Monatshefte für Chemie 113, 651—667 (1982)

Monatshefte für Chemie
Chemical Monthly

On the Binding in Carbides

Konrad Schubert

Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften, D-7000 Stuttgart, Federal Republic of Germany

(Received 26 August 1981. Accepted 2 December 1981)

The two-correlations model for the binding in alloy phases is applied to carbides. The model considers a valence electron spatial correlation (named *b* correlation) and a core electron spatial correlation (named *c* correlation) and assumes that they are in good commensurability with the crystal cell *a* and with one another; the types of the correlations together with the commensurability are named a binding. The well known concept of interstitial structures of carbides is extended by the assumption that the valence electrons of the C atoms and the peripheral d electrons of the transition metal atoms (T atoms) take part in the *c* correlation while the valence electrons of the T atoms form a *b* correlation which lies in good commensurability with the *c* correlation and contributes thus to the stability of a phase. This model explains the high melting temperature of TiC, it gives the sequence of structures for increasing C mole fraction in a mixture like WC_M (M = undetermined mole number) and it affords a simple interpretation of the martensite phenomenon. Only in B^n atom carbides, like Al_4C_3 or SiC, the valence electrons of B^n and of C appear to form a *b* correlation, so that the core electrons of the C and of the B^n atoms form the *c* correlation. By these assumptions becomes clear why great atoms like Tl, Pb, Bi do not form interstitial compounds with C, or why in the SiC compound and in $Al_4C_3(AlN)_M$ there are many homeotypic phases (polytypes). In three component carbides also, the occurrence of certain structural types is better understood by the analysis of the binding.

(Keywords: Crystal structures of carbides; Electron spatial correlation; Two-correlations model; Valence rules)

Über die Bindungstypen in Carbiden

Das Zweikorrelationenmodell für die Bindung in Legierungsphasen wird auf Carbide angewandt. Das Modell betrachtet eine Ortskorrelation der Valenzelektronen (genannt *b*-Korrelation) und eine Ortskorrelation der peripheren Rumpfelektronen (genannt *c*-Korrelation) und nimmt an, daß diese in guter Kommensurabilität mit der Kristallzelle *a* und miteinander stehen; die Typen der Korrelationen zusammen mit der Kommensurabilität zwischen ihnen kennzeichnen den Bindungstyp. Der bekannte Begriff der Einlagerungs-

0026-9247/82/0113/0651/$ 03.40

strukturen der Carbide wird erweitert durch die Annahme, daß die Valenzelektronen der C-Atome und die peripheren d-Elektronen der Übergangsmetallatome (T-Atome) an der *c*-Korrelation teilnehmen, während die Valenzelektronen der T-Atome eine *b*-Korrelation bilden, die in guter Kommensurabilität zur *c*-Korrelation steht und so zur Stabilität der Phase beiträgt. Das Modell erklärt die hohe Schmelztemperatur von TiC, es gibt die Abfolge der Strukturen für steigenden C-Molenbruch in einer Mischung wie WC_M (M = unbestimmte Molenzahl) und es liefert eine einfache Deutung des Martensit-Phänomens. Lediglich in B^n-Carbiden wie Al_4C_3 oder SiC scheinen die Valenzelektronen der B^n- und der C-Atome die *b*-Korrelation zu bilden, so daß die Rumpfelektronen der C- und B^n-Atome die *c*-Korrelation bilden. Durch diese Annahmen wird klar, warum große Atome wie Tl, Pb, Bi keine Einlagerungsverbindungen mit C bilden oder warum in der Verbindung SiC oder in $Al_4C_3(AlN)_M$ viele homöotypische Phasen (Polytype) auftreten. Auch in dreikomponentigen Carbiden wird das Auftreten bestimmter Strukturtypen besser verständlich durch die Analyse des Bindungstyps.

Introduction

Reviews on carbides have been written by *Goldschmidt*[1] and by *Nowotny*[2], carbide phase diagrams are reported in [3,4], carbide structures are discussed in [5,6], however, complete tables of two-component carbide phases with interpretations are missing as yet. This review tries to analyse the spatial correlations of electrons in two component carbides, it intends to find additional insight into their bonding. In order to follow the method of analysis, the two-correlations model should be known[7], see also appendix. Compounds of Li, Be, B have been reviewed previously[8a–c], the scope of the analysis is illustrated by these examples. The chemical elements have been analysed earlier with respect to the spatial correlation of electrons[9a] so that from this analysis the elemental electron distances may be taken.

The electron distances of C·r (graphite) in the *b* and *c* correlations $d_{b,c} = 1.42,\ 1.00$ Å follow from the binding proposal[9a]: C·r (H4, SR 1.28) H 2.46; 6.70 Å $= b_{FH}(\sqrt{3}; 5.8/3) = c_{CH}(\sqrt{3}; 12/3)$, in words: Carbon, room temperature phase, has a hexagonal *Bravais* group with 4 atoms in the cell, see Structure Reports A vol. 1 page 28, hexagonal basal coordinates, a_1 axis amounts to 2.46 Å, a_2 axis to 6.70 Å, this *a* cell equals the *b* cell of the valence electron correlation with the face centred cubic type in hexagonal aspect times the commensurability matrix $(\sqrt{3}; 5.8/3)$ (see appendix), and it equals the *c* cell of the correlation of the peripheral core electrons with the primitive cubic type in hexagonal aspect times the commensurability matrix $(\sqrt{3}; 12/3)$. On the other side for C·hp2 (F2, SR 1.21) 3.57 Å (diamond) holds $a = b_F(2) = c_C(4)$, so that $d_{b,c} = 1.26,\ 0.89$ Å, therefore $d_{b,c} = 1.4,\ 1.0$ Å is an acceptable value for the following analysis.

Results

A^1C_M. LiC (RbO type) has a deformed cubic primitive Li lattice in which C_2 dumbbells directed along the medium cell axis a_2 are inserted alternately into hexahedral interstices. The electrons of b and c correlation may be counted by $Li^{1,2}C^{0,4}$. The b correlation may be assumed of the B type (see Table 1) while for the c correlation $a = (3.7;5.4;4.8)\,\text{Å} = c_{FU}(2;3;4/2)$ could be chosen geometrically. But the formation of C_2 islets is not compatible with this c correlation as the electron places are partly too remote from the donors. Therefore the related $a = c_C(\sqrt{8};\sqrt{18};4)$ must be taken, forming a BC$\sqrt{8}$ binding, which may easily be extended to RbO (P2.2, SR21.236) as $a = (4.2;\ 7.1;\ 6.0)\,\text{Å} = b_B(1;1.66;1.5) = c_C(2\sqrt{2};5;3\sqrt{2})$. This homeotypism of binding explains the isotypism LiC-RbO which was before quite incomprehensible.

NaC (U8.8) is homeotypic to LiC, the C_2 dumbbells having different directions. The CC$\sqrt{8}$ binding yields an occupation $N_C^{/P''} = 0.55$. In the present model the "multiple bond" between the C atoms is favoured by the correlative interaction with the Na cores. A feature not understood is the commensurability element $K''_{33} = 11$. The close homeotypism of NaC with $CaC_2 \cdot r$ is caused by the homeodesmism CC$\sqrt{8}$-CC2 which is requested by the greater valence electron contribution of Ca^2.

In KC_M occurs besides KC(NaC) a series of so called graphite compounds. The arguments from atomic radii R [namely $R(K) = 2.36\,\text{Å} \approx |a_1(C \cdot r)| = 2.46\,\text{Å}$] show that in KC_8 there are alternating K and graphite layers. These arguments are supplemented by the assumption of a HFH$\sqrt{12}$ binding (see Table 1) which affords additional stability. The compound KC_{16} (SR2.181) has not been confirmed, the cell belongs to KC_{24} which yields with $a_3 = 2(5.41 + 3.36)\,\text{Å}$ (see SR 18.339) 32 C atoms in graphite layers, 4 C in mixed layers, and 2/3 K atoms in mixed layers. The reason for this atom ordering may be taken from the above interpretation: If less K are in the graphite then, not only the a_3 distance of the atoms is enlarged but also the distance of the K in some layer (by $\sqrt{3}$) in order that a new favourable b correlation may be built up.

A^2C_M. Be_2C (CaF_2) obeys the *Zintl* rule with octet completion, so that a FC2 binding is formed. An outstanding structure of the present mixture class is $CaC_2 \cdot r$ (U1.2 drawing Ref.[5] p. 222) and a CC2 binding for the count $Ca^{2,8}C^{0,4}$ is formed. A NaC type cannot be formed as Ca^2 contributes more valence electrons than Na^1, also the CC$\sqrt{8}$ binding is no more possible, but CC2 is neighboured and just this is chosen by $CaC_2 \cdot r$. At higher temperatures the structure transforms to cubic symmetry so that the C_2 dumbbells are no more parallel. In MgC_2 instead of CC2 binding a HH2 binding seems to exist. This suggests for CaB_6 and YB_6 the CC2 binding $a = (4.15)\,Å = b_C(1.5) = c_C(3)$ which was partially found earlier[8c].

T^3C_M. For YC_2 and $LaC_2 \cdot r$ the $CaC_2 \cdot r$ type is stable so that these phases must be considered as homeodesmic with $CaC_2 \cdot r$. In ScC_M no $CaC_2 \cdot r$ type is stable, therefore the electron count might be different here. Under the assumption $Sc^{1,2}C^{0,4}$ comes in $ScC \cdot h$ a FF2 binding. This makes probable for Sc_4C_3 (Th_3P_4, B6.8, drawing Ref.[5] p. 326) the b correlation $a = b_B(2)$ which excellently fits to the B1 position of the Sc atoms; the c correlation may be $a = c_B(4)$ and suggests once more the electron count $Sc_4^{1,2}C_3^{0,4}$. From this proposal it becomes also clear why $ScC \cdot h$ (NaCl) is only a high temperature phase: at lower temperatures the b correlation gets less places (see Table 1). For $Sc_{15}C_{19}$ might applly a BU2 binding. The phase Y_3C (Fe_4N) may be stabilized by a $FB\sqrt{8}$ binding. La_2C_3 (Rb_2O_3, B8.12, drawing Ref.[5] p. 224) has a B1 position of La with inserted C_2 dumbbells, the structure is therefore remotely homeotypic to $CaC_2 \cdot r$ so that the electron count will be $La_2^{1,10}C_3^{0,4}$ and a BF2 binding becomes probable. It is satisfactory that the distribution of the outer electrons in Scandium namely $Sc^{1,2}$ is similar to the spectroscopic finding in the gas state $Sc^{2,1}$.

T^4C_M. From the previous interpretations comes a proposal for TiC (NaCl) which may be described as FF2C4 binding (see Table 1) so that three commensurable correlations contribute to the stability. This favourable binding[9b] explains on the one side the high melting point of TiC following the commensurability rule[7] and on the other side that no other phases have been confirmed in the mixtures T^4C_M. The correlation of C-valence electrons with Ti-d electrons corresponds to what is known as *Hägg*'s interstitial concept (radius quotient $r_C/r_T < 0.6$) (see [2]) but it gives to the subject a new look because of its connection with electron numbers and commensurabilities. Magnetic arguments in favour to this electron count have been reported by *Stadelmaier*[13].

T^5C_M. The phase VC (NaCl) has also a high melting point, but not as high as that of TiC because of the presence of C-vacancies which are caused by the fact that the c correlation cannot be fully occupied. Several L-homeotypes (L = lacuna) of VC have been found. $V_2C \cdot h$ (W_2C, drawing Ref.[5] p. 267) has a Mg type partial V structure with statistical distribution of C atoms; the binding may be FHH2, a forerunner of FF2. At lower temperatures $V_2C \cdot r$ (Fe_2N_1, drawing Ref.[5] p. 257) has been reported with the C positions ordered. Probably the c correlation is in those compounds decisive for the structure so that the number of C atoms per V atom is of strong influence on the structure.

Table 1

LiC.h(M ,SR27.126)
LiC(RbO,P2.2,SR32.233)3.655;5.440;4.833A=bB(1;1.5;1.3)=cC(√8;√18;4) phdE219 NE4.24
NaC(U8.8,SR22.220)6.756;12.688A=bC(2;4)=cC(√32;11) NE16,128
NaC64(H8.512,SR23.102)H9.82;56A=hdm KC8 NE2056
KC(NaC,SR22.220)7.58;14.69A=idm NaC
KC8(H4.32,SR18.339)H4.91;21.64A=bH(1;4)=cFH(√12;20) NE4,160
KC10(Wells)
KC24(H2.48,SR18.339)H2.45;17.54A=hdm KC8, |a_1|is only subcell
KC36(H1.36,SR18,339)H2.45;12.12A=hdm KC8
KC48(H2.96,SR18.339)H2.45;30.98A
KC60(H1.60,SR18.339)H2.45;18.84A
RbC8(KC8,SR18.339),RbC24,RbC36,RbC48,RbC60(SR18.339)
CsC8(KC8,SR2.181)H4.95;22.8A=idm KC8
CsC24(KC24,71Ec)H4.95;18.55A=hdm KC8
CsC36,CsC48,CsC60(Wells)

Be2C(CaF2,SR3.20)4.34A=bF(2)=cC(4) NE32,24
Mg2C3(H16.24,SR11.75)H7.45;10.61A
MgC2(ThC2?,SR11.74)5.55,5.03A=bHT(2;2.1)=cHT(4;4.2)
CaC2.h(FeS2?,SR26.87)5.880A=hdm CaC2.r
CaC2.r(U1.2,SR1.740)3.89;638A=bC(√2;2.25)=cC(√8;4.5) NE4,32
CaC2.i?(Z8.16,SR27.117)Z93.4°92.5°89.9°8.42;11.84;3.94A
SrC2.h(FeS2,SR9.136)6.25A=idm CaC2.h
SrC2.r(CaC2,SR2.275)4.12;6.69A=idm CaC2.r
BaC2.h(FeS2,SR9.136)6.57A=idm CaC2.h
BaC2.r(CaC2,SR2.275)4.41;7.07A=idm CaC2.r

Sc2C(htpNaCl ,71Ec)9.4A
Sc4C3(Th3P4,SR34.59)7.207A=bB(2)=cB(4) NE16,80
ScC.h(NaCl,Sr26.103)4.51A=bF(1)=cF(2) NE4,24
ScC.r(H10.10,SR23.81)H5.46;10.24A=bH(√3;3.3)=cFH(√12;8/3) NE10,60
Sc15C19(T30.38,SR37.59)7.50;15.00A=bB(2;4)=cU(4;10) NE30,212
Y3C(Fe4N,SR22.184)5.11A=bF(1)=cB(√8;2.8)
Y2C.h(NaCl,SR34.60)5.115A
Y2C.r(R2.1,SR34.61)H3.617;17.96A
YC2(CaC2.r,SR22.185,23.81)3.664;6.169A=bF(1;3/2)=cC(√8;4.7)
La2C3(Rb2O3,B8.12,SR22.186)8.803A=bB(2)=cF(4) NE16,256
LaC2.h(KCN,SR33.53)6.022A=hdm YC2
LaC2.r(CaC2.r,SR33.53)4.00;6.58A=idm YC2
CeC(NaCl,SR29.106)5.135A=idm ScC.h
Ce2C3(Rb2O3,SR32.120)8.448A=idm La2C3
CeC2(CaC2,SR32.118)3.875;6.477A=idm YC2

TiC(NaCl,SR1.74,19.87)4.33A=bF(1)=cF(2)=eC(4) phdHEM cmp
TiC2?(C1.2,SR27.136)3.13A
ZrC(NaCl,SR1.74,24.89)4.698A=idm TiC phdES cmp
HfC(NaCl,SR4.6,19.87)4.637A=idm TiC phd SM cmp
ThC(NaCl,SR27.134)5.346A
ThC2.r(N2.4,SR33.56)M103.12°6.692;4.223;6.744A
ThC2.h1(U1.2,SR33.56)4.221;5.394A
ThC2.h2(KCN,SR33.56)5.806A

V2C.h(W2C,SR18.100,30.40)H2.881;4.547A=bFH(1;2/3)=cH(2;3) phdM NE2.12
V2C.i(Fe2N1,O8.4,71Ec)4.567;5,742;5.037A=hdm V2C.h
V2C.r(Nb2C.r,71Ec)11.49;10.06;4.554A
V2C.ε(Fe2N0.9,seeNb2C.h1)
V4.C3(R4.3,SR35.110)H2.917;27.83A=bFH(1;11.7/3)=cFH(2;23.4/3) cmp
V6C5(H18.15 ,SR33.57)H5.09;14.40A=bFH(√3;6,3)=cFH(√12;12/3)
V8C7(C32.28,SR38.68)8.330A=idm VC

VC(NaCl,SR27.127)4.173A=bF(1)=cF(2)=eC(4)
Nb2C.h2(W2C,SR23.97)H3.128;4.974A=idm V2C.h phdM
Nb2C.h1(Fe2N0.9;Nowotny, Progr.Sol.State Chem.5.1971.27-70)
Nb2C.r(O8.4,htp Fe2N1,Sr32.507)10.920;4.974;3.090A
Nb4C3(V4C3,SR35.110)H3.14;30.1A=idm V4C3 cmp
NbC0.75(htp NaCl,SR34.58)4.445A=idm VC
NbC(NaCl,SR30.118)4.47A=idm VC
Ta2C(CdI2,SR30.40)H3.103;4.938A=idm V2C.h
Ta4C3(V4C3,SR35.110)H3.116;30.00A=idm V4C3
TaC0.75(htp NaCl,SR34.58)4.424A=idm VC
TaC(NaCl,SR30.118)4.45A=idm VC

Table 1 (continued)

Cr23C6(F23.6,SR38.60)10.650A=bFU(4;6/2)=cHT(8;9/2) NE=92,556 phdM
Cr7C3(H56.24,SR3.363)H14.01;4.532A(?seeSR38.62)
Cr7C3(Mn7C3,SR38.60)4.526;7.010;12.142A
Cr3C2(O12.8,SR34.56)5.533;2.829;11.472A=bFUK"/2=cFU(4;2;11.5/2) NE12,96
CrC.h(NaCl,58Hansen-Anderko)3.62?A=idm TiC
Mo2.1C(Fe2N1,SR28.15)4.724;6.004;5.199A=hdm Mo2C.h phdS149
Mo2C.h(W2C,SR2.240)H3.007;4.778A=idm W2C FHUH2
MoC0.6.h(H6.4,SR18.90)H3.008;14.63A=bFH(1;6/3)=cFHK'(2) NE6,46
MoC0.7.h(NaCl,SR26.101)4.28A=idm TiC FF2
W2C.h(H2.1,SR1.575)H2.99;4.72A=bFH(1;2/3)=cUH(2;3.5/2) NE2,14 phdS167
W2C.r(CdI2,SR24.97)H2.98;4.71A=idm W2C.h
W2C.m(Fe2N1, seeNb2C.h1)
W2C.ε(Fe2N0.9, seeNb2C.h1)H5.184;4.721A
W3C 2.h(NaCl,SR.27.141)4.27A=idm TiC FF2 NE4.31
WC(H1.1,SR26.105)H2.907;2.837A=bH(1)=cFH(2;2.4) NE1.9

Mn4C.h?(T48.12,SR21.76)7.66;10.57A phdM
Mn23C6(Cr23C6,SR21.76)10.585A=idm Cr23C6
Mn15C4.h
Mn3C.h(Fe3C,SR21.76)4.53;5,11;6.76A=bFU(1.75;2;3.5/2)=cFU(3.5;4;7/2) NE12,88
Mn5C2(N10.4,SR18.88)M97.75°5.086;4.573;11.66A
Mn7C3(O28.12,SR30.36)4.546;6.959;11.976A
TcC(NaCl,SR26.104)3.985A compos. uncertain
ReCM nic phdE226

Fe20C.m(U1.(1/20),SR17.90)2.84;2.98A=bB(1;1.05)=cB(2;2.1)
Fe4C(C4.1,SR20.64)3.878A needs confirmationSR23.88
Fe3C.m(O12.4,SR9.40)4.524;5.089;6.743A=bFUK"/2=cFU(3.5;4;7/2) NE12,100
Fe2C(H6.3,SR23.89)H4.767;4.354A=hdm Ni3C
Fe2C(O4.2,SR38.64)4.704;4.318;2.830A
Fe5C2(Pd5B2,SR31.30)M97.73°11.563;4.573;5.058A=hdm Fe3C
Fe7C3(Mn7C3,SR32.139)4.537;6.892;11.913A=hdm Fe3C
RuC(WC,SR24.92)H2.908;2.822A=hdm WC phdM
OsC(WC,SR24.92)H2.908;2.822A=hdm WC phdM

Co3C.i(Fe3C,SR6.178)5.09;6.74;4.53A needs conf.,Hansen Anderko
Co2C(CaCl2,O4.2,SR15.31)2.897;4.447;4.371A=bBK"/2=cB(3;2) NE4.40
RhCM nic
IrCM

Cu2C2(Heslop&Jones) from aqueous solution
Ag2C2(see Cu2C2)
Au2C2(see Cu2C2)

Ni3C(R6.2,SR22.82)H4.553;12.92A=bFHK"/2=cF'H(√13;12/3) NE18.186
Ni3C.i(Fe3C,SR6.170) needs confirmation
PdCM nic phdM
PtCM nic

ZnCM nic
CdCM nic
HgCM nic

B50C2(T50.2,SR38.39)8.722;5.080A=bFU(6;4.5/2) NE158,104
B4C(R12.3,SR9.154)H5.63;12.14A=bH(4;9)=cC̃H(4;18) NE144,90
Al4C3(R4.3,SR3.56)H3.330,24.89A=bFH(2;18/3)=cCH(2;36/3) NE72,114
GaCM nic
InCM nic
TlCM nic

SiC(ZnS,F1.1,SR11.226)4.358A
SiC(H6.6,SR11.228)H3.080;15.098A=bFH(2;12/3)=cC̃H(2;18/3) NE48,60
many further homeotypes
GeCM nic
SnCM nic
PbCM nic

CN(gas), CPM nic, CAsM nic, CSbM nic, CBiM nic

Table 1 (continued)

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C3O2(SR29.290)
CO(C4.4,SR2.13)5.64A=bC(4)=cF(4)
CO2(FeS2.h,SR1.226)5.64=bC(4)=cF(4)
CS2(liquid,SR18.604,22.601)
CSeM nic, CTeM nic, CPoM nic

CF(H   ,SR3.228)
C4F(H   ,SR11.212)
CF4, and many additional gasous compounds
CCl4, and many additional gasous compounds
C6Br6(gas,SR24.648)
C2I4(gas,SR17.613)
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V_4C_3 (R 4.3) may have the FF 2 binding because of its congruent melting point. V_6C_5 (H 18.15) has to $V_2C \cdot h$ the commensurability $a = a_{V2C \cdot h}$ $(\sqrt{3}; 3)$. The FF 2 binding of V_4C_3 is probable here also. All other phases of T^5C_M are isodesmic to VC_M phases, i.e. of homeotypic binding.

T^6C_M. The fact that $CrC \cdot h$ (?), $MoC_{0.7} \cdot h$ and $W_3C_2 \cdot h$ have been reported as NaCl structures confirms the electron count $Cr^{1.5}C_M^{0.4}$ in analogy to VC_M. The structure of $Cr_{23}C_6$ (F 23.6, drawing Ref.[5] p. 259) is homeotypic to the Cu structure $a = a_{Cu}(3)$, but it is overfilled by 8 Cr atoms per cell. The C are formally substituted, but considering the inhomogenous deformation they are 8-coordinated. The b correlation $a = b_C(5)$ gives $N_{P'}^{/C} = 125$ b places per cell, and the c correlation $a = c_F(5)$ gives $N_{P''}^{/C} = 500$, so that 625 places are offered for 648 electrons. The observations $Mn_{23}C_6$ ($Cr_{23}C_6$, SR 3.60) and $Mo_2Fe_{21}C_6$ ($Cr_{23}C_6$, SR 3.60) clearly uncover the fact of *Hund* insertion[7], since only in connection with this effect the phases may be considered as isolectronic. Therefore it may be assumed that also in $Cr_{23}C_6$ some *Hund* insertion is present so that not all c electrons need have a place. Since the CF 1 binding is a filled homeotype of the FF 2 binding the relation to the previous FF 2 bindings is obvious, but the previous relation $a_{VC} = c_F(2)$ is here different: $a_{Cr23C6} = c_F(5)$. Another proposal would be the FUHT 2 binding of Table 1.

The structure of Cr_3C_2 (O 12.8, drawing SR 34.58) is commensurable to NaCl: $a_{Cr3C2} = (5.5; 2.8; 11.5)$ Å $= a_{NaCl}$ (—1, 0.5, 0; 1, 0.5, 0; 0, 0, 3). From this commensurability follows a c correlation $a_{Cr3C2} = c_{FU}$ (4; 2; 11.5/2) providing just $N_{P''}^{/C} = 92$ places and permitting on the basis of a FF 2 binding $N_{P'}^{/C} = 11.5$. The 4 C vacancies (as compared with the NaCl type) evidently have to do with the shifts of the Cr atoms in Cr_3C_2 as compared to NaCl. It must be assumed that the possibility of a FF 2 binding stabilizes the phase.

The structure of Cr_7C_3 (O 28.12) is commensurable to the Fe_3C type, this may be seen by comparing the drawings SR 38.61 and Ref.[5] p. 253: with $a_{Cr7C3} = (4.5; 12.1; 7.0)$ Å follows $a_{Cr7C3} = a_{Fe3C}$ (1; 2.5; 1). This homeotypism does not refer to the particular coordinations but to the cell as a whole. Transscribing the *c* correlation yields $a_{\mathrm{Cr7C3}} = c_{\mathrm{FU}}$ (3; 8; 6.5/2) with $\mathrm{N}_{\mathrm{P}''}^{/\mathrm{C}} = 156$; from this may be built a CF1 binding with 195 places so that the CF1 binding appears to be related to the structure when allowance is given for the *Hund* insertion.

The NaCl type phases $\mathrm{MoC}_{0.7}\cdot\mathrm{h}$ and $\mathrm{W_3C_2}\cdot\mathrm{h}$ yield the FF2 binding, although this binding is favourable the phases are only stable at high temperatures since the array of atoms is somewhat irregular because of the vacancies. If all octahedral interstices of $\mathrm{W_3C_2}\cdot\mathrm{h}$ are occupied for instance in WC, then there are too few valence electrons per core electron for the FF2 binding; therefore a HFH2 binding is formed. This binding causes a change of the stacking mode of the hexagonal W layers as compared to $\mathrm{W_3C_2}\cdot\mathrm{h}$. If there are more vacancies than in $\mathrm{W_3C_2}\cdot\mathrm{h}$, then instead of the *b* correlation the *c* correlation will be strained (see Table 1) which once more influences the stacking mode of the W partial structure. It becomes apparent, that the structures of the stable phases are closely related to the binding. The character of interstitial structures is conserved in MoC_M and WC_M while in CrC_M also substitutional structures occur, because of the smaller atom radius.

T^7C_M. $\mathrm{Mn_{23}C_6}$ ($\mathrm{Cr_{23}C_6}$) is as has been mentioned before a R-homeotype of Cu with interstitial atoms but $\mathrm{Mn_3C}\cdot\mathrm{h}$ ($\mathrm{Fe_3C}$) is a RI-homeotype of Cu (R = replacement, I = inhomogenous deformation) without interstitial atoms. The critical point is the electron count. From the isotypism $\mathrm{Mn_{23}C_6}$–$\mathrm{Cr_{23}C_6}$ becomes clear that *Hund* insertion plays a role. The phase $\mathrm{Mn_3C}$ ($\mathrm{Fe_3C}$, drawing Ref.[5] p. 253) may have the electron count $\mathrm{Mn}_3^{1,6}\mathrm{C}^{0,4}$ leading to $\mathrm{N}_{\mathrm{V,C}}^{/\mathrm{C}} = 12{,}88$. The *c* correlation is fundamental and may be $a = c_{\mathrm{FU}}$ (3.5; 4; 7/2), yielding $\mathrm{N}_{\mathrm{P}''}^{/\mathrm{C}} = 98$. If a FF2 binding is assumed then $\mathrm{N}_{\mathrm{P}'}^{/\mathrm{C}} = 12$, which fits well. The characteristic atom position permits *Hund* insertion, the most filled *c* correlation occurs in $\mathrm{Ni_3B}$.i (SR 22.58) which is compatible with the above electron place numbers. The *b* correlation may be changed so that even $\mathrm{Pd_3P}$ (SR 24.203) is compatible with the binding.

T^8C_M. For Fe·r the binding may be assumed as $a = 2.86\,\text{Å} = b_{\mathrm{B}}(1) = c_{\mathrm{B}}(2) = e_{\mathrm{C}}(4)$. If C enters interstices of Fe·r (B1) then the C valence electrons will populate the *c* correlation conforming to the previous interpretations. Since 5 atomic percent C in $\mathrm{FeC}_{.05}$ (martensite) increase the axial ratio $|a_3|/|a_1|$ by 5% (SR 17.91) it is obvious that 1 C atom ($\mathrm{N}'_{\mathrm{C}} = 0.33$) affords approximately one more layer of the *c* correlation per cell. It must therefore be understood that C may stabilizes the *c* correlation, and this explains the observation[2b] that even small C mole fractions may stabilize a new structure. It is known that also nitrogen martensites occur (see Ref.[5] p. 256) and that these fit into the present interpretation. For Fe·h_1 (F1) applies $a = b_F(1) = c_F(2)$ (cf.[10]) so that up to 1 C could be solved in the cell, really only less than 0.5 C is solved in order to avoid the occupation 1.00 of the c correlation.

The Fe_3C (O12.4) structure is as has been mentioned above a RI-homeotype of Cu(F1) and the R-homeotypism is of the Cu_3Au type (drawing Ref.[5] p.253). The electron distance d_C (Fe·r) $= 1.24$ Å suggests a FF2 binding for Fe_3C like as in Fe·h_1. The commensurability element $K''_{33} = 8$ indicates a fairly strong compression of the c correlation in the a_3 direction. This must be interpreted as caused by some *Hund* insertion: the c correlation is no more isometric and isotypic to the F type but more to a CuAu type which permits shorter distances of electrons with different spin. The compounds Fe_5C_2 and Fe_7C_3 are homeotypic[11] to Fe_3C and therefore also homeodesmic.

T^9C_M. The phase Co_2C ($CaCl_2$) is a D-homeotype (D = deformation) of TiO_2 (T2.4, drawing Ref.[5] p.275) and permits a BB2 binding. From the electron numbers *Hund* insertion must be present, and this will be responsible for the orthorhombic deformation; also the b correlation could be a little different from the B type and thus cause the deformation.

$T^{10}C_M$. While Fe_3C is a RI-homeotype of a Cu structure, in Co_2C and Ni_3C a Mg type T partial structure is supplemented by inserted C atoms. A FF′2 binding appears acceptable, where F′ indicates some *Hund* insertion.

$B^{1..2}C_M$. No compounds have been structurally described. Although much place in interstices is provided for C insertion, it appears that a d^{10} core with its B correlation[7] is not inclined to make a common correlation together with the C atoms at sufficient high temperatures.

B^3C_M. For B·r(R12) has been given the binding[8e] $a = H4.9; 12.6$ Å $= b_H(\sqrt{12};9)$, it is therefore satisfactory that for B_4C also a H binding is acceptable. The c correlation is less certain and may be left open.

The phase Al_4C_3 (R4.3, drawing Ref.[5] p.185) obeys the extended *Zintl* rule. The stacking of the Al is in *Zhdanov* notation[12] $(31)^3$ and the stacking of the C is $(21)^3$. The FC2 binding of Al_4C_3 is also acceptable to AlN (ZnO, H2.2, SR1.79): $a = H3.12; 4.99$ Å $= b_{FH}(2;4/3) = c_{CH}(2;8/3)$, it is therefore satisfactory that a series of $Al_4C_3\,(AlN)_n$ ($n = 0, \ldots, 4$: SR31.5) phases exists. By the correlations certain electric multipoles are caused at the atoms, these multipoles determine the stacking sequence of the structure. In Al_4C_3 come on 7 atom layers just 6 b correlation layers. This reminds somewhat to the rule for Cu_3Au shear homeotypes that an atom shear occurs just when 1 electron layer more or less than atom layers occurs[5].

CB^4_M. In the compound SiC which is homeodesmic to Al_4C_3 there occurs a phase SiC (ZnS, F1.1) but the most frequent type is SiC (H6.6). Clearly the FC2 type is possible (Table 1) but the suspicious frequency of the H6.6 type leads to the assumption, that the c correlation is not exactly of the CH type but of a hexagonally strained CH type (named $\tilde{\mathrm{C}}$H) so that the occupation of the c correlation is increased: $a_{\mathrm{H6.6}} = \mathrm{H}3.080;\ 15.098\,\mathrm{Å} = b_{\mathrm{FH}}\ (2;12/3) = c_{\tilde{\mathrm{C}}\mathrm{H}}\ (2;18/3)$. This assumption would immediately explain why in chemically pure SiC different stacking homeotypes may occur: if the phase has a little off-stoichiometry then the c correlation is strongly changed so that different stacking homeotypes will occur. This assumption could also explain why AlN is of the ZnO type: when the binding would be $a = b_{\mathrm{FH}}\ (2;4/3) = c_{\tilde{\mathrm{C}}\mathrm{H}}\ (2;6/3)$ then the number of c correlation places would be $\mathrm{N}^{/\mathrm{C}}_{\mathrm{P''}} = 24$ and the occupation $\mathrm{N}^{/\mathrm{P''}}_{\mathrm{C}} = 0.83$, a very frequent value.

$CB^{5..7}_M$. Several compounds are found. The best known are CO and CO_2 with cubic structures in which a b_{C} valence electron correlation may be assumed. However, most compounds are known in the gasous state.

Three component carbides. Carbides with more than one T component, not homogeneously connected to a carbide with one T component have been named "complex carbides" by *Nowotny*[2b], and the influence of octahedral or prismatic T_6C structural units has been discussed. It is a consequence of the interstitial filling property of the C atoms that many three component carbides may be classified by two component metallic structures which are filled.

A F-homeotype (F = filling) of Cu is Fe_4N (C4.1, SR1.487). A R-homeotype (R = replacement) of Fe_4N is for instance the F-homeotype of Cu_3Au[13]. It consists like the Cu type (see Ref.[5] p. 77) of different subtypes which have different bindings. The first subtype is described by the cummulative formula $\mathrm{T}^{3..4}_3\mathrm{B}^{3..4}\mathrm{C}$ (see [2b, 13]). The binding may be $a = b_{\mathrm{F}}(1) = c_{\mathrm{F}}(2)$. The second subtype has the cumulative formula $\mathrm{T}^{7..10}\mathrm{B}^{2..4}\mathrm{C}$ (see[2b]) and may have the binding $a = b_{\mathrm{F}}(1) = c_{\mathrm{B}}\ (\sqrt{8};2.8)$ which must be twinned. The valence electrons of C take part in the c correlation therefore C is inserted into the T octahedron. To the binding gap c_{F}–c_{B} there corresponds a chemical gap: $\mathrm{T}^{5..6}\mathrm{B}^{2..4}\mathrm{C}$ do not exist. In view of the fact that in the second subtype the cubic symmetry is formed thanks to twinning of the c correlation it is satisfactory that the tetragonal C-homeotype Cr_3AsN (U6.2.2, SR33.28; Ref.[13]) has been found with the binding $a = 5.36;\ 8.07\,\mathrm{Å} = b_{\mathrm{FU}}\ (2;4.2/2) = c_{\mathrm{B}}\ (4;6)$ having no more fractional commensurability elements in the c correlation. The binding fits to the electron numbers $\mathrm{N}^{/\mathrm{C}}_{\mathrm{V,C}} = 20{,}132$ if it is assumed that few As^5 electrons descend to the c correlation. F-homeotypes of CuAu are not possible as the T-octahedral surrounding of C is no more possible.

While the last subtype with FB $\sqrt{8}$ binding belongs to the Cu family of metallic structures there are types belonging to the BB2 binding of CuZn. The CsCl type is not appropriate for C insertion, but the Mn $\cdot$ h_1 (C20) type which occurs in brass like alloys also at $N_V^{/A} = 1.5$. For Mo_3Al_2C (C12.8.4, htp Mn $\cdot$ h_1, SR28.42) a binding homeotypic to that of the UU2 binding of $Ag_3Al \cdot r$ (Ref.[15]) is found: $a = b_B$ $(\sqrt{5}; 2.2) = c_B$ $(\sqrt{20}; 4.4)$.

A Mg type of metal packing displays Cr_2AlC (H4.2.2, SR28.3; Ref.[16]) although the stacking sequence BT(C)TBT(C)T leaving out (C) is not stabilized as a metallic phase for metric reasons. The cummulative formula is $T^{3..6}B^{2..6}C$ (Ref.[2b]). Assuming the electron numbers $N_{V,C}^{/C} = 6{,}48$ the binding may be accepted: $a_{Cr2AlC} =$ H2.866; 12.82 Å $= b_{FH}$ $(1; 6/3) = c_{FH}$ $(2; 12/3)$. It is clear that in these H4.2.2 phases the electron concentrations is not quite certainly to be assessed as it is unknown how many valence electrons descend into the c correlation. Making use of *Ekman*'s rule[5], that the descent is often small, the number of valence electrons per metal atom is near to one, like as in the C3.1.1 phases. The number of metallic core electrons per atom is probably smaller than in the core electron reach subtype of C3.1.1, therefore the c correlation is of the FH type.

A three component carbide S-homeotypic (S = shear) to H4.2.2 has been found in Ti_3SiC_2 (H6.2.4, SR32.46; Ref.[17]) just as for brasslike alloys S-homeotypes of the Mg type of $CuZn_4$ occur. The electron number may be assessed $N_{V,C}^{/C} = 8{,}56$ so that the binding might be $a =$ H3.068; 17.669 Å $= b_{\tilde{U}H}$ $(1; 8/2) = c_{\tilde{U}H}$ $(2; 16/2)$ where ŨH is a strongly compressed UH type which was for instance found in Zn: $a =$ H2.665; 4.947 Å $= b_{\tilde{U}H}$ $(\sqrt{1.33}; 3/2) = c_{\tilde{U}H} K'(2)$. The binding is homeotypic to the previous bindings and this opens the opportunity to choose appropriate series of mixed crystals and study the dependence of structures on electron concentrations.

For Mn_5Si_3 (H10.6, drawing Ref.[5] p. 306) the electron count $Mn^{0,7}Si_M^{4,8}$ conforms to the previous counts so that $N_{V,C}^{/C} = 24{,}118$ and the analysis affords the binding $a_{Mn5Si3} =$ H6.91; 4.81 Å $= b_{BH}$ $(2; \approx 6/3) = c_{BH}$ $(\sqrt{12}; 12/3)$. While the BB2 binding (say of the Mn $\cdot$ h_1-carbides) has $N_{P''}^{/P'} = 8$ places of the c correlation per place of the b correlation, the present BHBH $\sqrt{3}$ binding has only $N_{P''}^{/P'} = 6$, so that a Mn_5Si_3 structure with this binding cannot occur in brass like phases. According to *Nowotny*, F-homeotypes of Mn_5Si_3 obey the cummulative formula $T^{4..6}B^{3..5}E^{3..6}$ (where E is an element of the Li period) and this is compatible with the present interpretation.

The type of Re_3B (Q6.2, SR24.73) may be considered as a homeotype of CrB: $a_{\mathrm{Re3B}} = 2.890; 7.258; 9.313\,\text{Å} = a_{\mathrm{CrB}}\,(1; 2; 1)$. In the layers perpendicular to a_3 with support number 1 additional C or N atoms may be inserted.

For Ti_2Ni (F16.8, SR23.195) the electron count $\mathrm{Ti}_2^{4,8}\mathrm{Ni}^{0,10}$ may be assumed which is compatible with a FB2 binding $a = b_{\mathrm{F}}(4) = c_{\mathrm{B}}(8)$ (see[13,18]). The phase $Ti_4Zn_2C_x$ (F htp Ti_2Ni) may have a similar binding with $a = b_{\mathrm{C}}(4) = c_{\mathrm{F}}(4) = e_{\mathrm{B}}(8)$ where the C electrons take part in the c correlation for Ti electrons of presumable atomic vacancies. It becomes apparent, first, that the electron count is here fairly difficult and second, that to one and the same structural type may belong different bindings.

Discussion

To get an overview, in Table 2 the outstanding structure types for two component carbides are collected. The carbides of B^n elements have a valence electron concentration $N_{\mathrm{V}}^{/\mathrm{A}} > 2$ while all other carbides have $N_{\mathrm{V}}^{/\mathrm{A}} < 1$. Therefore the valence electron concentration is not appropriate here for classification purposes. The core electron concentration $N_{\mathrm{C}}^{/\mathrm{A}}$ is also not very appropriate since in A^nC_M and T^nC_M the electron count is different. However, for the typical T^nC_M compounds an increase of $N_{\mathrm{C}}^{/\mathrm{A}}$ with n is sensible. The most important binding is the FF2 binding which stabilizes for $M = 1$ the frequent NaCl type but for other compositions other structures may be stabilized. A remarkable feature is given by the fact that FHH2 and HFH2 bindings may replace the FF2 binding when the b and c correlations do not fit well enough together. The BB2 binding is rarer than in brass like alloys. Also the CC2 binding is rare although it stabilizes the important $CaC_2 \cdot r$ structure. The acetylides (percarbides) have a c_{C} correlation (or c_{H}), probably the A^n core requests it. The HH2 binding of MgC_2 is closely homeotypic to the CC2 binding.

It becomes clear from Table 2 that the manifold of bonding types (bindings) is smaller than the manifold of crystals structure types. Therefore the bindings are an appriopriate means for the classification and systematics of carbides and they indicate whether a phase is formed or not, i.e. the bindings represent a first valence model for carbides.

Several critics have suggested that a binding proposal could be made for any, also wrong, structure; others have blamed that not for all phases a proposal has been found. We avoid these extremes and consider the general necessity to analyse the binding.

Table 2. *Several structural types of two component carbides*

phase (type)	bonding type	$N_V^{/A}$	$N_C^{/A}$	$N_C^{/A}/N_V^{/A}$
LiC(RbO,P2.2)	BC√8	0.50	3.00	6.00
NaC(U8.8)	CC√8	0.50	6.00	12.00
KC8(H4.32)	HFH√12	0.11	4.44	4.00
Be2C(CaF2)	FC2	2.67	2.00	0.75
MgC2(ThC2?)	HTHT2	0.67	5.33	7.96
CaC2.r(U1.2)	CC2	0.67	5.33	7.96
Sc4C3(Th3P4)	BB2	0.57	2.88	5.01
ScC.r(H10.10)	HFH2	0.50	3.00	6.00
Sc15C19(T30.38)	BU2	0.44	3.12	7.09
Y3C(Fe4N)	FB√8	0.75	2.50	3.33
La2C3(Rb2O3,B8.12)	BF2	0.40	6.40	16.00
TiC(NaCl)	FF2C4	0.50	3.50	7.00
V2C.h(W2C.h)	FHH2	0.66	4.00	6.06
V4C3(R4.3)	FF2	0.57	4.00	7.02
Ta2C(CdI2)	FHH2	0.67	4.00	5.97
Cr 23C6(F23.6)	CF1	0.79	4.79	6.06
Cr3C2(O12.8)	FF2	0.60	4.60	7.67
MoC0.6.h(H6.4)	FF2	0.62	4.62	7.46
WC(H1.1)	HFH2	0.50	4.50	9.00
Fe3C(O12.4)	FF2	0.75	6.25	8.33
Co2C(CaCl2,O4.2)	BB2	0.67	6.67	9.95
B4C(R12.3)	HCH1	3.40	2.00	0.59
Al4C3(R4.3)	FC2	3.43	5.43	1.58
SiC(H6.6)	FHCH1	4.00	5.00	1.25
CO(C4.4)	CF1	5.00	2.00	0.40

The system of atomic radii, the rules of present day crystal chemistry for coordination and atomic interaction, have been found by efforts to build a systematics of experimental findings. Since electron spatial correlation is without any doubt real, there must be an influence of electron correlation on phase stability and structure. Therefore the task for the crystallographers emerges to analyse the type and commensurability of the electron spatial correlations. The two-correlations model is an attempt to approach this task.

A priori it is not clear how the different electron shells combine to form a spatial correlation. Only the success of the analysis may provide probability to one assumption or the other. The present analysis makes probable that the valence electrons of C form a spatial correlation not with the valence electrons of the T atoms but with their peripheral d electrons. This assumption is a remarkable supplement to the well known concept of interstitial structure occurring in carbides, since it explains why interstitial structures occur with T atoms but not with B^n atoms of comparable atomic radius. It becomes apparent here that two spatial correlations are necessary for finding an appropriate energetical insight. The earlier chemical models considered the influence of the core electrons on bonding as an electrostatic potential, but by this assumption all the interactions of these electrons go lost which are described here by the concept of commensurability. By the consideration of the correlative property of the core electrons a further degree of freedom enteres crystal chemical argumentation, and since this degree appears necessary for the systematics it must be concluded that the assumed property is real. In fact many problems of stability find an answer by the facilities of the model: Why occur acetylides only with $A^{1..3}$ components? Under the protection of the valence electron correlation supported only by the A atoms a *c* correlation establishes which favours C dumbbells. Why have TiC and its isotypes such a high melting or decomposition temperature? The electron numbers and electron distances allow a FF2C4 binding which is energetically very favourable and causes, following the commensurability rule, the stability of the structure against that of the melt. Why is the sequence of the W layers in the phases of the mixture WC_M of the types Mg (H2), Cu (F), and H1 for increasing mole fraction of C? With increasing mole fraction N'_C the number of electrons in the *c* correlation increases, but the commensurability of the *c* correlation in the hexagonal basal plane is conserved, therefore the commensurability in the direction perpendicular to the basal plane is changed and causes the change of the stacking sequence. Why occurs in the compound SiC also for great purity the phenomenon of polytypism? Under the protection of the *b* correlation develops a *c* correlation which is sensitive to very little deviations of stoichiometry which cannot be ruled strictly because of small local variations of the mole fraction. This interpretation poses the problem to find the connection between stacking sequence and small non-stoichiometry in SiC crystals.

By these examples the close correspondence of the model to the experimental findings becomes apparent. This is a first indication for the usefulness of the model. Another indication is, that the interpretations of the model should have a high degree of probability. This condition is approximated the more the better extended the interpretation is, because an extended interpretation yields many new rules and the rules make a proposal more probable. At the present state certainly mistakes may be contained in the Table 1. They will be found by preparing more interpretations for instance of nitrides, or oxides, and by finding more rules.

A usefulness is to be attributed to the two-correlations model also because of its heuristic abilities. Many suggestions for experiments emerge during the search for the binding, and such experiments are frequently helpful for the development of the model.

Note at proof reading: Analysis of binding in nitrides and oxide suggested in contrary to above assumptions electron counts $Al_4^{3,8}C_3^{0,4}$ and $Si^{4,8}C^{0,4}$.

Appendix: Short Review of Notation and Analysis Method

Phase designation by chemical symbols in the sequence of the homologous classes A^1 (alcali 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 phase, l = low temperature phase, p = high pressure phase, m = metastable phase, i = impurity stabilized phase.

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 is given by SR 1.1 = Structure Reports A Vol. 1, page 1. References for phase diagram (phd) are contained in *Hansen, Elliott, Shunk, Moffatt.* Few references are for *Eckerlin* or *Wells.*

Correlation kinds: As a, b, c correlation are designated 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. Non isometric correlation $\tilde{U}$: a H layer is stacked with distance $d_H/\sqrt{2}$. *Hund* insertion: into the octahedral holes of a b_F correlation with spin up several spin down electrons are inserted.

Matrix notation: $a_{iL} = (a_{11}, a_{12}, a_{13}; a_{21}, s_{22}, a_{23}; a_{31}, a_{32}, a_{33})$ 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 $M\beta°$ 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 $b = (2, 1, 0; -1, 2, 0; 0, 0, 1)$ may be written as $(\sqrt{5}; \sqrt{5}; 1)$ or even shorter

($\sqrt{5}$; 1). 5 is the determinant of b and a rotation matrix is omitted, further values of whole numbered determinants are collected in [Struct. Bond. 33 (1977) 139-177].

Commensurabilities: Names of commensurability matrices: $b^{-1}a =: K'$, $c^{-1}a =: K''$. An equation $a = b K' = c K''$ is named a bonding classification or *binding*. A quotient $a_{\mathrm{L}}^{-1} a_{\mathrm{L}'} =: K$ is a homeotypic commensurability between the lattices L and L′.

Derived properties: $\mathrm{N}_{\mathrm{A}}^{/\mathrm{C}}$, $\mathrm{N}_{\mathrm{V}}^{/\mathrm{C}}$, $\mathrm{N}_{\mathrm{C}}^{/\mathrm{C}}$, $\mathrm{N}_{\mathrm{P}}^{/\mathrm{C}}$ = number of atoms, — valence —, — core electrons, a places, per a cell. $\mathrm{N}_{\mathrm{V}}^{/\mathrm{A}}$, $\mathrm{N}_{\mathrm{P}'}^{/\mathrm{A}}$, $\mathrm{N}_{\mathrm{P}''}^{/\mathrm{A}}$ = number of valence electrons, b, c places per atom. d_b, d_c = smallest distances in b, c correlation. In this Tables 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, NE = numbers of electrons.

How to find a binding: Draw as abscissa the mole fraction $\mathrm{N}_2' = 0, \ldots, 1$ 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 $\mathrm{N}_2' = 0$ the values of $d_b(0)$, $d_c(0)$ of the first component, and for $\mathrm{N}_2' = 1$ 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 cited also in J. Less-Com. Met. 70 (1980) 167-180. For an empirical compound assume $d(\mathrm{N}_2')$ 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 above reference. The proposal with best fit to the rules is the probable binding.

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