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On the Binding in Transition Metal Disilicides[*]

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The two-correlations model for the bonding classification (binding) in metallic phases is applied to transition metal disilicides. The model considers the spatial correlations of the valence electrons (b correlation) and of the peripheral core electrons (c correlation) and proposes them to be simply commensurable to the crystal structure and to one another. A better understanding of the disilicides is possible by using the assumption that the electron contribution into the b and c correlations is essentially $T^{0,n}\mathrm{Si}_2^{4,8}$, where T represents a transition metal atom and n is its column number in the periodic system of elements. From this electron contribution it follows that the valence electron concentration in all $T^n\mathrm{Si}_2$ phases is nearly the same (i.e., not regarding a descent of valence electrons into the c correlation), and that the core electron concentration is not varying rapidly during increase of the column number n of the T component. Therefore the structure types of $\mathrm{TiSi_2}$, $\mathrm{CrSi_2}$, and $\mathrm{MoSi_2}$ are homeotypic and the stacking-homeotypism is caused by the increase of the core electron concentration. For $n = 7$ defect disilicide structures occur and an FU2 binding becomes stable, which is the cause for the incommensurability in one direction of the T and Si partial structures. The T atoms choose positions compatible with the c correlation and the B atoms adapt their position to the b correlation, since these component atoms mainly contribute into these separate correlations. For $n = 8$ the descent of valence electrons is reduced in quantity so that the binding becomes of the FB2 type which is formed in $\mathrm{FeSi_2}$.r, $\mathrm{CoSi_2}$, and $\mathrm{NiSi_2}$. The phase $\mathrm{FeSi_2}$.r is heterotypic to $\mathrm{CoSi_2}$ as the commensurability of the FB2 binding to the cell is different in both phases.

Introduction

It is a remarkable fact that all the chemical elements, beginning with A^2 (Be, Mg, Ca, Sr, Ba) up to T^{10} (transition metals Ni, Pd, Pt) form disilicides (*1*). Several of the structures formed are closely homeotypic: $\mathrm{TiSi_2}$(S2.4,SR7.12), $\mathrm{CrSi_2}$(H3.6,SR3.35, drawing (*2a*, p. 313)), and $\mathrm{MoSi_2}$ (U1.2,SR1.740, drawing (*2a*, p. 313)) (see Appendix for symbols). They are stacked up by hexagonal close-packed layers $T\mathrm{Si_2}$ (primitive submesh a_P, three atomic supermesh $a_\mathrm{S} = a_\mathrm{P}\,(1,1;\ -\ 1,2)$, for matrix notation see (*2b*) or Appendix), using the support number 2 (i.e., one atom of the second layer is supported by two atoms of the first layer) in different stacking sequences. The valence electron concentration $N_\mathrm{V}^{/\mathrm{A}}$ is important for the homeotypism as shown by Nowotny's diagram (*1a*), which displays in the sequence of increasing $N_\mathrm{V}^{/\mathrm{A}}$ the homogeneity ranges of the types $\mathrm{TiSi_2}$, $\mathrm{CrSi_2}$, $\mathrm{MoSi_2}$ for many two-component and three-component mixtures, the $N_\mathrm{V}^{/\mathrm{A}}$ being based on the electron count $\mathrm{Ti^4Si_2^4}$, etc. The $\mathrm{TiSi_2}$

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structure family ("supertype") gave an additional touch when the defect disilicides homeotypic to $Mn_{11}Si_{19}$(T44.76,SR29.64) were analyzed by Nowotny and his coworkers (*3*). Here the just-mentioned hexagonal layer TSi_2 is perturbed in such a way that the Si partial structure is a little strained in the $a_{S=1}$ direction as compared with the T partial structure. The stacking of these layers remains approximately with support number 2. Another electron count for the defect disilicides was proposed by Jeitschko and Parthé (*4*), who used the number of valence electrons per T atom site and applied a different electron contribution of the T component. Therefore the electron count in the disilicides is still controversial. In any case both electron counts (*1a* and *4*) consider one-electron gas as decisive for the structure stabilized, while the two-correlations model (*2b*) considers two-electron correlations. It appeared, therefore, of interest to examine the disilicide family by the concepts of the two-correlations model.

The questions to be answered are:

(1) Why is the tendency to form disilicides independent of the T^n component?

(2) Why are the types of $TiSi_2$, $CrSi_2$, and $MoSi_2$ closely homeotypic?

(3) Why are defect disilicides formed?

(4) Why have they such a rare structure type?

(5) What is the structural relation to the other disilicides?

A model which is able to bring energetic understanding into this remarkable phenomenon must be realistic, or, put otherwise, if the model interprets the facts, then the facts support the model.

Some chemists find difficulties in accepting the two-correlations model since they think that they have to assume an electron lattice in the structure. This is a misunderstanding of the model, which considers the spatial correlation (two-electron reduced spatial density function) and not the electron density. This spatial correlation may be calculated by a Hartree model and differs then from the function which exists in reality, by an excess density. If this excess density is subject to an averaging procedure (*2b,c*) then the result has some relation to a lattice. The kind of excess density may be assessed by a continuity consideration (*2c*), but it has the unfortunate property of being found only in high approximations of present-time *ab initio* calculations, so that it has not been carefully enough studied since. Nevertheless, the excess density governs phase formation since the Hartree spatial correlation cancels essentially in the energy of formation (energy of compound minus energy of unreacted components). This is the reason why the analysis by the two-correlations model is frequently very illuminating, for instance, in the present case where no other interpretation has been advanced so far.

Analysis

The remarkable feature that the phases T^nSi_2 are formed independently of the upper index n suggests that the valence electron correlation (b correlation) is exclusively filled by valence electrons of Si atoms (extended Ekman rule, see (*2a*)). The n peripheral d electrons of the T^n atoms must then populate the correlation of the peripheral core electrons (c correlation) together with the eight peripheral core electrons of Si. Therefore the electron count is assumed to be $T^{0,n}Si_2^{4,8}$, where the first numbers in the exponent indicate the contributions into the b correlation and the second numbers indicate the contributions into the c correlation. Therefore the valence electron concentration is the same in all considered disilicides and the core electron concentration varies only within narrow limits. This simple assumption already answers the first question, for if the valence electron concentration is approximately the same in all $T^n Si_2$ phases then this may favor just the formation of a phase (extended Hume–Rothery rule). The second question is also answered, for in the proposed count the change of core electron concentration must be slow, as the great contribution of the Si atoms is always present, and belongs to the majority component. A slowly varying core electron concentration will favor homeotypic structures.

In order to come to a binding (bonding classification) proposal it is appropriate to start from the binding in the marginal phase Si.

The binding in Si(F2 structure class (*2a*), Structure Report 1, p. 52) is given by a = 5.431 Å = $b_F(2) = c_B(4)$ (see (*2b*)). This is a factorial binding (*2b*) and therefore energetically favorable; it may be named briefly FB2. The disilicide $NiSi_2$(CaF_2 type, SR13.90) has (*5*) the same binding a = 5.406 Å = $b_F(2) = c_B(4)$, and the elementary cell is nearly that of Si with four Ni inserted and the Si atoms somewhat redistributed; only the occupation of the c correlation is strongly increased. From this independence of the degree of occupation of the c correlation, it is confirmed that the FB2 binding is quite stable. It appears, therefore, natural that the FB2 binding in $CaSi_2$ is also found: $CaSi_2$.p($ThSi_2$,U2.4, drawing (*2a*, p. 313), SR33.51)4.28; 13.54 Å = $b_{FU}(2;9/2)$ = $c_B(8^{1/2};9)$. The fact that the structure of $CaSi_2$.p is different from $NiSi_2$ stems from the circumstance that the electron count $Ca^{2,8}Si_2^{4,8}$.p is different from $Ni^{0,10}Si_2^{4,8}$, or, since the number of b correlation places is $N_{P'}^{/C} = 36$ there must be some descent of valence electrons into the c correlation: $Ca^{1,9}Si_2^{4,8}$.p. It is seen here that from the structure the electron count may be inferred. It is therefore satisfactory that $CaSi_2$.r permits an electron count $Ca^{2,8}Si_2^{4,8}$.r and the FB2 binding: $CaSi_2$.r(R1.2, SR33.51)H3.82; 15.98 Å = $b_{FH}(3.25^{1/2}; 9.2/3) = c_{BH}(3.25^{1/2}; 37/3)$. Since the FB2 binding also applies to $LaSi_2$($ThSi_2$, SR16.105)4.28;13.75 Å, the question arises what the binding is in $TiSi_2$.

The cell of $TiSi_2$, a = 8.25;4.78;8.54Å, permits us to find a quasi-tetragonal cell a_T which corresponds to the Si cell: $a_{Si} \approx a_T = a'_{TiSi2}(0.5,-0.5,0;\ 0,0,1;\ 0.5,0.5,0)$ and has the same atom content as the $NiSi_2$ cell (it should be noted that the last equation may be decomposed into $a_{T=1} = a'_1 0.5 + a'_2 0 + a'_3 0.5$, $a_{T=2} = a'_1(-0.5) + a'_2 0 + a'_3 0.5$, $a_{T=3} = a'_1 0 + a'_2 1 + a'_3 0$). Besides the redistribution of the Si atoms, a strong tetragonal deformation of the pseudocell a_T occurs, which also makes the cell a_{TiSi2} pseudohexagonal. The atom layer given by the fractional coordinates relative to the a_{TiSi2} cell as x_1, x_2, 0 permits, as has been mentioned, us to stack up the whole-type $TiSi_2$ and also the types $CrSi_2$ and $MoSi_2$ (see Fig. 1). Since in these types the concentration of the peripheral core electrons is less than in $NiSi_2$ it is clear that a less close-packed c correlation must be stabilized. To write it down it is advantageous to use the pseudohexagonal cell of $TiSi_2$ $a_H = a_{TiSi2}$ (0.5,−0.5,0; 0.5,0.5,0; 0,0,1), so that for c it follows that a_H = H4.78; 8.54 Å = $c_H(4; 7)$ quite similar to the correlation in the plane $(110)_{NiSi_2}$. This c correlation is conserved in the three homeotypic disilicide structures, only the matrix element $(c_H^{-1} a_H)_{33} = K''_{33} = 7$

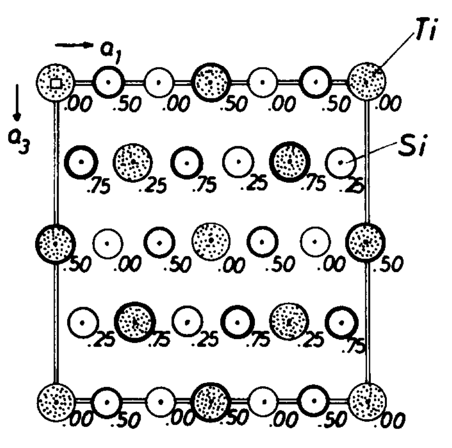

FIG. 1. $TiSi_2$(S2.4,SR7.12), D_{2h}^{24}Fddd a = 8.253; 4.783; 8.540 Å, 8Ti(a).0.0.0, 16Si(e).333.0.0.

changes a little and is probably responsible for the change of the structural stacking sequence. For $CrSi_2$ with a = H4.43; 6.36 Å comes K''_{33} = 5.7 and for $MoSi_2$ (a = 3.203; 7.855 Å or a_H = H4.530; 4.530 Å) comes K''_{33} = 4; taken relative to one atom layer the K''_{33} values are 1.75, 1.90, 2.00.

The b correlation in $TiSi_2$ could be $a_T = b_F(2;\ 1.6)$, which affords only 26 electron places. Concluding that six valence electrons have descended into the c correlation, there must be assumed $N^{/C}_{C}$ = 86 electrons in the a_T cell, which are distributed on $N^{/C}_{P''}$ = 112 c correlation places per cell leading to the reasonable occupation $N^{/P''}_{C}$ = 0.77. It is remarkable that the b correlation is approximately described also by a_H = H4.78; 8.54 Å = $b_{FH}(5.3^{1/2};\ 5/3) = c_H(4;\ 7)$. Therefore it may be written a_{CrSi_2} = H4.43; 6.36 Å = $b_{FH}(5.3^{1/2};\ 4) = c_H(4;\ 5.7)$ and $a_{MoSi_2} \rightarrow a_H$ = H4.53; 4.53 Å = $b_{FH}(5.3^{1/2};\ 2.8/3) = c_H(4;\ 4)$. It was assumed before that the last element of the second numerical matrix $K'' = c^{-1}\,a$ in the binding description is responsible for the stacking sequence of the hexagonal atom layers. This may be confirmed by the commensurability rule. The value K''_{33} = 7 of $TiSi_2$ is integral and favors, therefore, a 4-layer stacking sequence. The value K''_{33} = 5.7 has in fact for $3K''_{33}$ = 17 the first whole-number value and favors, therefore, a 9-layer sequence which is composed of three 3-layer sequences. Finally for K''_{33} = 4 the $MoSi_2$ sequence is appropriate. The increase of the axial ratio with increasing electron concentration is a frequently confirmed rule; it is caused by an electron correlation which is well commensurable in the basal plane, and less well in the direction of the unique axis.

It is clear that the present interpretation contains predictions on the change of axial ratio of a phase of the $TiSi_2$ family after substitution of appropriate T elements. Such investigations could confirm the present interpretation; also, it might be possible that more complicated stacking sequences may be found in three-component alloys at sufficiently low temperatures.

It is now possible to find the analysis of the binding in a defect disilicide. For this purpose it is helpful to analyze the binding in a complete mixture as this affords the $d_{b,c}(N'_2)$ relation (d_b = distance in b correlation, d_c = distance in c correlation, N'_2 = mole fraction of the second component) which helps to find the most probable binding (bonding classification). As an example the mixture $MoGe_M$ may be chosen (M = undetermined mole number). The binding of Mo is given by

$$\text{Mo(W,SR1.16)3.147 Å} = b\text{B}(1) = c\text{C}'(2) = e\text{C}(4).$$

The formula is written for simplicity with the indices on the line as in the tables (*5*); the b_B lattice is fully occupied, while the $c_{C'}$ lattice is occupied to $N^{/P''}_{C}$ = 1.25 (C = number of peripheral core electrons, P″ = number of places in the c correlation). The number of five electrons per atom in the c correlation leads to partial Hund insertion (see Appendix) and so to the effect found by neutron diffraction in Cr(SR23.113). Even a third correlation, e, may be commensurable and this fact is responsible for the high melting temperature of the $T^{4..6}$ elements following a well-confirmed rule (*2c*). The binding suggests the electron count $Mo^{0,6}$ $Ge^{4,10}_{M}$, i.e., only the Ge contribute to the b correlation which amounts to an extension of Ekmans rule (see *2a*). The binding in Mo may be named a BC′2 or a BB2 binding; it occurs also in CuZn with the distinction that the commensurability to the crystal cell a is different and the e correlation is not commensurable. Probably the Ge atoms favor a b_C correlation, therefore it is very satisfactory that the following to BB2 related binding is possible,

$$\text{Mo3Ge(Cr3Si,SR16.94)4.933 Å} = b\text{C}(2) = c\text{C}(4).$$

This CC2 binding satisfies the number of valence and core electrons per cell $N_{\mathrm{V,C}}^{/\mathrm{C}}$ = 8,56. The fairly high occupation of the c correlation perhaps has to do with the high supraconductivity transition temperature. Homeotypic to the binding in Mo_3Ge is

Mo5Ge3(W5Si3,71Ec)9.84; 4.97 Å
= bFU($18^{1/2}$;3/2) = cC($72^{1/2}$;4.3).

This FUC2 binding corresponds to the increase of valence electron concentration: The b_{C} correlation of Mo_3Ge is compressed to a b_{FU} correlation in Mo_5Ge_3, while the $c^{-1}b$ commensurability is preserved in the basal plane. The value $N_{\mathrm{P'}}^{/\mathrm{C}} = 54$ is a little greater than the value $N_{\mathrm{V}}^{/\mathrm{C}} = 48$, so that here Mo may have a little valence electron contribution. The next two phases are $Mn_{11}Si_{19}$ homeotypes:

Mo13Ge23(T52.92,SR32.72)5.987; 63.54 Å
= bF(2;42/2) = cU(4;52),

Mo9Ge16(U18.32,71Ec)5.994; 43.995 Å
= bF(2;29/2) = cU(4;36).

At first it is seen that the c correlation is no more of the H type of $c(MoSi_2)$ but of the U type which is formed by a compression in the direction of the hexagonal axis (and a plane shear of the c_{H} correlation). The transition $c_{\mathrm{H}} \rightarrow c_{\mathrm{U}}$ corresponds to the transition of (pseudo) hexagonality to tetragonality of the crystal structure. The compression of c_{H} to c_{U} is favored following the model by a great $N_{\mathrm{C}}^{/\mathrm{A}}$ (number of peripheral core electrons per atom) and by a small $N_{\mathrm{V}}^{/\mathrm{A}}$ (number of valence electrons per atom). Therefore, it remains possible that for greater $N_{\mathrm{V}}^{/\mathrm{A}}$ the c_{H} correlation reappears. The Mo partial structure of $Mo_{13}Ge_{23}$ and Mo_9Ge_{16} is exactly commensurate to the c correlation and the Ge partial structure is (less so because of descent) commensurate to the b correlation. This rare division is caused by the fact that all peripheral electrons of Mo contribute to the c correlation while (nearly) all valence electrons of Ge contribute to the b correlation. Since this is not generally the case (for instance, in brasslike alloys both components contribute to the b correlation) questions (3) and (4) are answered: The $Mn_{11}Si_{19}$ homeotypes are formed as the b_{F} and the c_{U} correlation are not well commensurate in a_3 direction and different numbers of Si defects are caused by different descent of valence electrons into the c correlation. The $Mn_{11}Si_{19}$ structure type is rare because the interdivision of the b and c electrons over the components is fairly rare. The descent of valence electrons is with 0.35 per atom smaller than in $TiSi_2$ (0.75). This is satisfactory since the descent must decrease with increasing column number n. For the second component mole fraction 0.67 follows

MoGe2.h(MoSi2,SR17.173)3.313;
8.195 Å → H4.69; 4.69 Å
= bFH($5.3^{1/2}$; 2.8/3) = cH(4; 4),

MoGe2.r(Ni2Si,SR30.21)6.343;
8.582; 3.451 Å = bFU(3; 4; ≈2.7/2)
= cU($3 \times 2^{1/2}$; $4 \times 2^{1/2}$; 2.8).

At lower temperatures the FU2 binding appears with strongly deformed b_{F} correlation. The good fit of the binding is displayed in the $d(N)$ diagram Fig. 2.

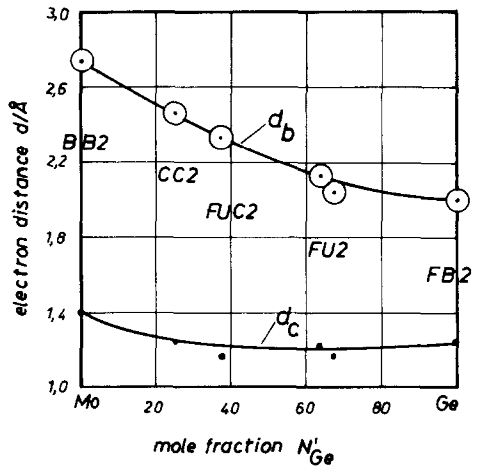

FIG. 2. Electron distances in phases $MoGe_M$.

The question now arises whether the above interpretation is valid for all $Mn_{11}Si_{19}$ homeotypes. This is in fact the case (NE = number of electrons per cell in *b* and *c* correlation):

V17Ge31(T68.124,SR32.74)5.91; 83.65 Å = *b*F(2; 56.5/2) = *c*U(4; 68), NE496,1580,

Cr11Ge19(Mn11Si19,SR32.70)5.80; 52.34 Å = *b*F(2; 36/2) = *c*U(4; 44), NE304,1024,

Mn11Si19(T44.76,SR29.64)5.52; 48.2 Å = *b*F(2; 35/2) = *c*U(4; 44), NE304,916,

Tc4Si7(T16.28,71Ec)5.737; 18.099 Å = *b*F(2; 12.6/2) = *c*U(4; 15.5≃16), NE112,336,

Ru2Sn3(T8.12,SR29.85)6.172; 9.915 Å = *b*F(2; 6.4/2) = *c*U(4; 7.9≃8), NE48,184,

Rh10Ga17(T40.68,SR32.68)5.813; 47.46 Å = *b*HT($8^{1/2}$; 26/2) = *c*U(4; 40), NE204,1040,

Rh17Ge22(U34.44,SR32.83)5.604; 78.45 Å = *b*HT($8^{1/2}$; 44/2) = *c*U(4; 68), NE352,1492,

Ir3Ga5(T12.20,SR32.69)5.823; 14.20 Å = *b*C($8^{1/2}$,7) = *c*U(4; 12), NE60,308,

Ir4Ge5(T16.20,SR32.80,33.84)5.612; 18.364 Å = *b*C($8^{1/2}$; 9.2) = *c*U(4; 16), NE80,344.

It becomes clear here why there are different subfamilies in the $Mn_{11}Si_{19}$ family: not only the different descent in the *b* correlation permits different crystal types but also the *b* correlation can have different types; the correlation type determines the family while the valence electron descent determines the different structural types.

The insight gained in the above interpretations permits the determination of the binding in further disilicides. The structure of $FeSi_2$.r(P8.16,SR37.101) is commensurable to the $NiSi_2$ by $a = 7.79; 7.83; 9.86$ Å = $a_{NiSi2}(1,-1.0;\ 1,1,0;\ 0,0,2)$. The binding is $a = b_{FU}(17^{1/2}; 7.4/2) = c_B(34^{1/2}; 7.4)$ so that the FB2 binding of $NiSi_2$ and $CoSi_2$ is conserved in $FeSi_2$.r. But there is some descent of valence electrons since $17 \times 7.4 = 125.8$ is smaller than the number of valence electrons per cell $N_V^{\prime C} = 128$. This descent has the tendency to make the structure tetragonally compressed. Therefore the Si chains along a_3 take zigzag form and this favors the increase of the basal mesh and the $17^{1/2}$ commensurability. The structure of $FeSi_2$.h remarkably has a different array of Fe atoms in the C1 partial structure of Si. The binding here is $a = 2.692; 5.137$ Å $= b_F(1; 2) = c_B(2; 4)$, i.e., once again of the FB2 type. The low occupation of the *c* correlation probably favors the layerlike array of the Fe, which is not possible for $CoSi_2$ and $NiSi_2$.

Concluding Remarks

It is clear that the proposed bindings are hypothetical; they are supported by the fact that they obey a set of rules, which is assumed to control all correlations. But this is not the first time in crystallography that hypotheses are used. From a hypothesis predictions may be inferred and afterwards examined by experiments. This property of suggesting new experiments is found in the present interpretation also. The universality of the increase of axial ratio with increasing core electron concentration in $TiSi_2$ homeotypes may be examined. New stacking homeotypes at lower temperatures may be searched for. The different descent of valence electrons into the *c* correlation (core electron band) may be scrutinized by magnetic measurements.

Besides this indication of new experimental problems there is a remarkable correspondence between observation and model, which gives confidence that there is some content of truth in the model. Some critics have found fault in too many free parameters of the model, which might allow one to find a binding proposal for mistaken structures. These critics must explain by their models why, for instance, in the mixture $\mathrm{MoGe_M}$ just for BB2, CC2, FUC2, FU2, and FB2 bindings phases are stabilized. While the present model leads to the correspondence between observed structures and favorable bindings the other models must calculate the stability of the structures as compared to other possible structures, and finally draw from the computational results a bonding classification which is desired by the experimental crystallographers. A possibility to falsify the present model would also be to prove that there are no latticelike spatial correlations in metallic phases, but such a proof has not appeared as yet. Therefore, the two-correlation model should be used and improved as long as severe deficiencies are not found.

Appendix: Summary of Model, Notation, and Analysis Method

A valence model for metallic phases needs not calculate the energy U as a function of volume, entropy, and mole numbers since it only wishes to indicate compositions which permit a low U in comparison to neighbored compositions. For this purpose the investigation of the potential energy is sufficient as in the electrostatic lattice theory. From $U^{\mathrm{pot}} = \int_{x1x2} H^{\mathrm{pot}}_{x1,x2} D^{\mathrm{SC}}_{x1,x2}$ (H^{pot} = potential energy function, D^{SC} = reduced density function = spatial correlation) it is seen that the function D^{SC} accounts for U^{pot}. The function $D^{\mathrm{av}}_{x} = \int_{x2} D^{\mathrm{SC}}_{x2+x,x2}$ gives an average of D^{SC} in three-dimensional space. It is assumed (1) D^{av} splits into an essentially attracting valence electron correlation (b correlation) and an essentially repelling correlation of the peripheral core electrons (c correlation); (2) the two correlations are latticelike with the cells b and c and have a coherency length of 50 Å; (3) the correlations obey the following rules.

Rule of types. Possible types for a correlation are the isometric lattices C,B,F,U,H which may also have the aspects CH,BH, FH,FU,UH,HT (see below).

Rule of occupation. The contributed valence electrons ($\mathrm{Ni^0}$,$\mathrm{Cu^1}$,$\mathrm{Zn^2}$,$\mathrm{Ga^3}$, . . .) fill the lattice of the b correlation fully, and the core electrons (d or sp shells) fill the c correlation to 83 ± 15% in BB alloys and to 50 ± 25% in AB alloys.

Rule of commensurability. $b^{-1}a$ and $c^{-1}a$ should have many whole-numbered elements. If $b = nc$ (n = whole number, factoriality) then congruent melting of the phase is frequent. A means to conserve factoriality is vacancy formation of the component with lowest valence electron contribution. The correlations b and c may be twinned in a thus generating a higher a symmetry.

Rule of place numbers. The number of c correlation places per atom $N^{/\mathrm{A}}_{\mathrm{P''}}$ decreases with decreasing valence electron concentration $N^{/\mathrm{A}}_{\mathrm{V}}$, with increasing atomic number $N^{/\mathrm{A}}_{\mathrm{E}}$, and with increasing external pressure.

Rule of distances. The distances of maxima in $D^{\mathrm{av}b}$ and $D^{\mathrm{av}c}$, d_b and d_c, depend smoothly on N'_2 of a mixture and quasi-periodically on $N^{/\mathrm{A}}_{\mathrm{E}}$. The distance becomes smaller with decreasing coordination number in the correlation.

Rule of Hund insertion. In a phase with a $\mathrm{B}^{n>4}$ component an F correlation of spin-up electrons may be partly filled in the octahedral interstices by spin-down electrons; this is indicated by F′.

Rule of classification. Different bindings in isotypic phases occur and define *subtypes*. Equal binding in different structures occurs and defines *isodesmic* phase sets. Nearly equal binding is named homeodesmism.

In order to describe the crystal–chemical relations the following notations are useful.

Phase designation. Phase designation by chemical symbols in the sequence of the homologous classes A^1 (alkali metals), A^2, T^3, T^4, . . . , T^{10}, B^1, B^2, . . . , B^8 (noble gases). Affixes to the chemical formula: h = high-temperature phase, r = room-temperature, l = low-temperature, p = high-pressure, m = metastable, i = impurity stabilized phase.

Structure types. Structure types are indicated by prototype. Prototypes themselves are indicated by Bravais group and numbers (separated by a point) of component atoms in the primitive cell. The symbols for the Bravais groups are following A. J. C. Wilson:

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, one face, all faces centered,
M,N,Z = monoclinic primitive, face centered, triclinic.

The two-character symbols of the Structure Reports cannot be taken as they must be used here in the binding description.

Citation. Citation is given by SR1.1 = Structure Reports A, Vol. 1, page 1. References for phase diagram (phd) are contained in Hansen, Elliott, Shunk, and Moffatt. A few references are for Eckerlin in Landolt-Börnstein (71Ec) or Wells.

Correlation kinds. a, b, c correlations are designated as the averaged correlations 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. An isometric correlation in a broader sence, $\tilde{C}$, may be generated by hexagonally straining C. Nonisometric correlation $\tilde{U}$: an H layer is stacked with distance $d_H/2^{1/2}$. Hund insertion: into the octahedral holes of a b_F correlation with spin up several spin-down electrons are inserted.

Matrix notation. $a_{iL} = (a_{11},a_{12},a_{13}; a_{21},a_{22},a_{23}; a_{31},a_{32},a_{33})$, 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, an M$\beta°$ refers to a monoclinic normal coordinate system with angle β.

Abbreviations. $(a_{11},0,0; a_{21},a_{22},a_{23}; a_{31},a_{32,33}) = :(a_{11}; a_{21},a_{22},a_{23}; a_{31},a_{32},a_{33})$, $(a_{11},0,0; 0,a_{22},0; 0,0,a_{33}) = :(a_{11}; a_{23}; a_{33})$, $(a_{11}; a_{11}; a_{33}) = :(a_{11}; a_{33})$, $(a_{11}; a_{11}) = :(a_{11})$. For brevity a matrix $b = (2,1,0; -1,2,0; 0,0,1)$ may be written as $(5^{1/2}; 5^{1/2}; 1)$, or even shorter as $(5^{1/2}; 1)$. 5 is the determinant of b and a rotation matrix is omitted; further values of whole-numbered determinants are collected in *Struct. Bonding (Berlin)* **33,** 139–177 (1977).

Commensurabilities. Names of commensurability matrices: $b^{-1}a = :K'$, $c^{-1}a = :K''$. An equation $a = bK' = cK''$ is named a bonding classification or *binding*. A quotient $a_L^{-1}a_{L'} = K$ 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 the tables the phase name, structure type, reference, cell, and binding are given for mixture classes. An A behind a numerical matrix means angström. 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, NE = numbers of electrons.

How to find a binding. Draw as abscissa the mole fraction $N_2' = 0, \ldots, 1$ of the second component over 10 cm. Draw as ordinate the average electron distance beginning with $d = 1$ Å so that the difference $\Delta d = 0.2$ Å corresponds to 1 cm. Plot for $N_2' = 0$ the values of $d_b(0)$, $d_c(0)$ of the first component, and 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 are also cited in *Struct. Bonding* (*Berlin*) **33,** 139–177 (1977). For an empirical compound assume $d(N_2')$ values interpolated corresponding to the atom volume curve. Insert these values into the possible correlation types to get possible b and c cells. Check (by slide rule) different commensurabilities $b^{-1}a$, $c^{-1}a$; for the different commensurability cases, check the fulfillment of the rules of the present summary. The proposal with best fit to the rules is the probable binding.

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