

ON THE BINDING IN $B^{0..2}B_M^2$ MIXTURES

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Summary

A useful classification principle in chemistry is given by valence rules based on electron numbers indicating a bonding type so that phases with the same bonding type form isodesmic sets of phases, and expectations may be expressed on the stability of isodesmic phases in a new mixture. For metallic phases valence rules related to valence electron numbers have been found by Zintl, Hume-Rothery, Grimm&Sommerfeld and others. A unifying model comprehending these rules and introducing additional rules is the two-correlations model. It assumes a lattice like spatial correlation in the ensemble of valence electrons with the cell \underline{b} and a lattice like spatial correlation in the ensemble of the peripheral core electrons with the cell \underline{c} and these correlations are commensurable to the crystal cell \underline{a} so that a simple commensurability exists also between \underline{b} and \underline{c} . The correlation types and the $\underline{c}^{-1}\underline{b}$ commensurability represent a bonding type and are named a binding. The binding may be analysed in homologous classes of alloy systems by simple methods. In the following, mixtures between T^{10} elements (Ni, Pd, Pt), or B^1 , (Cu, Ag, Au), or B^2 , (Zn, Cd, Hg) on the one side and B^2 elements on the other side are interpreted, (briefly $B^{0..2}B_M^2$, M=undetermined mole number). Since stable structures must have a low energy bonding type, one may claim to have found a confirmation of a crystal chemical rule when a low energy binding commensurable to the crystal cell is verified to be possible. In fact the two-correlations model yields a coherent interpretation of the $B^{0..2}B_M^2$ phases. A surprising result is, that two-factorial isotypic bindings (CC2, BB2, UU2, FF2) are so frequent, that their stability may be used to define the brass like property of a mixture.

Introduction

The knowledge of the crystal structures in brass like mixtures $B^{0..2}B_M^2$ is fairly complete thanks to the work of A.J.Bradley, A.Westgren and other investigators. Reviews on this knowledge have been written by W.Hume-Rothery and others [1,2,3,4]. Stability arguments for the different structures have been taken from the band model [5] but were doubted later on [6]. This instability of interpretation must be caused by the fact that the band model is an approximation for stability, corresponding to a series which does presumably not converge sufficiently fast. For this reason it appeared worthwhile to start from the density matrix formalism and try first a conceptual approach to the crystal chemical problem of these alloys [7]. It became apparent that the valence problem of alloys (which phase forms in a mixture?) could be separated from the stability problem (which energy has an alloy?) [8]. The solution of the valence problem is desirable for any chemical field since this solution is easier than the solution of the stability problem. It is probable that a solution of the valence problem is also of interest for the further development of the stability problem. The result of this approach was the two-correlations model [8]. To investigate the validity of this model and to contribute to its further development it is desirable to discuss chemically homologous sets of alloy systems as a whole with respect to the structures of the intermediary phases. Many authors have contributed to analyse these structures; unfortunately their valuable contributions cannot be cited fully here for the sake of brevity: instead the Structure Reports reference is given from which the author and journal references readily may be found. Also for the description of the particular structures reference must be made to reviews [7,9] on alloy phase structures. The method how to arrive at a binding, i.e. at a classification of the bonding, has been described earlier [7,8]. A short review of the symbols used and of an instruction how to find a binding is given in the appendix. It is helpful to visualize the different commensurabilities by consideration of the available structure drawings and by sketches of the fitting of the spatial correlations of the electrons. Also calculating the $d(N_2)$ diagram (d_b =smallest distance in the b cell, d_c =smallest distance in the c cell, N_2 =mole fraction of the second component) helps to learn the method of analysis of the bonding type. We shall now consider the interpretation of the empirical material.

Mixtures $T_{BM}^{10,2}$

$NiZn_M$. The CsCl structure of NiZn (high temperature phase of the compound NiZn) obeys Hume-Rothery's rule (number of valence electrons per atom $N_V^A=1.5$) because of the temperature dependent valence electron contribution of the Ni atoms [7p.62]. A binding which yields this rule has been found for AuCd.r [8,22], as this superstructure of AuCd.h (CsCl type) gives evidences for the electron correlations which are not so apparent in AuCd.h because of the quadruple twinning of the correlations which introduces a greater structural symmetry than in AuCd.r so that the indications of the binding become less distinct. If \underline{a} is the cell of AuCd.r and \underline{a}' the cell of AuCd.h then the following linear relation between the cell edge vectors holds: $\underline{a}_1 = \underline{a}'_1 - 2\underline{a}'_2 + \underline{a}'_3$, $\underline{a}_2 = \underline{a}'_1 + \underline{a}'_2 - 2\underline{a}'_3$, $\underline{a}_3 = \underline{a}'_1 + \underline{a}'_2 + \underline{a}'_3$. This may be abbreviated using matrix notation to $\underline{a}_{AuCd.r} = \underline{a}_{AuCd.h} (1,1,1; -2,1,1; 1,-2,1)$ and the binding in AuCd.r is expressed by the equations $\underline{a}_{AuCd.r} = \underline{b}_{BH} (2;7/3) = \underline{c}_{BH} (2;7/3) (2)$, where \underline{b} is the cell matrix of the valence electron correlation, \underline{c} is the cell matrix of the peripheral-core electron correlation, BH is the second matrix index (the first being omitted) and indicates additionally the bodycentered cubic correlation in hexagonal aspect, and the following brackets contain the commensurability matrices abbreviated as explained in the appendix. Since (2;7/3) may be divided out of the last equation, $\underline{b}_{BH} = \underline{c}_{BH} (2)$ holds, so that the binding may be named a BB2 binding where \underline{b} , \underline{c} , H have been omitted and from (2) only the first eigenvalue has been retained. It is easily verified that the smallest distance in \underline{b}_{BH} is $d_b = |\underline{a}'_{AuCd.h}|^{3/4}$ (where $|\underline{a}'|$ = lattice constant of AuCd.h), and this d_b value may be plotted in a $d(N_2)$ diagram as it has been explained earlier [8].

It should be appreciated that the correlation cells are a description of what has been named cybotactical areas in liquid theory. The commensurabilities describe energetically favourable relations between the correlations. The indirect proof for the reality of such correlations is given by many correspondences between the model and features of the empirical data. The \underline{b} correlation just mentioned comprehends Hume-Rothery's rule for CuZn homeotypes (like NiZn.h) since the number N_p^A of \underline{b} places per atom is $N_p^A = 1.55$ so that because of the occupation rule [8] the empirical valence electron concentration rule follows. The binding comprehends also Bradley's rule for partial atomic occupancy in iso-types and homeotypes of CuZn [7], as the factoriality of $\underline{c}^{-1}\underline{b}$ favours non-occupancy of places of the less valence electron rich component [8,10]. Finally the binding comprehends the Cu_5Zn_8 type of vacancy array in CuZn homeotypes

[10] as will be seen below for NiZn_3 .r. If the partial occupancy is only a consequence of the factorial commensurability of the binding (which occurs also in closed packed structures, like Au_5Sn , see below) it appears questionable why partial occupancy occurs only in CuZn homeotypes and not in Cu or Mg homeotypes. The cause for this lies in the fact that in CuZn homeotypes the neighbour atoms of a vacancy may move onto the vacancy without diminishing a smallest atomic distance while this is not the case for Cu homeotypes. About 700°C the phase NiZn.h transforms into NiZn.r (CuAu type) which shows a BU2 binding (Table 1). While the number of \underline{c} correlation places per atom in AuCd.r (and therefore also in NiZn.h) is $N_{\text{p}}^{\text{A}}=12.4$ it is in NiZn.r only $N_{\text{p}}^{\text{A}}=12.0$; this corresponds to the decrease of the valence electron concentration, going from NiZn.h to NiZn.r , by the rule of place numbers [8].

At the composition NiZn_3 an orthorhombic vacancy homeotype of the Cu_5Zn_8 type becomes stable [10], and at slightly greater Zn mole fractions a cubic homeotype of Cu_5Zn_8 is found which was refined [11] for the composition $\text{Ni}_2\text{Zn}_{11}$ although this composition lies a little outside the homogenous field of the phase. The wellknown commensurability $\underline{a}_{\text{Ni}_2\text{Zn}_{11}} = \underline{a}_{\text{NiZn.h}}(3)$ is compatible with the number of non-occupied atom places per cell $N_{\text{N}}^{\text{C}}=2$. Why has the Cu_5Zn_8 family more than 40 members [10] while for instance for Ni_3Ga_4 (SR34.137) no isotype is known? The answer to this question is given by the BB2 binding of NiZn.h which is to be assumed in NiZn_3 and $\text{Ni}_2\text{Zn}_{11}$ also. The BB2 binding may be extended to valence electron concentrations $N_{\text{V}}^{\text{A}} > 1.5$ by the homeotypism of Bradley partial occupation of \underline{a} places [8], i.e. by $N_{\text{N}}^{\text{C}} > 0$. It is easily understood that the commensurability of the BB2 binding to NiZn.h and $\text{Ni}_2\text{Zn}_{11}$ produces a stress field which favours just $N_{\text{N}}^{\text{C}}=2$: A great subset of the vacancy places of $\text{Ni}_2\text{Zn}_{11}$ is selfequivalent by the translation group of AuCd.r (see Tab.2, cf. also [12Fig.4]). Since the BB2 binding of AuCd.r produces also a little strain in the direction of the hexagonal axis, it must be assumed twinned in $\text{Ni}_2\text{Zn}_{11}$ in such a manner that its trigonal axis points statistically into all four [111] directions of $\text{Ni}_2\text{Zn}_{11}$. Since in AuCd.r the BB2 binding is untwinned (or as might be said singly twinned) it is conceivable that cases are found of double twinning (orthorhombic NiZn_3 and homeotypes) and triple twinning causing rhombohedral symmetry and $\alpha > 90^\circ$, for instance in Cu_7Hg_8 (SR34.77). The circumstance that a binding is twinned has not been considered by earlier bonding models, nevertheless it appears to be quite frequent. An anomaly of the lattice constant in $\text{Ni}_2\text{Zn}_{11}$ found by Schramm [10] could be interpreted by a particular vacancy mechanism [13] in Cu_5Zn_8 homeotypes. Since the neighbour atoms of a vacancy may freely move onto the vacancy and the second near neighbours follow

TABLE 1: Binding in the phases of $T_{10}^{10}B_M^2$ mixtures.
Designations see appendix.

NiZn.h(CsCl,SR4.241)2.914A→aH=H7.138;5.047A=bBH(2;7/3)=cBH(4;14/3)
 NiZn.r(CuAu,SR6.186)2.747;3.190A=bB(1;1.2)=cU(2;3)
 NiZn3(Q72.208,JLCM1980)33.33;8.87;12.50A=hdm NiZn.h
 Ni2Zn11(↔Cu5Zn8,SR33.108)8.92A→aH=bBH(2,2,0;-2,4,0;7/3),b=c(2)
 Ni3Zn22(N3.22,SR37.117)12.46;7.47;-4.86,0,7.65A=bB(5;3;-2,0,3)=cFU(7;6;-4,0,6)
 Pd2Zn(Ni2Si,SR26.225)5.35;7.65;4.14A=bC(2;2.75;1.5)=cB(4;5.5;3)
 PdZn.h(CsCl,SR15.112)3.05A=idm NiZn.h
 PdZn.r(CuAu,SR15.113)2.91;3.34A=idm NiZn.r
 Pd2Zn3.h(CsCl,SR15.113)3.05A=hdm NiZn.h
 PdZn2(Q8.16,SR44.87)7.525;7.363;12.30A=bB(2.5,1,0;-1,2.5,0;4.5)=cBK'(2)
 PdZn4(NiZn3,)34.0;9.0;12.7A=idm NiZn3
 Pd5Zn21(↔Cu5Zn8,SR15.114)9.10A=idm Ni2Zn11
 PdZn11.h(Mg,SR15.114)H2.776;4.331A=hdm CuZn4
 Pt3Zn(Cu3Au,SR16.132)3.893A=bB(1)=cB(√8;2.8)
 Pt3Zn2(CuAu,SR16.132)2.84;3.56A=bFU(1;1.8/2)=cU(2;3)
 PtZn1.7.h(↔B2A1,SR16.132)H4.11;2.74A
 Pt7Zn12(O14.24,SR34.120)28.79;6.94;2.76A=bB(10;2.5;1)=cB(20;5;2)
 PtZn3(↔Cu5Zn8,SR16.132)
 Pt3Zn10(↔Cu5Zn8,SR35.90)18.113A
 PtZn5.5(Ni2Zn11,SR35.56)9.08A
 PtZn8(,SR16.132)

Ni11Cd12(F11.12,SR30.33)11.39A→H8.05;19.73A=bCH(√5.3;14/3)=cBH(4;48/3)
 Ni2Cd5(↔Cu5Zn8,SR19.80)9.675A→aH=H13.682;8.379A=bBHK''/2=cBH(√43;20/3)
 NiCd5(↔Cu5Zn8,SR35.40)9.788→aH=H13.842;8.476A=bBHK''/2=cBH(√48 ;21/3)
 Pd3Cd2(CuAu,SR15.28)3.01;3.57A=idm Pt3Zn2
 PdCd.h(,SR15.28)
 Pd2Cd3.h(W,SR15.28)3.24A=idm Pd2Zn3.h
 PdCd3(↔Cu5Zn8,SR15.29)
 PdCd4(↔Cu5Zn8,SR15.30)
 Pd5Cd21(Cu5Zn8,SR15.29)9.96A=idm Ni2Zn11
 Pt3Cd(Cu3Au,SR16.39)3.97A=idm Pt3Zn
 PtCd(CuAu,SR16.39)2.95;3.81A=idm NiZn.r
 PtCd2(↔B2A1,SR16.40)
 Pt3Cd7(↔Cu5Zn8,SR16.40)
 PtCd3(↔Cu5Zn8,SR16.40)
 PtCd5(Cu5Zn8,SR16.40)9.90A=idm Ni2Zn11

NiHg4(B1.4,SR17.225)6.02A=bB(2)=cB(4)
 PdHg(CuAu,SR24.181)3.02;3.71A=idm NiZn.r
 PdHg2(↔B2A1)
 Pd2Hg5(Mn2Hg5,SR30.66)9.46;3.03A=bB(√10;1)=cBK'(2)
 PdHg4
 PtHg(CuAu,SR17.226)2.79;3.83A=idm NiZn.r
 PtHg2(T1.2,SR17.226)4.687;2.91A=bB(1.5,0.5,0;-0.5,1.5,0;1)=cBK'(2)
 PtHg4(NiHg4,SR17.227)6.187A=idm NiHg4

this displacement, around a vacancy atom clusters form which may be used to describe the displacement homeotypism of these structures to CuZn or W.

In Ni_3Zn_{22} (N3.22) a dilatation of the \underline{c} correlation is caused by the vacancies. A change to the \underline{c}_F correlation could decrease this stress. Also the expansion of the d shells of the Ni into the structure favours a \underline{c}_F correlation. Curiously enough the \underline{c} correlation is fully occupied. This assumption could be mitigated by choosing the binding $\underline{a}=\underline{b}_B(5;3;-2,0,3)=\underline{c}_{FU}(7.5;6;-4,0,6)$ which implies a little distortion (-) of \underline{c} but affords a better $\underline{c}^{-1}\underline{b}$ commensurability and allows an influence of the spins. The binding described in Table 1 seems to be the first argument in favour of the stability of the phase richest in Zn in this mixture.

At this occasion the binding of Zn(Mg,SR1.38) $\underline{a}=H2.665;4.947\text{\AA}$ should be reconsidered. The long axial ratio occurs only for Zn, Cd, and Zn_3Hg [7], evidently the B^2 homologous class is necessary for it. The neighbourhood of two opposite spins occurring in this class permits a correlation type which is non isometric and may be described [14] as a UH correlation which is compressed in the direction of the pseudo-hexagonal axis so that the layer distance is $d/\sqrt{2}$ (d =distance in the hexagonal basal plane of UH); this non-isometric correlation may be named $\bar{U}H$. It may be applied to Zn: $\underline{a}=\underline{b}_{\bar{U}H}(\sqrt{4/3};3/2)=\underline{c}_{\bar{U}H}K^1(2)$; where $K^1=\underline{b}^{-1}\underline{a}$. As a little disadvantage appears the low occupation $N_{\bar{U}H}^1/C=0.63$, so that instead of $\underline{c}_{\bar{U}H}$ also \underline{c}_F , \underline{c}_U , or \underline{c}_H might be considered. It is seen how very hidden the binding may be in a simple phase like Zn.

PdZn_M. The structure of $Pd_2Zn(Ni_2Si)$, drawing [7] p.322) is a displacive ordering homeotype of the Cu structure. The proposed CB2 binding is a forerunner of the BB2 binding and this is responsible for the stability of $PdZn.h$, $Pd_2Zn_3.h$, $PdZn_2$, $PdZn_4$ and Pd_5Zn_{21} . All these phases may be understood following Tab.1 as different adaptations of the BB2 binding to the crystal. This confirms that the BB2 binding is energetically favourable; it incidentally shows that very different structures may be formed by different commensurabilities of one and the same binding.

A new binding appears in $PdZn_{11}.h$ (Mg type) which may be understood by considering the binding in $CuZn_4$ below.

PtZn_M. The phase Pt_3Zn has a BB/8 binding like Pt itself, while Pt_3Zn_2 is homeodesmic to $NiZn.r$: the undistorted \underline{b}_F correlation (Tab.1) explains the unusual homogeneity range of the phase since it yields only $N_{\underline{b}_F}^1/C=1.8$. The compound $PtZn_{1.7}$ shows structures related to the B_2Al type with ordered vacancies in the Zn partial structure. The Pt atoms which formed in Pt_3Zn_2 quadratic nets are arranged here only in chains parallel to \underline{a}_3 , and the Zn too are so arranged; even the vacancies

of the Zn partial structure form chains parallel \underline{a}_3 . Since in $\text{Pt}_7\text{Zn}_{12}$ the number of vacancies per atom place $N_N^P = 4/42 = 0.095$ is greater than that for the Cu_5Zn_8 homeotypes, $N_N^P = 2/54 = 0.037$, a BB2 binding seems improbable when the number of \underline{c} correlation places $N_{p''}^A \approx 12$ like in Cu_5Zn_8 homeotypes. But just this is not the case. The BB2 binding of Table 1 gives $N_{p''}^A = 10.5$, and this corresponds to the place number rule [8] which states that low N_V^A and great atomic weight of the components favour small $N_{p''}^A$. The structure of $\text{Pt}_7\text{Zn}_{12}$ exemplifies that also a certain value of $N_{p''}^A$ may stabilize a structure. The low $N_{p''}^A$ is a necessary condition for the extension of the BB2 binding to low N_V^A values. The structure of $\text{PtZn}_{1.7}$ is a disorder variant of $\text{Pt}_7\text{Zn}_{12}$.

For the phase bundle of the Cu_5Zn_8 homeotypes in the mixture PtZn_M similar rules as in NiZn_M and PdZn_M must be assumed [10].

NiCd_M. The phase $\text{Ni}_{11}\text{Cd}_{12}$ (F 11.12) is not a CuAu isotype but is a vacancy homeotype of Ti_2Ni . The family of homeotypes of Ti_2Ni has been discussed thoroughly [15]. A homeotypism-commensurability is $\underline{a}_{\text{Ti}_2\text{Ni}} = \underline{a}_W(4)$, where W = Wolfram. The structural class F16.8 of Ti_2Ni suggests to consider the H cell of the structure, it is compatible with a CHBH/3 binding which is twinned here as in Cu_5Zn_8 . This binding is a forerunner of the BB2 binding. The number of \underline{c} correlation places per atom was $N_{p''}^A = 12.5$ in Cu_5Zn_8 while it is $N_{p''}^A = 11.1$ in $\text{Ni}_{11}\text{Cd}_{12}$. This is just what is to be expected by the place number rule [8] for smaller N_V^A values. The good commensurability of the \underline{c} correlation is an argument for the vacancies in the $\text{Ni}_{11}\text{Cd}_{12}$ structure. The cubic phases Ni_2Cd_5 and NiCd_5 both belong to the Cu_5Zn_8 family; (also a phase with $|\underline{a}| = 19.545\text{\AA}$ has been reported, SR19.80). A similar duplication of phases has been found for the FeSi type [16] and could be interpreted by a little finite rotation of the binding about a trigonal axis giving two neighboured whole number commensurabilities. For Ni_2Cd_5 and NiCd_5 an analogous interpretation is possible. The determinants of K'' in the hexagonal basal plane are following Tab.1 43 and 48. Not far from the $\sqrt{43}$ correlation comes the $\sqrt{36}$ correlation which occurs for $\text{Ni}_{11}\text{Cd}_{12}$ and NiHg_4 (Tab.1). This fact confirms the assumption of a small finite rotation of the binding between Ni_2Cd_5 and NiCd_5 . No other valence model has discussed this remarkable phenomenon.

PdCd_M. As in PtZn_M the CuAu type phase is stable near the composition Pd_3Cd_2 , which is stabilized by an undistorted b_F correlation. As in PdZn_M [17] metastable phases seem to exist. For the homeotypes of Cu_5Zn_8 see [10].

PtCd_M. The phases are isodesmic or homeodesmic to phases discussed earlier.

NiHg_M. In NiHg_4 (B1.4) a BB2 binding is simply commensurable with $N_{p''}^A = 12.8$. This fairly great number explains why NiHg_4 is stable down to $\text{Ni}_{25}\text{Hg}_{75}$ where $N_{p''}^A = 12$.

The composition NiHg is no more possible in this binding since $N_{Pn}^A=8$ would be too small. In NiZn.h is found $N_{Pn}^A=12.4$ which is greater than the value 12 of NiHg₃, this corresponds to the place number rule [8] that a heavy atom decreases N_{Pn}^A . The essential feature is that in a cell comparable to Cu₅Zn₈ the place number per cell of the NiHg₄ structure is smaller.

PdHg_M. The phase Pd₂Hg₅(Mn₂Hg₅, drawing [7] p.289) has a BB2 binding with $N_{Pn}^A=11.4$. The binding is to be assumed as twinned since in the untwinned state it is only well adapted to half of the Hg atoms.

PtHg_M. PtHg(CuAu) has the pre-BB2 binding of NiZn.r and PtHg₄ has the BB2 binding; for PtHg₂ a remarkable commensurability of the BB2 binding must be assumed (Table 1). It gives $N_{Pn}^A=13.3$, which hints that some more Pt are in the cell. Also $N_{Pr}^C=5$ is somewhat great for $N_V^C=4$.

Mixtures $B^1B^2_M$

CuZn_M. In the marginal phase CuZn_Q (Q=0..0.6), near Cu₃Zn a shear homeotype of Cu₃Au (Cu₃Au.S structure) is not confirmed but instead a maximum of the internal friction [18], and other effects [19] have been found, indicating that some transformation is to be expected at lower temperatures. It may be mentioned here that the interpretation of the shear homeotypes of Cu₃Au gave the first proof that the coherency radius of the b correlation in these alloys is about 50Å [7]. The interpretation of shear homeotypes of Cu₃Au by the two-correlations model [7,20] explains more facts than the band model interpretation [21], and it is not weakened by the pseudopotential-arguments against the band model explanations [6].

Since the model [7] for the Cu₃Au.S structures implies a tetragonal contraction of the b correlation it is natural that in CuZn the BB2 binding is found, the commensurability of which to the crystal cell was first analysed for AuCd.r [22]. As has been mentioned the binding causes the Hume-Rothery rule, the Bradley partial occupancy of the component with lower valence electron contribution [8], the well known homeotypism $a_{Cu_5Zn_8}=a_{CuZn}(3)$, and structures as Cu₂Zn₃ of lower symmetry [10]. At higher temperatures a hexagonal structure CuZn₃.h with non-occupancy $N_N^P=0.1$ (for Cu₅Zn₈ $N_N^P=0.037$) has been found. A higher non-occupancy is to be expected from the interpretation of the Bradley phenomenon, however, it must be kept in mind that the number of vacancies per sub-structure position is also dependent on the commensurability of the binding to the structure. It seems that the BB2 binding is no more present in CuZn₃.h (Tab.2).

The binding in CuZn₄ must be related to the binding in Zn. Although for Mg a CC2 binding is probable ($a_{Mg}=b_{CH}(1;4/3)=c_{CH}K'(2)$) [23] it is not acceptable

TABLE 2: Binding in phases of $B^1B_M^2$ mixtures

CuZn.h(W,SR1.533)2.997A=aH=H7.33;5.18A=bBH(2;7/3)=cBHK'(2)
 CuZn.r(CsCl,SR1.76)2.951A=idm CuZn.h
 Cu2Zn3(,SR2.694)=hdm Cu5Zn8
 Cu5Zn8(B10.16,SR1.499)8.87A=idm CuZn.h
 CuZn3.h(H(0.7).2,SR37.73)H4.275;2.590A=bH(2;1.2)=cUH(2,2,0;-2,4,0;1.2)
 CuZn-4(Mg,SR1.533)H2.738;4.294A=bUH($\sqrt{4/3}$);2.6/2)=cÜHK'(2)
 Ag-2Zn.r(H6.3,SR15.120)H7.636;2.820A=bBH(2;3.6/3)=cBHK'(2)
 AgZn.h(W,SR1.76)3.163A=aH=H4.47;5.48A=idm AuCd.r
 Ag5Zn8(Cu5Zn8,SR1.499)9.341A=idm Cu5Zn8
 AgZn-4(Mg,SR1.552)H2.826;4.485A=idm CuZn-4
 Au4Zn(Cu3Au,SS,SR21.110)4.026;6x4.034;5x4.062A=hdm Au3Zn.h1
 Au3Zn.h1(ZrA13,SR19.159)4.003;4x4.096A=bF(1;5)=cB($\sqrt{8}$;11.5)
 Au7Zn23.r(U24.8,SR23.155)5.586;33.41A=hdm Au74Zn26
 Au74Zn26.r(Q12.4,SR22.107)5.585;5.594;16.649A=bFU(2;5)=cB(4;12)
 Au5Zn3(P40.24,SR22.107)11.022;5.511;33.616A=bB(4;2;11)=cB(8;4;24)
 AuZn(CsCl,SR1.76)3.13=idm AuCd.r
 Au4Zn5
 Au32Zn68(Cu5Zn8.SR1.560)9.241A=idm Cu5Zn8
 AuZn3(C8.24,SR15.81)7.91A=bB(3)=cFU(6;9/2)
 Au18Zn82
 AuZn8.h(Mg,SR1.560)H2.82;4.38A=idm CuZn4
 Cu2Cd(Ni2Mg,SR27.106)H5.012;16.21A=bFH(2;8/3)=cÜH(4;18/2)
 Cu4Cd3(F160.121,SR32.36)25.871A=bHT(11;-13.3)=cHTK'(2)
 Cu5Cd8(Cu5Zn8,SR33.72)9.589A=idm Cu5Zn8
 Cu3Cd10(H6.20,JLCM1980)H8.12;8.75A=bHK''/2=cH($\sqrt{49}$;7.6)
 AgCd.h2(W,SR1.556)3.32A,aH=H8.12;5.74A=idm CuZn.h
 AgCd.h1(Mg,SR1.556)H2.99;4.82A=bFH(2/ $\sqrt{3}$;2.3/3)=cFHK'(2)
 AgCd.r(CsCl,SR28.42)3.33A=idm CuZn.r
 AgCd.l(Au1.05Cd0.95,SR21.63)3.116;4.890;4.778A=idm Au1.05Cd0.95
 Ag5Cd8.h(Cu5Zn8,SR1.556)9.98A=idm Cu5Zn8
 Ag5Cd8.r
 AgCd3(Mg,SR1.556)H3.07;4.82A=idm CuZn4
 Au3Cd(ZrA13,SR19.161,3032)4.117;16.524A=idm Au3Zn.h1
 Au2Cd.h(Mg,SR8.41)H2.92;4.82A
 Au2Cd.r(,JPCS31.1970.77,JPSJ22.1967.1509,27.1969.80)
 AuCd.h(CsCl,SR2.702)3.327A=idm CuZn
 Au1.1Cd0.9(LiSn,SR45.46)7.17;3.10;-1.98,0,4.90A=bHK''/2=cH(2,0,4;7,0,0;0,1.25,0)
 Au1.05Cd0.95(O2.2,SR2.11)3.15;4.86;4.76A=bHK''/2=cH(1.5,4,0;3,0,0;4)
 AuCd.r(H9.9,SR43.38)H8.109;5.80A=bBH(2;7/3)=cBHK'(2)
 Au5Cd8.h3(-Cu5Zn8,)10.03A=idm Cu5Zn8
 Au5Cd8.h2(-Cu5Zn8,)10.00A=idm Cu5Zn8
 Au5Cd8.h1
 Au3Cd5(W5Si3,SR45.46)10.728;5.352A=bHT($\sqrt{20}$;2.6/2)=cHTK'(2)
 AuCd3(Cu3P.r,SR43.39)H8.147;8.511A=bH($\sqrt{12}$;3.6)=cUH(6;7.2)
 AuCd-5(,JLCM51.1977.225)
 Cu7Hg6(-Cu5Zn8,SR34.77)a=9.402A alpha=90.425 Grd,hdm Cu5Zn8
 Ag5Hg4(Mg,SR26.248)H2.99;4.84A=idm AgCd.h1
 Ag3Hg4(Cu5Zn8,SR3.611)10.033A=idm Cu5Zn8
 Au4Hg(H ,JLCM13.1967.1)H8.74;9.58A superstructure of Au3Hg
 Au3Hg(Mg,SR21.125)H2.91;4.81A=bFH($\sqrt{1.15}$;2.2)=cFHK'(2)
 Au2Hg(H12.10,SR35.66)H6.994;10.148A=bUH(2,1,0;-1,3,0;4.5/2)=cÜHK'(2)

TABLE 3: Bindings in the phases of $B^2B_M^2$ mixtures

ZnCdM nic
 Zn8Hg3(Mg,SR11.165)H2.713;5.480A=bÜH($\sqrt{4/3}$);3.3/2)=cÜHK'(2)
 Zn3Hg2
 CdHg(CuAu,SR18.181)3.92;2.88A=bB($\sqrt{2}$;1.04)=cF(2;1.5)
 Cd2Hg.1(MoS12,AM14.1966.285)3.913;8.676A=idm CdHg
 CdHg2.1(MoS12,AM14.1966.285)3.965;8.607A=idm CdHg

for Zn since in the B^2 elements an occupation of the \underline{c} correlation of $N_C^{P''} = 0.8$ is probable while in Mg $N_C^{P''} = 0.5$. In order to find the binding of $CuZn_4$ it is helpful to consider a superstructure of the Mg type: $Au_5Sn.r$ (H15.3, [24]) has the cell $a = 5.09; 14.34 \text{ \AA}$ and yields the binding $\underline{a} = \underline{b}_{FH}(2; 7/3) = \underline{c}_{FH}(4; 14/3)$ which is a FF2 binding and confirms the important rule that many brass-like phases have a two-factorial isotypic binding. All Mg homeotypes with $N_V^A = 1.5$ have probably the FF2 binding. However, $CuZn_4$ has $N_V^A = 1.8$ and following Löhbergs rule [25, 26, 27] with increasing N_V^A the axial ratio $|\underline{a}_3|/|\underline{a}_1|$ decreases. This may be interpreted as follows. For $N_V^A = 1.5$ the FF2 binding of $Au_5Sn.r$ holds. With increasing N_V^A the commensurability in the basal plane remains but the type of the correlation is compressed gradually from the FH type to the $\bar{U}H$ type mentioned before. At the valence electron rich border of $CuZn_4$ the $\bar{U}H$ type is reached so that no more compression of the \underline{b} correlation is possible. Therefore a strong increase of the axial ratio begins [27c] until the value of Zn $|\underline{a}_3|/|\underline{a}_1| = 1.856$ is reached. Since the \bar{U} correlation is not an isometric correlation, (the shortest vectors span the whole lattice), the spin correlation is of influence and it is now clear that Zn isotypes have been found only for Zn homologues as only for these atoms the good spin ordering is possible. Also the isotypism of Zn to the H2 type becomes now clear: The atom in 0,0,0 and the atom in 0,0,1 get induced the same electro-dipole component parallel \underline{a}_3 because of $\underline{a} = \underline{b}_{\bar{U}H}(\sqrt{4/3}; 3/2)$, therefore they attract one another. It appears satisfactory that also in $CuZn_4$ a two-factorial isotypic binding may be assumed. It may therefore be stated that brass like alloys are defined by the preponderance of two-factorial isotypic bindings.

AgZn₄. The structure of $Ag_2Zn.r$ could have served to find the BB2 binding before $AuCd.r$ [22] was analysed, but the \underline{a}_3 axis did not give such a conspicuous commensurability as $\underline{a}_3(AuCd.r)$. The fact that $a_{Ag_2Zn.r} = a_{AuCd.r}(1; 0.5)$, must be caused by a stronger translational twinning of the binding which introduces a higher crystal symmetry. The remaining phases are isodesmic to phases in $CuZn_4$.

AuZn₄. The structure of Au_4Zn (drawing [7] p.97) is a double shear homeotype of Cu_3Au (briefly $Cu_3Au.SS$) analogous to $Pd_{30}Cu_{70}(Cu_3Au.SS)$. The normal shear system [7 p.98] with shear density $N_S^U = 0.210 = 1/5$ ($U =$ substructure cell) extrapolates well into the general shear density in function of mole fraction relation [7 p.94, 98], while the abnormal shear system with $N_S^U = 0.171$ serves to produce the off stoichiometry and incidentally reduces the energy of the array of the electric dipoles generated by the valence electron correlation. A simple shear structure is found in $Au_3Zn.h_1$ while $Au_{74}Zn_{26}.r$ is formed by a displacive transformation caused by the fact that the Zn core is essentially smaller than

the Au core. The correlation $\underline{a}=\underline{c}_B(4;12)$ shows that the commensurability \underline{K}'' is improved by the stress caused by the \underline{b} correlation. While for Au_3Zn_r the commensurability element ratio $K'_{33}/K''_{33}=5/12$, for Au_5Zn_3 is found $K'_{33}/K''_{33}=11/24$, just as the last step before the BB2 binding of AuZn. The phase $Au_{32}Zn_{68}$ is similar to Cu_5Zn_8 and belongs therefore also to the BB2 binding.

The structure of $AuZn_3.r$ (drawing [7] p.136) may be compared with a Cu structure: $\underline{a}=\underline{a}_{Cu}(2)$, no vacancies are contained in the structure so that the BB2 binding is no more probable. A post BB2 binding like the BFU1 binding must be considered. As in $NiZn_M$ phases rich in Zn show a \underline{c}_F correlation. \underline{CuCd}_M . The phase $Cu_2Cd(MgNi_2)$ is only homeotypic to $MgCu_2$ although it is homologous. From this must be concluded that Cu_2Mg and Cu_2Cd are only homeodesmic. A FHÜH2 binding seems to be realized (Tab.2); it is caused by $N_C^A=10.0$ as opposed to $N_C^A=9.3$ for Cu_2Mg . The observation $CuZnCd(Cu_2Mg)$ [28] indicates that the great volume of Cd favours the FHÜH2 binding, while $CuZnCd$ accepts the FF2 binding.

In Cu_4Cd_3 an HH2 binding seems to be the cause of stability, but the great size of the cell permits no certain analysis. This binding should be assumed twinned similarly as the BB2 binding in Cu_5Zn_8 . For Cu_3Cd_{10} a HH2 binding may be assumed.

\underline{AgCd}_M . In the marginal phase $AgCd_Q$ ($Q=0..0.5$) anomalies of the partial molar entropy of Cd in dependence of the mole fraction N_{Cd}^C seem to lie at whole number values of the shear length [7 p.101] of a shear system which has not yet reached its critical temperature. However superstructures have been postulated by other authors [29].

The compound AgCd has two phases of the W family, one phase of the Mg type and a low temperature phase of the $Au_{1.05}Cd_{0.95}$ type. The phases of the W family together with the Ag_5Cd_8 phases have the BB2 binding while $AgCd_3$ and Cd have the ÜÜ2 binding which is related to the FF2 binding of $AgCd.h_1$. \underline{AuCd}_M . The phase $Au_3Cd.r(ZrAl_3)$ is a shear homeotype of Cu_3Au and further phases have been described which are collected in Tab.2 under the name $Au_2Cd.r$ [30,31]. The phase $AuCd.h$ (isodesmic to CuZn) transforms depending on composition into three different superstructures permitting inference of the binding. $AuCd.r$ gives the BB2 binding already mentioned; the curious value $K'_{33}=7/3$ suggests that the binding is translatorically twinned to some degree in the \underline{a}_3 direction, so that no structural superperiod is found which makes K''_{33} a whole number. The fact that the \underline{b} correlation gives $N_P^C=28$ places per cell while the conventional offer of valence electrons is only $N_V^C=27$ confirms the anomalous valence electron contribution $N_V^{Au}=1.1$, [7].

Surprisingly for $Au_{1.05}Cd_{0.95}$ a HH2 binding is found; it may be conjectured that lower electrons find a good possibility of correlation into this binding. Satisfactorily $Au_{1.1}Cd_{0.9}$ (M3.3) too allows the HH2 binding with $N_p^C/C=8.8$ ($N_V^C=8.9$).

Conspicuously near Au_2Cd_3 at high temperatures a BB2 binding is found and lower temperatures a HH2 binding, this supports the assumption of participation of lower electrons in the binding.

In the phase $AuCd_3$ a two-factorial binding is no more possible; the proposal of Tab.2 shows that starting from HH2 the $c^{-1}b$ commensurability is made smaller in the hexagonal basal plane, but since the discrete step is too great, the c correlation is compressed to a UH correlation.

CuHg_M. It is satisfactory that the stable BB2 binding is realized in a Cu_5Zn_8 type phase (instead of in a CsCl type phase) since this type is better adapted to the binding than the CsCl type, because of the vacancies, which allow displacements of the atoms giving a better fit to the binding. If the components had the electron contribution Cu^1, Hg^2 then the compound should be expected for Cu_5Hg_8 following Hume-Rothery's rule $N_V^A=1.62$. However similarly as to Au [7] also to Hg a greater valence electron contribution should be attributed. For $Hg^{2.3}$ the composition would be $Cu_{53}Hg_{47}$, and from the experiment $Cu_7Hg_6=Cu_{54}Hg_{46}$ is reported.- The translation group is rhombohedral with $\alpha > 90^\circ$, this is caused by the binding: For $AuCd.r$ is found $|a_3|/|a_1|=0.716$ while the ideal ratio for cubic substructure is 0.707, and the ratio for ideal binding 0.714. Since $0.716 > 0.714 > 0.707$ it must be concluded that the binding is favoured by an additional strain of the cell which is made possible by the chain shear of the structure. Since for Cu_7Hg_6 $\alpha > 90^\circ$ it must be assumed that the correlation is twinned not in 4 directions but in 3 only.

AgHg_M. The electron contributions $Ag^1, Hg^{2.1}$ explain the shift of the Cu_5Zn_8 type of the phase to Ag_3Hg_4 .

AuHg_M. For Au_4Hg the commensurability $\underline{a}=a_{Au3Hg}(3;2)$ is reported [32]. In Au_3Hg a FF2 binding might be present. This binding has been discussed for $AuIn_M$ alloys [36]. The composition of Au_2Hg or Au_6Hg_5 is not yet settled, the structure permits a UU2 binding which is in favour of the composition Au_2Hg presupposing the electron contributions $Au^{1.1}, Hg^{2.1}$. Compounds $Au_5Hg_8, Au_2Hg_5, AuHg_4$ do not exist following [32], but it remains open whether these authors annealed their samples long enough.

Mixtures $B^2B_M^2$

ZnCd_M. No intermediary phases have been found in this mixture as no expansion energy of the valence electrons is available; a continuous series of mixed crystals does not occur because of the great difference of the atomic radii.

ZnHg_M. The axial ratio of the marginal phase ZnHg_Q (Q=0,...) increases with increasing Hg content (SR11.165). This is compatible with the binding under the assumption that the valence electron contribution of Hg $N_V^{Hg} > 2$. In the phase Zn₈Hg₃(Mg) the axial ratio $|a_3|/|a_1| = 2.019$ is found, what means that K_{33}^n has jumped one unit. The valence electron contribution must be assumed as $N_V^{Hg} = 2.5$ in this mixture.

CdHg_M. The phase CdHg(CuAu) has a broad homogeneity range at room temperature with decreasing axial ratio for increasing mole fraction N_{Hg} [33,34,35]. It is found, that the two correlations stress each other so that the change of the axial ratio is an expression for the change of elastic coefficients of the correlations which are as yet unknown.

Concluding remarks

The present analysis shows that the correlation energy must be a marked part of the energy of formation, therefore the correlation type and its commensurability to a may be used for the classification of phases. The spatial correlations of electrons are of influence on the valence problem similarly as atomic radii, discussed in the past, are of influence. Therefore as the system of atomic radii has been found by the analysis of the empirical data, the laws for the spatial correlations may be found also by the analysis of the empirical data. The model of two correlations in a crystal structure is also of mathematical interest: The influence of two electron correlations on the lattice energy has not yet been investigated. Also an influence on the structure type is effective as has been shown for the Cu₃Au shear homeotypes. The present analysis of the spatial correlation of the electrons gives new insight into the constitution of the $T^{10}B_M^2$, $B^1B_M^2$ and $B^2B_M^2$ alloys. The frequency of two-factorial isotypic binding suggests to identify this kind of binding with the brass-like character of an alloy. The customary planely empirical attitude towards the formation of intermediary phases in alloys may be replaced now by the expectation of a certain binding and by the search for additional parameters determining the stabilisation of a certain structure.

This analysis need not be taken on trust: the bindings may be checked by elementary calculations from the data given in the tables; the $d(N_2)$ curves

may be calculated and it may be verified that they satisfy the rules [8]; even better binding proposals may be found which possibly have been overlooked in the present first attempt. Also the conclusions which are drawn from the binding with respect to stability are not speculations since it is evident for instance that a factorial binding is of low energy.

Also "predictions" are easily possible, if for instance a new ternary mixture shall be studied then on the basis of the present analysis expectations as to the extension of a binary phase or stabilisation of a ternary phase may be derived from the rules the bindings are subjected to. Another facility similar to prediction is that the present analysis directs the attention to important new experimental problems. The fact that the bindings cannot be measured as yet is in common with many models, which remained supported only by indirect evidence for an extended period.

A surprise of the present analysis is, that such a simple model gives the possibility to understand many complicated structural phenomena for which no idea of explanation was available before. The simplicity of the model reflects a fundamental simplicity of alloy formation. However, although new understanding is opened, also the number of new problems with regard to stability posed by the model should not be overlooked. These problems will certainly be attacked at some time, but analysing further mixture classes with respect to binding should first fasten the ground for this future investigation.

Appendix: Review of notation and analysis method

Structure types are indicated by prototype. Prototypes themselves are indicated by Bravais group and numbers (seperated by a point) of component atoms in the primitive cell. The symbols for the Bravais groups are [7]:

C,B,F =cubic primitive, -body centered, -face centered,
I,U =tetragonal primitive, -body centered,
H,R =hexagonal primitive, -rhombohedrally centered,
O,P,Q,S =orthorhombic primitive, -body-, -one face-, -all faces centered
M,N,Z =monoclinic primitive, -face centered, triclinic.

The two-character symbols [9] cannot be taken as they must be used in the binding description here.

Citation is given by SRI.1=Structure Report A Vol.1, page 1, or LB=Landolt Börnstein. Inafew cases journals must be cited; AM=Acta Met., ACA=Acta Cryst.A, M=Metall, JPCS=J.Phys.Chem.Sol., JPSJ=J.Phys.Soc.Jap., JLCM=J.Less-Com.Met., ZK=Z.Krist..

Correlation kinds: a, b, c correlation=correlation of atoms, -valence electrons, peripheral core electrons. Cell matrices for a, b, c correlation are a, b, c. Isometric correlation types: C, B, F, U, H =cubic primitive, -body-, -face centered, tetragonal body centered with $|a_3|/|a_1|=0.816$, hexanormal. Aspect affixes: H,U,T=hexagonal, tetragonal body centered, tetragonal primitive. Non isometric correlation \bar{U} : a H layer is stacked with distance $d_H/\sqrt{2}$.

Matrix notation: $\underline{a}_iL=(a_{11},a_{12},a_{13};a_{21},a_{22},a_{23};a_{31},a_{32},a_{33})$ where i (mostly omitted) refers to an orthonormal coordinate system and L numbers the vectors and incidentally designates the phase or type. An H before a numerical matrix or behind the last index of a symbolic matrix indicates that i refers to hexanormal coordinates, a $M\beta^\circ$ refers to a monoclinic normal coordinate system with angle β .

Abbreviations: $(a_{11},0,0;a_{21},a_{22},a_{23};a_{31},a_{32},a_{33})=(a_{11};a_{21},a_{22},a_{23};a_{31},a_{32},a_{33})$, $(a_{11},0,0;0,a_{22},0;0,0,a_{33})=(a_{11};a_{23};a_{33})$, $(a_{11};a_{11};a_{33})=(a_{11};a_{33})$, $(a_{11};a_{11})=(a_{11})$. For brevity a matrix $\underline{b}=(2,1,0;-1,2,0;0,0,1)$ may be written as $(\sqrt{5};\sqrt{5};1)$ or even shorter $(\sqrt{5};1)$. 5 is the determinant of \underline{b} and a rotation matrix is omitted, further values of whole numbered determinants are collected in [8].

Commensurabilities: $\underline{b}^{-1}\underline{a}=K'$, $\underline{c}^{-1}\underline{a}=K''$. An equation $\underline{a}=\underline{b}K'=\underline{c}K''$ is named a binding. A quotient $\underline{a}_L^{-1}\underline{a}_{L'}=K$ is a homeotypic commensurability between the lattices L and L'.

Derived properties: $N_A/C, N_V/C, N_C/C, N_P/C$ =number of atoms, -valence-, -core electrons, a places, per a cell. $N_V/A, N_P/A, N_P''/A$ =number of valence electrons, -b-, -c- places per atom. d_b, d_c =smallest distances in b-, c- correlation. In Tables 1, 2, 3 the phase name, structure type, reference, cell and binding are given for mixture classes. An A behind a numerical matrix means Ångström. The symbol ~ stands for approximately. Blanks indicate missing information. The symbol M at the end of a chemical formula indicates a mixture. idm=isodesmic, hdm=homeodesmic, nic= no intermediary compound.

How to find a binding: Draw as abscissa the mole fraction $N_2=0, \dots, 1$ of the second component over 10cm. Draw as ordinate the average electron distance beginning with $d=1\text{Å}$ so that $\Delta d=0.2\text{Å}$ corresponds to 1cm. Plot for $N_2=0$ the values of $d_b(0), d_c(0)$ of the first component, plot for $N_2=1$ the values $d_b(1), d_c(1)$ of the second component. The marginal d values, produced by an analysis of structures of chemical elements [23] are cited also in [7,8]. For an empirical compound assume d_{N_2} values interpolated corresponding to earlier curves. Insert these values into the possible [7,8] correlation types to get possible b and c cells. Check by slide rule different commensurabilities $\underline{b}^{-1}\underline{a}, \underline{c}^{-1}\underline{a}$ [8]; for the different commensurability cases check the fulfillment of the rules [7,8]. The best fit to the rules affords the probable binding.

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