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On the Bindings in the Mixture $PtSn_M$

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As an example from a more extensive investigation, the binding analysis of the mixture $PtSn_M$ (M = undetermined mole number) is described. A phase becomes stable when a lattice-like correlation of the valence electrons (with cell b) and a lattice-like correlation of the peripheral core electrons of Pt (cell e) are in an energetically favourable commensurability to the crystal cell a and to one another. Surprisingly Pt_3Sn (of the Cu_3Au type) is not isodesmic to Cu, as with the Pt^{10} electrons the Sn^{10} electrons are not in correlation; the binding may be of the FF2 type which is also met in brass-like phases. For PtSn (NiAs type) a binding homeotypic to FF2 is found in which a strongly compressed e_{CH} correlation exhibits good commensurability. In Pt_2Sn_3 (homeotype of NiAs) the e_{CH} correlation is relaxed. In $PtSn_2$(CaF_2 type) the FU2 binding exists and in $PtSN_4$ (homeotype of CaF_2) the F'B2 binding, i. e. a FB2 binding with a noticeable amount of Hund insertion in the b correlation. It becomes apparent that the analysis of the binding is a new and effective instrument for developing structure systematics. The bindings classify Pt_3Sn to the brass-like phases, PtSn and Pt_2Sn_3 to the NiAs-like phases, and $PtSn_2$ and $PtSn_4$ to the Si-like phases. The knowledge of the bindings provides arguments which explain energetically the found crystal structures and afford new viewpoints for isotypism and heterotypism of homologic or quasi-homologic phases. As an example the phases of the mixture $PtPb_M$ are briefly considered.

INTRODUCTION

The phase diagram of the mixture $PtSn_M$ is reported (Doerinckel[1], Podkopayev[2]) to contain the intermediate crystalline phases Pt_3Sn, PtSn, Pt_2Sn_3, $PtSn_2$, and $PtSn_4$. The stability of these phases is not explained by valence rules of inorganic chemistry (see ref. 3.) since from the chemical formulae valence numbers of the components do not become obvious. The crystal structures of the intermediate phases will be considered below, they are simple, but appear not to indicate valence rules either. Since the inorganic valence rules for salt like and covalent phases are simple and distinct, it should be expected that valence rules for metallic phases will also be simple and distinct. In fact a phenomenological valence model for metallic phases, the plural-correlations-model[4,5,6] has been advanced, the concepts of which are founded on the quantum mechanical density matrix formalism (see ref. 7.) Therefore, the model is not invalidated by omitting a convergence proof, which would be inevitable for a molecular orbital model, as between the orbitals and the final density matrix lies a configuration interaction calculation which is a complex series development.

The plural-correlations model provides a procedure[8] to derive for an intermediate phase a bonding type, named binding; and a binding is all that can be expected from a valence theory; it is a hypothesis which is confirmed by the fulfilment of various empirical rules like electron distance rules, electron concentration rules, occupation rules[6] etc. By this procedure a binding analysis has been made[9] for many $A^1 B_M{}^4$, $A^2 B_M{}^4, \ldots, A^{14} B_M{}^4$ phases where A^n, B^n are homologic classes of the periodic system of chemical elements, and $A^{10+n} = B^n$. The present exposition shall make plain the result for one example, the $PtSn_M$ mixture. This mixture is quite simple so that it should be easy to find valence rules which rationalize the stability of the itermediate phases. Most chemists consider necessary a valence theory for alloy phases they appreciate the help which a valence model gives to the newcomer who wishes to learn and to memorize all these metallic phases; also they estimate the value of a valence model for finding interesting experimental problems. Some chemists find difficulty in the concept of a spatial correlation of electrons; they should realize that the concept is a moderate but expedient generalisation of the idea of a distribution of covalent bonds in a crystal used in any description of crystal chemistry. So far no argument against the plural-correlations model has been published. Its acceptability can only be doubted by indicating prohibitive mistakes in the fundamental assumptions.

ANALYSIS

The general features of the model are described in[5,8,10,6]. Without the knowledge of some of these expositions misinterpretations of the following become possible. It has been shown[8] how a lattice like correlation can exist despite a strong influence of the crystal structure. The correlation energy defined as difference between true energy and Hartree-Fock energy should not be confused with the energetic influence of the spatial correlation, as the Hartree-Fock wave functions contain already much spatial correlation. A spatial correlation of valence electrons is a probability density in a six dimensional space and therefore difficult to imagine. However, there is an averaging procedure[6] which yields a probability density in three dimensional space, the averaged correlation $D_x{}^{\mathrm{av}}$, which is quite different from eletcron density and conserves features bearing on energy of the spatial correlation while electron density looses them. It may be proposed that $D_x{}^{\mathrm{av}}$ ($x =$ spatial coordinates) is quasi periodic, similar as the radial distribution function of atoms in a liquid. It contains therefore a cell matrix b and one argument for a favourably low energy of a crystal (with cell a) is, that the commensurability $b^{-1} a = K'$ contains as many integer elements as possible (see ref. 5). The peripheral core electrons Pt5sp and Sn4d also form a correlation containing a cell c and the commensurabilities $c^{-1} a = K'''$ and $c^{-1} b$ should be favourable. It has been found of advantage to assume that the peripheral d electrons of Pt form a spatial correlation of their own; as the character d is already used for the distance, the correlation may be named and e correlation, $e^{-1} a = K''$. A bonding type is described by b, e, c,

K', K'', K'''. The matrices b, e, c may be classified into Bravais types following A. J. C. Wilson's symbols F, B, C, T, U, H, R, O, P, Q, S, M, N, Z (see e. g. 11 p. 17, and ref. 5, 8) used as an index.

The handling of the commensurability matrices is an essential part of the binding analysis, therefore some helpful conventions should be used. Since K', K'' and K''' may be decomposed into a symmetric matrix and a rotation matrix, it is a simplification to omit the rotation matrix (i. e. not to note it) and to use the eigenvalues for the description of the remaining symmetric matrix. The occurrence of a root sign in the numerical notation of a K matrix indicates that a rotation matrix different from unity has been left out. Furthermore, repeated eigenvalues are left out following an old tradition of crystallographers in the notation of an elementary cell.

The starting point of a binding analysis are the bindings of the component elements. For platinum the binding may be written[10].

$$a\,[\mathrm{Pt}] = (3.924)\ \text{Å} = b_C\,(\sqrt{2};\ 1.4) = e_B\,(\sqrt{8};\ 2.8) = c_C\,(4).$$

$a\,[\mathrm{Pt}]$ is the cell of Pt, b_C is the cell of the valence electron correlation and the index C notes its cubic primitive Bravais type. In brackets behind b_C follows the numerical value of the commensurability matrix K' in abbreviated notation. The root sign indicates that the full matrix is not completely diagonal but composed of submatrices. The submatrix 1.4 refers to b_3, it is to be understood $a_3 = b_3 \times 1.4$. The matrix element $\sqrt{2}$ contains a $\sqrt{\ }$ sign, indicating that a rotation (by 45° about a_3) has been omitted. The value $\sqrt{2}$ is then the quotient $|a_1|/|b_1|$ of two moduli of edge vectors. It is easily seen that the full submatrix is (1, —1; 1, 1) and that its determinant equals 2; the matrix is written linewise the lines separated by semicolon. The matrix $(\sqrt{2};\ 1.4)$ is not completely integer, nature appears to tolerate this. The number of b electrons per a cell is compatible with magnetic data of Ni (see Mott and Jones[12]). An analogous discussion is valid for the remaining equations. It becomes apparent that b_C and e_B have the same directions of axes. The geometrical figure formed by b_C and e_B is quite simple: in the b_C cell of the cubic primitive type there are 8 e_B cells of the cubic body centered type and they exhaust the volume of b_C. The equation $b_C = e_B\ (2;\ 2;\ 2)$ may be announced by CB2 where the 2 is the first eigenvalue of $e^{-1}b$ and this symbol CB2 may for brevity be named the binding of Pt although the commensurabilities $b^{-1}a$ and $e^{-1}a$ have not been mentioned, but are easily to be reconstructed from the electron numbers and occupation rules[5]. Since $e^{-1}b$ is a factor matrix the binding may be named a factorial binding, it is energetically favourable as for one b electron being in a favourable position relative to e, all electrons are in a favourable position. Clearly the binding might cause a tetragonal structure, however, when a single crystal is a three-crystal with respect to electron correlation, i. e. when the correlation is multiply »twinned«, then a cubic a crystal may result. The phenomenon of correlation twinning shows that the assumption of valence bond theory, the wave functions around one atom should be a representation of the corresponding point symmetry, is too narrow. For the spatial correlation of the peripheral d electrons (e correlation) in Pt earlier (ref. 11, p. 83) $a = e_C\ (4)$ was assumed, but this does not fit metrically to other propasals whence $a = e_B(\sqrt{8};\ 2.8)$ has been assumed which fits better. This choice is compatible with the commensurability rule[5] which suggests for good commensurability a high melting temperature. In the earlier e_C-assumption Cu should have a higher melting temperature than Ni by the commensurability rule while in the present e_B-assumption Ni has a higher melting temperature as it is observed indeed. The c correlation energetically below e may be $a = c_C(4)$, it is of minor influence.

The second binding to be known is that of Sn. The binding of the low temperature phase is[10]:

$$a\,[\text{Sn}, 1] = (6.47\ \text{Å}) = b_F\,(2) = c_B\,(4).$$

It is a FB2 binding and responsible for the large family of Grimm-Sommerfeld phases. The correlation of the Sn4d^{10} electrons is here named c as these electrons are shielded by the Sn5s^{2}p^2 electrons and therefore do not extend into the space like the Pt 5d^{10} electrons. The compatibility with the rules[5] is easily verified but the best confirmation of the binding is offered by interpretation of the room temperature phase Sn.r to be given below in the discussion of PtSn$_4$.

The distances d_b, d_e and d_c from the above bindings are now inserted into the $d\,(N_2')$, diagram, Figure 1, (N_2' = mole fraction of the second component, here Sn), which permits to derive d-values for intermediate phases by interpolation. The fulfilment of the distance rule[5] is not the only criterion

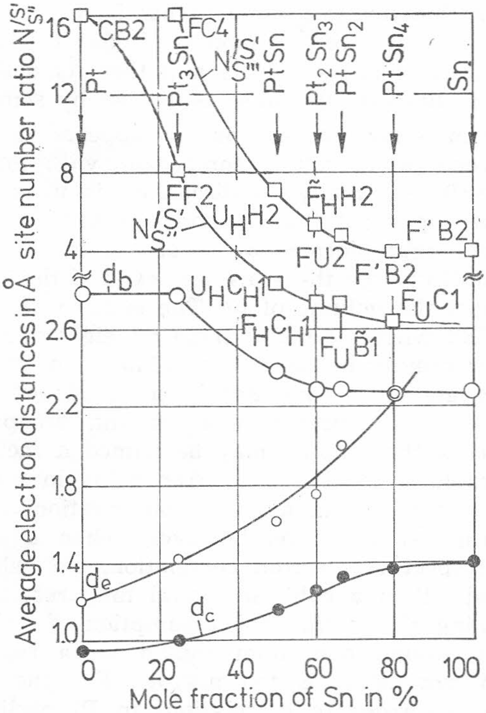

Figure 1. Binding diagram for Pt Sn$_M$ phases

which limits the set of possible binding proposals. Very valuable is the rule of the smoothness of the number of e or c correlation sites per b correlation site, $N_{S''}^{/S'}$ or $N_{S'''}^{/S'}$, as a function of N_2'. This function intuitively depicts what happens during alloy formation: The b correlation spreads over the e and c correlation and yields a stable phase when a favourable commensurability is possible. The $N_{S''}^{/S'}$ or $N_{S'''}^{/S'}$ value of the $CB2C\sqrt{8}$ binding in Pt is 16 for CB2 or 23 for $CC\sqrt{8}$ and of the FB2 binding in Sn.1 it is 4, so that in between these values various bindings are possible see ref. 6.

The first intermediate phase in the mixture $PtSn_M$, the phase Pt_3Sn(Cu_3Au type, Structure Reports 11 p. 177), is a simple replacement-homeotype of the Cu structure. When the b electron contribution of Pt is $N_b^{/Pt} = 0$, then Pt_3Sn might be isodesmic to Cu(F_UB2 binding[10]). But the corresponding electron distance d_e in Pt_3Sn does not fit well to the d_e values of the later phases of $PtSn_M$. The FF2 binding

$$a\,[Pt_3\,Sn\,(Cu_3\,Au,\,SR11.177)] = 3.993)\ \text{Å} = b_F\,(1) = e_F\,(2) = c_C\,(4)$$

has the advantage that e_B of Pt goes over to the homeotypic e_F in Pt_3Sn, that the b contribution of Pt is suppressed by the 4 b electrons of Sn and that the factorial relation $b_F = e_F\,(2)$ is energetically favourable and explains according to the commensurability rule[6] the congruent melting of Pt_3Sn. The suppression of the b-contribution of Pt (Ekmans rule) is probable since in Pd_3In e. g. the magnetic susceptibility as compared to that of Pd falls to zero at room temperature (Harris, Norman, Bryant ref. 13); also the simple binding should forbid any anomaly of the specific heat as a function of temperature, which may be verified. The number of e sites per b site, $N_{S''}^{/S'} = 8.0$, for the FF2 binding fits well to the $N_{S''}^{/S'}$ (N_{Sn}') function. — The closely related BB2 binding for Pt_3Sn[9] does not allow a favourable d_b distance in Figure 1 and appears therefore less probable. An indirect confirmation of the cubic binding of Pt_3Sn are the tetragonal structures of Pd_3In, Pd_3Tl (see ref. 19), and Pd_3Sn (see ref. 9), here the peripheral d electrons of the B component seem to take part in e.

Under the assumption, the BB2 binding were in fact realized in Pt_3Sn, the question should be raised whether Pt_3Sn is paramagnetic or diamagnetic; the diamagnetism would confirm the FF2C4 binding. Another question is related to the decrease of $N_{S''}^{/S'}$ from 16 to 8: why is no intermediate phase formed between Pt and Pt_3Sn? Since the b electrons are sustained by the Sn atoms, an intermediate phase would request a strong ionisation of Sn, i. e. the b electrons should move far away from the Sn core and this is energetically expensive. In the binding formulae the symbols $a\,[\,] =$ are not important and shall not be written in the following formulae.

The second intermediate phase in $PtSn_M$ is PtSn (NiAs), it is no more close packed like Pt and Pt_3Sn and this fact is caused by the increased valence electron concentration (ref. 11 p. 169). The pressure of the b gas on the structure is increased and the structure yields a less closed packe type. How will the binding change when the b electron concentration increases? Since the e electron concentration decreases in the heterotypism Pt_3Sn — PtSn it might be anticipated that the e correlation and the b correlation seak a new type of commensurability which allows a higher b concentration. The decisive arguments are the fulfilment of the electron count, and the smoothness of the $d\,(N_2')$ and $N_{S''}^{S'}\,(N_2')$ curves. The result of the binding analysis is in fact

$$\text{PtSn (NiAs, SR2.720) H4.11; 5.24 Å} = b_{\mathrm{UH}}\,(\sqrt{3};\,2.712) = e_{\mathrm{CH}}\,(\sqrt{3};\,6.7/3) = c_{\mathrm{H}}\,(\sqrt{2};\,4.6)$$

Here U_H (written UH in the equation) is the (pseudo) hexagonal aspect of U, therefore b has weakly changed its type F to U in the heterotypism Pt_3Sn — — PtSn. Furthermore it is seen that the two-factoriality is now for $c^{-1}b$ in the hexagonal basal plane, and that the c correlation has become more close packed by the transition c_C — c_H. The binding is therefore U_HC_HH2 with $N_{S'''}^{/S'} = 7$; and the $c^{-1}b$ commensurability is complicated in a single direction only. Quite striking is the high compliance of the d_c distance to the increase of the b concentration (Figure 1). Here the increased Sn content becomes apparent. The compliance of the Ptd electrons causes the separate e correlation and the compliance of the Snd electrons causes the increase of d_c. An examination of the binding of other NiAs-type phases shows that the isotypes of NiAs are not all isodesmic to one another, i. e. of the same binding, the binding analysis helps to describe the degree of heterodesmism. A further straining of the c correlation in the direction of the unique axis caused by increase of b concentration cannot be made; therefore the b correlation must be compressed in the next phase.

The third intermediate phase Pt_2Sn_3 = (H4.6) is homeotypic to PtSn and to $PtSn_2\,(CaF_2)$, see drawing (ref. 11 p. 341). The binding may be:

$$\text{Pt}_2\,\text{Sn}_3\text{ (H4.6, SR11.177) H4.34; 12.96 Å} = b_{\mathrm{F}}\,(\sqrt{3};\,8/3) = e_{\mathrm{CH}}\,(\sqrt{3};\,13/3) = c_{\mathrm{H}}\,(\sqrt{12};\,10).$$

The commensurability $(c^{-1}b)_{11}$ in the hexagonal basal plane has been conserved but it is strongly compressed in the a_3 direction. The main reason for the stability will be the relaxation of the e correlation.

The $N_{S'''}^{/S'}$ value has decreased from 7 to 5.2 as it is to be expected, and Ekman's rule that $N_b^{/Pt} = 0$ (see ref. 11) is fulfilled. The good commensurability of the new binding at the composition Pt_2Sn_3 causes a phase to become stable there. It is worth mentioning that the FB2 binding of Sn. 1 has a planar commensurability in the $(111)_F$ plane which is closely homeotypic to the $\sqrt{3}$ commensurability: a studded $(111)_B$ layer needs only be smoothed out to achieve the $\sqrt{3}$ type of commensurability.

The fourth intermediate phase is $PtSn_2\,(CaF_2)$. It may be described as a Sn.l structure in which the Sn are somewhat rearranged and 4 Pt are additionally inserted. Therefore it is not surprising that $PtSn_2$ has the b_F correlation of Sn.l. However, it cannot have the c_B correlation of Sn.l because the FB2 binding does not fit into the $N_{S'''}^{/S'}\,(N_2')$ curve. There is an easy possibility open to offer more c sites, by the FU2 binding[6]. The essentially tetragonal binding must be twinned in $PtSn_2$. Ekman's rule is fulfilled once more and a Hund-insertion[5] is not necessary to be assumed by the FU2 binding, therefore the magnetic susceptibility should be conjectured as diamagnetic. There is yet another reason for a FU2 binding. The peripheral d electrons of Pt which fill the e correlation suffer an astonishing increase of d_e and form the correlation $a = e_B\,(\sqrt{8};\ 2.5)$. This correlation supports the c_U correlation as may be seen from the summarizing formula

$$\text{Pt Sn}_2\text{ (Ca F}_2\text{, SR9.120) (6.426) Å} = b_{\mathrm{F}}\,(2) = e_{\mathrm{B}}\,(\sqrt{8};\,2.5) = c_{\mathrm{U}}\,(4;\,5).$$

Once more it may be stated that the tetragonal strain of e_B does not destroy its isometric property[6], and therefore its energetical favour. The striking endurance of the e correlation is repeated in the intermediate phase richest in Sn. This endurance effect is well known in transition metal chemistry as delocalisation of d electrons towards ligands and thereby lowering inter-electronic repulsion.[14] The reason why the crystal field theory could not approach the valence problem of the mixture $PtSn_M$ became apparent above in the analysis of the binding of Pt: The theory is unnecessarily limited by admitting only atomic orbitals which are a representation of the atomic point symmetry. This stipulation is violated in the present interpretations of all phases of $PtSn_M$ except Pt_3Sn.

The fifth and last intermediate compound, the phase $PtSn_4$ (Q 2.8), is homeotypic to $PtSn_2$ with the commensurability $a_{PtSn4} = a_{PtSn2}\,(1; 1; 2)$. The FB2 binding becomes probable here:

$$\mathrm{Pt\,Sn_4}\ (\mathrm{Q2.8,\ SR13.116})\ (6.39;\ 6.42;\ 11.36)\ \text{Å} = b_{\mathrm{F}},\ (2;\ 3.5) = e_{\mathrm{C}}\,(\sqrt{8};\ 5) = c_{\mathrm{B}}\,(4,\ 7).$$

This binding appeared inacceptable earlier[9] as the electron numbers are $N^{/a}{}_{b,c} = 64{,}192$ while $N^{/a}{}_{S', S'''} = 56{,}224$; this was one of the reasons why a defective proposal was chosen earlier. In fact, one important point of view had been overlooked, the inclination of Sn to form Hund-insertion which becomes apparent in the Sn room temperature phase[10]; Sn.r (U2, SR1.56) (5.83; 3.18) $\text{Å} = b_{F'}\,(\sqrt{3.25}; 1) = c_B\,(\sqrt{13}; 2)$; the prime on F indicates Hund-insertion of 3/4 b electrons per atom as is easily verified. A physical consequence of the Hund-insertion is the well-known paramagnetism of Sn.r, and the fact that Ge.p a high-pressure phase of Ge has the Sn.r structure (SR28.46). If it is assumed that also in $PtSn_4$ Hund-insertion occurs, then the last binding proposal becomes acceptable. The consequence, that $PtSn_4$ is paramagnetic, is still to be verified. The fact that $(c^{-1}a)_{33} = 7$, must be considered as cause for the Q translation group and the doubling of $a_3\,(PtSn_2)$ in $PtSn_4$ (following the homeotypic commensurability of both structures) which were not understood so far. The proof is like that[11] for the shear homeotypes of Cu_3Au. The concept of Hund insertion easily explains also the heterotypism Sn.l — Sn.r: Hund insertion is energetically expensive as the distances of the inserted electron to its neighbours are shorter than the average distances, therefore Hund insertion goes lost at lower temperatures and the Si type becomes stable (SR1.21). The easy formation of Hund insertion in Sn.r is the cause for the phenomenon, not understood before, that homeotypes of $PtSn_4$ mainly become stable in ASn_M alloys (11 p. 316); these phases, named »polyfluorite phases« by Hellner[15,16] are stabilized by the interplay of Hund insertion and FB2 binding. The temperature dependence of Hund insertion explains especially the thermal instability of $RnSn_2$.r at higher temperatures (Nial 17, see also 6). The phase $CoGe_2$ (Q4.8, SR11.96) is one of the homeotypes of $PtSn_4$ with a second component different from Sn, here Co does absorb b electrons.

The completed binding analysis of the mixture $PtSn_M$ suggests to compare the binding in the homologic but not completely isotypic mixture $PtPb_M$. It is found

$$\mathrm{Pt_3\,Pb\ (Cu_3\,Au,\ SR\ 10.66)\ (4.053)\ \text{Å}} = b_{\mathrm{F}}\,(1) = e_{\mathrm{F}}\,(2) = c_{\mathrm{C}}\,(4)$$

$$\mathrm{Pt\,Pb\ (Ni\,As,\ SR10.66)\ (H4.259;\ 5.467)\ \text{Å}} = b_{\mathrm{FH}}\,(\sqrt{3};\ 2.7/3) = e_{\mathrm{CH}}\,(\sqrt{3};\ 6.7/3) = c_{\mathrm{CH}}\,(\sqrt{3};\ 8/3)$$

$$\mathrm{Pt\,Pb_4\ (T2.8,\ SR15.90)\ (6.665;\ 5.978)\ \text{Å}} = b_{\mathrm{FU}}\,(\sqrt{9};\ 3.8/2) = e_{\mathrm{C}}\,(\sqrt{9};\ 2.7) = c_{\mathrm{C}}\,(\sqrt{36};\ 5.4)$$

$$\mathrm{Pb\ (Cu,\ SR1.14)\ (4.950)\ \text{Å}} = b_{\mathrm{B}}\,(2) = c_{\mathrm{C}}\,(4).$$

Pt_3Pb is isotypic and isodesmic to Pt_3Sn, the non-congruent melting is perhaps caused by the large atomic radius of Pb which increases the energy of the phase and decreases the melting temperature. The phase PtPb is homeodesmic to PtSn showing that the NiAs type contains different bindings. The number $N^{/\mathrm{S}(b)}{}_{\mathrm{S}(c)} = 9.0$ is essentially greater than in PtSn (6.9) and this causes presumably isotypes of Pt_2Sn_3 and $PtSn_2$ not to become stable and $PtPb_4$ to be heterotypic to $PtSn_4$. The stability of $PtPb_4$ is as that of $PtSn_4$ a consequence of the equality of distances $d_b = d_e$; it is not yet clear whether Pb^{10} electrons take part in the e correlation.

DISCUSSION

The above first valence theory of $PtSn_M$ alloys is simple and transparent. The four valence electrons of Sn form a lattice-like spatial correlation with the cell b; the $5d^{10}$ electrons of Pt form a lattice-like spatial correlation e; and the $5s^2c^6$ and $4d^{10}$ electrons of Pt and of Sn form a lattice like spatial correlation with the cell c. A phase becomes stable when b, e, and c have a good commensurability with one another and with the crystal cell a. The FF2 binding of Pt_3Sn is a binding of brass like phases[18]. After this, two intermediary bindings, U_HH2 and F_HH2 are found which stabilize PtSn and Pt_2Sn_3. Finally the FU2 and F'B2 bindings occur which are typical for silicon and for many BB_M' alloys and which stabilize the phases $PtSn_2$ and $PtSn_4$. Each binding determines besides the electron distances the number of c places per b place, $N_{\mathrm{S}'''}{}^{/\mathrm{S}'}$, and the function $N_{\mathrm{S}'''}{}^{/\mathrm{S}'}(N_{\mathrm{Sn}}')$ is a monotonous function decreasing with increasing valence electron concentration, Figure 1. The sequence of bindings is just what Hume-Rothery's generalized valence electron concentration rule[20] proposes, but the above analysis additionally gives suggestions for experiments. The present analysis shows for $PtSn_4$ how a little and hidden mistake may lead the binding analysis into a wrong line. This feature is common to any kind of analysis for instance also to early structure analysis; it must be reduced by further developing the analysis method. Also the experimental verifications of the electron correlations would be helpful, but is yet in a very undeveloped state. In the conjecture of the author the carreful comparison of the feet of different single crystal diffraction maxima could give indications for the real electron correlation. If the Compton effect were absent, distinct intensity differences at the feet of different diffraction maxima would be caused by the electron spatial correlations which are commensurable to the crystal cell a and represent strongly disturbed lattices. Unfortunately the Compton effect strongly decreases this contribution.

The plural-correlations model permits to find for each observed phase a bonding type (binding), but there are more bindings available than phases observed[6]. This is caused by the well-known energy minimum principle: When (for a given entropy) a two phase alloy has a lower internal energy than a structure which might form of the alloy, then the structure does not become stable.

The conventional valence theory considers only the subsystem of the valence electrons, but the plural-correlations model considers additionally one or two systems of peripheral core electrons. This greater freedom in the model permits to discriminate phenomena which have essentially to do with the b electrons (valence electrons) and such which have to do with the e or c electrons (peripheral core electrons). Instead of classifying the compounds by oxidation numbers, valence steps and the like, one gets some insight to how the electrons move really in a crystal to form a stable phase. There is no doubt that the assumption of covalent bonds in a crystal structure is an essentially phenomenological idea, but there is some doubt whether the inevitable proof of convergency ever has been delivered for such an interpretation of a crystalline phase. Therefore the distribution of covalent bonds in a structure must be considered as a hypothetical picture, since the interaction of the bonds which leads to the true correlations has not been accounted for. It appears more rewarding to ask what the electron correlations might look like in a crystal, than to study the first members of a series development, the result of which might exhibit a picture quite opposite to that afforded by the full series. In fact a long history of valence theory has not uncovered the correlative interaction of the core electrons with the valence electrons, which was apparent by the first look for the present model. As soon as we have understood that there are spatial correlations of electrons in a crystal, we are invited to investigate the kind of these correlations. Covalent bond is a picture of spatial correlations of electrons in a two-atomic molecule, it cannot simply be inserted into a crystal and even less into a metallic crystal.

It is not to be expected that the binding analysis is always as easy as in PtSn_M therefore the extension of the analysis to all $A^n B_M{}^4$ phases is desirable. Part of this problem has been solved[9], but more remains still to be done.

It will be found that the interpretations in[9] or [21] look somewhat different from the present proposals. This is partly caused by the fact that the necessity of a separate e correlation was appreciated only after these analyses had been finished. However, the old proposals contained already a considerable portion of truth. For instance[21] assumed $a\,(\mathrm{PtSn_4}) = b_F\,(2;\ 2;\ 3.5 \approx 4) = c_B\,(4;\ 4;\ 7)$, the difference between $N_b{}^{/a} = 64$ and $N_{S(b)}{}^{/a} = 56$ was attributed to a deformation of b, but the binding was essentially of the FB2 type just as in the present analysis. Since the deformation of F has energetic consequences, in[9] was assumed $a = b_{FU}\,(3;\ 7.7/2) = c_B\,(\sqrt{18};\ 7.7)$. This is once more a FB2 binding but it is rotated around a_3. Unfortunately this rotation could not be confirmed by later analyses. When the inclination of Sn to Hund insertion was found, the present version became most probable. For the interpretations of the other phases similar explanations may be given. It becomes apparent that the binding analysis procedes by trial and error and improves so at the same time the interpretation and the model. As in every trial some progress of understanding is contained (as compared with the previous valence theories which gave no explanation at all for $\mathrm{PtSn_M}$) it may be anticipated that the method of inductive analysis gains consistency and will provide further valuable results.

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SAŽETAK

O prirodi intermetalnih veza u Pt Sn_M

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Opisana je analiza intermetalnih veza u smjesi Pt Sn_M (M = neodređeni molni broj).