoAs3,SR24.48)could not be made, Moffatt                                  96
Pt5P2(N10.4,SR32.108)10.764;5.385;-1.185,0,7.343A=bC(6;3;4)=eFK'=cCK'(2)N=60,180
PtP2(FeS2.h,SR24.47)6.696A=bF(√5;2.2)=eFK'=cB(√20;4.5)  N=40,40,96            ,224
Ni5.1As1.9(htpPd5Sb2,JLCM22.1970.445)H6.824;75.66A=hdmNi5As2  phdS   N=75,285,336
Ni5As2(Pd5Sb2,H30.12,SR35.14)H6.825;12.513A=bH(√12;6)=eCH(√12;15/3)=cHK'(2)    ↓
Ni4.9As2.1(htpPd5Sb2,JLCM22.445)=hdmNi5As2
Ni11As8(T44.32,SR39.12)6.872;21.82A=bB(√10;10)=eFK'=cF̂U(√40;30/2) N=204,400,608
NiAs(H2.2,SR1.84)H3.618;5.032A=bH(2;2.8)=eĈ(2;5/3)=cUH(√12;5.6/2)N=11,19,32
NiAs2.h(FeS2.r,SR33.63)4.758;5.795;3.545A=bH(3/2;3.3/1;2)=cBH(3/2;16/3;2)N=20,20,48
NiAs2.r(AuSn2,SR38.27,33.34)5.753;5.799;11.407A=bFU(√10;9/2)=eFUK'=cU(√20;11)
NiAs3.i(CoAs3,SR1.253)8.28A=bB(4)=eC(4)=cC(8)                   N=86,192
NiAs2.p(FeS2.h,68Hul)                                       eFH(3/2;4/3;2)=
Pd5As(N10.2,SR44.26)5.52,0-1.32;7.74;8.32A  phdS
Pd3As(Fe3P.U12.4,SR29.102)9.974;4.822A=idmNi3PCHT√2C2  N=64,216,250 cmp
Pd2.65As
Pd5As2(PolytypesCanad.J.Chem.42.150,1511)=idmNi5As2  cmp                   cmp ↘
Pd2As.h(Fe2P,SR29.102)H6.650;3.539A=bH(√12;1.8)=eC(√12;4.5/3)=cHK'(2)N=21,54,72
Pd2As.r(Q8.4,SR34.25)3.25;16.84;6.58A=bUH(2/2;9;4/2)=eCH(4/3;9;4/2)=cUHK'(2)N=40,
PdAs0.3Bi0.7(NiAs,SR37.148)H4.030;5.735A=bH(2;2.8)=eĈH(2;6/3)=cUH(√12;6)     160,
                                                                              192
PdAs2(FeS2.h,SR1.781)5.983A=idmPtP2  FFB2  cmp
PtAs2(FeS2.h,SR1.125)5.967A=idmPtP2  FFB2
Ni15Sb,not confirmed,Trans.Jap.Inst.Met.11.1970.139
Ni3Sb(Cu3Sb.h,SR20.29)5.35;4.53;4.30A=bC(1.75√2;1.5√2;2)=eB(3.5;3;√8)=cCK'(2)
 N=16,54,64  phdHA
Ni2.7Sb.h(Fe3Si,SR20.29)5.96A=bF(2)=eFU(4;6)=cF(4)  N=32,98,136
Ni5Sb2(N10.4,SR44.13)11.46,0,-0.1;5.42;6.14A=hdmNi2.7Sb.h
NiSb(NiAs,SR9.28)H3.959;5.164A=idmNiAs  H.CH.UH√3
NiSb2(FeAs2,SR17.39)5.180;6.314;3.838A=idmNiAs2.h HFHBH1  N=20,20,48
Pd20Sb7(R20.7,SR43.16)H11.734;11.021A=bH(√28;5)  N=135,  phdHA      276,864,1128
Pd8Sb3(R32.12,SR42.20)H7.615;43.032A=bUH(√12;22/2)=eĈH(√12;66/3)=cUHK'(2) N=
Pd31Sb12(R31.12,JLCM22.1970.445)H7.613;42.240A
Pd5Sb2(H30.12,SR35.14)H7.606;13.863A=bFH(√13;8/3)=eCH(√13;16/3)=cFHK'(2)N=90,270
Pd2Sb(Pd2As.r,SR34.25)3.354;17.45;6.909A=idmPd2As                             336
Pd3.3Sb2.h(NiAs,SR17.41)H4.45;5.83A=bBH(1.33;11)=eCH(2;6/3)=cUH(4;6/2)
PdSb(NiAs,SR1.781)H4.078;5.594A=idmNiAs  HČHUH√3  cmp
PdSb2(FeS2.h,SR1.781)6.452A=idmPtP2  FFB2
Pt3.2Sb0.8(Cu3Au,JLCM17.1969.73)3.99A=bU(√2;1.7)=eF(2)=cC(4)  phdM
Pt3Sb(ZrAl3,JLCM17.1969.73)3.94;16.96A=bČ(2;8.5)=eF(2;8.5)=cC(4;17) N=32,108,136
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In $NiSb_M$ the brass set of phases is composed of Ni_3Sb, $Ni_{2.7}Sb$.h and $Ni_{2.5}Sb$. In $Ni_3Sb(Cu_3Sb.h_1)$ Sn may be substituted for Sb up to $Ni_{75}Sn_{15}Sb_{10}$ without appreciable effect on the axial ratios (78Hei), therefore the structure is not caused by the $\underline{b}$-correlation alone. This is expressed by the $CB\sqrt{2}C2$ binding. The observed value $2|\underline{a}_2|/|\underline{a}_1|=1.70<\sqrt{3}$ is reproduced by $2\underline{K}''_{12}/K''_{11}=6/3.5=1.71$. The distribution of Sb follows the electro-dipole rule (64Sch p.100) since in $\underline{a}_2$ direction dipoles are generated which attract one another. The phase $Ni_{2.7}Sb(Fe_3Si)$ is not homeodesmic to CuZn as the $\underline{b}$ electron contribution of the order 1 by Ni leads to a $\underline{b}$ electron concentration of the order 2. Therefore a FF2 binding fits much better than the BB2 binding of CuZn. The phase Ni_5Sb_2 is LDI-homeotypic to Fe_3Si with $\underline{a}=\underline{a}_{Fe3Si}(2;1;1)$. This suggests that the FF2 binding of $Ni_{2.7}Sb$.h is modified somewhat by the temperature dependent $\underline{b}$ electron contribution of Ni. Since the $\underline{e}$ correlation was fully occupied in $Ni_{2.7}Sb$.h, it too contributes to the structural transformation. It might be that parallel to (001) an additional $\underline{e}_F$ layer is introduced. This would introduce a monoclinic deformation as it is found in fact.

In $PdSb_M$ there is a wealth of phases homeotypic to W belonging to the brass set. As they are fairly complicated their binding analysis should be postponed. Pd_5Sb_2(H30.12) has a binding which is a little different from the bindings of Ni_5As_2, this problem deserves further consideration.

The phase $Pt_3Sb(ZrAl_3)$ certainly belongs to the brass set, and the rule of electrodipole vectors (64Sch) is obeyed in the $\underline{c}$ correlation. It is not quite certain whether $Pt_{3.2}Sb_{0.8}$ belongs to the CFC2 binding, tentatively another binding has been noted. Pt_3Sb_2(P6.4,drawing 69Bha) displays a LDI-homeotypism to Cu_2Sb(T4.2) with the commensurability $\underline{a}=\underline{a}_{Cu2Sb}(\sqrt{2};2;\sqrt{2})$; the deformation makes it pseudohexagonal. The binding analysis allows a $F_HC_HF_H2$ binding which is so favourable that it is not clear why the structure is not more frequent.

At this point it is of interest to consider the section $PtSn_NSb_{2-N}$ (69Bha). For $PtSn_2(CaF_2$,SR9.120) the binding $\underline{a}=\underline{b}_{FU}(3;4.2/2)=c_U(\sqrt{18};5.2)$ was found (82Sch) which is homeotypic to the FB2 binding, while for $PtSb_2(FeS_2.h)$ in this analysis the FB2 binding $\underline{a}=\underline{b}_F(\sqrt{5};2.2)=c_B(\sqrt{20};4.5)$ was found. Between these phases the following phases are stable: $PtSn_{1.3}Sb_{0.7}(CoSb_2)$, $PtSnSb(FeAs_2)$ and $PtSn_{0.7}Sb_{1.3}(FeS_2.r)$. The change of the axial ratio between PtSnSb and $PtSn_{0.7}Sb_{1.3}$ is continuous and the alloy $PtSn_{0.9}Sb_{1.1}$ has a hexagonal cell. It is seen that $PtSn_2$ has $\underline{N}_S^{/a}=38$ $\underline{b}$-sites per cell while $PtSb_2$ has $\underline{N}_S^{/a}=44$ because of the higher $\underline{b}$ contribution of $PtSb_2$. The homeotypism between $PtSb_2(FeS_2.h)$ and $PtSn_{0.7}Sb_{1.3}(FeS_2.r)$ is shown in (64Sch p.343,347), it is seen that the transition from the long $FeAs_2$ type to short FeS_2.r type is nothing else than

Pt3Sb2(P6.4,SR34.11)6.446;10.939;5.319A=bFH(3;6/2;3/3)=eCH(3;6/2;6/3)=cFHK'(2)↗
Pt56Sb44.m N=52,108,176↗
PtSb(NiAs,SR1.781)H4.138;5.483A=idmNiAs HCHUH/3
PtSb2(FeS2.h,SR24.47)6.440A=idmPtP2 FFB2 cmp
NiBi(NiAs,SR2.749)H4.069;5.360A=idmNiAs phdHA
NiBi3(O4.12,SR18.57)8.87;4.11;11.48A=bFH(5/2;2;7/3)=eFHK'=cBH(5/2;2;27/3)
Pd5Bi phdE N=60,40,152
Pd3Bi(O12.4,JLCM17.1969.73)9.4;5.8;4.9A=bCH(8/3;2;2/2)=eFH(8/3;4;4/3)=cCHK'(2)↖
Pd31Bi12.h(Pd31Sb12,JLCM63.1979.P75)H7.809;42.597A=bFH(√12;24/3) N=32,108,136
Pd5Bi2(N10.4,SR45.38)M119.04°14.430;5.780;6.752A
Pd3.3Bi2.h(NiAs,Naturwiss 40.1953.269)H4.51;5.81A=idmPd3.3Sb2.h
Pd5Bi3.r1(htpNiAs)subcellM91.834°4.478;7.794;5.838A
Pd5Bi3.r2(htpNiAs)subcellM91.574°7.772;4.496;5.833A
PdBi.h(Q8.8,SR17.57)7.20;8.71;10.66A=bH(4/2;4;5)=eCH(4/2;4;12/3)=cBH(4/2;4;24/3)
PdBi.r(M8.8,SR45.39)M89.70°7.20;10.66;8.71A N=80,160,320 cmp
PdBi2.h(U1.2,SR17.56)3.362;12.985A=bB(√2;5.5)=e..=cC(√8;11) N=20,20,56
PdBi2.r(N2.4,SR17.57)12.7,0-1.2;4.2;5.5A
PtBi(NiAs,SR27.86)H4.324;5.501A=bH(√4.3;2.7)=e..=cUH(√13;5.3/2) phdS
Pt1.3Bi2.h(NiAs,SR34.139)H4.12;5.56A=bH(2;2.7)=eĈH(2;5.4)=cUH(√12;5.4)N=11,12,27
PtBi2.h3(O4.8,Z.Metallk.71.1980.550)5.8;4.1;12.5A
PtBi2.h2(H3.6,SR34.137)H6,59;6.16A=bBH(2;9.5/3)=eH(√12;3.5)=cCH(4;10/3)N=36,24,72
PtBi2.h1(FeS2.h,SR9.34)6.697A=idmPtP2
PtBi2.r(AuSn2,SR46.35)6.732;6.794;13.346A=bF(√5;9/2)=eFK'=cB(√20;9)

TABLE 11: B1B5M

Cu3P.h(Cu3As.h,H6.2,SR38.82)H4.092;7.186A=bUH(2;4/2)=eBH(2;8/3)=cUH(4;8/2)
Cu3P.r(H18.6,SR38.86)H6.959;7.143A=idmCu3P.h N=16,60,64 phdM
CuP2(M4.8,SR30.45)5.353;4.807;-2.237,0,7.525A=bFU(4/2;2.5;4)=eFUK'=cB(4;2.5√2;4√2)
Cu2P7(N8.28,83Met)M107.46°12.658;7.256;14.630A N=44,40,96
AgP2(CuP2,SR30.45)M113.48°6.218;5.056;7.804A=idmCuP2
Ag3P11(,Inorg.Chem.20.1981.828)
Au2P3(N4.6,SR45.78) phdE
Cu8As(Mg,SR21.13)H2.59;4.24A=bFH(√3;2.3/3)=eFH(2;4/3)=cCH(2;8/3)N=29,18,17phdE
Cu12As4(B24.8,SR6.66)9.60A=bB(4)=eC(8)=cB(8) N=128,480,544
Cu3As.h(H6.2,Z.anorg.Chem.371.1969.172)H4.17;7.33A=idmCu3P.h cmp
Cu3As.r(Cu3P.r,SR30.268)H7.143;7.324A=idmCu3P.r UHBHUH2
Cu5As2.h(LhtpFe3Si,JLCM23.1971.232)5.82A=bF(2)=eFU(5.7/2;4)=cF(4) N=60,200,240
Cu5As2.m(Mg5Ga2,SR38.23)5.977;11.577;5.491A=bFU(4/2;2√8;√8)=eFU(2/2;8;4)=cFUK'(2)
Cu2As(Cu2Sb,SR38.23)3.788;5.942A=bHT(2;3.4)=eHT(√8;5/2)=cC(4;6) N=14,40,52
Ag9As.h(Mg,SR26.249)H2.899;4.735A=idmCu8As phdE
AuAsM(nic,phdM) N=32,20,16
Cu5.5Sb.h(Mg,SR22.31)H2.716;4.374A=bH(√7/2;2.1)=eUH(√21/2;4.2/2)=cHK'(2) phdE
Cu4.5Sb(htpMg,SR22.31)
Cu10Sb3.h(H20.6,SR22.32)H9.92;4.39A=bH(5;2)=eC(5;10/3)=cHK'(2) N=50,200,210
Cu3Sb.h2(Fe3Si,SR8.27)6.01A=bF(2)=eB(4)=cF(4) N=32,120,136
Cu3Sb.h1(O6.2,SR22.31)5.50;4.85;4.43A=bF'H(3/3;2.5/2;2)=eBH(12/3;2.5/2;2)=
cFHK'(2) N=16,60,68
Cu2Sb(T4.2,SR3.288)4.000;6.104A=bHT(2;3.5/2)=eHT(√8;5/2)=cHTK'(2) N=14,40,52
Ag9Sb(Mg,SR8.30)H2.928;4.783A=hdmCu5.5Sb.h phdHA
Ag3Sb.h(DhtpMg,SR8.29)2.990;5.225;4.820A=idmCu3Sb.h
Ag3Sb.r(DRhtpMg,SR8.30)=hdmAg3Sb.h
AuSb2.h(FeS2.h,SR21.30)6.659A=bF(√5;4.5/2)=eFK'=cB(√20;4.5) N=44,40,96 phdHA
AuSb3.m(C ,SR26.42)5.9A
CuBiM(nic,phdHA)
Cu5Bi2.m(SR26.63)
AgBiM(nic,phdHA)
Au2Bi(MgCu2,SR3.315)7.958A=bU(√8;3.5)=eC(√32;5.5)=cU(√32;7) N=56,160,208 phdHA

an increase of the $\underline{N}_{S'}^{/a}$ value caused by the increase of $\underline{b}$ electron concentration. The explanations (65Pea,75Fle) consider the $FeAs_2$ type as contracted by AA bonds while the present interpretation considers the FeS_2.r type as strained by increase of $\underline{b}$ electron concentration.

While NiBi(NiAs) is isodesmic to NiAs, no phase homeotypic to $NiAs_2$ or $PdSb_2$ is stable but instead $NiBi_3$, which is homeotypic to $PdBi_2$.r and $PtBi_2.h_3$ and should be compared with $CoSb_3(CoAs_3)$. Using the bindings of this analysis it is found for one atom (A) $\underline{N}_{S'}^{/A}(CoAs_3)=16.0$ and $\underline{N}_{S'}^{/A}(NiBi_3)=16.9$. Presumably the large volume of Bi causes the greater $\underline{N}_{S'}^{/A}$ value. The large electron distance is the cause that the phase with the property $\underline{d}_{\underline{e}}=\underline{d}_{\underline{c}}$ is shifted to a greater $\underline{N}_B^{-}$ mole fraction.

Pd_3Bi(O12.4) is homeotypic to $Cu_3Sb.h_1$ and $TiNi_3$ with the commensurability $\underline{a}=\underline{a}_{Cu3Sb.h}(2;1;1)$. A $C_HF_H2C_H2$ binding is assumed which could give an argument for the structure if it were compressed somewhat in the direction of the long axis. The phase $Pd_{3.3}Bi_2$.h(NiAs) has the $B_HC_H1.5U_H3$ binding, a fore-runner of $HU_H\sqrt{3}$. The occurrence of the NiAs type at the composition $Pd_{3.3}Bi_2$ makes the stability of the NiAs type at PdBi improbable because of the smoothness rule for $\underline{N}_{S''}^{/S'}$. In fact for PdBi.h(Q8.8,drawing 79Bha) a homeotype of TlI and Cu_2Sb with the commensurability $\underline{a}=\underline{a}_{TlI}(2;2;1)$, a HC_HB_H1 binding is possible which explains the shear-homeotypism to NaCl by the electro-dipole rule. The DI transformation into PdBi.r is probably caused by some change of the $\underline{e}$ correlation. In $PdBi_2$.h the Pd are no more uniformly distributed as in the FeS_2.r type, this is favoured by the large volume of Bi. The $\underline{e}$ electrons of Pd are now in a layered correlation. It is remarkable that in $PtBi_2$ the layered correlation is only found in h_2 and h_3 while in r and h_1 the Pt are uniformly distributed.

$\underline{B^1B^5_M\text{phases.}}$ $Cu_3P.h(Cu_3As.h$,H6.2) is I-homeotypic to Na_3As, a RS-homeotype of W like Pd_5Sb_2. The stacking sequence in the (001) direction is ABCBCABC=ccchhccc and contradicts to the rule of most uniform distribution of c and h (84cSch, 68Sch). The fact that the P atoms are in a partial structure isotypic to Mg corresponds to the rule (75Wop) that the valence electron rich component tends to a most uniform distribution because of spatial correlation of $\underline{b}$ electrons. The $U_HB_HU_H2$ binding shows that Cu_3P belongs to the brass set of phases. It is statisfactory that $Cu_3P.r(H18.6,IhtpCu_3P.h)$ obeys the rule of most uniform c,h distribution with the stacking ABCBACBC=ccchccch. The stacking causes 3 chains in $\underline{a}_3$ direction to contain 2 atoms per cell while all other chains contain 3 atoms. The phase is nearly isodesmic to Cu_3P.h. The phase CuP_2(M4.8) contains Cu_2 dumpbells surrounded octahedrally by 6P; it allows a FFB2 binding with 4 electrons in Hund insertion. However, with respect to $\underline{e}_F$ it is not clear how the Hund insertion finds space. Cu_2P_7 and Ag_3P_{11} have also the $\underline{b}$ electron concentration ≒4 and are therefore closely homeotypic to Si.

The phase Cu_8As(Mg) is compatible with a $F_HF_H\sqrt{3}C_H\sqrt{3}$ binding, a fore-runner of the XX2 bindings. $Cu_{12}As_4$(B24.8) is a L-homeotype of $Cu_{15}Si_4$ (not an isotype 72Nau) and is compatible with BB2. Since Cu_3As(Cu_3P) has a UU2 binding, it is gratifying that Cu_5As_2.m a RLD-homeotype of W permits a FF2 binding. Cu_5As_2.h (71Lie) is L-homeotypic to Fe_3Si and contains FF2. In Cu_2As(Cu_2Sb) a H_TC2 binding appears to exist. The observation of metastability has to do with the process of Hund insertion which is slow in the solid state. Metastability too was found in $PtSb_M$ and will occur in various later mixtures.

The phases $Cu_{5.5}Sb$.h(Mg) up to Cu_2Sb(T4.2) belong to the brass-like phases. There are no phases of the NiAs binding and no phases of the Si binding as the large Sb does not permit a favourable commensurability between Cu^{10} and Sb^5 electrons. However, $AuSb_2$.h(FeS_2.h) has a FFB2 binding as the electron rich Au presses the Au^{10} electrons outward. It appears that $Cu_3Sb.h_2$ and $Cu_3Sb.h_1$ have the same binding but in $Cu_3Sb.h_1$ there is a little amount of Hund insertion.

$B^2B^5_M$ phases. Phases with brass-like binding are no more possible in the following mixtures as the smallest valence electron concentration is $\underline{N}_{\underline{b}}^{/A}=2$ and the XX2 bindings occur near $\underline{N}_{\underline{b}}^{/A}=1.5$.

Zn_3P_2.r(T8.16) is homeotypic to Mg_3P_2(Mn_2O_3,B24.16) but the interference of the $\underline{e}$ correlation makes the structure tetragonal. ZnP_2(T 8.16) does not allow a FB2 binding but a BC2 binding which has the same site number ratio. In CdP_M several isotypic and isodesmic phases are stable. HgP_M contains no intermediary compounds, the high electron density of Hg prevents the $\underline{b}$ electrons of P to build a uniform spatial correlation.

$MgAs_4$(T4.16,drawing SR43.22) is homeotypic to MgP_4 and nearly isodesmic. The phases Zn_3As_2.h,r(T96.64,U48.32) are closely homeotypic, the slight heterotypism is caused by the interference of the $\underline{e}$ correlation. ZnAs.p(CdSb, drawing 64Sch p.186) is I-homeotypic to CdTe(ZnS.r), where the homeotypism causes a shrinking according to the volume rule. The good fit of the binding to the structure may be seen from 64Sch p.186. Four $\underline{b}$ electrons must be in Hund insertion and this agrees with the property that ZnAs.p is a high pressure phase. $ZnAs_2$(M8.16) has the $\underline{b}$ electron concentration $\underline{N}_{\underline{b}}^{/A}=4$ and is therefore homeotypic to Si or Ge. The composition $ZnAs_2$ causes that two ZnAs layers (100) are followed by one ZnZn layer, and the symmetry becomes monoclinic. The stacking is of the ZnO(H2.2) type. The relative compression in $\underline{a}_1$ direction

TABLE 12: B2B5M

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Zn3P2.h  phdM  cmp
Zn3P2.r(T24.16,SR3.51)8.11;11.47A=bFU(4;8/2)=eC(√32;8)=cU(√32;10) N=128,240,320
ZnP2(T8.16,SR30.83)5.08;18.59A=bB(√5;8)=eBK'=cC(√20;16) N=96,80,192
ZnP2.p(M8.16,SR28.37)M102.3°8.85;7.29;7.56A
Cd3P2.h  phdM  cmp
Cd3P2.r(Zn3P2.r,SR3.53)8.76;12.30A=idmZn3P2.r
Cd6P7.h
Cd7P10(S14.20,SR46.44)23.0;27.5;4.62A
CdP2.h(ZnP2,SR34.50)5.283;19.808A=idmZnP2
CdP2.r(O4.8,SR35.50)9.90;5.408;5.171A
CdP4(M2.8,SR20.59)M80.54°5.27;5.19;7.66A=idmMgP4
HgPM
Zn3As2.h(T96.64,SR42.34)11.789;23.635A=hdmZn3P2,  phdHA  cmp
Zn3As2.r(U48.32,SR42.34)11.778;23.643A                          N=56,80,144 ↘
ZnAs.p(CdSb,O8.8,SR42.24)5.679;7.277;7.559A=bFU(√13;4/2)=eU(√13;3.4)=cU(√26;5)
ZnAs2(M8.16,SR40.28)9.068;7.691;-2.005,0,8.010A=bFH(5/2;4.7/3;4)=eFHK'=cBH( )↑
Cd3As2.h(T24.16,SR34.15)8.963;12.680A=hdmZn3P2  phdHA,M            N=96,80,224
Cd3As2.r(U48.32,SR33.25)12.67;25.48A
CdAs.p(CdSb,SR42.24)5.993;7.819;8.011A=idmZnAs.p
CdAs2(U2.3,SR33.27,35.18)7.954;4.678A=bU(√10;2.3)=eUK'=cHT(√40;4) N=48,40,112
HgAsM(metastable compound,Bull.Sign.1978.161,8405)
Zn3Sb2.h(P   ,JLCM59.1978.43)25.0;14.6;7.6A
Zn4.Sb3.h                                                          N=214,360,588
Zn4Sb3.r(R12.10,SR44.17)H12.233;11.438A=bFH(√31;7/3)= eĈH(√31;14/3)=cBH(√31;28/3)
ZnSb(CdSb,SR29.22)6.202;7.742;8.099A=idmZnAs.p  FU√2U2
Cd3Sb2.m(see78May)
Cd4Sb3.m(78May)
Cd5Sb4.m(Phys.Stat.Sol.a78.1983.705)
CdSb(O8.8,SR11.32)6.471;8.253;8.526A=idmZnAs.p
Hg3Sb2?  phdS
ZnBiM(nic,phdHA)
CdBiM(nic,phdE)
HgBiM(nic,phdHA)
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TABLE 13: B3B5M

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AlP(ZnS.r,SR1.77)5.467A=bF(2)=cB(4)or=cU(4;5)
GaP(ZnS.r,SR22.139)5.451A=idmAlP  phdS
InP(ZnS.r,SR22.139)5.869=idmAlP  phdS
InP.p(NaCl,SR29.121)5.310A=idmAlP
TlPM(nic,phdHA)
AlAs(ZnS.r,SR1.77)5.660A=idmAlP
GaAs(ZnS.r,SR1.77)5.653A=idmAlP  phdHA
InAs(ZnS.r,SR22.139)6.058A=idmAlP  phdHA
InAs.p(NaCl,SR29.101)5.514A=idmAlP
TlAsM(nic,phdHA)
AlSb(ZnS.r,SR22.139)6.136A=idmAlP  phdHA
AlSb.p(Sn.r,SR28.42)5.375;2.892A=bF'U(√6.5;2/2)=cB(√13;2)
GaSb(ZnS.r,SR28.46)6.096A=idmAlP  phdHA
GaSb.p(Sn.r,SR28.46)5.348;2.973A=idmAlSb.p
InSb(ZnS.r,SR1.77)6.479A=idmAlP  phdHA
InSb.p1(Sn.r,SR28.47)5.92;3.06A=idmAlSb.p
InSb.p2(NaCl,SR28.47)5.84A
InSb.p3(DhtpSn.r,SR29.121)2.92;5.56;3.06A
In Sb.p4(CsCl,71Eck)3.38A
```

probably comes from the $\underline{e}$ correlation which favours this compression. Without doubt the commensurability $\underline{b}_{FH}=\underline{e}_{FH}$ contributes here essentially to stability.

The large Cd in $CdAs_2$(U2.4) cannot be surrounded tetrahedrally by As. A UUH_T2 binding appears possible, but it is not clear why no structure withFB2 binding is stable. Also the $\underline{c}_{HT}$ correlation indicates that the As site is perhaps only statistically true and requires confirmation.

The phase Zn_4Sb_3(R12.10) shows tetrahedral coordination of Sb to Zn as in Zn_3P_2. The FB2 binding is enforced by a $e\tilde{}_{CH}$ correlation, which probably causes the hexagonal symmetry. A phase with one-factorial $\underline{e}^{-1}\underline{b}$ commensurability is not stable as the Sb is somewhat large. The mixture $ZnSb_M$ has a positive volume of formation, and several metastable phases. Both phenomena may be interpreted by the plural correlations model (78May).

The absence of intermediate phases in $ZnBi_M$, $CdBi_M$, $HgBi_M$ points out that there is no strong stability contribution of the $\underline{e}$ correlation.

$B^3B^5_M$ phases. Most mixtures of this class have only one intermediate phase contrary to the fairly involved mixtures of $B^2B^5_M$. This observation suggests the assumption that the $\underline{e}$ correlation is no more of essential influence . Following the rule of anion packings (64Sch) the FB2 binding is now at the composition $B^3_1B^5_1$. The ZnS.r type seems to be somewhat more favourable at 1 bar than theNaCl type, but both types are probably isodesmic. In AlSb.p(Sn.r) there must be Hund insertion (see 82bSch) and from Table $B^3B^5_M$ may be concluded that Hund insertion is easier in Sb than in As. Also the phases with Sn.r structure may be expected to be paramagnetic (82bSch). In TlP_M, $TlAs_M$, $TlSb_M$ and $TlBi_M$ the atom radii are too large to build a ZnS.r structure. Instead various other structures become stable which are not possible in mixtures containing a favourable ZnS.r isotype.

The phase Tl_9Sb(Cu) is an interesting isodesmic successor of In(U_F1) for increasing $\underline{b}$ electron concentration. Instead of the commensurablity change $(\underline{c}_B{}^{-1}\underline{a})_{11}=\sqrt{8}\rightarrow 3$ of the FB2 binding also a different binding BC2 may be chosen which fits well in Tl_6Sb(W) and in Tl.h(W) (82bSch) which permits a $\underline{b}$ electron contribution $\underline{N}_{\underline{b}}^{/Tl}>3$. In confirmation of this interpretation it may be noted that the homogeneity of Tl.h is extended by Sb to lower temperatures. If in Tl_6Sb(W) the $\underline{b}$ electron concentration is increased then UH_T2 is favoured. This binding must be assumed to be twinned in Tl_7Sb_2(B21.6,drawing 64Sch p.175) and the structure, a homeotype of Fe_3Si, appears very plausible; the Sb atoms are shifted to render the $\underline{d}_{SbSb}$ more uniform. Without doubt the cause for the rare superstructure is the electron correlation.

The phase In_9Bi(In_3Sn,T3.1) is now a natural homeotype of Tl_9Sb(Cu). Once more a BC2 binding follows to the FB2 binding. The UF_U2 binding of In_5Bi_3 (Cr_5B_3) allows a greater site number ratio which apparently is requested by the large Bi atom. In InBi(PbO,T2.2,drawing 64Sch p.201) a ZnS.r structure cannot be formed. The numbers of sites per atom $\underline{N}_{S''}^{/A}$(InSb)=16 and $\underline{N}_{S''}^{/A}$(InBi)=15 clearly show that InBi is closer packed than InSb(ZnS.r).From the bindings a little Hund insertion may be inferred.Surprising is the BF1 binding of $TlBi_2$ which displays a completely filled $\underline{c}$ correlation confirmed by the independence of $|a_3|/|\underline{a}_1|$ of the mole fraction (79El1), while the $\underline{b}$ correlation is not completely filled. This variability of the $\underline{c}$ correlation lead above to many compounds with one-factorial $\underline{b}$,$\underline{e}$ correlations, also the increase of the $\underline{d}_c$ distance with increasing atomic number in chemical elements (77Sch Fig.5) belongs to this phenomenon.

$B^4B^5_M$ phases. The $B^4B^5_M$ mixtures have quasi homologous and therefore homeodesmic components, and the intermediate phases are also homeodesmic to the components. It is clear, therefore, that the number of intermediate phases must remain modest and their structures are homeotypic.

The phase SiP.p(ZnS.r) as prepared at high temperature under pressure has the F'B2 binding of all ZnS.r isotypes, and the electron count indicates that 1 electron per P must be in Hund insertion. Because of the high temperature the insertion is statistically distributed so that a cubic structure results. However, if SiP is prepared at normal pressure a Q12.12 structure is formed in which all Si have a tetrahedral coordination of 1Si+3P like Ga in GaS, and all P have a one sided coordination of 3Si. Surprisingly the structure leads to a $H_TF_U\sqrt{2}$ binding ($\underline{N}_{S''}^{/S'}$=3.5) which needs no Hund insertion at all. It must be concluded that the phase seeks to avoid Hund insertion at ambient circumstances like Sn.l, as it is energetically expensive. In SiP_2.p(FeS_2.h) also statistical Hund insertion into a FB2 binding may be assumed while in SiP_2($GeAs_2$, O8.16) a structure homeotypic to SiP is found. Every Si is tetrahedrally surrounded by 4P and the P are surrounded either by 3Si or by 1Si+2P; a $BU\sqrt{2}$ binding fits well.

In GeP.p(U1.1,drawing SR35.21) a DI-homeotypie of NaCl is stable for reasons of radius ratio, and a FB2 binding without Hund insertion is favourable. For GeP(SiAs) a homeotype of SiP is found. It may be homeodesmic to SiP.

Sn_4P_3(Sn_4As_3) is rhombohedrally strained as compared with SnP(NaCl), the strain is below that expected from $\underline{b}$ plane insertion along (001) (64Sch p.189). It must therefore be assumed that there is a common Hund insertion which corresponds to some spin ordering. For the rhombohedral deformation it is necessary that SnPSnPSnPSn layers are formed, in SnP(NaCl) such an array is not possible, therefore the binding is twinned and the structure becomes cubic.

Tl9Sb(Cu,SR24.52)4.860A=bFU(√4.5;3/2)=cB(3) N=13,40 phdHA
Tl6Sb(W,SR8.114)3.9A=bB(1.5)=cC(3) N=6.2,20
Tl7Sb2(B21.6,SR3.195,43.17)11.618A=bU(√18;5.2)=cHT(√72;10/2) N=186,540
AlBiM(nic,phdS) phdHA
GaBiM(nic,phdE)
In9Bi(In3Sn,JLCM62.13)4.910;4.495A=bFU(√4.5;2.75 /2)=cB(3;2.75) N=12.8,40
In2Bi(Ni2In,SR22.50,45.116)H5.496;6.579A=bBH(1.5;9/3)=cCH(3;9/3) N=22,60
In5Bi3(Cr5B3,U10.6,SR34.31)8.544;12.68A=bU(√10;5.7)=cFU(√40;13/2) N=120,320
InBi(PbO,T2.2,SR11.46)5.015;4.781A=bFU(√5;3/2)=cB(√10;3) N=16,40 cmp
Tl4Bi.h(Cu,SR3.648)4.91A=bFU(√4.5;3/2)=cB(3)
Tl4Bi.r
TlBi2(B2Al,SR3.648)H5.67;3.38A=bBH(√3;5/3)=cFH(√12;2.5)

TABLE 14: B4B5M

SiP(Q12.12,SR41.101)3.512;20.488;13.607A=bHT(2;12;9/2)=cFU(2√2;12√2;16) phdE
SiP.p(ZnS.r,SR31.58)5.241A=bF'(2)=cB(4) N=36,64
SiP2.hp(FeS2.h,SR31.58,33.36)5.705A=bF'U(√10;4.5)=cB(√20;4.5) N=56,96
SiP2.r(GeAs2,08.16,SR32.140)13.97;10.08;3.436A=bB(7;5;1.7)=cU(7√2;5√2;3)
GeP(SiAs,SR32.139)M101.1°15.14;3.638;9.19A=idmSiAs N=112,192
GeP.p(U1.1,SR35.20)3.544;5.581A=bF(√2;2.25)=cB(√8;4.5) N=18,36
GeP3.p(R2.6,SR38.137)
GeP5.p(,SR35.20)
Sn4P3(Sn4As3,SR3.650,35.88)H3.968;35.33A=bFH(2;22/3)=cBH(2;88/3) N=93,192 phdHA
SnP(H8.8,SR21.163)H8.78;5.98A
SnP(NaCl,SR35.88)5.536A=bF'(2)=cB(4) N=36,72
SnP.p(GeP.p,SR35.88)3.831;5.963A=idmGeP.p FB2
Sn3P4(,SR35.122)H4.433;28.394A
SnP3(GeP3,R2.6,SR38.137)H7.379;10.512A=bFH(4;7/3)=cBH(4;28/3) N=114,
PbPM(nic,)
SiAs(N6.6,SR30.22)M106.00°15.979;3.668;9.529A=hdmSiP N=108;216
SiAs2.h(FeS2.h,SR33.36)6.023A=idmSiP2.h
SiAs2(GeAs2,SR32.140)14.53;10.37;3.636A=idmGeAs2
GeAs(SiAs,SR32.139)M101.3°15.59;3.792;9.49A=idmGeP
GeAs.p(GeP.p,SR35.20)3.715;5.832A=idmGeP.p FB2 N=18,40
GeAs2(08.16,SR27.52)14.76;10.16;3.728A=bFU(8;7/2;2)=cB(4√8;8;√8) N=112,240
Sn4As3(R4.3,SR3.650,33.146)H4.090;36.06 A N=93,210 phdHA,M
SnAs(NaCl,SR3.649)5.728A N=36,80
PbAsM(nic,phdHA)
SiSbM(nic,phdHA)GeSbM(nic,phdHA)
Sn3Sb2(,J.Inst.Met.99,1971,169) phdHA
SnSb.h(NaCl,SR9.29)6.138A=bF'(2)=cB(4)
SnSb.r(R1.1,SR3.651)H4.32;10.77A=bFH(2;6.1)=cBH(2;24)
PbSbM(nic,phdHA)
SiBiM(nic,phdHA)
GeBiM(nic,phdE)
SnBiM(nic,phdHA)
Pb3Bi(Mg,SR28.44)H3.51;5.80A=bBH(1;8/3)=cUH(√7;5)

TABLE 15: B5B5M

PAsM(nic,SR21.45)
PSbM(nic,phdHA)
AsSbM.h(As,phdHA)
PBiM(nic,)
AsBiM(nic,phdHA)
SbBiM(As,phdHA)

However, this is not the case in SnSb.r but SnSb.h is cubic. SnP_3(R2.6) is R-homeotypical to As and allows a FB2 binding.

$B^5B^5_{\underline{M}}$ phases. Either miscibility or immiscibility is found. In $PAs_{\underline{M}}$ the black P appears to be stabilized.

Concluding remarks

The analysis for the bonding types (bindings) may be fully appreciated when it is taken in mind that a binding indicates an energetic favourable state of a phase, i.e. a reason for its stability. The improved understanding of metallic phases may be compared to the stability arguments which were revealed by the electrostatic lattice theory for the typically ionic compounds. Taking into account the ionic radii of the components the cause for the heterotypism ZnS.r-NaCl-CsCl became easily understood. Of course the field of metallic phases is larger and more involved than the field of ionic phases, but both belong to chemistry. Originally it was hoped that the valence bond theory could explain compounds like transition metal phosphides, but no binding analysis based on valence bond theory of for instance all intermediate phases of the mixtures $VP_{\underline{M}}$ or $NiP_{\underline{M}}$ has been offered so far. The tackling of such problems by the valence bond theory is insuccessful for reasons which have been announced by Franzen (78). A further reason may be that in the valence bond theory the interaction of the covalent bonds is neglected. The consideration of these effects immediately leads to a model which is similar to the plural correlations model. As is well-known the covalent bond is a molecular spatial correlation of electrons and it is not a very realistic idea to think of a binding in a crystal as an aggregate of independent molecular correlations, or if they are not independent, then they are in a relation which is energetically unfavourable.

Opposite to the valence bond arguments is the objection against the plural correlations model that in a crystal several different spatial correlations are not possible, as there is only one electrostatic repulsion. This argument oversees that the momentum of electrons also determines whether there is essential spatial correlation or not. It must therefore be considered as admissible to analyse bonding types under the propositions of the plural correlations model. The attentive reader will find in the bindings proposed many conspicious numerical relations, should they all be merely casual, are they not rather indications that different spatial correlations of electrons cooperate to produce the unique set of $A^nB^5_{\underline{M}}$ phases? Also the existence of several bands is compatible with the existence of several correlations. It may be used as a working hypothesic that different correlations are contained in the different bands, so that might be spoken equally well of $\underline{b}$, $\underline{e}$ or $\underline{c}$ bands. However, the concept of a correlation is superior to the concept of a band, as the band model is an approximation which neglects correlation while the plural correlations model takes it into account as the model is derived from the density matrix instead from the Bloch functions.

It might be objected to be impossible that the d electrons of Ni, say, change their distance from 1.1Å in the marginal phase Ni to 1.8Å in NiP_2. However, considering Fig.1 of (83Sch) reveals that the electron distance is not in first line a property of the atom, but a property of the space which is availabe to the atom. The essential maximum of the averaged pair density D^{av} (83Sch) may be shifted quite away from the unessential maximum near the atomic core and it appears that this shift is especially easy for d electrons. Perhaps the large distance causes that the $\underline{e}$ correlation stipulated by Franzen 1978 ist not the most influencial one and came therefore fairly late to attention.

The certainty that the binding proposals describe something real in the bonding of the $AB^5_{\underline{M}}$ phases originates from the integer number matrix elements entering the binding description while the electron distances form smooth $\underline{d}(\underline{N}'_2)$ relations. If there were no deeper reality in the proposals either the integral property or the smoothness of $\underline{d}(\underline{N}'_2)$ would be less strikingly fulfilled. Furthermore numerous rules valid for the binding proposals confirm the parallelism between model and empirical data. Also the relation between structure and binding, not yet investigated fully, may corroborate the validity of the model. Finally there is the objection that the bindings of the plural correlations model are hypothetical. It should, however, be appreciated that any valence model has begun by hypotheses. Also the oxidation states for many compounds are hypothetical, otherwise they could never be controversial. Clearly the relation between valence theory and magnetic data is a strong support of the valence bond theory, but who knows whether some day a relation between magnetism and plural correlations model becomes apparent?

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