On the bindings in $AC_{\underline{M}}$ phases

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Abstract

The earlier assumption of a common band of the valence electrons in carbides ($AC_{\underline{M}}$ phases) is replaced by an electron count distributing the valence electrons on different bands. The count was used successfully in the binding analysis of oxides and nitrides. Carbon gives its C2sp electrons into the $\underline{c}$ correlation of the peripheral closed noble gas shell of the cations. If energetically below that shell there is a d or f shell, it may also take part in the $\underline{c}$ correlation since these shells possess a high compliance to shift of electrons. Using these assumptions an improved attribution of bonding types (bindings) to the observed carbides may be established. The binding indicates electron correlations being favourable for stability and allowing to assess also structural features. In $A^{1}C_{\underline{M}}$, subcarbides or Lewis carbides are not to be expected, only supercarbides become stable. A supercarbide "KC_{16}" is not found because of the anisotropy of the $\underline{b}$ correlation. MgC_2 is heterotypic to $CaC_2.r$ conforming to the site number rule for the $\underline{c}$ correlation. The subcarbide $V_2C.h$ has a low axial ratio caused by the low electron offer, its stacking sequence is caused by electrodipoles induced by the binding. The striking heterotypism $V_2C.h-Cr_{23}C_6$ is an indication for the transition from a C to a B type of binding. Typical representatives of this binding are contained in the Fe_3C family. The basic phases of the compound SiC are stabilized by an excitation of electrons from the $\underline{b}$ correlation causing their observed stacking. The heterotypism $Mn_3GeC(U6.2.2)-Mn_3AlC(C3.1.1)$ is a consequence of the electron numbers.

Introduction

The crystal structures of the two-component carbides (AC_M phases) are generally quite simple, but since the times of Hägg 1931 only few energetical arguments to explain the stability of the phases have emerged. Recently it has been shown that a small number of simple assumptions (plural correlations model 83Sch, 86Sch) leads to new stability rules allowing to understand many crystal chemical facts. The constitutional and structural data of AC_M phases have been reviewed by 34Sta,58Han,63Kie,63Now,64Sch,67Gol,67Sto,69Rud,70Par,71Eck,71Now,71Tot,72 Now,72Pea,73Hol,73Now,78Mof,84Hol,85Vil,86Mas. In an earlier attempt to find energetical arguments in form of bonding types (bindings) for carbides (82Sch) several bindings were correctly or nearly correctly found (for instance for Be_2C,TiC), but the electron count used turned out to be not quite satisfactory so that changes became necessary. In the following, an improved proposal for the bindings in the carbides is presented. Once more it cannot be expected that it never will be furthermore improved. When the understanding of bindings grows, changes of proposals must occur, however, an improved proposal is frequently homeotypic to the earlier one and may be considered as a kind of consequence of the earlier proposal with respect to the new crystal chemical rules. The trial and error process of binding analysis is rewarding since the results provide a first insight into the causes of stability and suggest various problems for later calculations. After much thinking on electron density in recent years the consideration of electron pair density appears desirable. For symbols used in the following analysis see 64,83,86Sch.

Analysis

LiC(RbO,P2.2,Structure Reports 32.233) is a supercarbide, it has an orthorhombic body centered (P) cell $\underline{a}$ with 2 atoms of each component in the primitive subcell. The Li are in a site set of the cubic primitive type with one atom in the cubic primitive cell (Li_{C1}), compressed in $\underline{a}_1$ direction of the P cell, and obeying the commensurability $\underline{a}=\underline{a}_{C1}(1,0,-1;0,2,0;1,0,1)$. C_2 atom-couples directed along $\underline{a}_3$ are placed in each second hexahedral hole so that LiC is homeotypic to CaF_2 with C_2 in Ca sites and Li in F sites. LiC does not obey Lewis' rule of compensation of electron spins in C_1 by spins of Li. The mole fraction of a Lewis phase $\underline{N}_C^-=0.2$ would be too small for stability. In the observed phases having $\underline{N}_C^->0.2$ (supercarbides), spins must be compensated between the C atoms so that C_2 dumbbells are formed, described as $(C\equiv C)^{2-}$. The expected electron distances (83Sch) suggest the electron count $Li^{1,2}{}_C0,4$, so that the electron numbers per cell, $\underline{N}$, and the binding may be $\underline{a}(\underline{N}=4,24)=3.66;5.44;4.82\overset{R}{=}\underline{b}_B(1;\sqrt{2};\sqrt{2})=\underline{c}_B(2;2\sqrt{2};2\sqrt{2})$. $\underline{b}$ is the cell of the correlation of the valence electrons of Li, being of a (deformed) body centered cubic type (B), and $(1;\sqrt{2};\sqrt{2})$ is its

commensurability matrix to the $\underline{a}$ cell in an abbreviated notation (83Sch). The valence electrons of C, together with the core electrons of Li form the $\underline{c}$ correlation being also $c^{\mathfrak{f}}$ the (deformed) B type. The deformation is caused by the shape of C_2, and the low occupation of $\underline{c}$ with site number $\underline{N}_{\underline{c}}^{/\underline{a}}{=}32$ lets open whether $\underline{b}$ is solved in $\underline{c}$ so that a collective binding $\underline{a}{=}(\underline{b}{\cup}\underline{c})_B 2(1;\sqrt{2};\sqrt{2})$ is formed. The full spin compensation, i.e. + spins are neighbouring to - spins, is warranted by the B type of the correlation.

LiC.h(M , SR27.126) shall not be discussed here, and for $LiC_8, LiC_{12}, LiC_{18}$ see 73Hol.

NaC(U8.8,SR22.220) is heterotypic to LiC, it has a tetragonal body centered cell (U, with 8 atoms of each component in the primitive subcell) and a Na_{Cl} site set with $\underline{a}{=}\underline{a}_{Cl}(2;4)$. The spin-coupled C_2 dumbbells have not all the same direction. $\underline{a}(\underline{N}{=}16,192){=}6.76;12.69\text{Å}{=}\underline{b}_C(2;4){=}\underline{c}_B(4;7)$. The $\underline{c}$ correlation provides $\underline{N}_{\underline{c}}^{/\underline{a}}{=}224$ sites per $\underline{a}$ cell so that $\underline{b}$ may be solved in $\underline{c}$ and the binding may be considered as collective $\underline{a}{=}(\underline{b}{\cup}\underline{c})_B(4;7)$. The odd commensurability element 7 generates momentary dipole vectors in $\underline{a}_3$ direction that may be the cause for the variing direction of the C_2 dumbbells.

NaC_{64}(H8.512,SR23.102,drw ibid.) is an extreme super-carbide named a C.r (graphite) compound, $\underline{a}{=}\underline{a}_{C.r}(4;8)$. After 8 graphite layers parallel to $\underline{a}_1,\underline{a}_2$ with 32C per cell comes a Na layer with 4 Na per cell. From the bindings of C.r and Na, $\underline{a}$(C.r,H4,$\underline{N}{=}16,8){=}$H2.46;6.70$\text{Å}{=}\underline{b}_{FH}(\sqrt{3};5.8/3){=}\underline{c}_{CH}(\sqrt{3};11.5/3)$ and $\underline{a}$(Na,B1,$\underline{N}{=}2,16)$ $=4.29\text{Å}{=}\underline{b}_B(1){=}\underline{c}_C(4)$ (82Sch) follows that the $\underline{b}_{FH}$ correlation of C.r and the $\underline{c}_C$ correlation of Na may form a common $\underline{c}_{FH}$ correlation in NaC_{64} when the distance $\underline{d}_c$ (Na) is strongly strained: $\underline{a}(\underline{N}{=}8,2112){=}$H9.82;56.00$\text{Å}{=}\underline{b}\underline{x}_{FH}(1;8/3){=}\underline{c}_{FH}(\sqrt{48};48/3)$. The strain of $\underline{d}_c$(Na) may be the reason for the observation that "NaC_8" homeotypic to KC8 does not become stable. Super nitrides and oxides with such a composition are not possible since the elements N and O form molecular structures.

KC(NaC,SR22.220),$\underline{a}{=}7.58;14.69\text{Å}$, is isodesmic to NaC.

KC_8(H4.32,SR18.339,drw ibid.) contains alternating K and C layers parallel to $\underline{a}_1,\underline{a}_2$. A K-layer contributes 1K per $\underline{a}$ (atomic radius $\underline{r}_K{=}2.36\text{Å}\lessapprox|\underline{a}_1|$(C.r){=}2.46\text{Å}$) and a C layer 8C per $\underline{a}$. The share in $\underline{a}$ of one K+C double layer is $\underline{a}'{=}$H4.91;5.41\text{Å}. The $\underline{c}$ electrons of K and the valence electrons of C.r form the $\underline{c}$ correlation of KC_8: $\underline{a}(\underline{N}{=}4,160){=}$H4.91;21.64$\text{Å}{=}\underline{b}_H(1;4){=}\underline{c}_H(\sqrt{12};15/1)$. The K layer with only 8 $\underline{c}$ electrons allows an expansion of $\underline{b}_{FH}$ of C.r to $\underline{c}_H$ of KC_8. Since in KC_8 the number of $\underline{c}$ layers per K+C layer is 3.75 the K-stacking cannot be of the H1 type because of electro dipole vectors in $\underline{a}_3$ direction induced by the binding.

"KC_{16}"(SR2.181) has not been confirmed (SR18.338).

KC_{24}(H2.48,SR18.339) is in equilibrium with KC_8 (54Rüd) and contains two C layers per K layer. Since the distance of K layers in $\underline{a}_3$ direction is now greater than the distance of K atoms in the basal plane, the $\underline{b}$ correlation becomes more

anisotropic and therefore energetically unfavourable. To compensate for this the K layer is more loosely packed, isotypic (but not congruent) to the C layers, so that the C content per K is 16/0.66=24. The stacking of the K layers was statistical for the applied thermal treatment 20h400°C (54Rüd). It should be conjectured that the order of the stacking may be improved by an appropriate heat treatment. Using the experimental cell $\underline{a}$=H2.45;2(5.41+3.36)$\overset{\circ}{A}$ the binding becomes $\underline{a}(\underline{N}$=1.33,43)=H2.45;17.54$\overset{\circ}{A}$=($\underline{b}^v\underline{c}$)$_{FH}$($\sqrt{3}$;15/2) with an occupancy 0.98. The nearly full occupation of $\underline{b}^v\underline{c}$ contributes another reason for the looser packing of the K layers.

KC_{36},KC_{48},KC_{60} are homeotypic to KC_8 and KC_{24}(SR18.339).

RbC_8(KC_8,SR18.339), $\underline{a}(\underline{N}$=4,160,40)=H4.91;22.65$\overset{\circ}{A}$=($\underline{b}^v\underline{c}$)$_{UH}$($\sqrt{12}$;18/2). The expansion of the $\underline{b}_{FH}$(C.r) layers appears to be somewhat weaker.

RbC_{24},RbC_{36},RbC_{48},RbC_{60}(SR18.339) are homeotypic to RbC_8.

CsC_8(KC_8,SR2.181), $\underline{a}$=H4.95;22.80$\overset{\circ}{A}$ is isodesmic to RbC_8.

CsC_{24}(KC_{24},71Eck), $\underline{a}$=H4.95;18.55$\overset{\circ}{A}$ is isodesmic to RbC_{24}.

CsC_{36},CsC_{48},CsC_{60}, see 75Wel.

Be_2C(CaF_2,F2.1,SR3.20) is a brick-red Lewis phase, $\underline{a}(\underline{N}$=32,24)=4.34$\overset{\circ}{A}$=$\underline{b}_F$(2)= $\underline{c}_C$(4) or $\underline{a}$=($\underline{b}^v\underline{c}$)$_C$(4).

BeC_2(73Hol).

Mg_2C_3(H16.24,SR11.75) is not completely solved, the binding will be tentative. $\underline{a}(\underline{N}$=32,224)=H7.45;10.61$\overset{\circ}{A}$=($\underline{b}^v\underline{c}$)$_{BH}$($\sqrt{12}$;24/3). The phase may be described as Mg_4 ((C_2)$^{2-}$)$_2$(C_2)$^{4-}$. A Lewis phase is not stable in MgC_M and in the remaining homologic mictures, for the same reasons as in A^1C_M.

MgC_2(ThC_2,T4.8,SR11.74) has a Mg_{F1} site set with C_2 in octahedral holes. $\underline{a}(\underline{N}$=8,64)=5.55;5.03$\overset{\circ}{A}$=$\underline{b}_C$($\sqrt{5}$;2)=$\underline{c}_C$($\sqrt{20}$;4) or =($\underline{b}^v\underline{c}$)$_C$($\sqrt{20}$;4). Spin compensation is warranted by the C type.

CaC_2.h(F1.2,FeS_2.h?,SR26.87) $\underline{a}$=5.88$\overset{\circ}{A}$, will be homeodesmic to CaC_2.r.

CaC_2.r(U1.2,SR1.740,drw 64Sch.222) is homeotypic to NaCl with C_2 along $\underline{a}_3$ in Cl sites. $\underline{a}(\underline{N}$=4,32)=3.89;6.38$\overset{\circ}{A}$=$\underline{b}'_C$($\sqrt{2}$;2.25)=$\underline{c}_C$($\sqrt{8}$;4.5) or =($\underline{b}'^v\underline{c}$)$_C$($\sqrt{8}$;4.5). Conforming to the site number rule (86Sch) CaC_2.r has less $\underline{c}$ sites than MgC_2. $\underline{b}'$ means $\underline{b}^v\underline{e}$.

CaC_2.i?(Z8.16,SR27.117), discussion is postponed.

SrC_2.h(FeS_2.h,SR9.136), $\underline{a}$=6.25$\overset{\circ}{A}$, hdm CaC_2.h.

SrC_2.r(CaC_2,SR2.275), $\underline{a}(\underline{N}$=4,32,20)=4.12;6.69$\overset{\circ}{A}$=($\underline{b}'^v\underline{c}'$)$_B$($\sqrt{8}$;4.5). The ($\underline{b}'^v\underline{c}$)$_C$ correlation of CaC_2.r is simply filled to a ($\underline{b}'^v\underline{c}'$)$_B$ correlation. The smaller influence of the f correlation explains the admissibility of a low occupancy.

BaC_2.h(FeS_2,SR9.136), $\underline{a}$=6.57$\overset{\circ}{A}$, hdm CaC_2.h.

BaC_2.r(CaC_2,SR2.275), $\underline{a}$=4.41;707$\overset{\circ}{A}$, idm SrC_2.r.

Sc_2C(F8.4,71Eck) is homeotypic to NaCl, $\underline{a}(\underline{N}$=96,320)=9.4$\overset{\circ}{A}$=($\underline{b}^v\underline{e}^v\underline{c}$)$_B$(6). The phase is a sub-carbide since its mole fraction $\underline{N}^r_C$<0.43=3/7.

$Sc_4C_3(Th_3P_4$, B8.6, SR34.59, drw 64Sch.326) is a Lewis phase whith $\underline{a}=Sc_{B1}(2)$ and C_1 in some of the octahedral holes. $\underline{a}(\underline{N}=48,176)=7.21\text{Å}=(\underline{b}'\vee\underline{c})_C(6)$, the slight over-filling of the binding may be avoided by statistical Sc and C lacunae suggested by the comparatively small atomic volume.

ScC.h(NaCl, SR26.103), $\underline{a}(\underline{N}=12,48)=4.51\text{Å}=(\underline{b}'\vee\underline{c})_C(4)$.

ScC.r(H10.10, SR23.81), $\underline{a}(\underline{N}=36,144)=$H5.46;10.24Å$=(\underline{b}'\vee\underline{c})^\wedge_{CH}(\sqrt{12};15/3)$. The cell content of SR23.81 is doubtful because of the commensurability to ScC.h, probably it is H12.12.

$Sc_{15}C_{19}$(T30.38, SR37.5, drw 72Now) contains quadratic Sc_q nets with $(\underline{a}_1,\underline{a}_2)=Sc_q(\sqrt{5})$. These nets are only approximately stacked in F1 manner so that Sc_6C octahedra and Sc_6O_2 octahedra (as in CaC_2) occur. $\underline{a}(\underline{N}=90,392)=7.50;15.00\text{Å}=(\underline{b}'\vee\underline{c})_C(\sqrt{40};13)$. It should be noted that the commensurability of $(\underline{b}'\vee\underline{c})_C$ to $\underline{a}_1$, $\underline{a}_2$ is the same as in ScC.h. The commensurability element 13 causes the deviation from the Sc_F stacking similarly as in the Cu_3Au shear homeotypes (64Sch).

$Y_3C(Fe_4N$, SR22.184), $\underline{a}(\underline{N}=12,36,40)=5.11\text{Å}=(\underline{b}'\vee\underline{c}')_{FU}(4;5.6)$. The advantage of the binding as compared with that of Y_2C.h is, that it is undistorted.

Y_2C.h(NaCl, SR34.60), $\underline{a}(\underline{N}=12,40,40)=5.12\text{Å}=(\underline{b}'\vee\underline{c}')^\vee_{FU}(4;5.8)$. The high temperature makes spin compensation unnecessary.

Y_2C.r($CdCl_2$, R2.1, SR34.61), $\underline{a}(\underline{N}=18,60,60)=$H3.62;17.96Å$=\underline{b}'_H(\sqrt{3};8)=\underline{c}'_{BH}(\sqrt{3};42/3)$ Curiously a Lewis-carbide ($\underline{N}_C=3/7=0.43$) has not been reported in YC_M.

$YC_2(CaC_2$.r, SR22.185,23.81), $\underline{a}(\underline{N}=6,32,20)=3.66;6.17\text{Å}=(\underline{b}'\vee\underline{c})_B(\sqrt{8};4.75)$. The electronic difference to CaC_2.r is expressed by a little difference in $|\underline{a}_3|/|\underline{a}_1|$.

Y_2C_3.p(Rb_2O_3, SR48.85), $\underline{a}(\underline{N}=48,224,160)=8.23\text{Å}=(\underline{b}\vee\underline{c})_B(6)$.

$La_2C_3(Rb_2O_3$, B8.12, SR22.186, drw 64Sch.224), $\underline{a}(\underline{N}=48,224,160)=8.80\text{Å}=(\underline{b}\vee\underline{c})_B(6)$, the phase may be described as $La_4(C\equiv C)_3$, and the lengthening of $\underline{d}_{CC}$ has been observed (73Hol).

LaC_2.h(F1.2, SR33.53), $\underline{a}(12,64,40)=(\underline{b}'\vee\underline{c}')_B(4)$.

LaC_2.r(CaC_2.r, SR33.53), $\underline{a}(\underline{N}=6,32,20)=4.00;6.58\text{Å}=(\underline{b}'\vee\underline{c}')_B(\sqrt{8};4.7)$. Unlike CaC_2 the phase LaC_2.r is a conductor of electricity (73Hol).

Ti_2C(F8.4, 67Gor) is a lacuna homeotype of NaCl. $\underline{a}(\underline{N}=128,320)=8.6\text{Å}$. When the binding $\underline{a}=(\underline{b}'\vee\underline{c})_C(8)$ is assumed then it would be strongly under-occupied and it might be that a "Ti_2C.r" becomes stable at lower temperatures.

TiC(NaCl, SR1.74, 19.87) is a Lewis phase, melts at 3420K and is an electric conductor. Earlier for the electron count Ti^4C^4 the binding $\underline{a}=\underline{b}_F(2)$ was assumed (55Sch), but the preferable count $Ti^{4,8}C^{0,4}$ yields the homeotypic binding $\underline{a}(\underline{N}=16,48)=4.33\text{Å}=(\underline{b}'\vee\underline{c})_C(4)$, where $\underline{b}'=\underline{b}\vee\underline{e}$. It accounts for the high melting temperature and for the slight shift of the range of homogeneity to mole fractions $\underline{N}_C<0.5$. The collective property that $\underline{b}'\vee\underline{c}$ enters the binding is presumably supported by Ti3d and Ti3sp having the same main quantum number. Band calculations (87Zhu) show that Ti3d and C2p are energetically close together, this also

favours the collective binding. The high stability of TiC accounts for the absence of a phase homeotypic to Ti_4N(binding 88Sch).

TiC_2(C1.2,SR27.136) $\underline{a}$=3.13Å needs confirmation.

Zr_2 C(F8.4,67Gor) is homeodesmic to Ti_2C.

ZrC(NaCl,SR1.74,24.89,phase diagram 6/Sto) melts at 3690K. $\underline{a}$(N=16,48,40)= 4.70Å=$\underline{g}_B$(4). The range $Zr_{65}C_{35}$ - $Zr_{50}C_{50}$ illustrates the influence of the $\underline{f}$ electrons.

$Hf_{86}C_{14}$(FhtpMg,78Mof) is homeodesmic to Ti_4N, the high stability of HfC shifts the mole fraction to smaller values.

HfC(NaCl,SR4.6,19.87) melts at 4200K. $\underline{a}$(N=16,48,56)=4.64Å=$\underline{g}_B$(4). The high melting temperature illustrates the importance of the $\underline{f}$ correlation.

$V_2C.h$($N_2C.h$,SR18.100,30.40,drw 64Sch.267) is stable in the interval 1070-2460K. Contrary to many previous phases the A-stacking is of the kind hh=+- and $|\underline{a}_3|/|\underline{a}_1|$=1.58 is smaller than the ideal value 1.63. The ccc=+++ stacking and the ideal axial ratio will be reached in $VC_{0.9}$(NaCl). Since the commensurability of the $(\underline{b}'\smile\underline{c})_{CH}$ correlation of TiC in the hexagonal plane is very tight and since the compliant direction of C is $[111]_C$ a change of commensurability is to be expected in $[111]_{TiC}$=$[001]_{V2C.h}$. Therefore the binding in $V_2C.h$ may be $\underline{a}$ (N=10,20)=H2.88;4.55Å=$\underline{g}_{CH}^{\wedge}$(2;7.5/3). The number of $\underline{g}$ layers per atom layer parallel to the basal plane is only 0.25 smaller than in TiC where it is 4. The low $\underline{g}$ electron offer in $V_2C.h$ causes the low axial ratio. If it is assumed that the V2sp electrons weakly take part in the correlation forming $\underline{g}_{BH}$, then there are 15 $\underline{g}_{BH}$ layers per $\underline{a}$ cell so that the electro dipoles in $\underline{a}_3$ direction may be assessed by the sequence n2/15=0.00,0.13,...,0.93,1.07,...,2.00,2.13. In 0.00 lie an atom and an electron. To avoid this degeneracy the electron site n2/15-0.01 is considered. There in the atom 0.00 lies a + dipole and in 1.00 a - dipole favouring the +- stacking (84Sch).

$V_2C.i$(Fe_2N_1,08.4,71Eck), $\underline{a}$(N=40,80)=4.57;5.74;5.04Å=$\underline{g}_{CH}$(7.5/3;4;4/2).

$V_2C.r$(htp$V_2C.h$,71Eck), $\underline{a}$=11.49;10.06;4.55Å, more structural data are desirable.

V_4C_3(R4.3,SR35.110,70Yvo) is antiisotypic to Sn_4As_3(SR3.650). The stacking (+---)^3 is rare (70Yvo) and the V layers are not equidistant. The averaged and normed axial ratio $|\underline{a}_3|/6|\underline{a}_1|$ =1.59 is slightly greater than 1.58 of $V_2C.h$ but essentially smaller than 1.63 of $VC_{0.9}$. The binding may be $\underline{a}$(N=60,132)=H2.92; 27.83Å=$\underline{b}_H$(1;10)=$(\underline{e}\smile\underline{c})_{CH}^{\wedge}$(2;46/3). An assessment of the stacking must be postponed because of the non-uniform layer distance.

V_6C_5(H18.15,SR33.57) displays $\underline{a}$=$\underline{a}_{V2C.h}$($\sqrt{3}$;3) and the stacking cccccc. $\underline{a}$(N= 90,204)=H5.09;14.40Å=$\underline{b}_{CH}$(1;6/3)=$(\underline{e}\smile\underline{c})_{CH}$($\sqrt{12}$;24/3). The normalized axial ratio 1.63 indicates that $\underline{e}\smile\underline{c}$ is not strained. The strain of $\underline{b}$ is not of influence.

V_8C_{69}(C32.(27.6),SR38.68) has a NaCl structure with ordered C lacunae, $\underline{a}$(N= 160,366.4)=8.33Å=$\underline{b}_B$(2)=$(\underline{e}\smile\underline{c})_C$(8). The commensurability $\underline{a}$=$\underline{a}_{VC}$(2) must be caused

by electro dipole influences.

$VC_{0.9}$(NaCl,SR27.127) does not include the composition VC, but has a congruent melting point (71Tot). $\underline{a}(N=20,46.4)=4.17\text{Å}=\underline{b}_F(1)=(\underline{e}\vee\underline{c})_C(4)$. From the electron count it must be concluded that $\underline{a}=\underline{g}_C(4)$ is not possible, rather it must be assumed that a $\underline{b}$ correlation is precipitated. The lacuna homeotypes of VC may be interpreted by the assumption that a $\underline{b}$ correlation is precipitated from the $\underline{g}$ correlation, and seeks an appropriate commensurability. A Lewis phase "$A_4^5C_6$" is not stable in A^5C_M since the composition would not allow AA bonding. Also in $A^{6...10}C_M$ only subcarbides are found.

$Nb_2C.\bar{h}_2(W_2C.h,SR23.97)$, $\underline{a}(N=10,20,20)=3.13;4.97\text{Å}=\underline{g}_{BH}(2;15/3)$. The axial ratio 1.59 and the stacking are compatible with the binding.

$Nb_2C.h_1(Fe_2N_{0.9},H6.3,SR29.107)$, $\underline{a}(N=30,60,60)=H5.41;4.96\text{Å}=(\underline{b}'\vee\underline{c})_{CH}(\sqrt{12};7.5/3)$ $=\underline{f}_{CH}(\sqrt{12};7.5/3)$. Some rearrangement must occur in $\underline{f}$, but it is not easy to describe.

$Nb_2C.r$(08.4,SR32.507,52.94,drw 70Par), $\underline{a}(N=40,80,80)=10.91;3.10;4.97\text{Å}$. The phase is not isotypic to Fe_2N_1. A separate $\underline{b}$ correlation is not probable by extrapolation of the next phases. A supercell could not be detected by 85Lön.

$Nb_4C_3(V_4C_3,R4.3,SR35.110)$, $\underline{a}(N=60,132,120)=H3.14;30.10\text{Å}=\underline{b}_H(0.5;5)=(\underline{e}\vee\underline{c}')_{BH}$ (2;93/3). The phase is closely homeodesmic to V_4C_3 and also to $Nb_2C.h_2$.

$Nb_4C_{3.1}$(LhtpNaCl,SR34.58), $\underline{a}(N=20,44,40)=4.47\text{Å} =\underline{b}_C(1)=(\underline{e}\vee\underline{c}')_B(4)$. It appears that the cubic relation of $\underline{e}\vee\underline{c}'$ decreases the contribution to $\underline{b}$.

Nb_6C_5(H18.15,htpNaCl,SR52.31),$\underline{a}(N=90,204,180)=H5.46;15.42\text{Å}=\underline{b}_{CH}(1;6/3)=(\underline{e}\vee\underline{c}')_{BH}(\sqrt{12};48/3)$. See SR51.29.

NbC(NaCl,SR30.118), $\underline{a}(N=20,48,40)=4.47\text{Å}=\underline{b}_F(1)=(\underline{e}\vee\underline{c}')_B(4)$. If the $\underline{f}$ contribution is disregarded instead $(\underline{e}\vee\underline{c})_B$ the correlation $(\underline{e}\vee\underline{c})_C$ must be assumed, and it requires the b_F correlation.

$Ta_{64}C$(U64.1,65Vil) is homeodesmic to $Ta_{27}N$ (88Sch). The structure needs confirmation.

$Ta_2C.h(W_2C.h,67Sto)$ is isodesmic to $Ta_2C.r$.

$Ta_2C.r(CdI_2,SR30.40)$, $\underline{a}(N=10,20,28)=H3.10;4.94\text{Å}=\underline{g}_{BH}^{\wedge}(2;15/3)$.

$Ta_4C_3(V_4C_3,R4.3,SR35.110)$, $\underline{a}(N=60,132,168)=H3.12;30.00\text{Å}=\underline{b}_H(0.5;5)=(\underline{e}\vee\underline{c}')_{BH}$ (2;93/3).

$Ta_4C_{3.1}$(LhtpNaCl,SR34.58), $\underline{a}(N=20,44,56)=4.42\text{Å}=\underline{b}_C(1)=(\underline{e}\vee\underline{c}')_B(4)$.

TaC(NaCl,SR30.118), melts at 4270K. $\underline{a}(N=20,48,56)=4.45\text{Å}=\underline{b}_F(1)=(\underline{e}\vee\underline{c}')_B(4)$.

$Cr_{23}C_6$(F23.6,SR38.60,drw 64Sch.259) contains regions homeotypic to CaF_2 alternating with regions homeotypic to Cu. This is contrary to most earlier AC_M phases based on a close packed A site set. The pressure of the increased $\underline{e}$ contribution loosens the close packing locally and there must enter the C atoms. $\underline{a}(N=552,832)=10.65\text{Å}=(\underline{b}\vee\underline{e}\vee\underline{c})_B(9)$. The binding can no longer be of the C type as in $V_2C.h(W_2C.h)$, it must be closer packed. Substituted Mo and W atoms enter

only the tetrahedral interstices between the A_{12} cube octahedra, since the hexahedral interstices are filled with C. The $Cr_{23}C_6$ type is stable also in $Mn_{23}C_6$ contributing $\underline{N}$=644,832, and in $W_2Fe_{21}C_6$, contributing $\underline{N}$=720,832,112. Here new $\underline{b}$ bands might be opened.

$Cr_7C_3(Mn_7C_3,028.12,SR38.60,drw\ ibid.)$ is pseudo hexagonal. The close packed Cr sites form chains of octahedra along $\underline{a}_1$ sharing faces. On each free face is built a trigonal prism filled by C. $\underline{a}(\underline{N}$=168,272)=4.53;7.01;12.14$\overset{o}{A}$=$\underline{g}_B$(4;6;10). Evidently $Cr_{23}C_6$ and Cr_7C_3 are fairly homeodesmic.

$Cr_3C_2(012.8,SR34.56,drw.SR34.58)$ was very exactly refined (69Run). It is commensurable to NaCl: $\underline{a}$=$\underline{a}_{NaCl}(-1,0.5,0;1,0.5,0;0,0,3)$ but the atomic sites are strongly changed so that the C are not in Cr octahedra but in trigonal prisms. Nevertheless the binding may be $\underline{a}(\underline{N}$=72,128)=5.54;2.83;11.47$\overset{o}{A}$=$(\underline{b}^{1\nu}\underline{c})_B$(5;2.5;10). The commensurability element 10 must cause the structural shear.

$CrC.h(NaCl,51Epp)$, $\underline{a}(\underline{N}$=24,48)=3.62$\overset{o}{A}$=$\underline{b}_C$(2)=$(\underline{e}^\nu\underline{c})_C$(4).

$Mo_2C.h(W_2C.h,SR2.240)$, $\underline{a}(\underline{N}$=12,20,20)=H3.01;4.78$\overset{o}{A}$=$(\underline{b}^{1}\nu\underline{c})_{BH}$(2;15/3), $|\underline{a}_3|/|\underline{a}_1|$= 1.59, see $Nb_2C.h_2$. The $\underline{b}$ correlation is mainly on $\hat{C}_H$ of $\underline{c}$ and partly on $\hat{C}_H$ of $\underline{f}$. Another possibility would be to assume the precipitation of a $\underline{b}$ correlation.

$Mo_2C.r(Fe_2N,08.4,SR28.15)$, $\underline{a}(\underline{N}$=48,80,80)=4.72;6.00;5.20$\overset{o}{A}$, perhaps a better spin compensation is introduced to $\underline{b}$: $\underline{a}$=$\underline{b}_{FH}(2/3;2;2/2)$=$(\underline{e}^\nu\underline{c}')^\wedge_{BH}$(15/3;4;4/2). Since the C atoms obtain dipole vectors in $\underline{a}_1$ direction the change of C sites is favourable.

$Mo_3C_2.h(H6.4,SR18.90)$, $\underline{a}(\underline{N}$=36,64,60)=H3.01,14.63$\overset{o}{A}$=$(\underline{b}^{1}\nu\underline{c})^\wedge_{BH}$(2;42/3), $|\underline{a}_3|/3|\underline{a}_1|$ =1.62, stacking hcchcc=+++---, dipole sequence neglecting the weak $\underline{bf}$ correlations, $\underline{n}6/7$=0,0.86,1.71,(2.5),3.43,4.29,5.14,(6.00), +++---.

$MoC_{0.7}.h(NaCl,SR26.101)$, $\underline{a}(\underline{N}$=24,43,40)=4.27$\overset{o}{A}$=$\underline{b}_F$(1)=$(\underline{e}^\nu\underline{c}')_B$(4). Perhaps it is more appropriate to write the binding $\underline{a}$=$\underline{b}_F$(1)=$(\underline{e}^\nu\underline{c})_C$(4)=$\underline{f}_C$(4).

$W_2C.h(H2.1,SR1.575,drw\ 64Sch.267)$, $\underline{a}(\underline{N}$=12,20,28)=H2.99;4.72$\overset{o}{A}$=$\underline{g}_{BH}$(2;15/3).

$W_2C.r(CdI_2,SR24.97)$, $\underline{a}(\underline{N}$=12,20,28)=H2.98;4.71$\overset{o}{A}$=$\underline{b}_{FH}(1;2/3)$=$(\underline{e}^\nu\underline{c}')_{BH}$(2;15/3).

$W_2C.m(Fe_2N_1,08.4,68Yvo)$, $\underline{a}(\underline{N}$=48,80,112)=4.73;6.01;5.19$\overset{o}{A}$.

$W_2C.\varepsilon(Fe_2N_{0.9},H6.2,68Yvo,SR33.152)$, $\underline{a}(36,56,84)$=H5.18;4.72$\overset{o}{A}$.

$W_4C_{2.5}.h(NaCl,SR27.141)$, $\underline{a}(\underline{N}$=24,42,56)=4.27$\overset{o}{A}$=$\underline{g}_B$(4).

$WC(H1.1,SR26.105)$, $\underline{a}(\underline{N}$=6,12,14)=H2.91;2.84$\overset{o}{A}$=$\underline{g}_{BH}$(2;9/3). The NaCl type is not possible for WC since at elevated temperatures excited electrons are present. The excellently fitting binding causes a high hardness so that WC, in a binder of Fe or Co, may serve as cutting tool.

$Mn_4C.h(T48.12,SR21.76,phase\ diagr.78Mof)$ is homeotypic to $Mn_{23}C_6$. $\underline{a}(\underline{N}$=336,432) =7.66;10.57$\overset{o}{A}$=$\underline{b}_B(\sqrt{4.5};3)$=$(\underline{e}^\nu\underline{c})_B(\sqrt{41};9)$. The bindings for MnC_M contain the difficulty that they do not well compare with the binding of $Fe_{20}C.m$.

$Mn_{23}C_6(Cr_{23}C_6,F23.6,SR21.76)$, $\underline{a}(\underline{N}$=644+832=1476)=10.59$\overset{o}{A}$=$\underline{b}_C$(3)=$(\underline{e}^\nu\underline{c})_B$(9). The binding is homeotypic to that of $Mn_4C.h$.

$Mn_{15}C_4$.h(see phd 78Mof), structural details are desirable.

Mn_3C.h(Fe_3C.m,O12.4,SR21.76,drw 64Sch.253) is remotely homeotypic to Cu_3Au. $\underline{a}(\underline{N}=84,112)=4.53;5.11;6.76\mathring{A}=(\underline{b}'\cup\underline{c})_B(4;4.5;6)$. This is a collective binding compatible with the room temperature instability as $\underline{b}'\cup\underline{c}$ is strongly underoccupied.

Mn_5C_2(Pd_5B_2,N10.4,SR18.88,26.76,drw SR26.78) contains a sheared Pd_{HT} site set with C in trigonal prismatic coordination. $\underline{a}(N=140,192)=5.09;4.57;-1.57,0,$ $11.55\mathring{A}=(\underline{b}'\cup\underline{c})_B(4.5;4;10)$. The binding accentuates the homeotypism to Fe_3C.m. The sheer is caused by the binding.

Mn_7C_3(O28.12,SR30.36,38.61) is isotypic to Cr_7C_3, and pseudo hexagonal. $\underline{a}(\underline{N}=196,272)=4.55,6.96;11.98\mathring{A}=(\underline{b}\cup\underline{c})_B(4;6;10)$.

Tc_2C(htpNaCl,SR26.104), $\underline{a}(\underline{N}=28,40,40)=3.99\mathring{A}=\underline{g}_B(4)$.

ReC_M(73Bay) carbides have been suggested. The low number of subcarbides of the heavier elements is caused by the fact that the B type correlation cannot be as easily filled by $\underline{f}$ electrons as the C type of VC_M etc.

$Fe_{20}C$.m(U1.(0.05),SR17.90), $\underline{a}(\underline{N}=16,16.2)=2.84;2.98\mathring{A}=\underline{b}_B(\sqrt{5};1.9)=\underline{c}_B(\sqrt{5};1.9)$.

Fe_3C.m(O12.4,SR9.40,drw 64Sch.253), $\underline{a}(\underline{N}=96+112=208)=4.52;5.09;6.74\mathring{A}=(\underline{b}'\cup\underline{c})_B$ $(4;4.5;6)$.

Fe_2C(H6.3,SR23.89), $\underline{a}(\underline{N}=48,60)=H4.77;4.35\mathring{A}=(\underline{b}'\cup\underline{c})_{BH}(3;14/3)$.

Fe_2C(Co_2C ,O4.2,SR38.64,drw 64Sch.257), $\underline{a}(\underline{N}=32,40)=2.83;4.70;4.32\mathring{A}=(\underline{b}'\cup\underline{c})_B$ $(2.5;4.2;3.8)$. While Fe_2C(H6.3) appears to have 21 sites per Fe, in Fe_2C(0.42) are only 20. The deformation of the O4.2 phase might be a mechanism to save electron sites.

Fe_5C_2(Pd_5B_2,N10.4;SR31.30,drw SR26.78), $\underline{a}(\underline{N}=160+192=352)=5.09;4.57;-1.55,0,$ 11.45) is isodesmic to Mn_5C_2.

Fe_7C_3(Mn_7C_3,O28.12,SR32.139), $\underline{a}(\underline{N}=224,272)=4.54;6.89;11.91\mathring{A}=(\underline{b}'\cup\underline{c})_B(4;6;10.5)$. The last commensurability element is not integral, to conserve the rule that they are mostly integral, it should be investigated whether there are lacunae in Fe_7C_3. It appears suggestive to bring the orientation AB of the hexagonal columns (SR38.61,62) in relation to the binding.

RuC(WC,H1.1,SR24.92), $\underline{a}(\underline{N}=8,12,10)=H2.91;2.82\mathring{A}=(\underline{b}'\cup\underline{c}')_{BH}(2;9/3)$.

OsC(WC,SR24.92), $\underline{a}(\underline{N}=8,12,14)=H2.91,2.82\mathring{A}$ is isodesmic to RuC.

Co_3C.i(Fe_3C,SR6.178), $\underline{a}(\underline{N}=108,112)=5.09;6.74;4.53\mathring{A}=(\underline{b}'\cup\underline{c})_B(4.5;6;4)$, the binding is slightly overfilled.

Co_2C($CaCl_2$,O4.2,SR15.31,drw 64Sch.257), $\underline{a}(\underline{N}=36,40)=2.90;4.45;4.37\mathring{A}=(\underline{b}'\cup\underline{c})_B$ $(2.5;4;3.8)$.

Ni_3C(R6.2,SR22.82), $\underline{a}(\underline{N}=180+168=348)=H4.55;12.92\mathring{A}=(\underline{b}'\cup\underline{c})_{BH}(3;39/3)$. There are 13 electron sites per 6 layers of Ni parallel to $\underline{a}_1,\underline{a}_2$.

CuC(73Bai), a super-carbide, seems not yet to be structurally investigated.

Ag_4C(73Bai) suggested but not confirmed.

AgC(73Bai).

AuC(73Hol).

ZnC_2(73Hol) needs confirmation.

CdC_2(73Hol).

HgC_2(73Hol), Lewis phases become stable not earlier than in AlC_M where the equi atomic composition is approximated.

$B_{50}C_2$(T50.2,SR38.39), $\underline{a}(\underline{N}=158,104)=8.72;5.08\text{\AA}=\underline{b}_C(\sqrt{45};4)=\underline{c}_B(\sqrt{45};4)$. The $\underline{c}$ correlation has a occupancy 0.29 and is occupied only in the B_{12} icosahedra. In C.r also, $\underline{a}(N=16,8)=H2.46;6.70\text{\AA}=\underline{b}_{FH}(\sqrt{3};5.8/3)=\underline{c}_{CH}(\sqrt{3};11.5/3)$, the $\underline{c}$ correlation is very weakly occupied. However, molecular units as in boron cannot be formed since the $\underline{b}$ concentration is too high. In N the association to planes is no longer possible.

B_4C(R12.3,SR9.154,drw 64Sch.179), another subcarbide, $\underline{a}(\underline{N}=144,90)=H5.63;12.14\text{\AA}=\underline{b}_{CH}(3;16/3)=\underline{c}_{BH}(3;32/3)$. The $\underline{c}$ occupancy is 0.31. The C_3 fill the $\underline{b}$ correlation.

Al_4C_3(R4.3,SR3.56,drw 64Sch.185) is a pale yellow Lewis phase homeotypic to Si, but not isodesmic. Parallel to $\underline{a}_1,\underline{a}_2$ there are hexagonal close packed Al-layers and C-layers having just 1 atom per $\underline{a}_1,\underline{a}_2$ mesh. Only the projections $\underline{A}=0,0$, $\underline{B}=2/3,1/3$, $\underline{C}=1/3,2/3$ are geometrically possible. Both, the Al site set and the C site set are in zeroth approximation close packings and may be described by Zhdanows symbols (45Zhd,59Int). If B (or C) is stacked on A the layer is marked by + (or -). Analogously for the other characters. The Al stacking in Al_4C_3 is ++-+++-+++-+ or briefly $(13)^3$ and the C stacking is --+--+--+ or $(12)^3$. The binding is localized $\underline{a}(\underline{N}=36,132)=H3.33;24.89\text{\AA}=\underline{b}_{BH}(1;36/3)=\underline{c}_{CH}(2;36/3)$. The Al sites are influenced by $\underline{b}$ and $\underline{c}$ but the C sites by $\underline{c}$ only, therefore the C stacking should be considered. On 9 C-layers come $\underline{c}$ chains along $\underline{a}_3$ with 12 sites and the sites may be in $\underline{x}_3=\underline{n}/12$ ($\underline{n}=0,1,2,...$) or, with respect to the C layers in $9\underline{x}_3=\underline{n}9/12=0,0.75,1.50,2.25,3.00,3.75,4.50,5.25,6.00,6.75,7.50,8.25,9.00$, so that the electro dipole directions at the atoms may be +-++-++-+(+) i.e. favouring just the observed stacking following the rule (84Sch) that a change in dipole sign causes a change in stacking sign.

AlC_3(73Hol) lacks structural information.

$Al_4C_3(AlN)_1$(H10.6.2,SR28.3,31.5) is the first member of a homeotypic series of phases obtained by replacing the index $\underline{N}_{AlN}=1$ by 2,3,4. For $\underline{N}_{AlN}=1$ was found the Al stacking $(113)^3$ and the C,N stacking $(112)^2$=++-+--+-. For the binding in Al_5C_3N may be assumed $\underline{a}(\underline{N}=30,114)=H3.28;21.67\text{\AA}=\underline{b}_{BH}(1;32/3)=c_{CH}(2;32/3)$. The $\underline{a}_3$ axis contains $10.7\approx11$ $\underline{b}$ sites and 8C,N planes parallel to $\underline{a}_1,\underline{a}_2$. Normalizing $\underline{a}_3$ to 8 the 11 electron sites are (with $\underline{n}=0,1,..,8$) in $\underline{n}8/11=0,0.73,1.45,2.18,2.91,3.64,4.36,5.01,5.82,6.55,7.27,8.00$. From these numbers the momentary dipole vectors at the C or N layers have the signs ++-+--+- corresponding to the symbol $(112)^2$ under the assumption that conservation of sign leads to a

conservation of stacking while change leads to a change of stacking (84Sch).

SiC is a Lewis compound displaying the property of polytypism (25Ott). There are 4 basic structures F1.1,H4.4,R5.5,H6.6 from which metastable homeotypes (polytypes) may be derived (83Pan).

SiC.β(ZnS.r,F1.1,SR1.146,11.226) is formed near 1800°C and may be stabilized by N. The binding may be $\underline{a}(N=16,48)=4.36\overset{\circ}{A}=\underline{b}_\beta(2)=\underline{c}_r(4)$ or in hexagonal coordinates $\underline{a}_H(12,36)=H3.08;7.55\overset{\circ}{A}=\underline{b}_{BH}(1;12/3)=\underline{c}_{CH}(2;12/3)$. The binding might be considered as collective but basic phases obtained at higher temperatures do not allow this. At 1800 - 2100°C H4.4 is formed, above 2100°C H6.6.

SiC(H4.4,SR1.80,11.228) is a stacking homeotype of SiC(F1.1) with the stacking of the double layers parallel to $\underline{a}_1,\underline{a}_2$ ++--=chch. The binding may be $\underline{a}(N=16,48)=H3.08;10.08\overset{\circ}{A}=\underline{b}_{BH}(1;15/3)=\underline{c}_{CH}(2;15/3)$ meaning that $\underline{b}$ electrons are excited to a higher band so that $\underline{b}$ must expand into the $\underline{a}_3$ direction and $\underline{c}$ conforms to this strain. From the straining of $\underline{b}$ no conclusions may be drawn for the axial ratio of $\underline{a}$ since the influence of the new band is unknown. 4 Si layers parallel to $\underline{a}_1,\underline{a}_2$ are traversed by $\underline{b}$ electron chains parallel to $\underline{a}_3$ with 5 sites per cell. The dipole vectors generated by the chains at Si may be assessed as follows. When the normalized site parameter $x_3'=4x_3$ is used the Si have an integral x_3' parameter. The parameters of the electrons are $\underline{n}4/5=0,0.80,(1.60),2.40,$ 3.20,(4.00). Since the electron 0 lies in a Si, a little amount say 0.01, is subtracted from the chain. Then the signs of the dipoles in $\underline{a}_3$ direction are ++--. The value (1.60) does not cause a dipole. A neighbouring chain causes together with the first chain the average site $\underline{n}4/5-2/15=-0.13,0.66,(1.46),2.26,$ 3.06,(3.86) i.e. once more ++--. A chain giving another stacking will be weakened in the correlation. From this may be concluded that the dipoles in $\underline{a}_3$ direction cause the stacking (84Sch). From the site number $N_{S(C)}^{/a}=60$ it must be concluded that the binding in SiC is not collective, however, the conformity of $\underline{c}$ to $\underline{b}$ must be considered as the cause for the observation that all polytypes of SiC are hexagonal (or rhombohedral).

SiC(R5.5,SR1.83,11.228) has the stacking $(+++--)^3=(\text{hcchc})^3$ and the binding $\underline{a}(N=60,180)=H3.08;37.82\overset{\circ}{A}=\underline{b}_{BH}(1;54/3)=\underline{c}_{CH}(2;54/2)$. Both correlations are strained because of the excitation of $\underline{b}$ electrons. The dipole sequence is $\underline{n}15/18=0,0.83,$ 1.67,(2.50),3.33,4.17,5.00,5.83,6.66,(7.50),8.33,9.17,10.00,10.83,11.67,(12.50), 13.33,14.17,(15.00) and therefore the dipole signs become +++--++--+++--.

SiC(H6.6,SR1.82,11.226) is the most abundant phase in commercial SiC. It has the stacking +++----=hcchcc and the binding $\underline{a}(N=24,72)=H3.08;15.10\overset{\circ}{A}=\underline{b}_{BH}(1;21/3)=$ $\underline{c}_{CH}(2;21/3)$. The dipole sequence is $\underline{n}6/7=0,0.86,1.71,(2.57),3.43,4.29,5.14,$ (6.00) causing the dipole signs +++----. The electron count in TiC and SiC is quite similar. It appears that in TiC the binding is completely collective while in SiC it is more localized perhaps since the $\underline{b}$ electrons and $\underline{c}$ electrons of Si

have a different main quantum number. The strong influence of the excitation of $\underline{b}$ electrons on the stacking in SiC suggests that the stacking is not only a function of temperature but also of the impurity and defect concentrations. Therefore at room temperature only F1.1 might be stable and all other structures depend on history. Especially SiC(H2.2,59Ada) might contain hydrogen. If a crystal H6.6 is helt at a temperature being not its equilibrium temperature, then it tends to another stacking. However, since the $\underline{b}$ electrons are uniformly distributed the driving force for stacking change will be periodically distributed. This might be another cause for the striking phenomena observed.

Some ternary carbides

CaTiO$_3$(C1.1.3,perovskite,SR1.300) is a Lewis phase having Ti,with smaller atomic radius, in the O$_6$ octahedron. The binding may be $\underline{a}$(N=2,4,34)=3.80Å=(b^{v}e)$_C$(2)=$\underline{c}_F$(2) for instance, or $\underline{a}$=(b^{v}e)$_B$($\sqrt{2}$;1.5)=$\underline{c}_B$($\sqrt{8}$;3). The phase has a heterodesmic branch of isotypes (kind A$_3^{7...10}$A$^{12...14}$C) (69Sta) to be discussed for the following examples.

Mn$_3$AlC(3.1.1,SR13.3,19.13) displays C surrounded by Mn$_6$ as Mn has a smaller radius than Al. $\underline{a}$(N=3,21,36)=$\underline{b}_F$(1)=($\underline{e}^v\underline{c}$)$_C$(4). The binding may also be fully collective $\underline{a}$ =(b^{v}e^{v}c)$_C$(4). For Fe$_3$AlC$_{0.7}$(C3.1.1,SR3.614) comes N=3+24+35=62, for Co$_3$AlC$_{0.6}$(C3.1.1,SR22.7) N=3+27+34=64 and for Ni$_3$AlC$_{0.3}$(C3.1.1,SR22.7) N=3+30+33=66. The last binding would be overoccupied in $\underline{a}$=$\underline{g}_C$(4) whence it should be assumed that the $\underline{b}$ correlation is not collective with ($\underline{e}^v\underline{c}$). This is confirmed by the observation (SR22.7) that only Ni$_3$AlC$_{0.3}$ is not ferromagnetic.

Fe$_3$SnC(C3.1.1,SR23.83), $\underline{a}$(N=4,34,36,10)=3.86Å=$\underline{b}_F$(1)=($\underline{e}^v\underline{c}^v\underline{f}$)$_B$(4). The presence of Sn fills the $\underline{g}_C$ correlation of Fe$_3$AlC$_{0.7}$ partly to a($\underline{e}^v\underline{c}^v\underline{f}$)$_B$ correlation allowing thus a higher N$_C$. In Co$_3$SnC$_{0.7}$ comes N=4,37,35,10, apparently the higher $\underline{e}$ contribution repells the N$_C$ value although the correlation is partly filled to the B type.

Ti$_3$AlC(C3.1.1,SR29.97), $\underline{a}$(N=3,12,36)=4.15Å must be heterodesmic to Mn$_3$AlC. Perhaps a systematic introduction of unoccupied correlation sites is possible, $\underline{a}$=$\underline{b}_F$(1)=$\underline{e}_B$(2)=$\underline{c}_F$(2).

Mn$_3$GeC(Cr$_3$AsN,U6.2.2,SR33.28,drw SR33.30) has an Ir$_3$Si type (SR24.113) metallic structure with C in octahedral Mn$_6$ holes. The binding may be $\underline{a}$(N=16,124,144)=5.38;8.07Å=$\underline{b}_{FU}$(2;4.25/2)=($\underline{e}^v\underline{c}$)$_C$($\sqrt{32}$;8.5). In relation to the C3.1.1 type the electron numbers per cell would be N=4,31,36, being slightly too high for the binding of Mn$_3$AlC. Therefore the commensurability element in $\underline{a}_3$ direction is increased and the induced momentary dipoles cause the I-homeotypism to C3.1.1.

Mn.h$_1$(C20,SR2.3,drw 64Sch.142) is formed because the collective binding in Mn.h$_2$(Cu,SR18.210), $\underline{a}$(N=28,32)=3.86Å=$\underline{g}_C$(4), precipitates the $\underline{e}$ correlation. It may be found $\underline{a}$(N=140,160)=6.31Å=$\underline{b}_B$($\sqrt{20}$;3.8)=$\underline{c}_B$($\sqrt{20}$;3.8). The binding is homeo-

typic to that of Mn.h$_2$(Cu) written as a=$\underline{b}_F$(2)=$\underline{c}_F$(2), but has less sites per atom according to the site number rule. It is homeotypic to earlier proposals and is related to the screw axes in the space group. Analogously to the formation of perovskite carbides from the Cu type, also from the Mn.h$_1$ type carbides may be formed. When the sites of Mn.h$_1$ are occupied by atoms with lower electron contribution, then C may enter the cell as the C insertion increases the number of electrons per metal atom.

Nb$_3$Al$_2$C(C12.8.4,htpMn.h$_1$,SR28.42) contains Al in the eightfold position and Nb in the twelvefold position forming octahedra centered by C lying in a fourfold position. Although $\underline{r}_{Nb}$>$\underline{r}_{Al}$ the C lie in Nb$_6$ octahedra. From $\underline{N}$=24,60,176, 120 it must be inferred that the Nb3d electrons partly go into the $\underline{b}'$=$\underline{b}^{v}\underline{e}$ correlation and partly center the $\underline{b}'^v\underline{c}$ correlation.

Cr$_2$AlC(H4.2.2,SR28.3) has a hhhhhh type stacking of the metal atoms. The C are in Cr$_6$ octahedra sharing edges. $\underline{a}$($\underline{N}$=6,24,56)=H2.86;12.82Å=$\underline{b}_{FH}$(1;5.5/3)= ($\underline{e}^v\underline{c}$)$_{CH}$(2;22/3). The number of $\underline{c}$ sites per metal atom is 14.7, instead of 16 in Mn$_3$AlC, because of the smaller d electron contribution. In an ideal Mg type packing the axial ratio per 2 layers 1.63, here it is always, because of $\underline{c}$, smaller. Essentially smaller axial ratios occur in A$_2^5$A^{15}C.

V$_2$PC(Cr$_2$AlC,SR33.130), $\underline{a}$($\underline{N}$=10,20,56)=H3.08;10.91Å=$\underline{b}_{CH}$(1;9/3)=($\underline{e}^v\underline{c}$)$_{CH}$(2;18/3). The slight overfilling of the binding suggests statistically distributed lacunae, otherwise the binding would be compressed in the $\underline{a}_3$ direction.

Ti$_3$SiC$_2$(H6.2.4,SR32.46) has the metal stacking chhhchhh. $\underline{a}$($\underline{N}$=8,24,80)=H3.07; 17.67Å=($\underline{b}^v\underline{e}^v\underline{c}$)$_{CH}$(2;28/3). The stacking rules of 84Sch do not work since the layers are not equidistant.

Mn$_5$Si$_3$(H10.6,SR4.24,drw 64Sch.306) contains close packed Mn columns along $\underline{a}_3$, and a Mg-type Si site set with $\underline{a}$=$\underline{a}_{Mg}$($\sqrt{3}$;1). The binding may be $\underline{a}$($\underline{N}$=24,70,128) =H6.91;4.81Å=$\underline{b}_{FH}$($\sqrt{12}$;3/3)=$\underline{e}_{CH}$($\sqrt{12}$;6/3)=$\underline{c}_{BH}$($\sqrt{12}$;12/3). Since $\underline{c}$ is not fully occupied filling homeotypes are possible, and have been observed with C in Mn$_6$ octahedra.

Mn$_5$Ge$_3$(Mn$_5$Si$_3$,SR17.171), $\underline{a}$($\underline{N}$=24,130,128)=H7.19;5.05Å.
Fe$_5$Si$_3$.h(Mn$_5$Si$_3$,SR10.63), $\underline{a}$($\underline{N}$=24,80,128)=H6.74;4.72Å.
The carbides occur in the area A$_5^{4\ldots6}$A$_3^{13\ldots15}$C$_{c:7}$.
Mo$_{4.8}$Si$_3$C$_{0.6}$(Mn$_5$Si$_3$,SR20.182), $\underline{a}$($\underline{N}$=24,154,130). The Mo defect may come from the participation of the Mo3d electrons.

Discussion

The above used plural correlations model allows an attribution of a bonding type to most empirically found carbides. The understanding provided becomes apparent by answers to questions frequently raised:

Why include A^1C_M mixtures no Lewis phases (normal valence phases)? The composition of a Lewis phase would be "A_4^1C" and would not allow a strong ionic interaction, so that only supercarbides become stable. Earlier it was thought (34Sta) that the alcali interstices are not small enough for C_1 to be inserted.

Why is $Be_2C(CaF_2)$ stable but not "$Mg_2C(CaF_2)$"? The very favourable binding $\underline{a}=(\underline{b}^vc)_C(4)$ accepts 64 electons per cell but "Mg_2C" would offer 96 $\underline{b}^vc$ electrons.

Why is $Sc_4C_3(Th_3P_4)$ the only Lewis phase in A^3C_M? The 224 offered electrons find scarcely place in the binding $\underline{a}=(\underline{b}'v\underline{c})_C(6)$. But in "$Y_4C_3(Th_3P_4)$" or "$La_4C_3(Th_3P_4)$" there would be 384 electrons.

Why are in TiC_M no separate sub-carbides although in ScC_M and VC_M there are? The fit of the binding in the Lewis phase TiC is so favourable that no separate sub- or super-carbides become stable.

Why does TiC(NaCl) not include the equi atomic composition? The occupancy 1.00 of a binding is rare. A slight substitution Sc-Ti would presumably lead to an inclusion of the composition A_1C_1.

Why contains $Nb_2C.h_2(W_2C.h)$ a hh type of Nb-stacking? The binding $\underline{a}=g_B(2; 15/3)$ causes electron chains in $\underline{a}_3$ direction with 5 sites per cell. Therefore the electro dipoles in $\underline{a}_3$ direction of two neighbouring Nb with distance vector not normal to $\underline{a}_3$ have always $\underline{a}_3$ components with different sign. This causes the hh stacking (84Sch).

Why is $Cr_{23}C_6(F23.6)$ more complicated than $V_2C.h(W_2C.h)$? The binding being in $V_2C.h$ of the collective C1 kind condenses in $Cr_{23}C_6$ to a binding of the B1 kind since the $\underline{b}'$ concentration has increased. The Cr partial structure is partly of the F1 type and partly of the C1 type since the electron concentration does not admit all atoms from an ideal $\underline{a}=\underline{a}_{F1}(3)$ cell. The dismissal leads to a new commensurability $\underline{c}^{-1}\underline{a}$. It is no longer $\underline{a}=\underline{c}_C(12)$ as for a NaCl type but $\underline{a}=\underline{c}_B(9)$. Into the thinned regions of the Cr sites the C enter.

Why has $Mo_2C.h(W_2C.h)$ still a structure with close packed Mo site set? In $Cr_{23}C_6$ there come 15.8($\underline{b}^vc$) sites on one Cr, while in $Mo_2C.h$ for the partial $(\underline{e}^vc)_C$ correlation there are only 15 sites. This corresponds to the rule of the site numbers (86Sch) and presses the Mo stronger together. The pressure is caused by the additional interaction of the Mo3d electrons.

Why is $Mn_3C.h(Fe_3C.m)$ heterotypic to $Mn_{23}C_6$? The increase of C content and the elevated temperature cause that $Mn_3C.h$ has 9.0 B1 cells per Mn while $Mn_{23}C_6$ has 7.9 . This allows a more uniform distribution of Mn in $Mn_3C.h$.

Why is OsC isotypic to WC although the $\underline{b}'$ concentration of both phases is quite different? With respect to the high number of $\underline{c}'$ electrons the change of $\underline{b}'$ concentration has only a small influence.

Why is $Ni_3\underline{C}$ not isotypic to $Fe_3C.m$? The $\underline{b}'$ contribution is too high.

Why does CuC_M not contain Lewis carbides? Spin compensation can only come from Cu4s electrons and would cause a "Cu_4C" Lewis phase having small Coulomb interaction only.

Why is Al_4C_3 stable but no other $A^{13}C_M$ compounds? Al_4C_3 is a Lewis phase near the equi atomic composition. In the heavier A^{13} elements the peripheral filled sp shell has become too small, presumably, as to come into correlation with the C2sp electrons.

Why are all the polytypes of the lewis compound SiC hexagonal or rhombohedral? When in SiC(ZnS.r,F1.1) the binding is $\underline{a}=(\underline{b}\vee\underline{c})_C(4)$ at $1800^\circ C$ then at higher temperatures $\underline{b}$ will tend to dismiss excited electrons, so that it expands and draws $\underline{c}$ with it. Since $[111]_C$ is the compliant direction of C1, $\underline{c}_C$ will expand in this direction and causes the hexagonal symmetry and the observed stacking.

Crystal chemical rules are known, electron numbers are known, however, the interrelations of rules and numbers and their energetical meaning deserve investigation . The results will prove helpful for anyone having to do with chemical mixtures.

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