CROATICA CHEMICA ACTA CCACAA 64 (4) 649–654 (1991)

ISSN 0011-1643
UDC 541
CCA-2031

Original Scientific Paper

Bonding Types in the Mixtures $NiSn_M$, $PdSn_M$, and $PtSn_M$

K. Schubert

Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, Seestrasse 92, D-7000 Stuttgart, F. R. Germany

Received June 10, 1991

A remarkable improvement is introduced into the description of the bonding types of mixtures $NiSn_M$, $PdSn_M$, and $PtSn_M$ by considering the bonding type rules of confluence, collectivity, and spin compensation. The number of bonding figures has decreased to two in each mixture, namely to FU2 of Pt, Pd, Ni and FB2C4 of Sn. The stability of the FB2C4 figure with increasing valence electron concentration always begins in the NiAs homeotype. While the structures at lower valence electron concentrations are homeotypes of close packings, the structures at higher valence electron concentrations exhibit an anionic partial structure into which the A^{10} atoms are inserted. Structural features like lacuna homeotypism, stacking homeotypism, or deformation homeotypism may be explained by the bonding type. The proposed improved bonding types confirm that the electron correlations model is a useful valence model for intermetallic phases. No other model has provided explanation of these structures so far.

INTRODUCTION

Several years ago, a bonding type analysis of the phases in $PtSn_M$[1] provided the first energetic interpretation of the sequence of intermediate phases. In the meantime, several new crystal chemical rules have been found[2] so it is possible to improve the analysis.[1] It will be described in the following. If the present arguments appear somewhat brief, further reading will be helpful.[1,2]

The essential lattice-like spatial correlations are the valence electron correlation *b* lodging only Sn5sp electrons, the correlation *e* of the peripheral d electrons lodging the Pt5d and Sn4d electrons, and the ground correlation *g* lodging the electrons that still exert influence on the bonding, namely Pt5sp+4f and Sn3d+4sp. The participation of different shells in a correlation like Pt5sp+4f in *g* is named confluence, (ref. 2, p. 11, Figure 2). The participation of a higher correlation in a sublattice of a lower correlation is named collectivity (ref. 2, p. 9). The existence of such coalescences of correlations is confirmed by crystal chemical rules explaining the constitution of the mixtures.

The bonding type analysis has been described extensively.[2] Functions $d_b(N_{Sn}')$, $d_e(N_{Sn}')$, $d_g(N_{Sn}')$, play an important role in the analysis (d_b = electron distance in the averaged b correlation, N_{Sn}' = mole fraction of Sn) and the site number function $N_{Sg}^{'at}(N_{Sn}')$, which should be smooth, is also a sensitive check.

ANALYSIS

The bonding type is given first for the marginal phases of $PtSn_M$.

Pt(Cu,SR1.71,11.174) $a40,88 = 3.92$ Å $= e_{\breve{F}}2;2.5 = g_U$ 4; 5, $N_{Sg}^{'at} = 40$.

Here, Cu is the crystal type of Pt; SR1.71 = Structure Reports vol. 1, p. 71; a is the crystal cell matrix of Pt; 40,88 are the numbers of e and g electrons per a; 3,92 Å is the numerical value of a in abbreviated notation (ref. 2, p. 15); $e_{\breve{F}}$ is the cell matrix of the e correlation, it is of the face-centered cubic Bravais type F and this type is compressed (˘) along $[001]_F$ by an amount resulting from the above commensurabilities; 2;2.5 is the commensurability matrix in abbreviated notation (ref. 2, p. 15); g_U is the cell matrix of the ground correlation (ref. 2, p. 9) belonging to the U type (ref. 2, p. 14), a tetragonally compressed cubic body-centered Bravais type of the axial ratio $\sqrt{2}/\sqrt{3} = 0.816$; $N_{Sg}^{'at}$ is the number of g sites per atom. To conserve the symmetry of Pt, the bonding type must be twinned in a. It is seen that this bonding type exhibits confluence, collectivity, and spin compensation. The e correlation is similar to that in ref. 1, but in ref. 1 the importance of collectivity was not appreciated. If consecutive $(110)_U$ planes are occupied by alternating spins, then $e_{\breve{F}}$ allows spin compensation.

While Pt has no valence electrons (b electrons), the element Sn has four b electrons causing in the low-temperature phase a bonding type quite different from that of Pt.

Sn.l(Si,SR1.21) $a32,80,144 = 6.49$ Å $= b_F;2 = e_B;4 = g_C;8$, $N_{Sg}^{'at} = 64$.

The bonding type was partly already noted.[1] It now conforms to confluence and collectivity. If g_C contains a NaCl type of spin ordering, then spin compensation is possible in e, which is easily verified. It is not clear how the Sn2sp + 3sp electrons are correlated to g; the reported proposal (ref. 2, p. 46) does not solve the compensation problem. The semicolon behind b_F *etc.* indicates that the following figure is the abbreviation of a matrix, not a number.

It is helpful to consider, along with Sn.1, also the bonding type of Sn.r, the room temperature phase of Sn (ref. 2, p. 46).

Sn.r(U2,SR1.56) $a16,40,72 = 5.83;3.18$ Å $= b_F\sqrt{3.25};1 = e_B\sqrt{13};2 = g_C\sqrt{52};4$, $N_{Sg}^{'at} = 52$.

A small amount of Hund insertion (ref. 2, p. 12) is present in b. The low value of $N_{Sg}^{'at}$, as compared with 64 of Sn.1, is the cause of a decrease of the potential energy of the structure, compensating partly the increase related to the Hund insertion in b. The bonding figure is essentially that of Sn.1, only the commensurability to a is different in both phases. The use of the root sign in the commensurability element permits a diagonal form of the commensurability matrix, being in reality of a non diagonal type: $\sqrt{13};2 \leftarrow 3,2,0;2,-3,0;0,0,2$. The admissible numbers under the root sign are collected in (ref. 2, p. 17). The value $\sqrt{3.25}$ is harmonic to $a;2$.

The full occupation of the e correlation in Pt by e electrons does not allow a higher b correlation to be collective to e, even a full collectivity with g is not possible. It appears probable that this shortcoming is one of the reasons for the occurrence of the

shear homeotypes of Cu_3Au (ref. 2, p. 20). The bonding type of Pt_3Sn assumed in [1] is still related to the present bonding type:

$Pt_3Sn(Cu_3Au,SR11.177)$ $a4,40,84 = 3.99$ Å $= b_F;1 = e_{\check{F}}2;2.5 = g_U4;5$.

The $N_{Sg}^{/at}$ value remained 40, as in Pt, since the partial structure of Pt in Pt_3Sn is a Cu structure with one lacuna per cell only. With respect to the above weak commensurability of b to e, the following phase is of interest:

$Pt_3Sb(ZrAl_3,JLCM17.1969.73)$ $a20,160,336 = 3.94;16.96$ Å $= b_{\check{F}}1;5 = e_{\check{F}}2;10 = g_U4;20$.

Although b and e are not collective, the harmony between them is favourable and conforms to the shearing rules (ref. 2, p. 20). The next phase in $PtSn_M$ contains Pt-chains along a_3 as homoatomic elements.[3]

Since the valence electron concentration does no longer admit a close packing, the FB2C4 bonding of Sn might be preferred to the ŤU2 bonding of Pt.

PtSn(NiAs,SR2.720), $a8,40,80 = H4.11;5.44$ Å $= b_{FH}\sqrt{3.25};3.2/3 = e_{BH}\sqrt{3.25};12.6/3 = g_{\check{C}H}\sqrt{13};12.6/3$. Here, H indicates the hexagonal coordinate system of a and the hexagonal aspects of F,B,C. The commensurability element 12.6 has been accepted to obtain $N_{Sg}^{/at} = 41$, fitting best the neighbouring values, and $12.6/3 \approx 4$ favours the stacking with support number 1 of the Pt layers parallel to $(001)_a$ according to the rules of stacking (ref. 2, p. 21), while the b correlation favours the stacking of the Sn layers parallel to $(001)_a$.

The following homeotype of PtSn (drawing in ref. 4, p. 341) displays interrupted Pt-chains parallel to a_3. According to the number of 6 Sn per cell, a relation $a_{Pt_2Sn_3} = a_{PtSn}1;3$ might be expected, but the Pt lacunae cause strong compression along a_3. A new harmony in the plane a_1, a_2 yields the remarkable bonding type:

$Pt_2Sn_3(H4.6,SR11.177)$ $a24,100,196 = H4.34;12.96$ Å $= b_{FH}2;6.5/3 = e_{BH}2;26/3 = g_{CH}4;26/3$.

b is not collective to e, the commensurability element 26/3 just allows the site number $N_{Sg}^{/at} = 41.6$, fitting well into the $N_{Sg}^{/at}(N_{Sn}')$ function. The bonding type is weakly related to the reported.[1]

The fourth intermediate phase is filling and rearrangement homeotypic to Sn.l, and it turns out that it is also homeodesmic to Sn.l.

$PtSn_2(CaF_2,SR.9,120)$ $a32,120,232 = 6.43$ Å $= b_F;2 = e_B;4 = g_C;8$, $N_{Sg}^{/at} = 42.7$.

Hund insertion in b is not necessary and b is not collective to e. The high occupation of e by Pt electrons shifts the b sites into the interstices of e, and the good harmony of the bonding type stabilizes the structure.

The last intermediate phase in $PtSn_M$ is a lacuna and shearing homeotype of $CuAl_2$ (drawing in ref. 4, p. 317), which is also homeotypic to Sn.l as revealed by the bonding type.

$PtSn_4(Q2.8,SR13.116)$ $a64,200,376 = 6.39;6.42;11.36$ Å $= b_F2;3.5 = e_B4;7 = g_C8;14$.

Although e is collective to g, b is not collective to e but to g. The b sites are in interstices of e. Moreover, 1/2 electron per Sn is in Hund insertion. The present bonding type is related to the bonding type assumed[1] and, therefore, some consequences are conserved, for instance the shearing as caused by the commensurability element

7 (see ref. 2, p. 20). The g site number per atom has risen to 44.8, and extrapolates over the mole fraction N_{Sn}' well to the site number 52 of Sn.r.

The easy bonding type analysis in $PtSn_M$ suggests a look at $PdSn_M$ and $NiSn_M$. The first intermediate phase of $PdSn_M$ is a deformation homeotype of Cu_3Au.

$Pd_{3.1}Sn_{0.9}$(DhtpCu$_3$Au,SR23.123) a3.6,40,72 = 4.07;3.73 Å = $b_{F'}$1;1.1 = $e_{\tilde{F}}$2;2.25 = = g_U4;4.5.

Four e electrons are excited to b and this latter correlation has a better harmony to e than in Pd_3Sn, although it is not collective with it. Presumably, the structure contains a shearing which was not found because of the similarity of nuclear charges of the components. The small N_{Sg}^{at} = 36 yields the cell volume 61.8 Å^3 against 62.6 Å^3 of Pd_3Sn.

Pd_3Sn(Cu$_3$Au,SR23.123) a4,40,72 = 3.97 Å = b_F;1 = $e_{\tilde{F}}$2;2.5 = g_U4;5.

Pd_2Sn(Ni$_2$Si,SR23.120) a16,120,216 = 8.12;5.65;4.31 Å = b_{FU}3;2;1.3 = $e_{\tilde{F}\,U}$6;4;5.3/2 = = g_U6$\sqrt{2}$;4$\sqrt{2}$;5.3.

The phase is a nonconservative shear homeotype of Cu_3Au with a_2, a_3 as shear planes (ref. 2, p. 20). The commensurability element 3 favours the shearing. The element 5.3 increases the N_{Sg}^{at} value to 42.5; this value appears, however, somewhat high.

The next phase is a filling homeotype of NiAs.

$Pd_{3.3}Sn_2$.h(FhtpNiAs,SR11.173) a8,53,95 = H4.39,;5.65 Å = b_{FH}2;3.2/3 = e_{BH}2;12.5/3 = g_{CH}4;12.5/3. Surprisingly, the FB2C4 bonding figure of Sn occurs already here. The b correlation indicates that e electrons are excited into it. Then, e is fully occupied, and collectivity $b \subset e$ is not realized. However, e and g are collective and both permit spin compensation when the spin ordering in g is of the NaCl type. $b^{-1}a$ favours the stacking of Sn layers parallel to a_1, a_2.

The phase $Pd_{20}Sn_{13}$ is another filling-homeotype of NiAs but it also contains three anomalous substitutions of Sn in the Pd chains.

$Pd_{20}Sn_{13}$(H39.27,[5],SR48.55) a104,660,1188 = H8.80;16.98 Å = b_{FH}4;9.5/3 = e_{BH}4; 38/3 = g_{CH}8;38/3. This bonding type can only be tentative since many e electrons should be excited to b. The related phases $Pd_3Sn_2.h_2$, $Pd_3Sn_2.h_1$, Pd_3Sn_2.r and $Pd_{59}Sn_{41}$ found by Sarah *et al.*[5] and presumably further phases not yet described appropriately cannot be analyzed at present as the structures are not known well enough.

The phase PdSn is a deformation homeotype of NiAs with a = a_{NiAs}1,–1,0;1,1,0; 0,0,1. Since no filling of a is applied, the N_{Sg}^{a} must decrease. This is possible as follows.

PdSn(MnP,O4.4,SR11.174) a16,80,144 = 3.87;6.13;6.32 Å = b_F1.25;2;2 = e_B2.5;4;4 = g_C5;8;8. Once more, e is fully occupied so that collectivity is not possible between b and e.

The next three phases are homeotypes of CaF_2, as it was already stated by Hellner.[6] This observation is now explained by the homeodesmism to Sn.l. Remarkably, all three homeotypes contain Hund insertion in b.

$PdSn_2$(U8.16,SR20.168) a64,480,864 = 6.49;24.38 Å = $b_{F'}$2;7.5 = e_B4;15 = g_C8;30.

In the next two phases, e contains vacancies in order to facilitate the Hund insertion.

$PdSn_3$(Q4.12,SR23.123, drawing in ref. 4, p. 317) a96,320,576 = 17.20;6.47;6.50 Å = $b_{F'}$2;5.25 = e_B4;10.5 = g_C8;21.

$PdSn_4$($PtSn_4$,Q2.8,SR13.116) $a64,200,360$ = 6.40;6.43;11.60 Å = $b_{F'}2;3.5$ = $e_B4;7.3$ = $g_C8;14.5$.

In the following, the intermediate phases of $NiSn_M$ will be considered. The first phase is homeodesmic to CuZn, *i.e.* it is a Hume-Rothery β phase and has the following bonding type:[7]

Ni_3Sn.h(Fe_3Si,SR20.29) $a16,160,264$ = 5.98 Å = $b_{\tilde{F}}\sqrt{2.5};2$ = $e_{\tilde{F}}\sqrt{10};4$ = $g_U\sqrt{40};8$.

Since $e_{\tilde{F}}$ is fully occupied by e electrons, b is not collective to e, but it is harmonic to e. It is seen that e electrons are excited to b.

Ni_3Sn.r(H6.2,SR5.7) $a8,80,132$ = H5.29;4.24 Å = $b_{\tilde{B}}2;3;1.7$ = $e_{\tilde{B}}4;6;3.5$ = $g_{UH}\sqrt{48};7/2$.

For convenience, the first two commensurabilities are written for $a1,-1,0;1,1,0;\ 0,0,1$. The bonding type occurred already for Co.r.[7]

In the next phase, the bonding figure of Sn emerges.

Ni_3Sn_2.h(FhtpNiAs,SR1.765) $a8,50,84$ = H4.11;5.19 Å = $b_{F'H}2;3.1/3$ = $e_{BH}2;12.5/3$ = $g_{CH}4;12.5/3$.

4 e electrons per a are excited to b, e has vacancies to support the Hund insertion.

Ni_3Sn_2.r(O12.8,SR32.107) $a32,200,336$ = 7.11;8.23;5.21 Å = $b_{FH}\sqrt{3};2.7$ = $e_{BH}2;12.5/3$= = $g_{CH}4;12.5/3$.

The bonding type is written for the NiAs type subcell. e is now fully occupied. Since there is no collectivity between b and e, also the harmony between b and e is low.

NiSn (drawing in ref. 8) is homeotypic to a completely filled Ni_3Sn_2.h. In order to describe the homeotypism, the unconventional aspect of NiSn a' = 4.09;24.45;5.20 Å will be compared with the orthorhombic aspect of Ni_3Sn_2.h, a'' = 4.11;7.11;5.19 Å. The commensurability is then $a' = a''1;3,4;1$, and would suggest $12 \cdot 3.4 \approx 40$ atoms in a'. The observation yields only 32 atoms because the thick a_1'',a_3'' layers, from which a' is built, have a thickness of less than a_2''. In fact, there are not 3.4 layers in a' but 4, so that in each layer 2 Ni per a' are left out. It has been proposed[8] that the suppression of Ni chains in a_3'' direction is easier than the suppression of Ni in the filling positions. These geometrical relations result in the following bonding type:

NiSn(O16.16,SR39.88) $a64,320,544$ = 24.45;5.20;4.09 Å = $b_{FH}14/2;3.2/3;2$ = $e_{BH}14/2;12.7/3;2$ = $g_{CH}28/2;12.7/3;4$.

The abbreviated commensurability should be read as follows: (ref. 2, p. 16). In $g_{CH}28/2;12.7/3;4$ the number 4 multiplies g_1 to equal a_3, the number 28/2 multiplies $-g_1+g_2$ to equal a_1, and 12.7/3 multiplies g_3 to equal a_2. The number of g sites per atom is N_{Sg}^{at} = 44.5, lying between 40 of Ni and 52 of Sn.r. The number of e sites per a cell is 356; it forbids collectivity with b. The number of b sites is 90, but it could be reduced because of non-collectivity with e. The e chains parallel to a_1 contain 7 sites per $|a_1|$, they favour the shearing in the structure according to ref. 2 (p. 20). The thick a_1'', a_3'' layers contain potentially 6 monoatomic layers and 28/4 = 7 parallel triple g layers. This might give the thick layers a certain compactness, which explains the stability of numerous close homeotypes.[8]

The phase Ni_3Sn_4 is in fact such a homeotype. With respect to the low symmetry, the bonding type is less easy to formulate and is, therefore, left out here.

CONCLUDING REMARKS

The assumption[1] that, besides the valence electron correlation *b*, two further correlations play a role in alloy phase formation has been confirmed by the present analysis. Improvement of the bonding types consists in a better consideration of the rules of confluence, collectivity, and spin compensation. Especially the latter rule causes certain deformations of the originally simple correlation types so that the simplicity of the earlier bonding type proposals seemingly gets lost. In reality, a correlation figure like F̆U2 is very satisfactory as compared with say FB2 because it admits spin compensation in both collective correlations. The low symmetry of F̆U2 is compensated by correlation-twin formation. A single crystal *a* generally contains a polycrystal of *b* *i.e.* *b* is generally twinned in *a*. Such a structure is well known from ferromagnets containing twinned spin directions, which provide an easy experimental proof.

A new crystal chemical rule which already emerged[7] is the persistence of the bonding figure in sets of chemically related phases. A bonding figure like FB2C4 may be so favourable that, with the aid of different commensurabilities, it causes different phases.

REFERENCES

1. K. Schubert, *Croat. Chem. Acta* **59** (1986) 685.
2. K. Schubert, *Bonding types of two-component phases*, Part I, Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, Stuttgart 1990, obtainable free from the author upon request.
3. A. Simon, *Angew. Chem.* **100** (1988) 163.
4. K. Schubert, *Kristallstrukturen zweikomponentiger Phasen*, Berlin 1964, Springer Verlag.
5. N. Sarah, K. Alasafi, and K. Schubert, *Z. Metallk.* **72** (1981) 517.
6. E. Hellner, *Z. Krist.* **107** (1956) 99, 124.
7. K. Schubert, *Cryst. Res. Technol.*, accepted.
8. M. K. Bhargava and K. Schubert, *J. Less-Comm. Metals* **33** (1973) 181.

SAŽETAK

Tipovi vezivanja u smjesama $NiSn_M$, $PdSn_M$, i $PtSn_M$

K. Schubert

Tipovi vezivanja u smjesama $NiSn_M$, $PdSn_M$, i $PtSn_M$ mogu se bolje opisati, ako se u obzir uzmu pravila konfluencije, kolektivnosti i spinske kompenzacije. Broj veznih oznaka smanjuje se na dva u svakoj smjesi, tj. FU2 za Pt, Pd i Ni te FB2C4 za Sn. Stabilnost oznake FB2C4 (s rastućom koncentracijom valentnih elektrona) započinje uvijek homeotipom NiAs. Dok su strukture s nižim koncentracijama valentnih elektrona homeotipi gustih pakiranja, strukture s višim koncentracijama valentnih elektrona jesu anionske parcijalne, s umetnutim A^{10} atomima. Predloženi, poboljšani tipovi vezivanja potvrđuju da je model elektronskih korelacija koristan za intermetalne faze.