

On the bindings in AN_M phases

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Abstract

An analysis of the bonding types (bindings) in two-component nitrides confirms the rule that the $N2sp$ electrons are in correlation with the electrons of the outmost filled noble gas shell of the A atoms (\underline{c} correlation). This circumstance causes the stability of the well-known interstitial phases (Hägg's rule), and the occurrence of isotypic series (with changing homologic number) observed in $A^{4...10}N_M$ mixtures as $Mn_4N, Fe_4N, Co_4N, Ni_4N$. The binding proposal for KN_3 reveals that the reason for the stability of the azide ion $(N_3)^-$ is the \underline{c}_C correlation, fitting well to the linear array of N_3 . The stable phase ScN (NaCl type) exhibits a collective binding, such as influences also the stability of many $A^{4...7}N_M$ phases and causes the so called metallic nitrides as opposed to the ionic nitrides like Mg_3N_2 (MnFeO₃ type) and to the covalent nitrides like AlN or Si_3N_4 , containing a localized binding. In the localized binding the higher correlations \underline{b} and \underline{c} are trapped by \underline{c} , and the trapping occurs when the \underline{b} and \underline{e} concentration is sufficiently high. In AlN (ZnO type) there are 14 \underline{c} sites per AlN while in ScN there are 16, therefore in ScN a collective binding is possible but in AlN not. In the collective binding the spin compensation is easily recognized while in the localized binding the spin array appears to be more complicated. Many details of stability and structure such as lacunae in TiN , tetragonal deformation of Mo_2N and Mn_3N_2 , hexagonality of Fe_3N , heterotypism of Cu_3N and Ag_3N , hexagonality of AlN etc. are interpreted by the binding analysis and thus contribute to the confidence into the assumed model.

Introduction

The study of the interrelations between electron numbers and stability of chemical compounds and phases lead G.N. Lewis at the beginning of this century to the detection of what may be called electron spin compensation (electron pairs and octets). Another early result, W. Hume-Rothery's valence rule, was already interpreted by its discoverer as an indication for a lattice-like spatial correlation of electrons in crystals. Simultaneously the theory of electron motion in crystals by F.Bloch and others revealed that the electrons are distributed over energy bands stemming from the electron shells of the constituent atoms. A continued pursuit of these models of bonding suggests that each energy band contains a lattice-like correlation (64Sch,86Sch 1) and this leads to the question how the various correlations of the binding might coexist. Two possibilities appear in first line. In the "collective" binding the correlations contribute to one and the same lattice (fluctuating in the crystal) while in the "localized" binding there are two or more interpenetrating lattices being so arranged that the electrons are as remote as possible from one another (87Sch 1). The localization is caused by the proximity of the core electron correlation (c) to the central part of an atom, while the valence electron correlation (b) is trapped by c, instead of flowing around c as in the collective binding. The collective binding transforms with increasing homologic number to the localized binding when the b and e electron concentration in the phases surmounts a critical limit.

In a recent analysis of the bindings in oxides of many elements A i.e. in AO_M phases (87Sch 1), an assumption was sought as to how the various correlations are occupied by electrons. The result was that the O2sp electrons are in a common c correlation with the A3sp electrons of a 3d component, not with the A3d electrons as was earlier assumed with respect to the octet completion of Lewis' rule. Another uncommon result said that in 4d elements not only the A4sp electrons were in correlation with the O2sp electrons but also the A3d electrons because of the high compliance of their orbitals (see also 86Sch 2). Likewise in 5d elements the A4f electrons contributed to c.

It appears desirable to examine these results not only in oxides but also in AN_M phases. An earlier binding analysis of these phases (82Sch 1) must be modified in the light of the recently found rules. Reviews on AN_M phases by 67Gol, 68All, 71Tot, 75Jon, 78Pie, report a gross classification of nitrides into ionic (Mg_3N_2 e.g.), metallic (TiN), diamond-like (AlN) and covalent (Si_3N_4) phases. The ionic radii in nitrides permit an estimation of the atomic distances with 0.02Å precision (87Bau), but do not predict stability beyond the knowledge on oxidation numbers. Two stability rules have been especially helpful in the earlier systematics of nitrides. The rule on electron numbers by Lewis said that

the peripheral unfilled noble gas shell of N is filled by the valence electrons of the A component, i.e. the unpaired electron spins of A compensate the unpaired spins of N. A rule by Hägg considering the structural geometry of the phases said that N with the atomic radius $r_N=0.69\text{\AA}$ is inserted into the interstices of a simple lattice of $A^{4\cdots 10}$ atoms when $r_N/r_A < 0.59$. Unfortunately the validity of both rules is limited. Therefore rules of more extended validity must be sought and may be found by an analysis combining the earlier numerical and geometrical considerations (86Sch 1). The following analysis tries to demonstrate that for stable nitrides energetically favourable electron correlations are possible. Therefore the spatial correlation represents an additional stability argument supplementing the earlier rules of systematic crystal chemistry. For symbols used in the following see 64,86,87Sch.

Analysis

Li_3N (H3.1,SR3.325,42.107,drw64Sch.229) is a Lewis phase melting at 1088K; H3.1 is the structure type indicated by the symbols of 64Sch; SR3.325 and 42.107 are references to Structure Reports, volume and page; drw refers to a drawing to be found in 64Sch p.229. The N site set is of the H1 type and Li is in 2 and 3 coordination causing by the way a high ionic conductivity (81Rab). Since the average valence electron distances in Li and N are considerably different (86Sch Fig.2) an electron count $\text{Li}_3^{1,2}\text{N}^{0,5}$ may be used. It suggests the binding $\underline{a}(\underline{N}=3, 11)=\text{H}3.65; 3.87\text{\AA}=(\underline{b}\underline{v}\underline{c})_{\text{CH}}(\sqrt{3}; 4.7/3)$; here \underline{a} is the crystal cell matrix of Li_3N ; \underline{N} gives the numbers of $\underline{b}, \underline{c}$ electrons per \underline{a} to be calculated from electron count and structure symbol; $(\underline{b}\underline{v}\underline{c})_{\text{CH}}$ is the cell of the united \underline{b} and \underline{c} correlation being of the cubic primitive C type in hexagonal aspect H; $(\sqrt{3}; 4.7/3)$ is the symmetrical part of the commensurability matrix $(\underline{b}\underline{v}\underline{c})^{-1}\underline{a}$, in abbreviated notation(86Sch), the rotatory part of the commensurability matrix is not of interest and has been omitted. The binding has the collective property, it has a good commensurability in the basal plane of \underline{a} (86Sch Tab.1), while the non integral property of the commensurability matrix in \underline{a}_3 direction is tolerable (86Sch). The last commensurability element 4.7/3 indicates by the denominator the number of $(\underline{b}\underline{v}\underline{c})$ layers parallel to $\underline{a}_1, \underline{a}_2$ so that the correlation is fully occupied. The correlation is slightly compressed in \underline{a}_3 direction for structural reasons. Finally the binding displays a full spin compensation and therefore stabilizes the phase.

LiN_3 (H3.3,SR33.168,drwSR33.170) is an azide, the stability of the $(\text{N}_3)^-$ ion may be understood from the binding of KN_3 below. The discussion of LiN_3 shall be postponed.

$\text{NaN}_3 \cdot \text{h}$ (R1.3,SR1.276,33.168,drw64Sch.239) is a D-homeotype of NaCl with Cl replaced by N_3 . $\underline{a}(\underline{N}=3,69)=\text{H}3.65; 15.21\text{\AA}=(\underline{b}\underline{v}\underline{c})_{\text{CH}}(2; 18/3)$. Because of the considerable difference of the electron distance of Na2sp and N2sp it might perhaps be that the Na2sp electrons do not take part: $\underline{a}(\underline{N}=3,45)=\text{H}3.65; 15.21\text{\AA}=(\underline{b}\underline{v}\underline{c})_{\text{CH}}(\sqrt{3}; 18/3)$.

$\text{NaN}_3.r(\text{LiN}_3, \text{SR33.168})$, discussion will be postponed.

$\text{KN}_3.r(\text{U2.6, SR1.276, 289, drwSR1.276, 64Sch.240})$ is homeotypic to CsCl with K^+ ,⁸ in the Cs site and $(\text{N}_3)^-$ in the Cl site, $\underline{a} = \underline{a}_{\text{CsCl}}(\sqrt{2}; 2)$. The electron count $\text{K}^{1,8} \text{N}_3^{0,5}$ yields the binding $\underline{a}(\underline{N}=4, 92) = 6.11; 7.07 \underline{A} = \underline{b}_{\text{FU}}(\sqrt{2}; 2.5/2) = \underline{c}_{\text{C}}(\sqrt{18}; 5)$. The remarkable fit of the binding to the structure (see 64Sch.240) incidentally reveals the cause for the stability of the azide ion $(\text{N}_3)^-$. Isodesmic isotypes of $\text{KN}_3.r$ are KHF_2 and $\text{KCNO}(\text{SR1.279})$. The homeodesmism of $\text{CaC}_2(\text{U1.2, SR1.740})$, $\underline{a}(4, 32) = 3.84; 6.37 \underline{A} = \underline{b}_{\text{C}}(\sqrt{2}; 2.4) = \underline{c}_{\text{C}}(\sqrt{8}; 4.7)$ to KN_3 is interesting. It may be mentioned that the binding for KN_3 revives an old finding of the octet theory (see 28Eph p.120).

$\text{KN}_3.h(\text{cubic, see 78Pie})$, $\underline{a} = 9.6 \underline{A}$ should be further elaborated structurally.

$\text{RbN}_3.h(\text{cubic, see 78Pie})$, $\underline{a} = 4.35 \underline{A}$ is homeotypic to CsCl .

$\text{RbN}_3.r(\text{KN}_3.r, \text{SR38.187})$, $\underline{a}(\underline{N}=4, 92, 40) = 6.31; 7.52 \underline{A} = \underline{b}_{\text{B}}(\sqrt{2}; 1.7) = \underline{c}_{\text{B}}(\sqrt{18}; 10/2)$. The filling in of \underline{c}_{C} of KN_3 to \underline{c}_{B} occurs resumably only near the Rb atoms. Perhaps also $\text{Rb}3\text{sp}$ electrons take part.

$\text{CsN}_3.h(\text{cubic, see 78Pie})$, $\underline{a} = 4.54 \underline{A}$, is homeotypic to CsCl .

$\text{CsN}_3.r(\text{KN}_3.r, \text{SR38.187})$, $\underline{a} = 6.54; 8.09 \underline{A}$ is isodesmic to $\text{RbN}_3.r$.

$\text{Be}_3\text{N}_2.h(\text{H6.4, SR34.29})$ has a chch close packed N site set and Be lie in tetrahedral interstices. The electron count must be $\text{Be}_3^{2,2} \text{N}_2^{5,2}$ considering the electron distances (86Sch1). $\underline{a}(\underline{N}=32, 20) = \text{H}2.84; 9.69 \underline{A} = (\underline{b} \underline{c})_{\text{CH}}(2; 17/3)$. The CH correlation provides good spin compensation and favours the chch stacking following the rules of 84Sch. The $\underline{b} \underline{c}$ site number is greater than in the r phase following a general rule.

$\text{Be}_3\text{N}_2.r(\text{MnFeO}_3, \text{B24.16, SR3.353, drw64Sch.231})$ has a N_{F1} site set and Be in part of the tetrahedral interstices. $\underline{a}(\underline{N}=256, 160) = 8.15 \underline{A} = \underline{b}_{\text{F}}(4) = \underline{c}_{\text{F}}(4)$, i.e. $\underline{a} = (\underline{b} \underline{c})_{\text{C}}(8)$.

$\text{Mg}_3\text{N}_2(\text{MnFeO}_3, \text{B24.16, SR38.120})$, $\underline{a}(\underline{N}=96, 544) = 9.97 \underline{A} = \underline{b}_{\text{B}}(4) = \underline{c}_{\text{C}}(8)$. Mg_3N_2 is a Lewis phase, but the spins to compensate each other belong to different correlations. One electron per N is excited into the \underline{b} correlation.

$\text{Ca}_2\text{N}(\text{CdCl}_2, \text{R2.1, SR33.163})$ contains a Ca_{F1} site set with N in octahedral holes, it does not follow Lewis' rule. $\underline{a}(\underline{N}=12, 63) = \text{H}3.64; 18.78 \underline{A} = \underline{b}_{\text{CH}}(1; 12/3) = \underline{c}_{\text{CH}}(\sqrt{3}; 21/3)$. The good fit of \underline{b}_{C} makes Lewis compensation unnecessary.

$\text{Ca}_3\text{N}_2.r(\text{H?SR3.352})$, $\underline{a} = \text{H}3.55; 4.11 \underline{A}$, needs further elaboration.

$\text{Ca}_3\text{N}_2.h_1(\text{MnFeO}_3, \text{B24.16, SR33.50})$, $\underline{a}(\underline{N}=96, 544) = 11.42 \underline{A} = \underline{b}_{\text{B}}(4) = \underline{c}_{\text{C}}(8)$. Although Ca is a large atom the phase contains a N_{F1} site set.

$\text{Ca}_3\text{N}_2.h_2(024.16, 78Pie)$, $\underline{a}(\underline{N}=48, 272) = 17.82; 11.56; 3.85 \underline{A} = \underline{b}_{\text{FU}}(6; 4; 2) = \underline{c}_{\text{HT}}(12; 8; 3/2)$.

$\text{Ca}_3\text{N}_2.p(\text{O} \quad , 78Pie)$, $\underline{a} = 5.63; 11.40; 13.61 \underline{A}$, structure needs further elaboration.

$\text{Ca}_{11}\text{N}_8(\text{T2.16, SR34.54})$, $\underline{a}(\underline{N}=44, 256) = 14.45; 3.60 \underline{A} = \underline{b}_{\text{FU}}(5; 2/2) = \underline{c}_{\text{C}}(10; 2.5)$. As is seen Ca_{11}N_8 is cosely homeodesmic to $\text{Ca}_3\text{N}_2.h_1(\text{BC2})$. The compression of $\underline{b}_{\text{FU}}$ improves the spin compensation.

$\text{CaN}_6(\text{SrN}_6, \text{S2.12, 78Pie, drw64Sch.241})$ confirms the stability of azides found in

A^1N_M . $\underline{a}(N=16,304)=11.62;10.92;5.66\bar{A}=b_{FU}(\sqrt{8};2/2)=c_{HT}(8;4.8/2)$.
 $Sr_2N(CdCl_2, R2.1, SR38.135)$, $\underline{a}(N=12,63,60)=H3.85;20.69\bar{A}=b_{CH}(1;12/3)=c_{BH}(\sqrt{3};45/3)$.
 $Sr_8N_5(M, 78Pie)$, further elaboration is desirable.
 $SrN(NaCl, SR38.169)$, $\underline{a}(N=8,52,40)=5.50\bar{A}=b_C(2)=c_{FU}(4;6/2)$.
 $SrN_6(S2.12, SR11.357, drw64Sch.241)$, $\underline{a}(N=16,304,80)=11.82;11.47;6.08\bar{A}=b_{FU}(\sqrt{8};2/2)=c_{FU}(8;6/2)$. The proposal is tentative as in c no spin compensation is provided.
 $Ba_3N_4(H3.4, 78Pie)$, $\underline{a}(N=6,44,30)=H5.22;5.50\bar{A}=b_{CH}(1;4.5/3)=c_{CH}(\sqrt{7};7/3)$. The cell content is tentative and so is the binding proposal.
 $BaN_6(M2.12, SR34.169, drwibid.)$, $\underline{a}(N=4,76,20)=9.63;4.41;0.89,0,5.35\bar{A}=b_{FU}(2.3;1.5;1.3)=c_C(7;3;4)$. C' means that C is inserted by f electrons near the Ba atoms. The proposal can only be approximate with respect to the monoclinic symmetry. The binding analysis for complicated structures must remain tentative because there are very many possibilities available.

$ScN(NaCl, SR1.74, 139)$ melts at 2800K. $\underline{a}(N=12,52)=4.45\bar{A}=b'_B(2)=c_C(4)$, $b'=b^*e$. Presumably b , and the d electron correlation e , and c are united, $b^*e^*c=g$ (collective binding), so that $\underline{a}=g_C(4)$. It is to be assumed that the b correlation somehow exists in g , however, the binding analysis becomes very simple using g .

$YN(NaCl, SR21.160)$, $\underline{a}(N=12,52,40)=4.88\bar{A}=b_B(2)=c_B(4)$ or $\underline{a}=g_B(4)$.

$LaN(NaCl, SR16.105)$, $\underline{a}(N=12,52,40)=5.30\bar{A}=g_B(4)$. The Lewis composition $A_1^3N_1$ is so favourable that no other phases become stable.

$Ti_4N.h(Mg, 58Han)$ decomposes on heating at 2623K and is homogeneously connected with $Ti.r$. For a recent assessment of the phase diagram see 87Wri. $Ti_4N.h$ opens a series of subnitrides, and a Lewis phase does not become stable as the high number of spins in Ti moves the stability to a too high N content. If the binding $\underline{a}(Ti.r, N=8,16)=H2.95;4.68\bar{A}=(b^*e^*c)_{CH}(2;6.5/3)$ is accepted, it must be concluded that the insertion of N stabilizes the phase. $\underline{a}(Ti_4N.h, N=8,18.5)=H2.95;4.68\bar{A}=(b^*e^*c)_{CH}(2;7.5/3)$.

$Ti_2N(antiTiO_2.r, T4.2, SR27.308)$, $\underline{a}(N=16,42)=4.95;3.03\bar{A}=(b^*e)_{FU}(\sqrt{8};2.5)=c_C(4;2.5)$. The binding must be written $\underline{a}=g_{FU}(4;3.6)$ as the lattice constants suggest.

$Ti_2N_{1.2}.m(U4.(2.4), SR43.88)$ is topologically not isotypic to $ThSi_2(SR43.88)$ since $x_3(Ti)=0.268+x_3(Si)=0.417$, rather it is a Lhpt of $NaCl$ with ordered lacunae of the N site (77Nag). $\underline{a}(Ti_2N_{1.2}, N=32,88)=4.19;8.59\bar{A}=b_B(2;4)=c_C(4;8)$ or $\underline{a}=g_C(4;8.5)$. The value $(g^{-1}\underline{a})_{33}=8.5$ is necessary since also N lacunae may request c sites.

$TiN(NaCl, SR27.308)$ melts at 3500K and has a range of homogeneity $Ti_{68}N_{32}-Ti_{45}N_{55}$ at 1270K, if $N_N^<0.5$ N -lacunae and if $N_N^>0.5$ Ti -lacunae are found. $\underline{a}(N=16,52)=4.23\bar{A}=b_B(2)=c_C(4)$ or $\underline{a}=g_C(4)$. It must be assumed that $Ti_{1.0}N_{1.0}$ contains lacunae too (see 78Pie). A study of lacunae in TiO by the band model (84Sch) cannot be applied here since it does not lead to an electron count like that used above and appearing necessary for the whole problem. For earlier band theories see 71Tot.

$\text{Zr}_4\text{N}(\text{Mg}, \text{SR20.165})$, $\underline{a}(\underline{N}=8, 19, 20)=\text{H}3.2; 5.2\bar{A}=(\underline{b}\cdot\underline{e}\cdot\underline{c})_{\text{BH}}(2; 16/3)$.

$\text{ZrN}(\text{NaCl}, \text{SR18.253})$, $\underline{a}(\underline{N}=16, 52, 40)=4.54\bar{A}=\underline{b}_{\text{B}}(2)=\underline{c}_{\text{B}}(4)$ or $\underline{a}=\underline{g}_{\text{B}}(4)$. No lacunae are contained (78Pie).

$\text{Hf}_4\text{N}(\text{Mg}, \text{SR26.73})$, $\underline{a}(\underline{N}=8, 19, 28)=\text{H}3.22; 5.16\bar{A}=(\underline{b}\cdot\underline{e}\cdot\underline{c})_{\text{BH}}(2; 16/3)$.

$\text{Hf}_3\text{N}_2(\text{R}3.2, \text{SR35.68})$ contains a close packed Hf site set with the stacking sequence hchhchhch. $\underline{a}(\underline{N}=36, 102, 126)=\text{H}3.21; 23.26\bar{A}=\underline{g}_{\text{BH}}(2; 72/3)$. The comparison of 24 \underline{g} layers parallel to $\underline{a}_1\underline{a}_2$ with 9 Hf layers affords the above stacking sequence following the rule of 84Sch.

$\text{Hf}_4\text{N}_3(\text{V}_4\text{C}_3, \text{R}4.3, \text{SR35.69})$ displays a stacking cchhchhchh. $\underline{a}(\underline{N}=48, 141, 168)=\text{H}3.21; 31.12\bar{A}=\underline{g}_{\text{EH}}(2; 96/3)$. The stacking cannot obey the rule 84Sch since it is not uniformly distributed as requested in 84Sch.

$\text{HfN}(\text{NaCl}, \text{SR17.70})$, $\underline{a}(\underline{N}=16, 52, 56)=4.52\bar{A}=\underline{g}_{\text{B}}(4)$. Curiously lacunae are preported (78Pie).

$\text{V}(\text{W}, \text{B1}, \text{SR1.56}, 26.275)$, $\underline{a}(\underline{N}=10, 16)=3.02\bar{A}=\underline{g}_{\text{C}}(3)$. This binding evidently may be conserved when some N is solved.

$\text{V}_{16}\text{N}(\text{Q16.1}, \text{ActaMet}19.1971.881)$ has a V_{B1} site set, $\underline{a}=\underline{a}_{\text{B1}}(4; 1; 4)$, the insertion of N deforms the tetragonal cell. $\underline{a}(\underline{N}=160, 266)=12.14; 3.04; 12.50\bar{A}=\underline{g}_{\text{C}}(12; 3; 12)$.

$\text{V}_3\text{N}(\text{Fe}_3\text{N}, \text{H}6.2, \text{SR39.117}, 45.100, \text{drw64Sch.257})$ has a $\text{V}_{\text{H}2}$ site set, $\underline{a}=\underline{a}_{\text{H}2}(\sqrt{3}; 1)$, with H in octahedral interstices. $\underline{a}(\underline{N}=30, 58)=\text{H}4.91; 4.55\bar{A}=\underline{g}_{\text{CH}}(\sqrt{12}; 7/3)$. The strain of \underline{g}_{C} causes the axial ratio $|\underline{a}_3|/\sqrt{3}/|\underline{a}_1|=1.605\sqrt{8/3}$, and the V stacking is favoured by 7/3 following 84Sch.

$\text{VN}(\text{LhtpNaCl}, \text{SR11.171})$, $\underline{a}(\underline{N}=20, 52)=4.14\bar{A}=\underline{g}_{\text{C}}(4)$. It remains to be verified that the lacunae decrease $\Sigma \underline{N}=72$ down to 64.

$\text{Nb}(\text{W}, \text{SR1.754})$, $\underline{a}(\underline{N}=10, 16, 20)=\underline{g}_{\text{FU}}^*(3; 5.1/2)$. This curious interpretation of the Nb phase suggests to seek in VNb_{M} and NbTa_{M} for irregularities of properties in dependence of the mole fraction \underline{N}_2 . It should be noted that this binding proposal is homeotypic to an earlier one (82Sch2).

$\text{Nb}_2\text{N}(\text{W}_2\text{C}, \text{H}2.1, \text{SR23.99}, \text{drw64Sch.267})$, $\underline{a}(\underline{N}=10, 21, 20)=\text{H}3.06; 4.99\bar{A}=\underline{g}_{\text{FH}}(3; 6/3)$. The high electron density chooses \underline{g}_{F} and resigns to spin compensation.

$\text{Nb}_4\text{N}_3(\text{T}8.6, \text{SR26.215}, 78\text{Pie})$, $\underline{a}(\underline{N}=40, 94, 80)=4.38; 8.63\bar{A}=\underline{g}_{\text{FU}}(\sqrt{18}; 12/2)$. The F correlation does not contain spin compensation as has been said, presumably the collective binding in close packing is so favourable that it compensates for this.

$\text{NbN}_{0.8}(\text{WC}, \text{H}1.1, \text{SR18.236}, \text{drw64Sch.267})$, $\underline{a}(\underline{N}=5, 12, 10)=\text{H}2.95; 2.77\bar{A}=\underline{g}_{\text{UH}}(3; 3.3/2)$. A \underline{UH} correlation has a better spin compensation than a FH correlation, however, it has a similar axial ratio in the hexagonal aspect.

$\text{NbN}_{0.95}(\text{h}(\text{NaCl}, \text{SR23.100})$, $\underline{a}(\underline{N}=20, 51, 40)=4.39\bar{A}=\underline{g}_{\text{FU}}^*(4; 7/2)$. The compression of $\underline{g}_{\text{FU}}$ improves spin compensation. The number of sites per Nb is $\underline{N}_{\text{S}(\underline{g})}^{\text{Nb}}=28$.

$\text{NbN}_{0.98}(\text{antiNiAs}, \text{SR26.216})$, $\underline{a}(\underline{N}=10, 26, 20)=\text{H}2.97; 5.54\bar{A}=\underline{g}_{\text{UH}}^*(3; 6.7/2)$. The number of sites has a little increased, $\underline{N}_{\text{S}(\underline{g})}^{\text{Nb}}=30$.

$\text{NbN}(\text{TiP}, \text{H}4.4, \text{SR26.216}, \text{drw64Sch.267})$, $\underline{a}(\underline{N}=20, 52, 40)=\text{H}2.95; 11.25\bar{A}=\underline{g}_{\text{UH}}^*(3; 14/2)$.

The stacking sequence of atoms is cchccch and this sequence follows from \underline{g} according to the rules of 84Sch, $N_{S(\underline{g})}^{Nb} = 31$.

$Ta_{27}N(B27.1, SR27.307)$. The striking influence of a mole fraction $\underline{N}_N = 0.036$ on the structure must be connected with the exact fitting of the binding in Ta, $\underline{a}(Ta, N=10, 16, 28) = 3.30\text{\AA} = \underline{g}_B(3)$. When 2 N are contained in $\underline{a}(Ta_{27}N)$ then \underline{g}_B of Ta goes over to \underline{g}_B' : $\underline{a}(Ta_{27}N) = 10.11\text{\AA} = \underline{g}_B'(9; 9; 9+1/16)$ i.e. the \underline{g} correlation finds a new harmony in $\underline{a}' = \underline{a}_{Ta}(3; 3; 8)$. The tetragonal phase to be expected occurs in fact:

$TaN_{0.06}(DhtpTa, U1.1, SR22.177)$, $\underline{a} = 3.31; 3.38\text{\AA}$. In this finding the rule is contained that a \underline{g}_B binding deforms tetragonally.

$Ta_2N(W_2C.h, H2.1, SR18.245)$, $\underline{a}(N=10, 21, 28) = H3.04; 4.91\text{\AA} = \underline{g}_{UH}'(3; 6.5/2)$. The \check{U}_H correlation is homeotypic to the B correlation but closer packed and therefore more favourable in the Ta atom with high electron density.

$TaN_{0.85}(WC, H1.1, SR18.246)$, $\underline{a}(N=5, 12.3, 14) = H2.93; 2.88\text{\AA} = \underline{g}_{UH}'(3; 3.5/2)$. The \underline{g}_{UH} correlation has here a layer distance like a F_H type.

$TaN(CoSn, H3.3, SR23.102, drw64Sch.310)$, $\underline{a}(15, 39, 42) = H5.19; 2.91\text{\AA} = \underline{g}_{UH}'(\sqrt{27}; 3.6/2)$. The \underline{g} correlation is still of the \check{U}_H type with favourable spin array, $N_g^{g(\underline{g})} = 0.99$.

$TaN.h(NaCl, SR35.121)$, $\underline{a}(N=20, 52, 56) = 4.39\text{\AA} = \underline{g}_B(4)$. It should be noted that \underline{g}_B is less close packed than \underline{g}_F , it is chosen because of the high symmetry and spin compensation.

$Ta_5N_6(H10.12, SR34.168)$ is a close packing of \underline{N} with sequence hchc, the Ta being in octahedral holes. $\underline{a}(N=50, 140, 140) = H5.18; 10.35\text{\AA} = \underline{g}_{UH}(\sqrt{27}; 12.5/2)$. It should be noted that in this binding also $\underline{a} = \underline{b}_H(3; 6)$ is contained.

$Ta_4N_5(U4.5, SR34.168)$ is Lhtp to NaCl. $\underline{a}(N=40, 114, 112) = 6.83; 4.27\text{\AA} = \underline{g}_B(6; 3.75)$. With higher N content the less close \underline{g}_B is favoured. In this binding is contained $\underline{a} = \underline{b}_C(\sqrt{18}; 2.5)$.

$Ta_3N_5(Ti_3O_5, Q6.10, SR39.91, drw64Sch.275)$ exhibits a N_{F1} site set with Ta in some of the octahedral interstices. $\underline{a}(N=60, 196, 168) = 3.89; 10.26; 10.26\text{\AA} = \underline{g}_B(3.4; 9; 9)$. The low occupancy of this binding suggests that 60+196 electrons are in a \underline{g}_C correlation which is centered near Ta by the \underline{f} electrons.

$Cr.h(W, SR1.61, 20.68)$, $\underline{a}(N=12, 16) = 2.89\text{\AA} = \underline{e}'_F(\sqrt{2}; 3/2) = \underline{c}_C(\sqrt{8}; 2.8)$ perhaps.

$Cr_2N(W_2C.h, H2.1, SR2.792, drw64Sch.267)$, $\underline{a}(N=12, 21) = H2.78; 4.48\text{\AA} = \underline{b}'_{UH}(\sqrt{3}; 4/2) = \underline{c}_{CH}(\sqrt{3}; 7/3)$, $\underline{b}' = \underline{b} \cdot \underline{e}$. Although the $W_2C.h$ type occurred above with collective binding, here the localized binding appears inevitable. It causes the Mg-type stacking following 84Sch. It is closely homeotypic to $Cr_2AlC(H4.2.2, SR28.3)$ so called H phase, with $\{2Cr+Al\}_{H2}$, $\underline{a} = \underline{a}_{H2}(1; 3)$, and C in octahedral holes. These phases have been discussed by 69Sta and 72Now.

$CrN.h(NaCl, SR2.792)$, $\underline{a}(N=24, 52) = 4.15\text{\AA} = \underline{b}'_U(\sqrt{5}; 2.6) = \underline{c}_B(\sqrt{10}; 2.6)$. The binding is no longer collective. Since \underline{b}'_U is a sublattice of \underline{c}_B selfdeformation is possible.

CrN.r(htpNaCl,78Pie), $\underline{a}(N=12,26)=2.88;2.97;4.13\text{\AA}$. To be sure a binding analysis of such a phase should not be undertaken without full consideration of the magnetic data.

$\text{Mo}_2\text{N}_{0.8}\cdot\text{hU4}(.1.6), \text{ActaCryst.10.833}$ is homeotypic to NaCl. $\underline{a}(N=48,80,80)=4.20;8.01\text{\AA}=\underline{b}'_{\text{B}}(\sqrt{6.5;4})=\underline{c}'_{\text{B}}(\sqrt{13;6.25})$. The binding is homeotypic to that of CrN.h(NaCl), it shows that a cubic NaCl structure can only be an exception. The strain of B must be understood as a tendency to higher electron density.

$\text{Mo}_2\text{N.h}(\text{F1}(.0.5), \text{SR2.793})$ is L homeotypic to NaCl. $\underline{a}(N=24,42,40)=4.16\text{\AA}=\underline{b}'_{\text{B}}(\sqrt{6.5;2})=\underline{c}'_{\text{B}}(\sqrt{13;3.25})$. The reason for the cubic \underline{a} must lie in the high temperature since at lower temperature another tetragonal phase appears.

$\text{Mo}_2\text{N.r}(\text{U4}(.2,78\text{Pie}), \underline{a}(N=48,84,80)=4.21;8.04\text{\AA}=\underline{b}'_{\text{B}}(\sqrt{6.5;4})=\underline{c}'_{\text{B}}(\sqrt{13;6.5})$. This phase is identical with $\text{Mo}_2\text{N}_{0.8}\cdot\text{h}$ (57Eva).

$\text{MoN}_{1.0}(\text{H8.8}, \text{SR26.197}), \underline{a}=\text{MoH}_1(2). \underline{a}(N=48,104,80)=\text{H5.67;5.52}\text{\AA}=\underline{b}'_{\text{FH}}(\sqrt{12;4/3})=\underline{c}'_{\text{BH}}(\sqrt{12;16/3})$.

$\text{MoN}_{1.1}(\text{H8.8}, \text{SR18.224}, 26.197) \text{ htp MoN}, \underline{a}(N=48,104,80)=\text{H5.73;5.61}\text{\AA}$. The cell \underline{a} is so similar to $\underline{a}(\text{MoN})$ that no different binding appears possible. Therefore the difference of the phases needs confirmation. Perhaps there is only a difference of thermal treatment.

$\text{W}_2\text{N}(\text{F1}(.0.5), \text{SR2.795}, 22.178) \text{ Lhtp NaCl}$, preparation: W powder + NH_3 at 1000K, chemical analysis proved absence of H. Stability at lower temperatures appears to be unknown, but a reaction at 800K afforded other phases (SR22.178). $\underline{a}(N=24,42,56)=4.13\text{\AA}=\underline{b}'_{\text{C}}(\sqrt{8;3})=\underline{c}'_{\text{FU}}(4;6/2)$. The near homeotypism of $\underline{c}'_{\text{F}}$ to $\underline{c}'_{\text{F}}$ is caused by the high electron density in W.

$\text{W}_2\text{N.r}(\text{H6.3}, \text{SR24.201}, \text{drwSR26.220})$. The phase is only known from nitrided W foils. Preparation from W powder appears desirable. The structure has $\underline{a}\approx 8\underline{a}(\text{WN}_{0.7})$ but is said to contain only 6W, this difficulty should be solved.

$\text{WN}_{0.7}(\text{WC}, \text{H1}(.0.7), \text{SR18.225}, 22.178)$ was prepared from W powder and from W foil at various temperatures. $\underline{a}(N=6,11.5,14)=\text{H2.89;2.83}\text{\AA}=\underline{b}'_{\text{FH}}(\sqrt{3;2.1/3})=\underline{c}'_{\text{BH}}(\sqrt{3;8.3/3})$. The \underline{c} correlation displays a favourable spin compensation. The next 3 structures are known only from nitrided W foils and need confirmation as they do not yield a smooth dependence of the atomic volume on the mole fraction.

$\text{WN}_{0.85}(\text{H7.6}, \text{SR27.303}), \underline{a}=\text{H2.89;23.35}\text{\AA}$,

$\text{WN}_{0.87}(\text{H6.5}, \text{SR22.178}), \underline{a}=\text{H2.89;15.30}\text{\AA}$,

$\text{WN}_{0.91}(\text{H}(2.2).2, \text{SR28.32}), \underline{a}=\text{H2.89;10.80}\text{\AA}$,

$\text{W}_3\text{N}_4(\text{C3.4}, \text{SR15.110}, 18.244, 31.54), \underline{a}(N=18.44,42)=4.12\text{\AA}=\underline{b}'_{\text{C}}(\sqrt{8;2.8})=\underline{c}_{\text{FU}}(4;5.6/2)$.

$\text{WN}_{1.5}(\text{H}(2.6).4, \text{SR26.222}, 28.32), \underline{a}=\text{H2.89;11.00}\text{\AA}$, needs confirmation.

It must be admitted that a part of the binding proposals for $\text{A}^6\text{N}_\text{M}$ phases is not very convincing. Perhaps an important idea for these phases is still missing.

$\text{Mn}_4\text{N}_{0.3}\cdot\text{h}(\text{T4}(.0.3), \text{SR2.790}), \underline{a}(N=28,34)=3.78;3.69\text{\AA}=\underline{g}_{\text{C}}(4;3.9)$. At temperatures near 1000K the binding appears to be collective.

$\text{Mn}_4\text{N}_{0.6} \cdot \text{h}(\text{C4} \cdot (0.6), \text{SR21.150})$, $\underline{a}(\underline{N}=28,35)=3.78\text{\AA}=\underline{c}_{\text{C}}(4)$.

$\text{Mn}_4\text{N}(\text{Fe}_4\text{N}, \text{C4.1}, \text{SR2.790})$, $\underline{a}(\underline{N}=28,37)=3.86\text{\AA}=\underline{b}'_{\text{F}}(2;3.5/2)=\underline{c}_{\text{B}}(\sqrt{8};2.3)$. The binding is similar as in $\text{Mn}_4\text{N}_{0.3} \cdot \text{h}$ but of the localized kind. A collective binding would not be possible because of high electron number.

$\text{Mn}_2\text{N}(\text{W}_2\text{C}, \text{H2.1}, \text{SR2.791})$, $\underline{a}(\underline{N}=14,21)=\text{H2.83}; 4.54\text{\AA}=(\underline{b}\underline{v}\underline{e})_{\text{FH}}(2;4/3)=\underline{c}_{\text{CH}}(\sqrt{3};7/3)$. The increase of $\underline{N}/\underline{a}$ has changed the type of \underline{c} from $\underline{c}_{\text{B}} \approx \underline{c}_{\text{FU}}$ to \underline{c}_{C} . The odd value of $(\underline{c}^{-1}\underline{a})_{33}$ favours the Mg type stacking of Mn according to 84Sch.

$\text{Mn}_2\text{N.1}(\text{Fe}_2\text{N.1}, 08.4, \text{SR33.111}, \text{drw64Sch.257})$, $\underline{a}(\underline{N}=56,84)=5.67; 4.91; 4.54\text{\AA}$. The antiferromagnetic structure must be homeodesmic to Mn_2N .

$\text{Mn}_3\text{N}_2 \cdot \text{r}(\text{U3.2}, \text{htpNaCl}, \text{SR27.27}, 51.68)$, $\underline{a}(\underline{N}=42,68)=2.97; 12.13\text{\AA}=(\underline{b}\underline{v}\underline{e})_{\text{C}}(\sqrt{5};8)=\underline{c}_{\text{B}}(\sqrt{5};8)$. The compound transforms to $\text{Mn}_3\text{N}_2 \cdot \text{h}$ at 930K and decomposes at 1420K (84Jac). From Xray data it is confirmed that no N^{3-} is present (84Jac). The deformation of \underline{c}_{B} is caused by $(\underline{b}\underline{v}\underline{e})$. The strain of $(\underline{b}\underline{v}\underline{e})_{\text{C}}$ keeps $|\underline{a}_3|/|\underline{a}_1|$ independent on \underline{N}_{N} (SR27.271). A second phase of this type has been described:

$\text{Mn}_4\text{N}_{3.5}(\text{LDhtpNaCl}, \text{SR16.112}, 27.271)$, $\underline{a}(\underline{N}=28,50)=4.22; 4.13\text{\AA}=(\underline{b}\underline{v}\underline{e})_{\text{C}}(\sqrt{10};2.8)=\underline{c}_{\text{B}}(\sqrt{10};2.8)$. $\text{Mn}_4\text{N}_{3.5}$ is homeodesmic to $\text{Mn}_3\text{N}_2=\text{Mn}_4\text{N}_{2.7}$, only the commensurability has jumped to another value. The less favourable commensurability element $(\underline{c}^{-1}\underline{a})_{33}$ causes a lower maximum decomposition temperature for $\text{Mn}_4\text{N}_{3.5}$ than for Mn_3N_2 (SR27.271). Since $|\underline{a}_3|/|\underline{a}_1|$ increases with increasing \underline{N}_{N} the existence of a cubic phase (SR16.112) appears conceivable. The example of the MnN_{M} phases clearly shows how helpful (although sometimes tentative) the bindings of the plural-correlations model are for the understanding of stability in simple mixtures.

$\text{TcN}_{0.8}(\text{LhtpNaCl}, 78\text{Pie})$, $\underline{a}(\underline{N}=28,48,40)=3.98\text{\AA}=(\underline{b}\underline{v}\underline{e})_{\text{FU}}(\sqrt{6.5};4.5/2)=\underline{c}'_{\text{B}}(\sqrt{13};3.5)$, $\underline{c}'_{\text{B}}$ is not deformed since $\underline{b}'=\underline{b}\underline{v}\underline{e}$ is not in good commensurability to \underline{c}' . For "TcN(NaCl)" would come $\underline{N}=28,52,40$ so that $\underline{c}'_{\text{B}}$ would be filled too much.

$\text{ReN}_{0.43}(\text{LhtpNaCl}, \text{SR13.142})$, $\underline{a}(\underline{N}=28,41,56)=3.93\text{\AA}=(\underline{b}\underline{v}\underline{e})_{\text{FU}}(\sqrt{6.5};4.5/2)=\underline{c}'_{\text{B}}(\sqrt{13};3.75)$. The high f electron contribution causes the low N content.

$\text{Fe}_{12}\text{N.h}(\text{FhtpCu}, \text{SR15.84})$, $\underline{a}(\underline{N}=32,34)=3.64\text{\AA}=\underline{b}'_{\text{FU}}(\sqrt{8};4.3/2)=\underline{c}_{\text{FU}}(\sqrt{8};4.3/2)$. In Fe.h_2 (Cutype) the binding was found (87Sch2) $\underline{a}=\underline{b}_{\text{F}}(1)=\underline{e}_{\text{F}}(2)=\underline{c}_{\text{F}}(2)$, it is here slightly compressed. For a recent review of FeN_{M} see 87Wri.

$\text{Fe}_{12}\text{N.m}(\text{FDhtpN}, \text{SR15.84})$, $\underline{a}(\underline{N}=16,17)=2.85; 3.09\text{\AA}=\underline{b}'_{\text{B}}(\sqrt{5};1.8)=\underline{c}_{\text{B}}(\sqrt{5};1.8)$. The binding should be compared with the bindings of Fe.r and Fe.h_1 (87Sch2). The \underline{e} and \underline{c} correlation deform each other. The deformation cannot attain the cubic NaCl type because of packing density. The dependence of $|\underline{a}_3|/|\underline{a}_1|$ on \underline{N}_{N} (64Sch.256) is compatible with the binding proposal.

$\text{Fe}_4\text{N}(\text{C4.1}, \text{SR2.784}, 87\text{Jac})$, $\underline{a}(\underline{N}=32,37)=3.79\text{\AA}=\underline{b}'_{\text{B}}(\sqrt{8};2.3)=\underline{c}_{\text{B}}(\sqrt{8};2.3)$. The binding must be twinned, of course, to yield the crystal symmetry. $\underline{b}\underline{v}\underline{e}$ and \underline{c} suffer from self deformation (87Sch2). The partial occupation of the $(\underline{b}\underline{v}\underline{e})$ correlation is compatible with the ferromagnetism of Fe_4N (87Jac). While neutron diffraction (58Fra) suggested $9\mu_{\text{B}}$ per \underline{a} the present proposal yields $5\mu_{\text{B}}$. Fe_4N is a member of

the comprehensive type of perovskites discussed by 69Sta using the model of electron pair bonds.

Fe_3N (H6.2,SR2.302,drw64Sch.257), $\underline{a}(\underline{N}=48,58)=\text{H}4.67;4.37\text{\AA}=\underline{b}'_{\text{FH}}(\sqrt{12};4/3)=\underline{c}_{\text{CH}}(3;7/3)$. If the \underline{c}_{B} correlation of Fe_4N is described approximately by $\underline{a}=\underline{c}_{\text{F}}(2)$ then in the hexagonal mesh of Fe_4N four sites are accepted. In the neighbouring Fe_3N there are only three sites, but the stacking of the planes is much closer. The same binding was observed in Mn_2N .

Fe_2N (08.4,SR11.143,drw64Sch.257), $\underline{a}(\underline{N}=64,84)=5.52;4.83;4.43\text{\AA}$. The phase is homeotypic to Fe_3N and will also be homeodesmic. Two azides, FeN_6 and FeN_9 have been mentioned by 87Wri.

Co_4N (Fe_4N ,SR24.128), $\underline{a}(\underline{N}=36,37)=3.74\text{\AA}=\underline{b}'_{\text{B}}(\sqrt{8};2.3)=\underline{c}_{\text{B}}(\sqrt{8};2.3)$.

Co_3N (Fe_3N ,SR10.44), $\underline{a}(\underline{N}=54,58)=\text{H}4.61;4.36\text{\AA}$, is isodesmic to Fe_3N .

Co_2N (04.2,SR15.31,drw64Sch.257), $\underline{a}(\underline{N}=36,42)=2.85;4.61;4.34\text{\AA}$. Consideration is postponed.

Ni_4N (Fe_4N ,SR24.192), $\underline{a}(\underline{N}=40,37)=3.72\text{\AA}=\underline{b}_{\text{F}}(1)=\underline{e}_{\text{B}}(\sqrt{8};2.3)=\underline{c}_{\text{B}}(\sqrt{8};2.3)$. The isotypism of Mn_4N , Fe_4N , Co_4N and Ni_4N is caused by the fact that the \underline{c} correlation is always the same, while the \underline{e} correlation undergoes only slight change. The \underline{b} correlation is separated from the \underline{e} correlation.

Ni_3N (Fe_3N ,SR13.140), $\underline{a}(\underline{N}=60,58)=\text{H}4.62;4.31\text{\AA}$ is isodesmic to Fe_3N .

Cu_3N (ReO₃C3.1,SR6.67,8.65) is a Lewis phase while in $\text{A}^{4...10}\text{N}_{\text{M}}$ such phases were rare because the many free spins of the A component preferred a compensation between A. Since it is not probable that the N2sp electrons form a correlation together with the Cu4s electrons because of the difference of the electron distances, the assumption must be continued that Cu3sp and N2sp form a common correlation. $\underline{a}(\underline{N}=3,30,29)=3.81\text{\AA}=\underline{b}_{\text{F}}(1)=\underline{e}_{\text{F}}(2)=\underline{c}_{\text{F}}(2)$. This proposal is only an approximation because the spin compensation in \underline{e} and \underline{c} has not been taken into account. If \underline{e} and \underline{c} are united then a $\hat{\text{C}}$ type correlation is formed providing good spin compensation.

CuN_3 (U4.12,SR11.356,drw64Sch.241) contains Cu-N_3 strings like KN_3 but the Cu do not form a simple site set. $\underline{a}(\underline{N}=8,80,184)=8.67;5.60\text{\AA}=\underline{b}_{\text{FU}}(2;2.3/2)=\underline{e}_{\text{FU}}(\sqrt{20};4/2)=\underline{c}_{\text{HT}}(\sqrt{40};4.7/2)$. The binding proposal is only tentative.

CuN_6 (04.24,SR33.510), the binding analysis must be postponed.

Ag_3N (Fe_4N ,SR13.142) is apparently heterotypic to Cu_3N as has been proven by mass density measurements. $\underline{a}(\underline{N}=4,40,37,40)=4.3\text{\AA}=\underline{b}_{\text{F}}(1)=(\underline{e}\underline{c}\underline{v}\underline{f})_{\text{B}}(4)$. The heterotypism must be caused by the \underline{f} electrons.

AgN_3 (P2.6,SR3.75) is D-homeotypic to KN_3 .r. $\underline{a}(\underline{N}=4,40,92,40)=5.59;5.94;6.04\text{\AA}=\underline{b}_{\text{FU}}(\sqrt{2};2.2/2)=(\underline{e}\underline{v}\underline{c}\underline{v}\underline{f})_{\text{B}}(\sqrt{18};4.8)$.

Zn_3N_2 (MnFeO_3 ,B24.16,SR8.104,drw64Sch.231) shows a $\text{N}_{\text{F}1}$ site set with $\underline{a}=\underline{a}_{\text{F}1}(2)$. $\underline{a}(\underline{N}=96,480,544)=9.74\text{\AA}=\underline{b}_{\text{FU}}(4;6)=\underline{e}_{\text{C}}(8)=\underline{c}_{\text{C}}(8)$. \underline{b} must be twinned and \underline{c} gives electrons to \underline{e} . The binding could also be written $\underline{a}=\underline{b}_{\text{B}}(4)=(\underline{e}\underline{v}\underline{c})_{\text{B}}(8)$.

$\text{Cd}_3\text{N}_2(\text{MnFeO}_3, \text{B24.16, SR8.44})$, $\underline{a}(\underline{N}=96, 480, 544, 480)=10.79\text{\AA}$. The isotypism of Cd_3N_2 to Zn_3N_2 suggests that in Cd_3N_2 the correlation of the Cd3d electrons is not of a high influence.

$\text{CdN}_6(08.48, \text{SR5.66})$ the structure appears to be unknown so far.

$\text{HgN}_6(04.24, \text{SR39.137})$, the consideration must be postponed.

$\text{BN}(\text{H2.2, SR1.95, 13.44, drw64Sch.180})$ has depending on the preparation, slightly different atomic sites. $\underline{a}(\underline{N}=16, 8)=\text{H2.52}; 6.69\text{\AA}=\underline{b}_{\text{UH}}(\sqrt{3}/6/2)=\underline{c}_{\text{CH}}(\sqrt{3}/12/3)$. For BN (R1.1, SR22.217) $\underline{a}=\text{H2.50}; 10.01\text{\AA}$ an isotypic binding applies. The $\underline{b}_{\text{UH}}$ correlation allows a good spin compensation. Two \underline{b} sites may be occupied by impurity electrons.

$\text{BN.p}(\text{ZnS, F1.1, SR21.194})$, $\underline{a}(\underline{N}=32, 16)=3.62\text{\AA}$. The homeotypism to BN becomes apparent in the hexagonal aspect: $\underline{a}_{\text{H}}(\underline{N}=24, 12)=\text{H2.56}; 6.27\text{\AA}=\underline{b}_{\text{UH}}(\sqrt{3}/6/2)=\underline{c}_{\text{CH}}(\sqrt{3}/10/3)$. This may be contracted to $\underline{a}_{\text{H}}=(\underline{b}\underline{v}\underline{c})_{\text{CH}}(\sqrt{3}/12/3)$, a collective binding.

$\text{AlN}(\text{ZnO, H2.2, SR1.79, 20.18})$, $\underline{a}(\underline{N}=6, 26)=\text{H3.12}; 4.99\text{\AA}=\underline{b}_{\text{BH}}(1/7/3)=\underline{c}_{\text{CH}}(2/7/3)$. The $\underline{b}_{\text{BH}}$ and $\underline{c}_{\text{CH}}$ correlations are strained in \underline{a}_3 direction, and therefore $|\underline{a}_3|/|\underline{a}_1| < \sqrt{8/3}=1.63$. If the correlations are smeared in $\underline{a}_1, \underline{a}_2$ direction then electrodiopole vectors in \underline{a}_3 direction are generated that favour the Mg type stacking of the Al layers parallel to $\underline{a}_1, \underline{a}_2$ (see84Sch).

$\text{GaN}(\text{ZnO, H2.2, SR6.4})$, $\underline{a}(\underline{N}=6, 20, 26)=\text{H3.19}; 5.18\text{\AA}=\underline{b}_{\text{BH}}(1/7/3)=\underline{c}_{\text{BH}}(2/14/3)$.

$\text{InN}(\text{ZnO, SR6.4})$, $\underline{a}(\underline{N}=6, 20, 26, 20)=\text{H3.54}; 5.70\text{\AA}=\underline{b}_{\text{BH}}(\sqrt{1.06}/8/3)=\underline{c}'_{\text{BH}}(\sqrt{4.25}/16/3)$. The geometrical possibility of a $\sqrt{13/4}$ commensurability allows the stability of InN. Conspicuously a "TIN" has not been found so far, as a further favourable commensurability element is not available.

$\text{TlN}_3(\text{KN}_3, \text{U2.6, SR38.187})$, $\underline{a}(\underline{N}=12, 40, 92, 56)=6.21; 7.36\text{\AA}=\underline{b}_{\text{FU}}(2/3/2)=\underline{e}_{\text{F}}(2/2.5)=\underline{c}_{\text{B}}(4/4.7)$.

$\text{Si}_3\text{N}_4 \cdot \text{h}(\text{H6.8, SR26.292, drwibid.})$ contains SiN_4 tetrahedra sharing corners such that a N belongs to 3 tetrahedra. $\underline{a}(\underline{N}=24, 88)=\text{H7.61}; 2.91\text{\AA}=\underline{b}_{\text{CH}}(3/3/3)=\underline{c}_{\text{UH}}(\sqrt{27}/3/2)$. The \underline{c} correlation is slightly overoccupied, this could be corrected by the homeotypic binding $\underline{a}=\underline{b}_{\text{CH}}(\sqrt{31}/3/3)=\underline{c}_{\text{UH}}(\sqrt{31}/3/2)$. The commensurability element $(\underline{c}^{-1}\underline{a})_{33}=3/2$ suggests that a r phase must be stable.

$\text{Si}_3\text{N}_4 \cdot \text{r}(\text{H12.16, SR34.166, drwibid.})$, $\underline{a}(\underline{N}=48, 176)=\text{H7.77}; 5.62\text{\AA}=\underline{b}_{\text{UH}}(\sqrt{12}/4/2)=\underline{c}_{\text{UH}}(6/6/2)$. At lower temperatures the occupancy of the \underline{c} correlation decreases.

$\text{Ge}_3\text{N}_4 \cdot \text{h}(\text{Si}_3\text{N}_4 \cdot \text{h, H6.8, SR22.125})$, $\underline{a}(\underline{N}=24, 60, 88)=\text{H8.04}; 3.07\text{\AA}=\underline{b}_{\text{CH}}(\sqrt{31}/3/3)=\underline{e}_{\text{H}}(\sqrt{31}/2)=\underline{c}_{\text{UH}}(\sqrt{31}/3/2)$.

$\text{Ge}_3\text{N}_4 \cdot \text{r}(\text{Si}_3\text{N}_4 \cdot \text{r, H12.16, SR22.125})$, $\underline{a}(\underline{N}=48, 120, 176)=\text{H8.20}; 5.94\text{\AA}$ is homeodesmic to h.

$\text{PbN}_6(012.72, \text{SR34.170})$, $\underline{a}=11.33; 16.28; 6.64\text{\AA}$. The discussion is postponed.

Discussion

The purpose of the present investigation is to seek new valence rules in AN_M phases. The instrument for this search is the plural-correlations model (86SchI) giving an advantage over an intuitive search because it is founded on the density matrix concept. A comparison of 82SchI with the present analysis shows that many bindings have remained essentially the same (KN_3, Mg_3N_2, ScN , etc.), and that many phases not interpreted earlier are now interpreted ($Ta_{27}N, W_2N, Co_4N, Ag_3N$, etc.). On the other hand many phases have changed somewhat their binding proposal due to the new electron count. The internal consistency of the interpretation has thus increased. This is also confirmed by the following explanations of phenomena not understood earlier.

Why alternates the direction of the $(N_3)^-$ ion in KN_3 when the observer proceeds in \underline{a}_3 direction? The \underline{c} correlation proposed above generates at the ions electro dipoles and quadrupoles which would have a higher energy when the direction would remain the same.

Why has $ScN(NaCl)$ no lacunae and TiN has? In both phases applies the collective binding $\underline{a}=\underline{g}_C(4)$. This would be overfilled in the case of a fully occupied TiN , but it is completely filled in the case of ScN .

Why is Ti_4N stabler than Ti_r although both phases are homogeneously connected? The collective binding is essentially the same in Ti_r and Ti_4N , but in Ti_r it is strained and in Ti_4N it is not, so that its stability is higher.

Why is $Ta_{27}N$, a subnitride of an uncommon composition, stable? This phenomenon is a consequence of the peculiar binding of Ta : $\underline{a}(Ta, N=10,16,28)=3.30\underline{a}=\underline{g}_B(3)$. The binding is completely filled and reacts sensitively to the filling in of N . $\underline{a}(Ta_{0.037}, N=10,16,37,28)=\underline{g}_B(3;3;3.02)$ so that for $25 \underline{a}_3 \approx 8 \times 3 \underline{a}_3$ a new harmony is found. It should be expected that samples may be prepared with other harmonies.

Why has $VN(hcpNaCl)$ lacunae and $TaN.h(NaCl)$ has not? This follows from the bindings $\underline{a}(VN, N=20,52)=\underline{g}_C(4)$ and $\underline{a}(TaN, N=20,52,56)=\underline{g}_B(4)$. Only the first binding is overfilled in the ideal $NaCl$ type.

Why is the perovskite phase $Fe_4N(C4.1)$ stable? The binding in the high temperature phase Fe_4 , $\underline{a}(Fe_4, N=32,32)=3.65\underline{a}=\underline{b}_F(1)=\underline{c}_F(2)=\underline{c}_F(2)$ is fully occupied in \underline{c} but has no good spin compensation. When additional \underline{c} electrons are filled in and the commensurability in $\underline{a}_1, \underline{a}_2$ direction is conserved then \underline{c}_B will be approached. However, this would not be stable in the presence of \underline{e}_B because of self deformation (87SchII). Since $\underline{a}(Fe_4) = \underline{c}_F(2) = \underline{c}_B(\sqrt{8};2)$ and $\underline{a}=\underline{c}_B(\sqrt{8};2.8)$ in the case of a deformed B correlation, the expected binding of Fe_4N would be $\underline{a}=\underline{b}_F(1) = \underline{e}_B(\sqrt{8};2.4) = \underline{c}_B(\sqrt{8};2.4)$. This is near to the binding of Fe_4N proposed in the analysis.

Why are $Cu_3N(ReO_3)$ and $Ag_3N(Fe_4N)$ heterotypic? The bindings may be $\underline{a}(Cu_3N, N=3,30,29)=3.81\underline{a}=\underline{b}_F(1)=(\underline{e} \vee \underline{c})_C(4)$, and $\underline{a}(Ag_3N, N=4,40,37,40)=4.38\underline{a}=\underline{b}_F(1)=(\underline{e} \vee \underline{c} \vee \underline{f})_B(4)$

corresponding for instance to $\underline{a}(\text{TiN})=\underline{g}_C(4)$ and $\underline{a}(\text{ZrN})=\underline{g}_B(4)$.

Why is $\text{AlN}(\text{ZnO})$ not of the NaCl type like ScN or of the ZnS.r type like AlP? The ionic radius $\underline{r}(\text{Al}^{3+})$ is smaller than $\underline{r}(\text{Sc}^{3+})$, therefore only the ZnO or ZnS.r types are possible for AlN. In the case " $\text{AlN}(\text{ZnS.r})$ " the electron count $\underline{N}=12,52$, is not sufficient for a localized correlation binding $\underline{a}=\underline{c}_C(4)$. Therefore \underline{c}_C must be strained and since $\underline{C}_{[111]}$ is the easy strain direction, the structure becomes hexagonal. For the reasons mentioned in the analysis above the ZnO type is favourable.

The series of questions could be further extended, and answers become possible when there is a sufficient number of crystal chemical rules. This number has been considerably increased by the plural-correlations model (83,86Sch) and additional rules presumably will be found by application of the model to additional classes of phases, for instance to the three component nitrides (78Pie).

It is an indication for a useful model that it not only answers numerous old questions but also poses numerous new ones. The electrostatic implications of a spatial correlation for instance are related to the electrostatic implications of the electron density (Born, Madelung). But they go beyond those since they have to do with the pair density not with the number density of electrons. It is clear that before working on this problem at first the plural-correlations model must be more firmly established and this is possible only by inference from empirical data, i.e. once more by applying the model to additional classes of phases.

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