

ON THE BINDING IN $A^nB_M^1$ PHASES

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Summary

The $A^nB_M^1$ mixtures display the striking feature of an alloying gap: $A^{8,9}B_M^1$ mixtures do not form intermediate compounds. The cause for this gap is seen in a change from the Ekman type electron count (for instance in $A^{10}B_M^1$) to a non-Ekman type count (for instance in $A^4B_M^1$). The alloying gap is therefore briefly named the Ekman gap. The non-Ekman type count accepts all peripheral d electrons of an $A^{n<8}$ atom into the b correlation while these electrons enter under Ekmanian count the c correlation. Therefore in $A^{n<8}B_M^1$ mixtures brass-like bindings (XX2, X=CHBUF) and even silicon-like bindings may occur. The place number ratio $N_{p,u}^{/P'}$ holds as a good compass in the search for the appropriate electron-count and binding. For $A^2B_M^1$ it is found that $N_{p,u}^{/P'}(N_2)$ (N_2 = mole fraction of the second component) is not always a monotonous function. A monotonous function seems to occur only when the participating components are sufficiently similar. It appears that the outstanding energetic property of the XX2 binding, forces down the $N_{p,u}^{/P'}(N_2)$ curve to the value 8 and causes thus the exceptional non-monotonous character. The phenomenon of crystallographic shears occurs in several mixtures, its compatibility with the earlier theory is a strong indication for the validity of the present approach. The bindings found are compatible with magnetic data by the phenomenon of Hund-insertion, this furthermore contributes to the confidence into the binding interpretations.

Concordance of symbols used in binding analysis

Homologous classes (columns of the periodic system of elements): A^1 (alkali metals), A^2 (Be,...), A^3 (Sc,...), A^4 , A^5 , ..., A^{10} , B^1 (Cu,...), B^2 (Zn,...), B^3 (B,...), ..., B^8 (nob.g.).

This notation is especially appropriate to describe subsets of mixtures or phases. Phase designation by chemical formula with element symbols in the sequence of the above homologous classes; within a homologous class the lighter element first. Affixes separated by a point: p= high pressure phase, h= high temperature-, r= room temperature- (mostly omitted), l= low temperature; i= impurity stabilized, m= metastable phase. The stoichiometric index M (undetermined mole number) serves to designate a whole mixture. Sometimes the mole fraction designates composition. Structural type is noted by formula of prototype i.e. of the first found representative. The prototype itself is described (not exhaustively) by a letter for the Bravais group (Amer.Soc.Test.Mater.Standard E157-77), the number of atoms of the first component in the primitive cell, point, number of atoms of sec.comp. Bravais groups: C,B,F = cubic primitive, body centered, face centered T,U= tetragonal primitive, body centered H,R= hexagonal primitive, rhombohedrally centered O,P,Q,S= orthorhombic primitive, body centered, one face centered, all faces c. M,N;Z= monoclinic primitive, face centered; triclinic. Homeotypisms: R= replacement of atoms, L= formation of vacancies (lacunae), F= filling of interstices, D= homogeneous deformation, I= inhomogeneous deformation, S= shear of layers, C= shear of chains. The symbols may be placed with the affix htp (homeotypical to) before a prototype formula.

Densities: $\underline{D}_{XX'}$ = density matrix, X = configuration (spin and spatial coordinates)

\underline{D}_X = diagonal of $\underline{D}_{XX'}$, $\underline{D}_{X_1 X_2}^{SC}$ = spatial correlation, \underline{D}^{av} = averaged spatial correl., \underline{D}^{ed} = electron density, X = spatial coordinate.

Cells and commensurabilities: \underline{a} = cell (matrix) of crystal, \underline{a}_1 = edge vector of \underline{a} , \underline{b} = cell of valence electron correlation, \underline{c} = cell of peripheral core el. corr. $\underline{a}^{-1} \underline{a}' = \underline{K}$ = homeotypic commensurability, similarly $\underline{b}^{-1} \underline{a}' = \underline{K}'$, $\underline{c}^{-1} \underline{a}' = \underline{K}''$, $\underline{c}^{-1} \underline{b}' = \underline{K}'''$. \underline{d}_a , \underline{d}_c = distances of essential maxima in the \underline{D}^{av} function, $\underline{a} = \underline{bK}' = \underline{cK}''$ is the binding.

Isometric lattices (containing three linearly independent shortest vectors) are written omitting the 1 for one atom in the cell, as C,B,F,R,U,H. A lattice aspect different from the conventional aspect may be indicated by the (pseudo) symmetry of the aspect and noted behind the Bravais group. Sometimes the lattices are deformed (for instance by spin correlation) this is indicated by ~. Sometimes at certain places Hund insertion of spin down electrons into a spin up lattice occurs, this is indicated by a prime behind the isometric lattice symbol.

Particle numbers: $N_A^{\underline{a}}$ = number of atoms per cell,

$N_B^{\underline{a}}$, $N_C^{\underline{a}}$, $N_P^{\underline{a}}$, $N_P^{\underline{a}}$ = number of \underline{b} , \underline{c} electrons, atom places, \underline{b} -places, per \underline{a} cell, $N_A^{\underline{a}}$ = number per atom, $N_P^{\underline{a}}$ = number of \underline{c} places per \underline{b} place

Matrix notation: $\underline{a}_i = (\underline{a}_{11}, \underline{a}_{12}, \underline{a}_{13}; \underline{a}_{21}, \dots)$, i (mostly omitted) refers to an orthonormal spatial coordinate system, P numbers the edge vectors and incidentally designates the phase. An H before a numerical matrix or behind the last index of a symbolic matrix indicates that i refers to a hexanormal i coordinate system, analogously MB³ for a monoclinic normal system. Following abbreviations are convenient: $(\underline{a}_{11}, 0, 0; \dots) = (\underline{a}_{11}; \dots)$, $(\underline{a}_{11}; \underline{a}_{11}; \underline{a}_{33}) = (\underline{a}_{11}; \underline{a}_{33})$, $(\underline{a}_{11}; \underline{a}_{11}) = (\underline{a}_{11})$. Furthermore $(2, 1, 0; -1, 2, 0; 1) = (\sqrt{5}; 1)R$, where $5 = \det(2, 1; -1, 2)$ and R = rotation matrix which is generally not noted.

Alphabetical index of symbols used in binding analysis

A=class of homologous elements left to the Cu class in the periodic system; atom
a=elementary cell of crystal, \underline{a}_1 =edge vector of el. cell; \underline{a}_p =matrix element
B=class of homologous elements right to the Ni class; body cent. cub. Bravais group
 \underline{b} =elementary cell of valence electron correlation; \underline{b} -electrons=valence electrons
C=cubic primitive Bravais group; chain shear homeotypism
 \underline{c} =cell of peripheral core electrons; \underline{c} -electrons=peripheral core electrons
 \underline{D} = density, \underline{D}_{XX} =density matrix; \underline{D} =deformation homeotypism
 \underline{D}^{SC} = spatial correlation; \underline{D}^{AV} = averaged spatial correlation; \underline{D}^{ed} = electron density
 \underline{d}_b = distance of essential maxima in $\underline{D}^{AV,b}$; \underline{d}_c = the same for $\underline{D}^{AV,c}$
 \underline{E} = electrical dipol vector, \underline{E}_3 = its third component
F= cubic face centered Bravais group; filling homeotypism
H= hexagonal Bravais group; hexagonal aspect
h= high temperature phase
I= inhomogeneous deformation homeotypism
i= impurity stabilized phase; matrix index referring to orthonormal coord.system
 \underline{K} = commensurability matrix, $\underline{K}=\underline{a}^{-1}\underline{a}'$, $\underline{K}'=\underline{b}^{-1}\underline{a}$, $\underline{K}''=\underline{c}^{-1}\underline{a}$, $\underline{K}'''=\underline{c}^{-1}\underline{b}$
k= running index for components
L= vacancy formation (lacuna) homeotypism
l= low temperature phase
M= monoclinic primitive Bravais group; undetermined mole number
m= metastable phase
N= monoclinic face centered Bravais group; number; N_2 = mole fraction of the second component
n= exponent indicating the homologous class; number index of electron
O= orthorhombic primitive Bravais group; orthorhombic aspect
P= atom place, $P'=\underline{b}$ -correlation place; $P''=\underline{c}$ -correlation place; index counting edge v.
P= orthorhombic body centered Bravais group
p= high pressure phase
Q= orthorhombic one face centered Bravais group
R= rhombohedral Bravais group; replacement homeotypism
r= room temperature phase
S= orthorhombic all faces centered Bravais group; layer shear homeotypism
T= tetragonal primitive Bravais group; tetragonal aspect
U= tetragonal body centered Bravais group
W= wolfram type
 \underline{X} = spin spatial configuration
 \underline{x} = local coordinate of an electron
Z= triclinic Bravais group

Introduction

The analysis of binding (i.e. bonding type) by the two-correlations-model (82aSch) is of interest for the numerous phases between A^n and the B^1 elements, Cu, Ag, Au, as no valence rules have been advanced so far for them. The meaning of the symbols used to describe the bindings, homeotypisms etc. is the same as in the earlier communications of this series, so that the explanation needs not be duplicated here. For the sake of brevity the authors of the many structure determinations used here, can only be named indirectly by the Structure Reports reference; this does not mean a disregard of these valuable contributions.

In $A^n B_M^2$ phases (83Sch) the generalised Ekman rule was valid in the form that for $\bar{A}^n > 2$ and $\bar{N}_B < 0.5$ the \underline{b} electron contribution was $\bar{N}_B^{\bar{A}^n} - 1$ and for $\bar{N}_B > 0.5$ $\bar{N}_B^{\bar{A}^n} = 0$. This is an empirical rule and may have therefore exceptions. A greater \underline{b} electron contribution of A^n might be expected for $B^{\leq 2}$ components for instance in the present mixtures as the density of the \underline{b} gas of B^n atoms is here small and does not request descent of A^n electrons into the core. The real electron count of a metallic phase is assumed to be the one which permits the simplest and most natural binding proposal. Thus the change of the electron count independence of the mixture class amounts to a new valence rule for metallic phases.

It should be taken in mind that an examination or improvement of a binding assumption presupposes considering all the neighbouring structures and inserting the values of quantities determined by the binding into the $\underline{d}_{b,c}$ (\bar{N}_2) and $\bar{N}_P^{\bar{P}'}(\bar{N}_2)$ diagrams. Many phases allow a surprisingly good fit of the binding, and alone the fact that the two-correlations-model permits a more complete classification of the $A^n B_M^1$ phases than the earlier theories, shows that the model contains features which call for a serious examination. It should also be remembered that stability arguments coming from atomic radii and atomic charges are always taken for granted. When in the following analysis the word expansion of the electron gas is used, this means an increase of the \underline{d} value; the electron density generally does not reveal this remarkable process.

Analysis

A¹B_M¹ phases. The rules of the two-correlations model require a redistribution of electrons and this contributes to the energy of formation. As may be inferred from TAB.1 the energy contribution of Ag and Au is greater than that of Cu as the expansion of the d electrons reduces a greater electron density. The A¹ elements with their BC4 binding (3!Sch) and the B¹ elements with a FB√8 binding present the place number ratios $N_{p''}^{P'}=32$ and $N_{p''}^{P'}=11.3$, and following the monotonous property of the $N_{p''}^{P'}(N_2)$ function (N_2 =mole fraction of the second component) the bindings of A¹B_M¹ phases should belong to $N_{p''}^{P'}$ values lying between 32 and 11.3. A factorial binding falling into this interval is BF2 with $N_{p''}^{P'}=16$, the binding of W and its quasi-homologues. In fact RbAu(CsCl) and CsAu(CsCl) are compatible with this binding. To be sure NaAu and KAu are not isotypic to CsCl, probably as the electron rich components Rb and Cs easier form the c_F correlation than Na and K. A phase richer in A¹ than A¹Au is Na₂Au(CuAl₂), it permits BB√8 binding which yields $N_{p''}^{P'}=22.1$, and since BB√8 is only partially factorial it is gratifying that Na₂Au has not a congruent melting point. The HTFU2 binding of NaAg₂(MgCu₂) is slightly deformed in order to give a full occupation of the b correlation; the binding is closely homeotypic to FF2. Also the HUH2 binding of KAu₅(CaCu₅) is homeotypic to UU2 but it brings a contradiction to the monotonous condition for $N_{p''}^{P'}$. Probably the strong expansion of the c correlation near B¹ into the A¹ atoms causes this anomalous effect.

A²B_M¹ phases. It appears that in MgCu_M the $N_{p''}^{P'}(N_2)$ function is not monotonous once more, as starting from Cu an expansion of c in MgCu₂ causes a decrease of $N_{p''}^{P'}$ to the value 8 of the favourable FF2 binding. The phase MgCu₂(F4.2, drawing 64Sch p.158) may be derived from Cu by replacing 8 times 2Cu by 1Mg (see 64Sch); this mechanism conserves the b correlation of Cu but strongly decreases the number of c electrons per cell. Therefore the c correlation jumps into a better K₃₃ value, by straining the B type in Cu into F and this improvement of the binding is rewarded by a congruent melting point. Further decrease of $N_{p''}^{P'}$ may result in a HUH2 binding which permits a good extrapolation of $N_{p''}^{P'}$ from the value 9.2 of Mg₂Cu into the value 11.1 of the CHH3 binding of Mg.

Leaving aside Ca₂Cu(htpFeB), CaCu.h(htpT1I) and CaCu.r(htpFeB) leads to the famous phase CaCu₅(H1.5, drawing 64Sch p.165) which is isotypic to KAu₅ and RbAu₅. For chemical and geometrical discussion of this remarkable structure and its homeotypes see 40Hau, 42Now, 50Heu, 52Bys, 64Sch, 73Ram, 74Kha,

75Dep, 77Ray, 80Pea. The fact that every Cu is neighbouring to 3 or 4 Ca favours a strong increase of d_c as compared with Cu. This stabilizes a UU2 binding and it appears remarkable that less Ca than Mg is needed in alloys with Cu to reach the $N_{p''}^{P'}$ value 8.

SrCu(BaCu, H4.4, drawing SR46.25) is a LS-homeotype of B_2Al with the commensurability $\underline{a} = \underline{a}_{B_2Al}$ (1;4). There is no more a three dimensional connection of Cu atoms like in $SrCu_5$, but the Cu positions are gathered into separated planes parallel to (001); this must be considered to be the cause for the commensurability element $(\underline{a}_{B_2Al}^{-1}, \underline{a})_{33} = 4$ instead of 2, as the inhomogeneous Cu distribution causes electrical quadrupoles at the layers which favour a shift of the layers in the basal plane against one another. The binding may be tentatively assumed as $\check{C}HH/12$ which is an example of a \underline{b} correlation with a distorted $\check{C}H$ type.

The phase $BaCu_{13}(NaZn_{13})$ is an exception among the $NaZn_{13}$ representatives with respect to electron count, the BU2 binding is not as favourable as the FF2 binding of $NaZn_{13}$, but the radius ratio of both phases is comparable.

Assuming for $MgAg(CsCl)$ the BB2 binding as in $CuZn$ leads to the $\check{F}UB2$ binding for $Mg_{22}Ag_{78}(ZrAl_3)$, which explains the shears of the structure as compared with Cu_3Au (64Sch), provided that Ag contributes in the presence of Mg $N_{\underline{b}}^{Ag} = 1.04 \underline{b}$ electrons. The structures of the homeotypes with smaller mole fraction $N_{\underline{b}}^{Ag}$ are described in TAB.2 by the Zhdanov symbol (for $ZrAl_3$ $\check{2}\check{2}$ or simpler $2\check{2}$). As requested by the model (64Sch) the shear density increases with increasing \underline{b} electron concentration $N_{\underline{b}}^{Ag}$ as TAB.2 shows.

While Ca(Cu type) permits CB2 with $N_{p''}^{P'} = 16$ it appears that $Ca_3Ag(Fe_3C)$ and $Ca_5Ag_3(Cr_5B_3)$ are stabilized by the HTFU2 binding ($N_{p''}^{P'} = 9.8$). $CaAg(TII)$ permits a BB2 binding ($N_{p''}^{P'} = 8$) which causes the shear generating to TII type from the NaCl type and $CaAg_2(KHg_2)$ and $Ca_3Ag_8(H4.14)$ probably too. A UHFH2 binding may be chosen for the remaining analysed structure. The $SrAg_M$ and $BaAg_M$ phases as far as they are analysed are mainly isodesmic to earlier structures.

For $Mg_3Au(htpNa_3As)$ a HH2 binding appears probable and for $MgAu(CsCl)$ the BB2 binding of $CuZn$ homeotypes. The $\check{F}B\check{y}/8$ binding of $Mg_{22}Au_{78}(ZrAl_3)$ yields $N_{p''}^{P'} = 8.8$ which is so far from the value for Au $N_{p''}^{P'} = 11.3$ that additional structures are heterotypic to $Mg_{22}Au_{78}$ and show homeotypism to Nd (see drawing SR30.58); they contain a $\check{B}B2$ binding which explains the shears of the Mg sites in the close packed layers and probably also the shears in the stacking sequence of the layers.

The mixtures $CaAu_M$, $SrAu_M$ and $BaAu_M$ show isotypes to earlier phases and few new structures which yield admissible bindings (see TABLE 2).

TABLE 1: A1B1M

NaCuM(nic,phdHA)
 KCuM(nic,)
 RbCuM(nic,)
 CsCuM(nic,)
 NaAg2(MgCu2,SR26.250)7.923A=bHT($\sqrt{8};3/2$)=c $\sqrt{4}(\sqrt{32};8)$ N=24,224 phdE
 KAgM
 RbAgM
 CsAgM
 Na2Au(CuA12,SR5.55)7.417;5.522A=bB(2;1.5)=cB($\sqrt{32};4.2$) N=12,104 phdE
 NaAu
 NaAu2(MgCu2,SR5.54)7.803A=idmNaAg2 cmp
 K2Au phdE
 KAu
 KAu2
 KAu5(CaCu5,SR29.103)H5.659;4.483A=bH(2;1.6)=cUH(4;3,7/2) N=6,58
 RbAu(CsCl,SR23.78)4.105A=bB(1)=cF(2) phdE
 RbAu2
 RbAu5(CaCu5,SR29.103)H5.760;4.448A=idmKAu5 cmp
 CsAu(CsCl,SR23.78)4.263A=idmRbAu phdE

TABLE 2: A2B1M

Mg2Cu(S8.4,SR8.64)9.07;18.25;5.28A aH=bH($\sqrt{5.3};8$)=cUH($\sqrt{21};18/2$)N=80,416 phdHA
 MgCu2(F2.4,SR1.531)7.03A=bF(2)=cF(4) N=32,224 cmp
 Ca2Cu(O8.4,ACB38.2235)6.126;4.161;14.531A phdM
 CaCu.h(O20.20,ACB37.1981.500)38.80;4.271;5.894A
 CaCu.r(M10.10,ACB37.1981.500)M94.3⁰,19.47;4.271;5.880A
 CaCu5(H1.5,SR11.59)H5.092;4.086A=bH(2;1.8/2)=cUH(4;3,7/2) N=7,58 cmp
 SrCu(BaCu,SR46.128)H4.341;15.38A=bC(H(1;12)=cH($\sqrt{12};12$) N=12,72 phdM
 SrCu5(CaCu5,SR37.155)H5.261;4.058A=idmCaCu5
 BaCu(H4.4,SR46.24)H4.495;16.230A=idmSrCu phdM cmp
 BaCu13(NaZn13,SR23.45)11.719A=bB(4)=cU(3;10) N=120,1104
 Mg3Ag
 MgAg(CsCl,SR1.488)3.31A(1,1,1,-2,1,1;1,-2,1)=bBH(2;7/3)=cBHK'(2)
 Mg26.5Ag73.5(221221,ActCryst.A35.181)=hdmMg22Ag78
 Mg25Ag75(2221,ActCryst.A35.181)=hdmMg22Ag78
 Mg24Ag76(222122221,ActCryst.A35.181)=hdmMg22Ag78
 Mg23Ag76.5(222221222221,ActCryst.A35.181)=hdmMg22Ag78
 Mg22Ag78(ZrAl3,SR19.162)4.109;16.440A=bF(1;5)=cB($\sqrt{8};11$) phdHA phdM
 Ca3Ag(Fe3C,71Ec)7.99;6.86;10.17A=bHT($\sqrt{8};0.86\sqrt{3};4/2$)=cU($\sqrt{32};0.86\sqrt{32};5$)N=28,136
 Ca5Ag3(Cr5B3,SR27.119)8.039;15.011A=bHT($\sqrt{3};\sqrt{6.5}$)=cH($\sqrt{3235/2}$) N=52,280
 CaAg(TlI,71Ec)4.08;11.48;4.65A=bB(0.88 $\sqrt{2};3.5;\sqrt{2}$)=cBK'(2) N=12,72 cmp
 CaAg2(KHg2,71Ec)7.26;4.68;8.14A=bBH0(7.5/3;1;2/2)=cBHOK'(2) N=16,112
 Ca3Ag8(B6.16,SR29.33)9.81A=bB(3)=cB(6) N=56,416
 Ca2Ag7(H4.14,71Ec)H5.50;14.1A=bH(2;6/2)=cFH(4;3,7/3) N=22,172 cmp
 Ca2Ag9
 Sr3Ag2(Er3Ni2,83Mer)H9.962;18.61A [Sr7Ag3(Th7Fe3,83Mer)H11.385;7.277A phdHA,M cmp
 SrAg(O8.8ActCryst.37.1981.500)16.558;4.783;6.385A cmp
 SrAg2(KHg2,SR30.101)4.817;7.710;8.263A=idmCaAg2 cmp
 SrAg4
 SrAg5(CaCu5,SR13.31)H5.675;4.619A=idmCaCu5 cmp
 BaAg(FeB,ActCryst.37.1981.500)8.657;4.982;6.651A
 Ba2Au3 phdHA cmp
 Ba3Ag5(KHg2,SR30.100)4.95;8.06;8.45A=idmCaAg2
 BaAg5(CaCu5,SR13.31)H5.720;4.645A=idmCaCu5

$A^3B_M^1$ phases. Unfortunately under A^3 here only Sc, Y, La are considered. For the important set of compounds left out the excellent report of Iandelli and Palenzona (1979) should be consulted.

For ScCu(CsCl) the electron count may be taken contrary to the extended Ekman rule as $Sc^{3,8}Cu^{1,10}$ so that a FF2 binding may be assumed. A FF2 binding is possible also for $ScCu_2(MoSi_2)$ in a different commensurability. For $YCu_2(KHg_2)$ the ratio r_Y/r_{Cu} is greater than r_{Sc}/r_{Cu} so that a homeotype of B_2A1 becomes possible. The heterotypism YCu_2-B_2A1 is caused by the bad fit of b in a_3 direction. The phase $LaCu_2(B_2A1)$ has less c places per atom by virtue of the place number rule.

In $ScAg_M$ the phase $ScAg_4(MoNi_4)$ permits the BU2 binding, and the phase $Y_{14}Ag_{51}(Gd_{14}Ag_{51}, H14.51)$ may have a BHFH/12 binding.

$A^4B_M^1$ phases. For Ti.h(W) there is not much doubt into the binding $a=b_B(1)=c_F(2)$ with $N_{p''}^{P'}=16$, but it could alternatively be written $a=b_B^1(1)=b_C^1(2)=c_F(2)$. When the Cu^1 electrons, as it seems to be, are in correlation with $b''(Ti)$, then it must be written $N_{p''}^{P'}(Ti)=4$ following TAB.12 of 82Sch and the mixture $TiCu_M$ is non-Ekmanian, i.e. in its count an exception of Ekman's rule; the Cu^1 electrons cannot expand into the direction of the Ti atoms, but the Ti^4 electrons expand into the direction of the Cu atoms. The first result of the expansion is $Ti_2Cu(Zr_2Cu)$ with a $\tilde{B}C2$ binding (see 82aSch): the $N_{p''}^{P'}$ ratio is 4.4 near the value 4 and the c electrons form a C correlation. The FB2 binding cannot become stable for $TiCu(T2.2)$ as for further increase of N_{Cu}^C the $N_{p''}^{P'}$ must grow too, therefore the FU2 binding is formed while the homeotypism to CsCl is conserved. In order to account for the decreasing volume per atom the commensurability element K_{33}^u decreases from 2.60 in $TiCu$ to 2.50 in Ti_3Au_4 , to 2.44 in Ti_2Cu_3 , to 2.34 in $TiCu_2.h$, and these differences cause different phases to become stable. The $b^{-1}a$ commensurability too changes, as it needs not be exactly cubic because of the anisotropy of the crystal. It appears that the full occupation of the b correlation is more important than its exact symmetry.

The structures of $ZrCu_M$ and $HfCu_M$ are mainly complicated so that the binding assumptions are only a first attempt. The heterotypism $TiCu_4-ZrCu_5$ obeys the place number rule.

The phase $Ti_2Ag(Zr_2Cu)$ has a cell which is quite different from the cell a_{Ti_2Cu} ; therefore it is heterodesmic. However, its HTB/2 binding is not very different from $\tilde{B}C2$ of Ti_2Cu .

Following a rule $TiAu_M$ has more intermediate phases than $TiAg_M$ as the

TABLE 2 continued:

Mg3Au(htpNa3As,H18.6,Meta1123.4)H8.04;8.46A=bH($\sqrt{12}$;3.6)=cHK'(2) N=42,204
Mg5Au2
Mg2Au(htpPbC12,Met23.1969.4)18.34;8.26;13.56A
MgAu(CsC1,SR4.101)3.266A=idmMgAg
Mg27.5Au72.5
Mg27Au73(Q20.60,SR30.57)5.740;19.83;23.59A=hdmMg24Au76
Mg25.5Au74.5
Mg24Au76(Q8.24,SR30.58)5.747;19.95;9.437A=bB̄(2;5 $\sqrt{2}$;2 $\sqrt{2}$)=cB(4;10 $\sqrt{2}$;9 $\sqrt{2}$)N=80,608
Mg23Au77(H82.26,SR33.89)H14.927;9.441A
Mg22Au78(ZrA13,SR30.113)4.073;16.30A=idmMg22Ag78 $\bar{F}B/3$
Ca2Au phdHA \uparrow Ca5Au3(Cr5B3,Mer)7.867;14.39A
Ca4Au3
Ca1.1Au(TTI,JLCMet36.1982.241)3.961;11.075;4.573A
CaAu2(KHg2,RendAcNazLin48.1970.235)4.600;7.085;8.055A=idmCaAg2
CaAu3
CaAu5(PdBe5,F1.5,SR29.103)7.747A=bHT($\sqrt{8}$;~3.5/2)=cF(4) N=28,232
Sr9Au phdE
Sr3Au \uparrow Sr7Au3(Th7Fe3,83Mer)H11.07;7.161A
Sr3Au2.h
Sr3Au2.r
SrAu cmp
SrAu2(KHg2,RendAcNazLin48.1970.235)4.700;7.489;8.234A=idmCaAg2 cmp
SrAu5(CaCu5,SR24.149)H5.62;4.61A=idmCaCu5 UU2 cmp
Ba2Au3
BaAu2(B2A1,RendAcNazLin48.1970.235)H4.804;4.119A=bH($\sqrt{3}$;1.5)=cHK'(2) N=4,28
BaAu5(CaCu5,SR13.31)H5.67;4.58A=idmCaCu5 UU2

TABLE 3: A3B1M

ScCu(CsC1,SR27.342)3.256A=bF(1)=cF(2) N=4,18 phdM cmp
ScCu2(MoS2,71Ec)3.290;8.388=bF(1;2.5)=cF(2;5) N=10,56 cmp
ScCu4 cmp
YCu(CsC1,SR23.77)3.477A=idmScCu FF2 phdM cmp
YCu2(KHg2,SR28.21)4.305;6.800;7.315A=bFH($\sqrt{3}$;3.3/3;3)=cFHK'(2) N=20,112 cmp
Y2Cu7
YCu5(CaCu5,SR23.222)H4.984;4.117A=bH(2;1.6)=cUH(4;3.8) N=8,58 cmp
YCu6(H,71Ec)H6.83;4.07A \uparrow YCu7(TbCu7,SR37.156)H4.940;4.157A
LaCu(FeB,SR43,103)7.543;4.616;5.724A phdM
LaCu2(B2A1,SR28.45)H4.346;3.807A=bH($\sqrt{3}$;1.5)=cHK'(2) cmp
LaCu5(CaCu5,SR11.60)H5.169;4.116A=idmYCu5
LaCu6(CeCu6,SR43.103)8.165;5.148;10.23A
ScAg(CsC1,SR27.342)3.412A=idmScCu FF2 phdM cmp
ScAg2(MoS2,71Ec)3.519;8.922A=idmScCu2 cmp
ScAg4(MoNi4,SR35.116)6.574;4.069A=bB($\sqrt{5}$;1.4)=cU($\sqrt{20}$;3.4) N=14,96
YAg(CsC1,SR23.77)3.620A=idmScCu phdM
YAg2(MoS2;SR30.101)3.691;9.241A=idmScCu2 FF2
YAg3(Gd14Ag51,H14.51,SR35.116)12.637;9.300A=bBH(3;10.5/3)=cFH($\sqrt{108}$;9/3)N=93,622
YAg4
LaAg(CsC1,SR9.46)3.768A=idmScCu phdM cmp
LaAg2(KHg2,JLCM15.1968.273)4.825;7.287;8.196A=idmYCu2 N=20,112
La14Ag51(Gd94Ag51,SR35.116)H12.955;9.525A=idmY14Ag51 cmp
LaAg4.h(RhtpMgZn2,SR35.116)H5.569;9.078A
LaAg4.r(DhtpMgZn2,SR35.116)

TABLE 3 continued:

Sc₂AuNi₂Si,) phdM
 ScAu(CsCl,SR27.343)3.370A=idmScCu FF2 cmp
 ScAu₂(MoSi₂,SR37.151)3.508;8.725A=idmScCu₂ FF2 cmp
 ScAu₄(MoNi₄,SR37,151)6.536;4.031A=idmScAg₄ BU2 cmp
 Y₂Au(Ni₂Si,)
 YAu(CsCl,71Ec)3.559A=idmScCu
 YAu₂(MoSi₂,SR30.114)3.66;9.00A=idmScCu₂
 YAu₃(Cu₂Sb,₇₉Ian)6.096;5.084;4.968
 YAu₃.6(Gd14Ag51,)
 La₂Au(Ni₂Si,SR37.150)7.397;5.107;9.410A=bC(3;2;4/2)cCK'(2) N=28,104 phdM
 LaAu.h(TlI ,SR37.150)3.95;11.20;4.78A=bHT($\sqrt{2.5;5/2}$)=cHT($\sqrt{10;5;4/10}$) N=16,72
 LaAu.r(FeB,SR37.150)7.52;4.69;5.96A cmp
 LaAu₂(KHg₂,JLcM15.273)4.700;7.295;8.155A=idmYCu₂ FF2 cmp
 LaAu₃.6(Gd14Ag51,SR34.138)12.83;9.25A=idmY14Ag51 cmp
 LaAu₆

TABLE 4: A4B1M

Ti₂Cu(Zr₂Cu,SR28.20)2.944;10.786A=b \bar{B} ($\sqrt{2;5\approx 4.5}$)=cC($\sqrt{8;10}$) N=18,52 phdM
 TiCu(T₂.2,SR15.69)3.118;5.921A=bF($\sqrt{1.25;2.1^2}$)=cU($\sqrt{5;5.2}$) N=10,36
 Ti₃Cu₄(U₃.4,SR30.47)3.13;19.94A=bF($\sqrt{1.25;7.1\approx 6.4}$)=cU($\sqrt{5;17.5}$) N=32,128
 Ti₂Cu₃(T₄.6,SR30.47)3.13;13.95A=bF($\sqrt{1.25;5\approx 4.4}$)=cU($\sqrt{5;12.2}$) N=22,92 N=24,112
 TiCu₂.h(YAu₂,Q₂.4,SR30.47)4.38;7.97;4.49A=bF($\sqrt{2.5;28\approx 2.4;2.5}$)=cU($\sqrt{10;7;\sqrt{10}}$)
 TiCu₄(ZrAu₄,O₄.16,SR33.152)4.530;4.342;12.930A=bFU(2;2;8/2)=cFUK'(2) N=32,192
 Ti₂Cu(U₂.1,SR13.110,27.234)3.220;11.183A=idmTi₂Cu phdHA
 ZrCu N=152,624
 Zr₇Cu₁₀(Zr₇Ni₁₀,Q₁₄.20,SR41.127)12.673;9.316;9.347A=bHT(7/2; $\sqrt{20}$)=cU(10; $\sqrt{40}$)
 Zr₃Cu₈(Hf₃Cu₈ ,SR42.139)7.869;8.157;9.987A N=80,416
 Zr₂2Cu₇(GdAg₃.6,SR41.127)H11.244;8.246A=seeY14Ag51 N=107,622
 ZrCu₅(PdBe₅,SR46.67)6.87A=bF(2)=cF(4) N=36,232
 Hf₂Cu(Zr₂Cu,SR27.234)3.170;11.133A=idmTi₂Cu phdM
 Hf₂Cu₃
 Hf₃Cu₈(O₁₂.32,SR42.70)7.811;8.101;9.947A=idmZr₃Cu₈
 HfCu₃.6(GdAg₃.6,SR41.56)H11.179;8.235A=idmZrCu₃.6
 HfCu₅
 Ti₂Ag(Zr₂Cu,SR30.101)2.95;11.8A=bHT($\sqrt{2.5;7/2}$)=cB($\sqrt{5;9}$) N=18,52 phdE
 TiAg(TiCu,SR30.101)2.90;8.14A=bU($\sqrt{1.25;4}$)=cB($\sqrt{5;6}$) N=10,36
 Zr₂Ag(Zr₂Cu,SR27.234)3.246;12.004A=idmTi₂Ag phdHA
 ZrAg(TiCu,SR16.138)3,47;6.61A=idmTiCu
 Hf₂A (Zr₂Cu,SR29.96)3.20;11.84A=idmTi₂Ag
 HfAg(TiCu,SR29.96)3.41;6.48A=idmTiCu
 Ti₃Au(Cr₃Si,SR16.100)5.089A=bHT($\sqrt{8;3.2/2}$)=cB(4) N=26,68 phdS cmp
 TiAu.h(Au₁.05Cd_{0.95},SR27.224)2.94;4.88;4.63A=bB(1.25;2;2)=cFU(3.5;4;4)N=10,36
 TiAu.r(TiCu,SR27.224)3.33;6.02A=bF($\sqrt{1.25;2}$)=cU($\sqrt{5;5}$) N=10,36
 TiAu₂(MoSi₂,SR27.224)3.43;8.53A=bB($\sqrt{2;6/2}$)=cFU($\sqrt{8;10/2}$) N=12,56 cmp
 TiAu₄(MoNi₄,SR27.223)6.48;4.00A=bU($\sqrt{5;1.7}$)=cU($\sqrt{20;3.4}$) N=16,96
 Zr₃Au(Cr₃Si,SR27.224)5.486A=idmTi₃Au FB2 phdS
 Zr₂Au(Zr₂Cu,SR27.224)3.272;11.50A=idmTi₂Cu BC2
 Zr₅Au₄
 Zr₇Au₁₀(U ,SR27.224)6.966;13.292A
 ZrAu₂(MoSi₂,SR27.224)3.532;8.718A=idmTiAu₂ BFU2
 ZrAu₃(Cu₃Sb,SR27.224)6.062;4.865;4.785A=bFU(3.5/2;2;2)=cFUK'(2) N=14,76
 ZrAu₄(O₄.16,SR27.224)14.295;5.006;4.845A=idmTiCu₄ FF2
 Hf₂Au(Zr₂Cu,SR27.225)3.217;11.538A=idmTi₂Cu BC2

highly populated Au core tends to expand and this contributes to the energy of formation. With the non-Ekmanian electron count $Ti_4^{.8}Au_M^{1,10}$ the phase Ti_3Au may be classified. If at higher temperatures Au contributes more than one \underline{b} electron, a FB2 binding might be assumed. The good commensurability of this binding is partly conserved in the HTB/2 binding of Ti_3Au at lower temperatures. For $TiAu.r(TiCu)$ the FU2 binding is found; the non uniform distribution of Cu is a result of the stronger interaction of Cu cores and of the commensurability element $K_{33}^n \approx 5$. At higher temperatures $TiAu.h(Au_{1.05}Cd_{0.95})$ appears which allows a BFU2 binding. A fore-runner of XX2 is FF2 of $TiAu_2(MoSi_2)$. The deformation of $\underline{b} \approx$ is an indication that the simple composition is chosen at the cost of a little deformation of \underline{b} or \underline{c} . The phase $TiAu_4(MoNi_4)$, a RD-homeotype of Cu, permits a UU2 binding.

Several interesting structures in $ZrAu_M$ and $HfAu_M$ appear to be not yet known. The interpretation $HfAu_4(ZrAu_4, FF2)$ and $HfAu_5(MoNi_4, UU2)$ obeys the rule that for $N_{p,n}^P=8$ the closer packed binding is stable for the greater \underline{b} electron concentration.

$A^5B_M^1$ phases. This mixture class begins with six mixtures containing no intermediate compounds. Only the alloys with Au form intermediate phases. The gap represented by mixtures without intermediate phases is perhaps caused by the change of non-Ekmanian electron count to Ekmanian electron count; it may therefore be named the Ekman gap. The A^5Au_M mixtures have a greater energy of formations than A^5Cu_M and they do therefore not belong to the gap. The non-Ekmanian electron count yields for $V_3Au(Cr_3Si)$ and its A^5_3Au homologues a FB2 binding which might suggest that also Ti_3Au uses this binding by an only partial occupation of the \underline{b} correlation. $Ta_2Au(U.h)$ is homeotypic to $Ta_3Au(Cr_3Si)$ with $\underline{a}=\underline{a}_{Ta_3Au}(2;1)$ but the hexagons generated by the tetrahedral stars (64Sch) are closer packed in Ta_2Au in consequence of the smaller \underline{b} electron concentration; the cell does not contain 32 atoms as suggested by the commensurability to Ta_3Au but only 30. A homeotype of W is $Nb_3Au_2(U3.2, drawing 64Sch p.287)$ with the commensurability $\underline{a}=\underline{a}_W(1;5)$; the distribution of Au is not most uniform but displays association because of the interaction Au-Au which is more favourable than Nb-Au; the binding comes as UFU2 which has the place number ratio $N_{p,n}^P=4.6$. For $VAu_2(Q2.4)$ a RDI-homeotype of W a FUHT2 binding is found and for $VAu_4(MoNi_4)$, an isotype of $TiAu_4$, the brass binding UU2.

$A^6B_M^1$ phases. The only exception of the Ekman gap is $CrAu_4(MoNi_4)$ which must be homeodesmic to $VAu_4(MoNi_4)$. However, the electron numbers do not fit to the UU2 binding. Assuming that Cr absorbs 1.5 \underline{b} electrons in Hund-insertion

TABLE 4 continued:

HfAu.h
HfAu.r(TiCu,SR27.225)3.467;6.323A=idmTiCu FU2
Hf7Au10(U,SR27.225)6.894;13.19A
HfAu2(MoSi2,SR27.225)3.525;8.649A=idmTiAu2
HfAu3(Cu3Sb,SR27.225)6.022;4.868;4.779A=idmZrAu3 FF2
HfAu4(ZrAu4,SR27.225)5x2.850;4.995;4.835A=idmTiCu4 FF2
HfAu5(MoNi4,SR27.225)6.529;4.028A=idmTiAu4 UU2 N=15,97

TABLE 5: A5B1M

VCuM(nic, phdM)
NbCuM(nic, phdE)
TaCuM(nic, see S)
VAgM(nic, see HA)
NbAgM(nic, see S)
TaAgM(nic, see HA)
V3Au(Cr3Si,SR20.114)4.876A=bF(2)=cB(4) N=32,68 phdM
VAu2(Q2.4,SR27.226)4.684;8.482;4.810A=bFU($\sqrt{5}$;5.5/2)=cHT($\sqrt{20}$;9/2) N=28,112
VAu4(MoNi4,SR27.226)6.382;3.981A=bU($\sqrt{5}$;1.7)=cUK'(2) N=18,96
Nb3Au(Cr3Si,SR20.114)5.20A=idmV3Au FB2 phdM
Nb3Au2(U3.2,SR24.121)3.38;15.18A=bU($\sqrt{2}$;8)=cFU($\sqrt{8}$;18/2) N=34,88
NbAu2(B2A1,SR24.120)H4.61;2.72A=bFH(2;1.5)=cH(4;2.3) N=7,28
Ta3Au(Cr3Si,SR26.161)5.223A=idmV3Au FB2
Ta2Au(U.h,SR26.161)10.06;5.23A=bHT($\sqrt{32}$;3.3/2)=cB(8;4) N=110,260
Ta3Au2(Nb3Au2,SR26.161)3.38;15.25A=idmNb3Au2

TABLE 6: A6B1M

CrCuM (nic, phdHA)
MoCuM (nic, seeHA)
WCuM (nic, see HA)
CrAgM (nic, phdHA)
MoAgM (nic, seeHA)
WAgM (nic, see HA)
CrAu4(MoNi4,SR27.226)6.403;4.040A=bU($\sqrt{5}$;1.7)=cUK'(2) N=20,96 phdE
MoAuM (nic, see HA)
WAuM (nic, see E)

TABLE 7: A7B1M

MnCu3(Cu, phd S)
MnCu5(Cu, phd S)
TcCuM
ReCuM(nic, see S)
MnAgM(nic, phd E)
TcAgM
ReAgM(nic, see S)
Mn2Au(MoSi2,SR27.227,SR35.66)3.346;8.579A=bFU(2;7/2)=cB($\sqrt{8}$;7) N=30,52
MnAu.h(W,SR17.177,seeHA)3.256A=bU($\sqrt{2}$;1.7)=cF(2) N=8,18
Mn1.1Au.r(DhtpCsC1,SR27.227,seeH)3.146;3.182;3.291A=hdmMnAu.h
MnAu.r(DhtpCsC1,SR17.178,27.220)3.16;3.30A=hdmMnAu.h
MnAu2(MoSi2,SR27.227)3.374;8.778A=bB($\sqrt{2}$;4)=cFU($\sqrt{8}$;10/2) N=18,56

(see 80Sch) easily permits Hund-insertion also for $\text{MnAu}_4(\text{MoNi}_4)$; in fact CrAu_4 is antiferromagnetic (61Wac) and MnAu_4 is ferromagnetic (59Mey).

$A^7B_M^1$ phases. The phases $\text{MnCu}_3(\text{Cu})$ and $\text{MnCu}_5(\text{Cu})$ are not yet known well enough to warrant binding analysis. Besides these phases no intermediate compounds have been found in A^7Cu_M and A^7Ag_M .

The mixture MnAu_M confirms the rule that in a part of the Ekman gap the gold alloys exceptionally form compounds, to be sure, in TcAu_M and ReAu_M no compounds have been found either.

The phase $\text{Mn}_2\text{Au}(\text{MoSi}_2)$ yields under the non-Ekmanian count $\text{Mn}^{7,8}Au_M^{1,10}$ a FB2 binding which belongs to the silicon plateau; unfortunately $N_{pT}^{a/28}$, while $N_b^{a/30}$, therefore it must be assumed that one half electron per Mn is in Hund insertion so that only 6.5 \underline{b} electrons are contributed by Mn. In fact Mn_2Au displays weak paramagnetism (59Gia). This observation is supported by MnAu_2 ; the r phases are caused by entering of Hund-insertion. In MnAu_2 the Hund-insertion has increased to 1 electron per Mn according to Ekman's rule and the BFU2 binding is a good successor of the UFU2 binding of MnAu_2 . Mn_2Au_5 (N2.5, drawing 77Sch) is a R-homeotype of Cu with $\underline{a}=\underline{a}_{Cu}(-1,0,1.5;2,0,0.5;0,1,0)$ and a S-homeotype of MoPt_2 with abnormal shears which dilute the minority component. The CB $\frac{1}{2}$ binding permits a fully occupied \underline{b} correlation which is according to the rule of correlation density less close packed than the BFU2 binding of MnAu_2 ; the distance \underline{d}_b is shorter than the expectation according to the distance rule (80Sch). For $\text{MnAu}_4(\text{MoNi}_4)$ a FF2 binding appears which permits 1 electron to be Hund-inserted as the magnetic measurements require (59Mey). It appears therefore that there are two heterodesmic subtypes of the MoNi_4 type in the AB_M^1 phases; this is confirmed by two classes of axial ratio (see 64Sch p.102).

$A^8B_M^1$ and $A^9B_M^1$ phases. These mixtures do not show intermediate phases as the d electrons of the $A^{8,9}$ component are neither in a correlation with the d electrons of the B^1 component nor in a correlation with the s electron of the B^1 component.

$A^{10}B_M^1$ phases. The d electrons of A^{10} are in correlation with the d electrons of B^1 here. In accordance with Ekman's rule the \underline{b} electron contribution of A^{10} is 0.6 for $M=0$ and 0 for $M>2$. This causes a FUU2 binding for $\text{Pd}_{0.8}\text{Cu}_{1.2}(\text{CsCl})$. The high value of $N_{p''}^{P'}$ requires the \underline{c}_U correlation. The \underline{b} electron contribution of Pd is already small so that the homogeneity of $\text{Pd}_{0.8}\text{Cu}_{1.2}$ is shifted from 0.5 to greater mole fractions N_{Cu}^c . For greater N_{Cu}^c the \underline{c} correlation takes the

TABLE 7 continued:

N=38,132

Mn2Au5(N2.5,SR29.60)a/(-1,0,1.5;2,0,0.5;0,1,0)=4.10;3.95A=bC(2)=cB($\sqrt{8}$;2.8)
Mn28-23Au72-77(H,R,SR32.89)
Mn24Au76(Mg,SR27.219)2.858;4.730A
Mn9Au31(T9.31,SR46.84)12.6;4.0A drawing
Mn21Au79(ShtpCu3Au,SR24.148)2x4.08;4x4.05;4.03A drawing
MnAu4(MoNi4,SR21.128,24.149)6.45;4.03A=bFU($\sqrt{8}$;2.5/2)=cFUK'(2) N=22,96
TcAuM
ReAuM(nic,see S)

TABLE 8: A8B1M

FeCuM(nic, phd HA)
RuCuM(nic, see HA)
OsCuM(nic, see HA)
FeAgM(nic, see HA)
RuAgM(nic, phd M)
OsAgM
FeAuM(nic, phd HA)
RuAuM(nic, phd M)
OsAuM(nic, see HA)

TABLE 9: A9B1M

CoCuM(nic, phd HA)
RhCuM(nic, phd M)
IrCuM(nic, phd M)
CoAgM(nic, see HA)
RhAgM(nic, phd E)
IrAgM(nic, see E)
CoAuM(nic, phd HA)
RhAuM(nic, phd E)
IrAuM(nic, see E)

TABLE 10: A10B1M

NiCuM(Cu,SR1.513,2.624) phdHA
PdCuM.h(Cu,SR1.515) phdHA
Pd0.8Cu1.2(CsC1,SR1.515)2.99A=bFU(1;1.4/2)=cU(2;2.5)
Pd30Cu70(ShtpCu3Au,SR19.146)3.70;6x3.70;8x3.70A
PdCu3(ShtpCu3Au,SR19.150)3.705;8x3.655A=bF(1;7)=cB($\sqrt{8}$;22)
Pd15Cu85(Cu3Au,SR19.150)3.67A=bF(1)=cB($\sqrt{8}$;2.8)
PtCuM.h(Cu,SR9.75)
Pt7Cu(Pt7Mg,SR9.76)7.77A=bB($\sqrt{5}$;2.2)=cF($\sqrt{20}$;4.5)
Pt3Cu(htpPt7Mg,SR15.66)7.71A
PtCu(R1.1,SR1.485)H2.70;12.9A=bH(1;4.8)=c \tilde{C} H($\sqrt{3}$;24/3) N=45,60
PtCu3(ShtpCu3Au,SR19.153)3.708;3.692A=idmPdCu3
Pt22Cu78(Cu3Au,SR19.153)3.686A=idmPd15Cu85
NiAgM(nic, phdHA)
PdAgM.h(Cu,SR1.519) phdHA
Pd3Ag2(see E)
PdAg(see E)
Pt3Ag.h phdHA

B type instead of U, the \underline{b}_F correlation is strained to have the appropriate $N_{Pn}^{P'}$ value and the strain decreases with increasing N_{Cu}^A . Because of the strain of \underline{b}_F the axial ratio $|\underline{a}_3|/|\underline{a}_1| < 1$, where L =shear length, and the negative shear density $1/L$ increases towards the value 0 as the valence electron concentration approaches 1 (see 64Sch). For $N_b^A < 0.75$ the off-stoichiometry against $PdCu_3$ causes a second shear system the shear vector of which is not normal to the shear normal. It decreases the \underline{a}_1 axis as the radius $r_{Cu} < r_{Pd}$, so that the axial ratio returns to 1 (see drawings 64Sch or SR19.149). It should be appreciated that the line through the points $N_{Pn}^{P'}(Pd_{0.8}Cu_{1.2})$, $N_{Pn}^{P'}(Pd_{25}Cu_{75})$ and $N_{Pn}^{P'}(Pd_{15}Cu_{85})$ does not extrapolate to $N_{Pn}^{P'}(Pt)=16$ because of the composition dependent \underline{b} contribution of Pd.

$Pt_7Cu(Pt_7Mg, F7.1)$ is a R-homeotype of Cu with $\underline{a}=\underline{a}_{Cu}(2)$; the binding is only a first attempt. $Pt_3Cu(HPt_7Mg)$ is postponed as the structure is not certain enough. The phase $PtCu(R1.1)$ is a RD-homeotype of Cu with layers of Pt and Cu parallel $(111)_{Cu}$ alternating in $[111]_{Cu}$ direction; the $HCH/3$ binding has a favourable internal commensurability and has a $N_{Pn}^{P'}$ value 15 which fits well to the values occurring in $PdCu_M$. The phases $PtCu_3$ and $Pt_{22}Cu_{78}$ are isotypic to phases in $PdCu_M$.

The mixture $PdAg_M$ and $PtAg_M$ appear to have intermediate compounds but the structures are not known well enough to warrant binding analysis. $A^{10}Au_M$ displays no new structures.

B_M^1 phases. The rule that Au easier forms intermediate phases than Cu and Ag is confirmed in this mixture class. The FUB2 binding of Cu, Ag, Au is essentially conserved in all phases. This binding is indeed responsible for $CuAu(T1.1)$ instead of "CuAu(PtCu)": the composition favours ordering of atoms in alternating planes. This ordering causes, as is easily verified, a contraction in the direction perpendicular to the basal plane. As for a \underline{b}_F correlation the contraction is easiest in $[001]_{\underline{b}}$ direction the $(001)_{Cu}$ planes are chosen as ordering planes. In $PtCu$ which has not a \underline{b}_F correlation the $(111)_{Cu}$ planes are chosen which permit a stronger interaction of atoms of the same kind. The Cu_3Au structure is energetically preferred by the fact that every Au is surrounded by 12 Cu and no Cu is not bound to an Au. The class of B_M^1 phases displays a special feature, the stability of shear homeotypes which are caused by a mismatch of \underline{b}_F to \underline{a} (see 64Sch). The mismatch is caused by an anomalous and temperature dependent \underline{b} electron contribution of Au (45Ray, 64Sch). Once more the additional correlation planes (which accept the electrons of the anomalous \underline{b} contribution of Au) are parallel to $(001)_{Cu}$ and the energetic

TABLE 10 continued:

Pt3Ag.r
PtAg.h
Pt2Ag3
PtAg3.h
PtAg3.r(Cu3Au,SR9.118)3.895A=idmPd15Cu85
NiAuM.h(Cu,SR4.227) phdHA
Pd3Au(,71Ec) phdHA
PdAu(CuAu,SR29,103)4.0;3.9A
PdAu3(Cu3Au,JphysSocJap20.1965.1881)=idmPd15Cu85
PtAuM.h(Cu,SR15.77) phdHA
PtAu3(Cu3Au,SR15.78)3.91A=idmPd15Cu85

TABLE 11: B1B1M

CuAgM(nic, phdHA)
CuAuM.h(Cu,SR1.506) phdHA
Cu3Au.h1(ShtpCu3Au,JApp1Cryst6.1973.371)
Cu3Au.r(C1.3,SR1.486)3.76A=bF(1)=cB($\sqrt{8}$;2.8)
CuAu.h1(P10.10,SR33.75)3.956;10x3.972;3.676A
CuAu.r(T1.1,SR1.485)3.99;3.73A=bF(1;1)=cB($\sqrt{8}$;3)
CuAu3.m(ShtpCu3Au,PhysStatSola14.1972.123)
CuAu3.r(Cu3Au,PhysStatSola14.1972.123)
AgAuM(Cu,SR1.510) phdHA

reason is the same as earlier: the system of $(001)_{Cu}$ planes accepts easiest additional electron planes, or $[001]_{Cu}$ is a soft direction. The softest direction of $CuAu.h_1(P10.10)$ is $[010]$ and therefore it is the normal of the shear planes. The mechanism of electrical dipole vectors at the minority component has been explained earlier (64Sch). Additional features of the shear phenomenon may be found in 73Sch.

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