On the Bindings in AF_M phases

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Summary

The attribution of bonding types (bindings) to fluorides containing one additional component A is improved. The change became necessary by the extension of the draught of the bonding types, found in the elements. The correlation in the outmost d band has been introduced below the valence band b as e correlation, and below the outmost noble gas band c, a closing ground correlation g has been inserted providing an idea as to where the lowest electrons influencing the bonding might preferentially lie. In most cases considered below the correlations are collective i.e. the energetically higher correlation lattice is a sublattice of the lower correlation lattices. Thus the bonding type is a geometrical figure displaying a certain commensurability to the crystal structure and suggesting its real existence by numerous striking relations to the crystal cell and the atomic sites. The obtained interpretations of the stable fluorides exceed the interpretations provided by the models of ionic and covalent bond and by the band model because important crystal chemical rules (e.g. the site number rule) have only been formulated in the electron correlations model. The new interpretations lead to interesting experimental problems.

Introduction

The crystal structures of fluorides are reported in 31Ewa,68Can,69Col,72Win, 73O'Do, -73Pie,82Gre. Arguments for the bonding types may be found in 70Hop,73O'Do, 75Wel, -79Has,82Sch. In the following the binding proposals of 82Sch shall be improved by taking into account the larger draught of the binding found in the structures of the elements (89Sch). Nevertheless the above references shoud bee consulted for additional structural remarks. Although some of the proposals of 82Sch are the same as in the following, the difference in the electron count introduces numerous changes. The electron count of the atomic shells enjoys general agreement, but the combination of shells to bands is still a matter under discussion. One combination may provide easy bonding type analysis, the other not. It appears that the valence electrons of fluorine are mostly in correlation with the c shell of A. For every compound the assumed electron count is noted in the following between the crystal cell symbol a and its numerical value. The occupancy of b is mostly 1.0 but it becomes smaller in r, c, g, the latter being quite sparsely occupied. Nevertheless, g is important for the structure as may be seen in UF_6 or $13F.r$. Each binding proposal determines a set of electron distances d and these, conforming to the distance rule, permit smooth interpolation curves over the mole fraction N_2^c (86Sch). It appears instructive to draw the $d(N_2^c)$ diagram of a mixture and to compare it with neighbouring diagrams. Mostly the dilution of a component leads to an increase of its electron distances being equivalent to an expansion of the correlation. This finding appears natural since the correlation between electrons of the same kind of atom must be especially strong. Since the expansion in the lower shells is smaller than in the higher shells, changes of commensurability occur which correspond to changes in energy of formation. Also since with increasing N_F^c the d_{AA} increase but the d_{FF} decrease, compositions of optimum harmony will exist which must correspond to compositions of phase formation.

Analysis

LiF(NaCl,SR1.73) obeys Lewis' spin compensation rule and Zintl's electron supply rule. $a(4,28,16) = 4.03\text{Å} = b_F(1) = c_C(4) = q_B(4)$ for symbols see 86Sch. b is collective with c, i.e. it is a sublattice of c, so that it is trapped in c. The c correlation is only half occupied since a correlation $a = c_F(2)$ is weakly present just as in the noble gas structures.

NaF(NaCl,SR1.73) $a(4,32+28,16) = 4.63\text{Å} = b_F(1) = c_C(4) = q_F(4)$. The ionic radii of the components yield a ratio $0.98/1.33 = 0.74$ favouring the CsCl type (see e.g.64Sch.42). But NaCl contains a q_F correlation while CsCl contains q_C (see KF.p), that might be a bonus for the NaCl type. The occurrence of a q_F correlation may be caused by a high electron density, it often appears also in actinon fluorides. The fully occupied c_C correlation cannot contribute to electrical conductivity because its band is filled.

KF.r(NaCl,SR1.73), $a(4,60,40) = 5.34$ is isodesmic to NaF by $F_1C_4F_4$.

KF.p(CsCl,73Pie) confirms that the radius of F^{1-} is easier decreased by pressure than

that of K^{1+} so that 8-coordination is stabilized. $a(1,15,10)=3.06Å=b_C(1)=c_B(2)=g_C(4)$.
Since c is closer packed in p than in r, it must be assumed that c is decisive for the structure adopted.

RbF.r(NaCl,SR1.73), $a(4,60,48)=5.63Å$ idmNaF.

RbF.p(CsCl,SR27.425), $a(1,15,12)=3.27Å$ idmKF.p.

CsF.r(NaCl,SR1.73), $a(4,60,48)=6.02Å$ idmNaF.

CsF.p(CsCl,73Pie), $a(1,15,12)=3.39Å$ idmKF.p.

$BeF_2.h_2(SiO_2.h_2,F2.4,SR20.216,drw64Sch.200)$ has an ionic radius ratio that stabilizes a BeF_4 coordination (SR20.216) but the atomic volume requests FBe_2 coordination. $a(16,112,48)=6.79Å=b_B(2)=c_B(4)=g_C(8)$. Several b sites are quite appart from the atoms so that the structure is stable only as h_2, $N/At_{S(c)}=5.3$.

$BeF_2.h_2m(SiO_2.h_2m,T8.16,73Pie)$, $a(16,112,48)=6.61;6.75Å$, binding proposal is postponed. Note that $SiO_2.h_2m$ has a C-centred cell and $|a_3|/|a_1|$ is underideal while in $BeF_2.h_2$ it is overideal.

$BeF_2.h_1(O64.128,htpSiO_2.h_1,73Pie)$, binding proposal is postponed.

$BeF_2.r_2(SiO_2.r_2,H3.6,SR16.167,73Pie)$, $a(6,42,18)=H4.73;5.25Å=b_{BH}(1;5.5/3)=c_{BH}(2;11/3)=g_{CH}(4;11/3)$. $N/At_{S(c)}=4.9$ has decreased conforming to the site number rule.

$BeF_2.r_1(SiO_2.r_1,H3.6,73Pie)$, $a(6,42,18)=H4.73;5.19Å$ exhibits a further decrease of axial ratio and therefore of site number per atom.

$MgF_2(TiO_2.r,T2.4,SR1.158,drw64Sch.275)$ is a Lewis phase with $MgF_{6/3}$ coordination. It may be considered as a remote lacuna and deformation homeotype of NaCl (LDhtpNaCl), therefore Zintl's rule is poorly fulfilled. $a(4,16+28,12)=4.65;3.12Å=b_C(\sqrt{5};1.5)=c_C(\sqrt{20};3)=g_B(\sqrt{20};3)$. $N/a_{S(c)}=60$ while it was 64 in NaF.

$CaF_2.r(F1.2,SR1.148)$ is a Lewis phase with $CaF_{8/4}$ coordination and it is LhtpCsCl. $a(8,32+56,48)=5.46Å=b_C(2)=c_B(4)=g_C(8)$, $N/At_{S(c)}=10.7$.

$CaF_2.p>100kb(PbCl_2,O4.8,73Pie,drw64Sch.322)$ RDhtpCu, $a(8,32+56,48)=3.58;5.96;7.01Å=b_C(1.5;2.5;3)=c_C.(3;5;6)=g_B(3;5;6)$, $N/At_{S(c)}=7.5$. The homeotypism of some two-cation fluorides may be briefly mentioned (89Sch).

$Ca_{1-N}Y_NF_{2+N}$(filling htpCaF$_2$ up to $N=0.28$,SR44.324,78Get) has Y on Ca sites of CaF_2 and additional F in octahedral interstices of the cation site set. For larger N the additional F take ordered sites.

$Ca_2YF_7(a_T=a_{CaF2}(\sqrt{2.5};3),78Get)$ has a substructure axial ratio 1.008.

$Ca_9Y_5F_{33}$(rhombohedral superstructure,78Get).

$Ca_{8-\delta}Y_{5+\delta}F_{31+\delta}$(rhombohedral superstructure,78Get).

$Ca_3Y_7F_{27}.h$(monoclinic superstructure,78Get).

$CaY_4F_{14}(Na_3As,H2.(5.6),78Get,65Man)$ will be considered below.

$SrF_2(CaF_2,SR1.150)$, $a(8,32+56,56)=5.79Å$ idmCaF$_2$.

$SrF_2.p>60kb(PbCl_2,SR31.243)$, $a(8,88,56)=3.79;6.31;7.43Å$ idmCaF$_2$.p.

$BaF_2(CaF_2,SR1.150)$, $a(8,88,128)=6.20Å$ idmCaF$_2$.

$BaF_2.p > 50kh(PbCl_2, SR31.243)$, $a(8,88,128) = 4.04;6.71;7.91Å$ idmCaF$_2$.p.

$RaF_2(CaF_2, SR4.8)$, $a(8,72,56,200) = 6.38Å$ idmCaF$_2$.

$ScF_3.h(ReO_3, SR23.288)$ LhtpNaCl, $a(3,8+21,14) = 4.01Å = c_C(1.5) = c_B(3) = q_C(6)$.

The b correlation of KF(NaCl) or CaF$_2$(F1.2) is here named c. Non-Lewis phases are not stable.

$ScF_3.r(R1.3, SR7.12,96)$ was doubted SR23.288, a binding proposal must be postponed.

$YF_3.h(UO_3, H1.3, 73Sob, drwSR11.224)$, the fluorine form a C1 partial structure similar as in CaF$_2$, which is hexagonally compressed. The Y are in $F_{6/3}F_{2/2}$ coordination, the structure is also htpLi$_3$N (drw64Sch.229). $a(3,8+21,10+6) = H4.12;4.23Å = r_{CH}(1;2.5/3)$ $= c_{BH}(2;10/3) = q_{CH}(4;10/3)$, $N_{S(c)}^{At} = 10$. YF$_3$.h is closely hdmCaF$_2$. The bonding type is collective and has 0.7 c sites per atom less than CaF$_2$. This decrease is caused by Lewis' rule requiring less metal per fluorine than in CaF$_2$. Earlier (66Tho) a larger cell $a = a_h(\sqrt{3};2)$ was assumed using high temperature powder diffractograms of limited angular extension. These data were reindexed by 73Sob. With respect to the bonding type the structure of YF$_3$.h might be more complicated.

$Ca_1Y_4F_{14}(Na_3As, H(0.4)(1.6)(5.6), 78Get, 65Man)$ yields the binding $a(5.6,16+39.2, 30.4) = H3.92;6.96Å = c_{CH}(\sqrt{1.33};5/3) = c_{BH}(2;17/3) = q_{CH}(4;17/3)$. The binding offers the normalized layer coordinates, $n17/6 = 0.2.8,5.7,8.5,11.3,14.2,17$ and after subtracting 0.1 from every coordinate the electro-dipole sequence is obtained as the sign of the smallest value that must be added in order to get an integer (see 84Sch,64Sch.229).

$YF_3.r(O4.12, SR17.328,40.134, drw79Has)$ is homeotypic to Na$_3$As but has quite different axial ratios and a volume decreased by 23% explaining the observation (66Tho) that YF$_3$.h may not be retained by quenching. The binding might imply a slight disharmony: $a(12,32+84,40+24) = 6.35;6.85;4.39Å = c_C(2;3;2) = c_C(6;6;4) = q_F(6;6;4)$. $N_{S(c)}^{At} = 9$ while it was 10 in h. LaF$_3$...HoF$_3$ have a h(LaF$_3$) and ErF$_3$...LuF$_3$ have a h(YF$_3$.h) phase, SmF$_3$...LuF$_3$ have a r(YF$_3$.r) phase (66Tho,82Gre), i.e. the phases with many core electrons favour the site-poor structure at low temperatures conforming to the site number rule (86Sch). For LnF$_M$ phases see 82Gre.

$LaF_3(H6.18, SR30.267,31.84, drw64Sch.229,79Has)$ is DhtpNa$_3$As(drw64Sch.229) and therefore htpCaF$_2$. The fluorine partial structure is DShtp to C$_H$ with stacking sequence $+ + + - - -$. The La is in F$_9$ coordination and in $+ -$ stacking. For history and structure description see 76,79Has. $a(18,48+126,60+108+36) = H7.19;7.35Å = b_{CH}(\sqrt{4.3};4.7/3) = c_{BH}(\sqrt{13};19/3) = q_{CH}(\sqrt{52};19/3)$. $N_{S(c)}^{At} = 10.3$, $n19/6 = 0,3.2,6.3,9.5,12.7,15.8,19.0$ i.e. the fluorine stacking is favoured by c_{BH}. The commensurability element $\sqrt{13}$ causes the atom displacements as compared with Na$_3$As. To this assumption fits the observation (78Gre) that LaF$_3$ crystals smaller than 1000Å (becoming hotter) are transformed in the primary ray of an electron microscope to the Na$_3$As type while larger crystals remained in the LaF$_3$ type. A thermal analysis of LaF$_3$ up to high temperatures appears desirable.

$CeF_3(LaF_3,SR42.166)$, $a(18,54+126,60+36+108)=H7.11;7.27Å$. The phase must be isodesmic to LaF_3. This remark shall be omitted in the following itpLaF_3, the structural prototype indicates here sufficiently the binding.

$CeF_4(ZrF_4,N6.24,SR12.168,drwSR29.261)$ has a CeF_8 coordination in antiprismatic from. A binding proposal must be postponed.

$PrF_3(LaF_3,SR18.576)$, $a=H7.08;7.24Å$.

$PrF_4(ZrF_4,73Pie)$, $a=N12.47;10.54;8.18Å126.4°$.

$NdF_3(LaF_3,SR21.208)$, $a=H7.03;7.20Å$.

$NdF_4(ZrF_4?,73Pie)$.

$PmF_3(LaF_3,73Pie)$, $a=6.97;7.19Å$.

$SmF_{2...2.29}(CaF_2,73Pie)$, $a(8,56+56,112+16)=5.87Å=e_C(2)=c_B(4)=g_C(8)$.

$SmF_{2.35}(htpCaF_2,T,73Pie)$, $a=4.106;5.825Å$.

$SmF_{2.45}(htpCaF_2,R,73Pie)$.

$SmF_3.h(LaF_3,SR17.328)$, $a=H6.96;7.16Å$.

$SmF_3.r(YF_3.r,73Pie)$, $a=6.07;7.06;4.41Å$.

$EuF_2 (CaF_2,SR7.80)$, $a=5.83Å$, half filled f shell.

$EuF_2.p(PbCl_2,73Pie)$, $a=3.80;6.32;7.35Å$.

$EuF_3.h(LaF_3,SR17.328)$, $a=H6.92;7.09Å$.

$EuF_3.r(YF_3.r,73Pie)$, $a=6.62;7.02;4.40Å$.

$GdF_3.h(LaF_3,73Pie)$, $a=H7.06;7.20Å$.

$GdF_3.r(YF_3.r,73Pie)$, $a=6.57;6.94;4.39Å$.

$TbF_3.h(LaF_3,73Pie)$, $a=H7.03;7.10Å$.

$TbF_3.r(YF_3.r,73Pie)$, $a=6.52;6.95;4.39Å$.

$TbF_4(ZrF_4,SR18.354)$, $a=12.11;10.15;7.92Å126.1°$, half filled f shell.

$DyF_3.h(LaF_3,73Pie)$, $a=H7.01;7.05Å$.

$DyF_3.r(YF_3.r,73Pie)$, $a=6.47;6.90;4.38Å$.

$HoF_3.h(LaF_3,SR17.328)$, $a=H6.83;6.98Å$.

$HoF_3.r(YF_3.r,73Pie)$, $a=6.40;6.88;4.38Å$.

$ErF_3.h(LaF_3,73Pie)$, $a=H6.97;8.27Å$.

$ErF_3.r(YF_3.r,73Pie)$, $a=6.35;6.85;4.38Å$.

$TmF_2(CaF_2,73Pie)$, $a(8,32+56,112+16)=5.60Å=e_C(2)=c_B(4)=g_C(8)$. It appears that the Tm4f electrons take part in the $g_C$correlation.

$TmF_3.h(YF_3.h,73Pie)$, $a=H7.03;8.35Å$.

$TmF_3.r(YF_3.r,73Pie)$, $a=6.29;6.82;4.41Å$.

$YbF_2 (CaF_2,73Pie)$, $a=5.60Å$, fully filled f shell.

$YbF_3.h(YF_3.h,73 Pie)$, $a=H6.99;8.32Å$.

$YbF_3.r(YF_3.r,73Pie)$, $a=6.22;6.79;4.43Å$.

$LuF_3.h(YF_3.h,73Pie)$, $a=H6.96;8.30Å$.

$LuF_3.r(YF_3.r,73Pie)$, $a=6.15;6.76;4.47Å$.

AcF_3(LaF$_3$,SR12.165), $a(18,234,300+36)$=H7.41;7.55Å=b_{CH}^{-}($\sqrt{4.3};4.7/3$)= c_{BH}^{-}($\sqrt{13};19/3$)=g_{CH}^{-}($\sqrt{52};19/3$).

ThF_4(ZrF$_4$,SR12.168), a=13.1;11.0;8.6Å126°.

PaF_4(ZrF$_4$,SR18.354).

Pa_2F_9(C4.18,73Pie), a=8.49Å.

PaF_5(UF$_5$.r,U4.20,73Pie).

UF_3(LaF$_3$,SR20.220), $a(18,126+126,300+36)$=H7.20;7.35Å=e_{CH}^{-}($\sqrt{4.3};4.8/3$)= c_{BH}^{-}($\sqrt{13};19/3$)=g_{CH}^{-}($\sqrt{52};19/3$).

UF_4(ZrF$_4$,SR12.168,drwSR29.261),a=12.82;10.74;8.41Å126.17°.

UF_4.p(F ,73Pie), a=6.34Å.

U_2F_9(B4.18,SR11.290,drw64Sch.284) shows UF_9 coordination with all U equivalent. $a(36,156+252,400+72)$=8.47Å=e_F(2)=c_C(8)=g_F(8). Apparently the electron density is so high that spin compensation is no longer important.

UF_5.h(U1.5,SR12.169,drw64Sch.284) contains a slightly strained F1 partial structure of fluorine with a=a_{F1}($\sqrt{2.5};1$). The U are in $UF_4F_{2/2}$ coordination so that the phase is not volatile. The pale blue crystal is an isolator and suggests the c correlation of Ne and the Ue electrons will be trapped near the F. $a(12,36+70,100+20)$=6.53;4.47Å=e_F($\sqrt{2.5};1.1$)= c_C ($\sqrt{40};4.5$)=g_F($\sqrt{40};4.5$). The e correlation is nearly fully occupied while c is only occupied to 0.7. The slight strain of the fluorine packing is caused by g_F forming a CuAu type compressed for spin compensation.

UF_5.r(U4.20,SR12.170,drwibid.) has a $UF_3F_{4/2}$ coordination with all U equivalent. This closer packing must result in a smaller electron site number per atom. $a(48,144+280,400+80)$=11.47;5.21Å=e_F($\sqrt{8};2.5/2$)=c_C^{-}($\sqrt{128};5$)=g_F($\sqrt{128};5$). The g site number has decreased from 57 in h to 53 in r, as in h the $|a_3|/|a_1|$ ratio is strained for spin compensation of g.

UF_6(O4.24,SR14.33) exhibits a close packing of fluorine with a stacking along a_1 of + + - - and with UF_6 coordination. It boils at 57 °C. The numerous core electrons of U favour the close packing of the fluorine atoms. The strong ionisation of the U means that the correlation density of the Ue electrons moves from the summit of the d shell to its spur. $a(24,72+168,200+48)$=9.90;8.96;5.21Å=e_{FH}($4/3;3;\sqrt{3}$)=c_{CH}($16/3;6;2\sqrt{3}$)=g_{FH}($16/3;12;4\sqrt{3}$). The g correlation favours the sequence of signs of dipole vectors in a_1 direction $n4/5.3$= 0,0.8,1.5,2.25,3.0, i.e. + + - -.

NpF_3(LaF$_3$,SR12.165) a=H7.13;7.29Å.

NpF_4(ZrF$_4$,SR12.168) a=12.70;10.64;8.33Å126.17°.

NpF_6(UF$_6$,73Pie), a=9.91;8.97;5.21Å.

PuF_3(LaF$_3$,SR12.165), a=H.7.09;7.25Å

PuF_4(ZrF$_4$,SR12.168), a=12.62;10.57;8.28Å126.17°.

PuF_6(UF$_6$,73Pie), a=9.95;9.02;5.26Å.

AmF_3(LaF$_3$,SR12.165;17.328), a=H7.07;7.25Å.

AmF_4(ZrF$_4$,SR18.354), a=12.50;10.47;8.20Å126°.

$CmF_3(LaF_3,73Pie)$, $a=H4.04;7.18Å$.

$CmF_4(ZrF_4,SR21.206)$, $a=12.45;10.45;8.16Å126.50°$.

$BkF_3 \cdot h(LaF_3,73Pie)$, $a=H6.97;7.14Å$.

$BkF_3 \cdot r(YF_3 \cdot r,73Pie)$, $a=6.70;7.09;4.41Å$.

$BkF_4(ZrF_4,73Pie)$, $a=12.47;10.58;8.17Å125.9°$.

$CfF_3(YF_3 \cdot r,73Pie)$, $\underline{a}=6.65;7.04;4.40Å$.

$TiF_3(VF_3,R2.6,SR18.351,drw64Sch.283)$ is $DhtpReO_3$, i.e. Ti are surrounded by nearly regular F-octahedra slightly rotated around a_3 and sharing corners. Since the basal plane decreases by the inhomogeneous deformation the axial ratio $|a_3|/|a_1|$ increases. There are 6 Ti and 6 F layers parallel to a_1,a_2. $a(84,96+126,48+36)=H5.44;13.61Å=e_H(\sqrt{4.3};5.5/3)$ $=c_{CH}(\sqrt{13};22/3)=g_{FH}(\sqrt{52};22/3)$. The e correlation is only partly occupied and d_e is strongly strained. The parameter x describing the rotation of the F octahedra is a function of the axial ratio (71Mic). Just as $CaTiO_3(C1.1.3,SR1.300)$ is $FhtpReO_3$(filling), the ferro-electric phase $LiTaO_3(R2.2.6,SR32.312)$ is $FhtpVF_3$ and fits, together with further isotypes, to the $x-|a_3|/|a_1|$ relation mentioned.

$TiF_4(C,73Pie)$, $a=8.24Å$.

$ZrF_2(O4.8,73Pie)$, $a=4.09;4.91;6.56Å$.

$ZrF_3(htpReO_3,73Pie)$, $a=3.96Å$.

$ZrF_4 \cdot h(UF_4,N6.24,SR12.168,drw29.261)$, $a=11.71;9.89;7.66Å126.15°$.

$ZrF_4 \cdot r(M52.208,SR29.439)$.

$ZrF_4 \cdot i(F2.8,73Pie)$, $a=7.88Å$.

$HfF_4(T7.28,73Pie)$, $a=(28,154+196,196+56)=7.85;7.67Å=e_{FU}(\sqrt{8};4/2)=c_B(\sqrt{32};5.5)=$ $g_C(\sqrt{128};11)$. The binding suggests that the filling of c is more important than that of ϵ, it appears to be noncollective.

$HfF_4(UF_4,ZrF_4 \cdot h,SR12.168)$, $a=11.70;9.86;7.64Å126.8°$.

$VF_2(TiO_2 \cdot r,MgF_2,SR45.383)$, $a(10,32+28,8)=4.80;3.24Å=e_{C'}(\sqrt{5};1.5)=c_B(\sqrt{20};3)=g_C$ $(\sqrt{80};6)$. The e_C correlation displays overoccupation which may be the cause for the magnetic structure at low temperatures (73Pie,82Bau). The $TiO_2 \cdot r$ type does not become stable in NbF_M and TaF_M because of its high c site number.

$V_2F_5(\approx T,73Pie)$ is reported $htpVF_2$.

$VF_3(R2.6,see \quad TiF_3,SR15.145)$, $a(30,96+126,48)=H5.17;13.40Å=e_{FH}(\sqrt{4.3};7.7/3)=c_{CH}$ $(\sqrt{13};23/3)=g_{FH}(\sqrt{52};23/3)$. It is seen that the increase of $|a_3|/|a_1|$ as compared with TiF may be caused by the e correlation. Since VF_3 is $DhtpReO_3$ the site number rule (86Sch) forbids its occurrence in NbF_M because ReO_3 is loosely packed.

$VF_4(O4.16,73Pie)$ is pseudo hexagonal with $a=a_{VF3}(-1,1,0;1,1,0;0,0,1/3)$. $a(20,64+112,32)=9.35;5.33;5.16Å=c_{CH}(3;2/2;4/3)=c_{BH}(6;\sqrt{12};16/3)=g_{CH}(12;4\sqrt{3};32/3)$.

$VF_5(O8.40,SR34.172)$ LhtpNaCl with $a=a_{NaCl}(1,0,-1.5;0,4,0;1,0,1.5)$. Forming the determinant shows that 48 F sites are available and 40 are occupied i.e. $N_F^{S(F)}=5/6$ while in ReO_3 only $3/4=4.5/6$ are occupied because of a higher c electron offer per F in say ScF_3

(ReO$_3$). Each VF$_6$ octahedron shares two F lying in a_1 direction with another octahedron to establish the composition. Therefore the V atoms form separated zigzag chains in a_1 direction and there are 4 chains in the cell. The binding may be $a(40,128+280,80)=5.40;16.72;$ 7.53Å$=e_{FU}(2;6;4/2)=c_C(4\sqrt{2};12\sqrt{2};8)=g_F(4\sqrt{2};12\sqrt{2};8)$, e is here underoccupied but in CrF$_5$ (VF$_5$) fully occupied. The number of c sites per 4 fluorine sites is 64, but $N_{S(c)}^{cF}=19.2$. This is with respect to the NbF$_M$ structures, a typical example of the site number rule.

Nb$_2$F$_5$(B6.15,SR30.261) LhtpNaCl, $a=a_{NaCl}(2)$, 20 Nb-lacunae, the 12 Nb form two octahedral clusters (64Schä,81Sim) centered by a fluorine lacuna. $a(60,216+210,192+60)=$ 8.19Å$=e_C(4)=c_C(8)=g_F(8)$. It appears that in NbF$_M$ compound formation begins when $d_e=2d_c$.

NbF$_3$.i(ReO$_3$,SR20.223,73Pie), $a(5,18+21,16+6)=3.90$Å$=e_{HT}(\sqrt{3.2};2/2)=c_C(4)=g_F(4)$.

NbF$_4$(SnF$_4$,U1.4,73Pie) LhtpNaCl, $a=a_{NaCl}(1;2)$, the fully occupied fluorine partial structure yields NbF$_{2+4/2}$ coordination. $a(10,36+56,32+16)=4.08;8.16$Å$=e_{HT}(\sqrt{3.2};4/2)=c_C(4;8)=g_B(4;8)$. The rare H$_T$ correlation only approximates the collective property of the bonding type

NbF$_5$(MoF$_5$,N4.20,SR29.258) LhtpNaCl, $a=a_{NaCl}(3,5,-1;-3,5,1;-2,0,2,)/8$, 32 Nb-lacunae. Contrary to NbF$_4$ each (001)$_{NaCl}$ layer is occupied by Nb forming squares with $d=a_{NaCl}$ as in NbF$_4$. From the cell $a=9.62;14.43;5.12$Å96.1° follows the NaCl type subcell and the tentative binding $a'(4,15+28,13+8)=4.1$Å$=e_B(\sqrt{2};1.5)=c_C(4)=g_F(4)$, e is fairly occupied by the electrons of the e united with the c correlation.

TaF$_3$.i(ReO$_3$,SR15.147), $a(5,22+21,28+6)=3.90$Å idm NbF$_3$.i.

TaF$_5$(MoF$_5$,SR29.258), $a=9.64;14.45;5.12$Å96.3° idm NbF$_5$.

CrF$_2$(CuF$_2$,M2.4,SR21.204), DhtpTiO$_2$.r, $a(12,32+28,12)=4.73,0,-0.40;4.72;3.48$Å $=e_{FU}(\sqrt{5};2.35/2)=c_B(\sqrt{20};3.5)=g_C(\sqrt{80};7)$, The e correlation shows weak Hund insertion but takes an interesting kind of commensurability to c and g. The matrix element 3.5 seeks more commensurability which may cause the monoclinic deformation. With this structure also the irregular axial ratio of TiO$_2$.r isotypes should be compared (71Bau).

Cr$_2$F$_5$(N4.10,SR29.255,drwibid.) has 4Cr in CrF$_{4/2+2/3}$ and 4Cr in CrF$_{4/3+2/2}$ coordination. It was inferred from this that the phase is to formulate Cr^{3+}Cr^{2+}F$_5$. However, since such an explanation is not generally possible, the electron correlation must be considered, $a(48,128+140,56)=6.43;7.54;-4.38,0,7.44$Å$=e_B^-(3;\sqrt{8};\sqrt{8})=c_C(7;8;8)=g_C$ ($10;\sqrt{128};\sqrt{128}$), as written for the diagonal cell. $N_{S(c)}^{cF}=22.4$ while in a L$_A$htpNaCl $N_{S(c)}^{cF}=16$ (see NbF$_4$ e.g. cf 82Sch).

CrF$_3$(VF$_3$,R2.6,SR21.204,24.272), $a(36,96+126,48)=$H4.99;13.22Å$=e_{FH}^-(\sqrt{4.33};8/3)$ $=c_{CH}(\sqrt{13};24/3)=g_{FH}(\sqrt{52};24/3)$. The oxidation number 3 must be formed by Cr^{4+}Cr^{2+}.

CrF$_5$(VF$_5$,O8.40,73Pie), $a(48,128+280,94)=5.5;16.3;7.4$Å$=e_{FU}(2;6;4/2)=c_C(4\sqrt{2};12\sqrt{2};8)=g_F(4\sqrt{2};12\sqrt{2};8)$. The Cr^{5+} must be understood as Cr^{6+}Cr^{4+}. A phase A^{6}F$_6$ occurs with Mo and W. Here it does not become stable because it requests a too high ionization.

$MoF_3(VF_3,R2.6,SR24.274)$ has a slightly higher axial ratio $|a_3|/|a_1|$ than CrF_3 since the additional core electrons provide a compression of the cell. $a(36,108+126,96+36) =$ H5.21;14.41Å $=e_{FH}^{\sim}(\sqrt{4.3};8/3)=c_{CH}(\sqrt{13};24/3)=g_{FH}(\sqrt{52};24/3)$. The compression of e favours commensurability.

$MoF_5(N4.20,NbF_5,SR27.445)$ cannot be itp$CrF_5(VF_5)$ since that structure has too many fluorine lacunae, it is L_{Mo}htpNaCl conforming to the site number rules. Mo in the Na sites form squares with edge a_{NaCl}. $a=$M9.61;14.22;5.16Å94.35°, a plane corresponding to $(001)_{NaCl}$ is (101). A binding has been proposed for NbF_5.

MoF_6.r$(OsF_6,B1.6,SR41.151)$ contains isolated MoF_6 octahedra with F on fourfold axis but suffering rotational disorder. The melting temperature is 17.4 °C. $a(12,36+84,32+24) =$ 6.22Å $=e_B(2)=c_F(4)=g_B(8)$. The $OsF_6(B1.6)$ type is not restricted to A^6 elements, it occurs also in $TcF_6,RuF_6,RhF_6,PtF_6,TeF_6$ etc.

MoF_6.l$(UF_6,O4.24,SR41.151,drwibid.)$ transforms at 263 K with 14% volume decrease from r. $a(24,72+168,64+48)=9.61,8.75;5.07$Å $=e_{FH}(4/3;3;\sqrt{3})=c_{CH}(16/3;6;2\sqrt{3})=g_{FH}$ (16/3; 12;4$\sqrt{3}$). The cause of the transition r→l is a higher density of e and g. While $N_{S(g)}^{/At}=73$ in h, here $N_{S(g)}^{/At}=55$. It has been shown at UF_6 that the element 16/3 reproduces the $++--$ stacking of the fluorine partial structure. The stability of the UF_6 type in TcF_6.l, RuF_6.l,RhF_6,PtF_6.l suggests that c is decisive for the structure.

$WF_5(MoF_5,NbF_5,73Pie)$, $a=$M9.61;14.26;5.32Å94.6° idm NbF_5.

WF_6.r$(OsF_6,B1.6,SR42.165)$ melts at 1.9 °C, $a(12,44+84,56+24)=6.30$Å idm MoF_6.r.

WF_6.l$(UF_6,O4.24,SR41.152)$, $a(24,88+168,160)=9.68;8.81;5.09$Å idm$MoF_6$.l.

$MnF_2(TiO_2$.r,VF_2,SR18.348), is antiferromagnetic (SR15.359), $a(14,32+28,12)=4.87$; 3.31Å $=e_B(\sqrt{5};1.5)=c_B(\sqrt{20};3)=g_C(\sqrt{80};6)$. While $e_{FU}^{\sim}$ of CrF_2 caused a deformation of the structure here e_B is fully commensurable, $N_{S(c)}^{/At}=20$. The low c occupation causes various p phases.

MnF_2.p_1>20kb$(PbO_2$.m,O4.8,SR28.72,30.449, antiitpFe_2N,drw64Sch.257) has a F(Mg) partial structure with $a=a_{Mg}(0,2-1;0,2,1;1,0,0)$ and $MnF_{6/3}$ coordination. The Mn form zigzag chains along a_3 whence a_2 is "too small". $a(28,64+56,16)=4.96;5.80;5.36$Å $= e_{BH}^{\sim}$ (7.5/3;1.9;2/2)$=c_{BH}^{\sim}(15/3;3.8;4/2)=g_{CH}^{\sim}(15/3;7.6;8/2)$. The commensurability element 15/3 favours the $+-$ stacking of the fluorine layers perpendicular to a_1. The e correlation is fully occupied. $N_{S(c)}^{/At}=19$ conforming to the rule that pressure decreases the site number.

MnF_2.p_2>50kb(T4.8,SR30.449), $a(28,64+56,24)=5.20;4.97$Å $=e_{FU}^{\sim}(\sqrt{8};3.5)=c_{FU}^{\sim}$ ($\sqrt{32}$; 7/2) $=g_C^{\sim}(8;7)$, $N_{S(c)}^{/At}=18.7$.

MnF_2.p_3>80kb$(PbCl_2,CaF_2$.p,O4.8,73Pie), $a(28,64+56,24)=3.32;5.56;6.45$Å $= e_{FU}(2.5/$ 2;3;3.5)$=c_{FU}(5/2;6;7)=g_C(5;6\sqrt{2};7\sqrt{2})$, $N_{S(c)}^{/At}=17.5$.

$MnF_3(N6.18,SR21.207)$ DhtpVF_3, $a(84,192+252,96)=8.90;5.04;13.45$Å92.7° $= e_{CH}^{\sim}$ ($\sqrt{3.25}$;13/3)$=c_{CH}(\sqrt{13};24/3)=g_{FH}(\sqrt{52};24/3)$ as written for the hexagonal cell.

$TcF_5(VF_5,73Pie)$, $a=5.76;7.75;17.01$Å idmVF_5.

TcF_6.r$(OsF_6,MoF_6,73Pie)$, $a(14,36+84,32+24)=6.16$Å $=e_B(2)=c_F(4)=g_C(8)$.

$TcF_6.l<268K(UF_6,MoF_6.l,73Pie)$, $a(28,72+168,48)=9.55;8.74;5.02Å$ idm$MoF_6.l$.

$ReF_4(T24.36,73Pie)$, $a(168,528+672,672+192)=10.12;15.95Å$.

$ReF_5(VF_5,O8.40,73Pie)$, $a=5.70;17.23;7.67Å$.

$ReF_6.r(OsF_6,MoF_6.r,73Pie)$, $a=6.26Å$.

$ReF_6.l(UF_6,73Pie)$, $a=9.61;8.76;5.06Å$. The oxidation number 7 does not occur because it requests a too high ionization.

$FeF_2(TiO_2.r,MgF_2SR18.348,17.327)$, $a(16,32+28,12)=4.70;3.31Å=e_B(\sqrt{5};1.5)=$ $c_B(\sqrt{20};3)=g_F(\sqrt{20};3)$. As with all bindings this proposal can be no more than an aproximation, for instance the commensurability element 1.5 might be replaced by 1.6 to provide a better b occupation.

$Fe_2F_5(T12.30,73Pie)$, $a(96,192+210,84)=8.05;9.56Å=e_C(\sqrt{18};5)=c_C(\sqrt{72},10)=g_F(72;10)$. The over-occupation of e suggests the presence of a b correlation. It should be appreciated that $d_g(Fe_2F_5)>d_g(FeF_2)$.

$FeF_3(VF_3,R2.6,SR21.206)$ is stable although MnF_3 was strongly deformed. $a(48,96+126,48)=H5.20;13.33Å=e_{CH}(\sqrt{3.25};11.5)=c_{CH}(\sqrt{13};23/3)=g_{FH}(\sqrt{52};23/3)$,

$RuF_3(VF_3,R2.6,SR21.206)$, $a(48,108+126,96+36)=H4.97;13.76Å$ idm FeF_3.

$RuF_5(M8.40,SR29.260)$ DhtpMoF_5 and Lhtp$NaCl$ with no fluorine lacunae. $a=12.47;10.01;5.42Å99.83°$.

$RuF_6.r(OsF_6.r,MoF_6.r,B1.6,73Pie)$, $a(16,36+84,32+24)=6.11Å$, idmTcF_6.

$RuF_6.l(UF_6,MoF_6.l,73Pie)$, $a=9.44;8.59;4.98Å$, idm$TcF_6.l$.

$OsF_5(RuF_5,SR37.177)$, $a=5.53;9.91;12.59Å99.5°$.

$OsF_6.r(B1.6,SR22.233)$, $a=6.23Å$ idm$TcF_6.r$.

$OsF_6.l(UF_6,73Pie)$, $a=9.59;8.75;5.04Å$, idm$TcF_6.l$.

$CoF_2(TiO_2.r,VF_2,SR21.209)$, $a(18,32+28,12)=4.70;3.18Å=e_C(\sqrt{10};2)=c_B(\sqrt{20};3)=g_C$ ($\sqrt{0},6$). It appears curious that the F2sp electrons are in the c correlation together with the Co2sp+3sp electrons instead of entering the e correlation with a more similar electron distance. However, the problem which electrons from a common correlation depends on their interaction, and this depends also on the angular quantum number. Furthermore the strong dependence of the distance d_e on the mole fraction N'_F should not be understood as an ionization since the correlation point needs not be in the summit of a shell but is preferentially in the spur of the summit (83SchFig.1).

$CoF_2.p>130kb(htpCaF_2,73Pie)$ indicates that the pressure decreases essentially the fluorine ionic radius, so that a CoF_8 coordination becomes stable. $a(36,64+56,24)=4.91Å=e_B^-(\sqrt{8};2.5)=c_F(4)=g_C(8)$. Apparently the spin compensation is sacrificed to the close packing in c.

$CoF_3(VF_3,R2.6,SR21.206)$, $a(54,96+126,48)=H5.04;13.58Å=e_{CH}^-(\sqrt{4.3};12/3)=c_{CH}(\sqrt{13};24/3)=g_{FH}(\sqrt{52};24/3)$. A higher fluoride is not formed since Co is not electropositive enough. The calculation of the average atomic volume shows that higher fluorides should have a higher atomic volume. The difficulty to increase d_e prevents the stability of higher

Co-fluorides but not of higher Rh- or IrF_M phases.

RhF_3(PdF$_3$,R2.6,SR21.206,drw64Sch.283) has the same space group as VF_3, but the parameters form now 6 undistorted hexagonal planes parallel to a_1,a_2 of fluorine, stacked in + - sequence in a_3 direction. $a(54,108+126,96+36)$=H4.88;13.58Å$=e_{C'H}(\sqrt{3.25};12/3)$ $=g_{CH}(\sqrt{13};25/3)=g_{FH}(\sqrt{52};25/3)$.

RhF_5(RuF$_5$,SR39.138), a=12.34;9.92;5.52Å100.42°.

RhF_6.r(OsF$_6$,73Pie), $a(18,36+84,32+24)$=6.13Å$=e_C(\sqrt{8};2.8)=c_F(4)=g_C(8)$.

RhF_6.l(UF$_6$,73Pie), a=9.40;8.54;4.96Å, idm MoF$_6$.l.

IrF_3(PdF$_3$,SR21.207), $a(54,132+126,168+36)$=H4.93;13.83Å$=e_{C'H}(\sqrt{3.25};12.5/3)$ $=c_{CH}$ $(\sqrt{13};25/3)=g_{FH}(\sqrt{52};25/3)$. The c correlation is collective with e, and highly occupied.

IrF_4(S2.8,SR40.294), has a $IrF_{4/2+2}$ coordination, see PdF$_4$ isotype, $a(72,176+224,224+64)$=9.64;9.25;5.67Å$=e_B(4;4;2.4)=c_B(8;8;4.8)=g_C(16;16;9.6)$.

IrF_5(RuF$_5$,73Pie), a=12.5;10.0;5.40Å99.8°.

IrF_6.r(OsF$_6$,SR22.233), $a(18,44+84,56+24)$=6.23Å$=e_C(\sqrt{8};2.8)=c_F(4)=g_C(8)$.

IrF_6.l(UF$_6$,O4.24,73Pie), $a(36,88+168;112+48)$=9.58;8.73;5.04Å$=e_{F'H}(4/3;3;\sqrt3)=$ c_{CH} $(16/3;6;2\sqrt3)=g_{FH}(16/3;12;4\sqrt3)$. The Hund insertion in e causes the isotypism MoF$_6$.l $-IrF_6$.l.

NiF_2(TiO$_2$.r,SR21.209), $a(20,32+28,12)$=4.65;3.08Å$=e_B^-(\sqrt5;2)=c_B(\sqrt{20};3)=c_C(\sqrt{80};6)$. g is highly occupied and strongly compressed.

NiF_2l<73K(htpTiO$_2$.r,73Pie), a=4.648;4.647;3.074Å. Perhaps in e spins are odered.

NiF_2.p(htpCaF$_2$,73Pie), $a(40,64+56,24)$=4.84Å$=e_B^-(\sqrt8;2.5)=c_F(4)=g_C(8)$. The higher compessibility of fluorine favours the NiF$_8$ coordination.

PdF_2(TiO$_2$.r,SR22.233), $a(20,36+28,40)$=4.96;3.39Å, idmNiF$_2$.

PdF_2.p(CaF$_2$,SR45.384), $a(40,72+56,64+16)$=5.32Å$=e_B(\sqrt8;2.8)=c_F(4)=g_e(8)$.

PdF_3(R2.3,SR21.206,drw64Sch.283), $a(60,108+126,96+36)$=H5.01;14.13Å= e_{BH} $(\sqrt3.25.19/3)=c_{CH}(\sqrt{13};25/3)=g_{FH}(\sqrt{52};25/3)$. unfortunately, e is quite underoccupied.

PdF_4(IrF$_4$,S2.8,SR44.140,drw ibid.) LhtpTiO$_2$.r $a=a_{TiO2.r}(2)$. $a(80,144+224,128+64)$ =9.34;9.24;5.83Å$=e_{FU}(\sqrt{20};4/2)=c_C^-(\sqrt{80};6)=g_F(\sqrt{80};6)$. The compliance of the e correlation is impressive.

PtF_4(M4.16,73Pie, itpPdF$_4$?) a=6.68;6.68;5.71Å92.02°.

PtF_6.r(OsF$_6$,SR26,301), a=6.21Å, idmIrF$_6$.r.

PtF_6.l(UF$_6$,SR26.301), a=9.55;8.71;5.03Å, idmIrF$_6$.l.

CuF(ZnS,SR3.7) a=4.26Å was doubted (SR18.350).

CuF_2(M2.4,SR21.205), DhtpTiO$_2$.r, $a(2,20,32+28,12)$=4.59,0,0.39;4.54;3.30Å $=b_C(\sqrt{2.5};1.1)=e_C(\sqrt{10};2.3)=c_B(\sqrt{20};3.2)=g_C(\sqrt{80};6.4)$. The monolinic deformation provides an improved commensurability for c. A higher oxidation number does not occur since the d shell lies now deeper than in A$^{4..10}$.

Ag_2F(CdI$_2$,H2.1,SR31.83,drw64Sch.349) has a brass-like colour and contains Ag in

close packing with stacking + - and with F in octahedral holes. $a(2,20,36+7,32+2)=$H3.00; 5.69Å $=b_{FH}(1;2.7/3)=c_{FH}^-(2;5.5/3)=c_{BH}(2;19/3)=g_{CH}(4,19/3)$.

AgF(NaCl,SR1.73), $a(4,40,72+28,64+8)=4.93$Å $=b_C(\sqrt{2.5};1.6)=e_{FU}(\sqrt{10};4.5/2)$ $=c_B(\sqrt{20};4.5)=g_C(\sqrt{80};9)$, $N_{S(c)}^{At}=22$. The phase is stongly heterodesmic to NaF etc. and has therefore different physical properties.

AgF$_2$(CuF$_2$,SR37.178), $a(2,20,36+28,32+8)=4.61,0,-0.40;4.59;3.41$Å. The atomic volume of this phase is so similar to that of CuF$_2$ that a confirmation of the cell appears desirable.

AgF$_2$(O4.8,SR37.178) has a quadratic AgF$_{4/2}$ coordination. $a(4,40,72+56,64+16)$ $=5.07;5.53;5.81$Å $=b_F(1)=e_B(\sqrt{8};\sqrt{8};3)=c_C(\sqrt{32};\sqrt{32};6)=g_F(\sqrt{32};\sqrt{32};6)$. It appears possible that g_F has a deforming influence similar to that in TlF.r.

AuF$_3$(H6.18,SR32.155) is said to have a strongly distorted AuF$_6$ coordination which should be described as AuF$_4$ coordination. There are 6 equidistant F layers parallel to a_1,a_2. $a(6,60,132+126,168+36)=$H5.15;16.26Å $=b_{CH}(1;6/3)=e_{FH}(\sqrt{4.3};16)=c_{CH}(\sqrt{13};28/3)$ $=g_{BH}(\sqrt{13};56/3)$.

ZnF$_2$.r(TiO$_2$.r,SR21.209), $a(4,20,32+28,12)=4.70;3.13$Å $=b_B(\sqrt{2.5};1)=e_{FU}(\sqrt{10};3/2)=c_B$ $(\sqrt{20};3)=g_C(\sqrt{80};6)$, $N_{S(c)}^{At}=20$. b is strained while e, c, g are quite weakly compressed.

ZnF$_2$.p$_1$(MnF$_2$.p$_2$,T4.8,73Pie), $a(8,40,64+56,24)=4.91;4.66$Å $=b_{FU}(2;2.7/2)=e_B(\sqrt{8};$ $2.7)=c_C(\sqrt{32};5.5)=g_B(\sqrt{32};5.5)$, $N_{S(c)}^{At}=14.6$. e_B does not completely imply b, but c is somewhat underoccupied so that p_2 becomes possible.

ZnF$_2$.p$_2$(ZrO$_2$.r,M4.8,73Pie,drw64Sch.278) D'htpCaF$_2$, $a(8,40,64+56,24)=5.05,0,0.97$; 4.96;5.20Å. Since this phase has a larger cell (V$=130.2$Å^3) than p$_1$(V$=112.3$Å^3) something must be mistaken.

CdF$_2$(CaF$_2$,SR15.144) $a(8,40,72+56,64+16)=5.39$Å $=b_U(1.5;1.8)=e_B(3)=c_C(6)=g_B(6)$, $N_{S(c)}^{At}=18$. At lower temperatures a symmetry decrease might be expected because of the b correlation.

CdF$_2$.p(PbCl$_2$,O4.8,73Pie,drw64Sch.322) RDhtpCu. $a(8,40,72+56,64+16)=3.37$; 5.69; 6.73Å $=b_{FU}(1.7/2;1.5\sqrt{2};1.75\sqrt{}$ 2)$=e_C(2.5;3\sqrt{2};3.5\sqrt{2})=c_{FU}(5/2;6;7)=g_C(5;6\sqrt{2};7\sqrt{2})$, $N_{S(c)}^{At}=$ 17.5 conforming to the site number rule.

HgF(HgCl,U2.2,SR20.214,drw64Sch.191) RDShtpNaCl with $a=a_{NaCl}(1/\sqrt{2};2)$. $a(8,40,$ $88+28,112+8)=3.66;10.90$Å $=b_F(1;3)=e_B(2;6)=c_C(4;12)=g_F(4;12)$. b is only partially occupied but e is fully occupied by b and e electrons. The matrix element 3 causes the shear in HgF as compared with NaCl (64Sch.100). A low temperature phase corresponding to TlF.r has not yet been found.

HgF$_2$(CaF$_2$,SR3.20), $a(8,40,88+56,112+16)=5.54$Å $=b_U(1.5;1.8)=e_B(3)=c_C(6)=g_B(6)$.

B$_2$F$_4$.l(M4.8,SR22.230) is a molecular structure. $a(12+56,24)=5.49;6.53;4.83$Å102.5°. Analysis is postponed.

AlF$_3$.h(htpReO$_3$,SR18.440), $a(3,29,8)=3.58$Å $=b_F(1)=c_F(2)=g_C(4)$.

$AlF_3 \cdot r(htpVF_3, R2.6, SR3.40)$, $a(18,48+126,48) = H4.92; 12.48Å = b_{II}(2;5) = c_{FH}(4;12/3)$ $= g_{CH}(4;12/3)$.

$AlF_3 \cdot i(T2.6, 73Pie)$, $a(6,16+42,16) = 3.54; 6.00Å = b_F(1;3.5/2) = c_F(2;7/2) = g_C(4;7)$.

$GaF_3(VF_3, R2.6, SR23.289)$, $a(18,60,96+126,12+36) = H5.00; 12.97Å = b_{FH}(\sqrt{3}.2; 5.6/3)$ $= e_{BH}(\sqrt{3}.25; 23/3) = c_{CH}(\sqrt{13}; 23/3) = g_{FH}(\sqrt{52}; 23/3)$.

$InF_3(VF_3, SR31.260)$, $a(18,60,108+126,96+36) = H5.42; 14.43Å = b_{FH}(\sqrt{3}.25; 6/3)$ $= e_{BH}$ $(\sqrt{3}.25; 24/3) = c_{CH}(\sqrt{13}; 24) = g_{FH}(\sqrt{52}; 24/3)$.

$TlF \cdot h(U1.1, SR33.171)$ $DhtpNaCl, a = a_{NaCl}(1/\sqrt{2}; 1)$. $a(6,20,44+14,56+4) = 3.77; 6.12Å$ $= b_F(1;3.2/2) = e_B(2;6.5/2) = c_C(4;6.5) = g_F(4;6.5)$. The fact that e_B is fully occupied by the b and c electrons while b_B is not fully occupied indicates the e electrons to be decisive for the structure.

$TlF \cdot r(S1.1, SR3.9, 40.131)$ $DhtpNaCl$ $a = a_{NaCl}$. $a(12,40,88+28,112+8) = 5.18; 6.10; 5.49Å$. The axes $a_1 \pm a_2$ of h split into a_1 and a_3 of r because g_F of h is transformed into $g_{\bar{F}}$ to improve the spin compensation. The direction of compression is mixed, $a_1 + a_3$ and elsewhere $a_1 - a_3$ of r. The present explanation must replace the early assumption of 35 Ketelaar that merely the polarisation of Tl causes the deformation homeotypism to NaCl. This interpretation confirms the importance of the g correlation.

$Tl_2F_3(CaTiO_3, 73Pie)$, $a(6,20,44+21,56+6) = 4.60Å = b_{\bar{B}U}(\sqrt{2}; 1.5) = e_{\bar{F}U}(\sqrt{8}; 3.25/2) = c_C$ $(\sqrt{20}; 4.6) = g_F(\sqrt{20}; 4.6)$.

$TlF_2(O8.16, 73Pie)$ $htpCaF_2$. $a(24,80,176+112,224+32) = 8.35, 8.23; 6.26Å = b_{FU}(\sqrt{8}; 3)$ $= e_B(4;3) = c_C(8;6) = g_F(8;6)$. Once more the g_F correlation displays the above deformation.

$TlF_3(YF_3, O4.12, SR38.194)$, $a(12,40,88+84,112+24) = 5.83; 7.02; 4.85Å = b_F(1.5; 1.75; 1.25)$ $= e_B(3;3.5;2.5) = c_C(6;7.5;5) = g_F(6;7.5.5)$.

CF_M phases are homeotypic to organic structures and will be omitted here. $SiF \cdot l(B1.4, SR2.37, 18.353)$ shows a fluorine partial structure of the Cl type with $a = a_{C1}$ (2), and SiF_8 coordination. Small displacements of the F provide that the exact coordination is SiF_4 conforming to Lewis' rule. $a(8,16+56,20) = 5.42Å = b_C(2) = c_B(4) = g_C(8)$.

$GeF_2 \cdot h(M4.8, 73Pie)$ $a = 7.55; 8.58; 4.87Å$ has been considered as tentative by the authors.

$GeF_2 \cdot r(O4.8, SR31.82)$ is homeotypic to $PbCl_2$ with $a = a_{PbCl_2}[1], a(16,40,64+56,24) = 4.68;$ $5.18; 8.31Å = b_{FH}(2/2; 2; 4/3) = e_{FH}(4/2; 4; 8/3) = g_{CH}(4/2; 4; 16/3)$.

$Ge_5F_{12}(M10.24, SR39.137)$.

$GeF_4 \cdot l(SiF_4, 88Köh)$, $a(80,20,32+56,20) = 5.49Å = b_C(2) = e_U(\sqrt{8}; 3.5) = c_F(4) = g_C(8)$, $N^{/At}_{S(c)} = 25.6$.

$SnF_2 \cdot h(N8.16, SR27.430, 42.163, 45.143)$.

$SnF_2 \cdot r(O16.32, 73Pie)$.

$SnF_4(U1.4, NbF_4, SR27.442)$ $LhtpNaCl$, $a(8,20,36+56,32+16) = 4.04; 7.93Å = b_F(1;2) = e_B$ $(2;4) = c_C(4;8) = g_B(4;8)$. e is not fully occupied, but in PbF_4 it is. A deformation of e may produce momentary dipole vectors at Sn, normal to a_3, and favouring the observed Sn site, $N^{/At}_{S(c)} = 26$.

$PbF_2 \cdot h(CaF_2, SR15.145)$, $a(16,40,88+56,112+16)=5.94\text{Å}=b_B(2)=e_c(4)=c_F(4)=g_c(8)$; $N_{S(c)}^{At}=22$. It might be that two b electrons per Pb enter e when they exhibit internal spin compensation.

$PbF_2 \cdot r(PbCl_2, O4.8, SR15.145)$, $a(16,40,88+56,112+16)=6.44;3.90;7.65\text{Å}=b_{F'U}(2.5;1.5; 4/2)=e_B(2.5\sqrt{2};1.5\sqrt{2};4)=e_c(5\sqrt{2};3\sqrt{2};8)=g_B(5\sqrt{2};3\sqrt{2};8)$, $N_{S(c)}^{At}=20$.

$PbF_4(SnF_4, SR27.442)$, $a(8,20,44+56,56+16)=4.24;8.03\text{Å}=b_F(1;2)=e_B(2;4)=c_C(4;8)=g_B(4.8)$.

NF(gas, SR28.360).

NF_3(gas, SR13.419)

N_2F_4(F,73Pie), $a=24.95\text{Å}$.

PF_3(gas, SR34.172).

PF_5(gas, SR30.266).

AsF_3(gas, SR40.313).

AsF_5(gas, SR40.314, see 88Köh).

SbF_3(Q2.6, SR9.152, 35.147) is composed of SbF_3 but there are three more F forming with the closest neighbours a SbF_6 coordination. $a(20,40,72+84,64+24)=7.26;7.46;4.95\text{Å}=b_{C'}(\sqrt{8};2)=e_C(\sqrt{32};4)=c_F(\sqrt{32};4)=g_C(\sqrt{128};8)$. The Hund insertion in b expresses the internal spin compensation.

Sb_4F_{16}(M16.64, SR43.119), $a=9.32;12.07;11.60\text{Å}107.1°$.

SbF_5(N8.40, SR37.353), $a=19.00;14.10;5.29\text{Å}94.0°$.

$BiF_3 \cdot i$(H2.6, SR19.342) LhtpLaF$_3$, $a(10,20,44+42,56+12)=H4.08;7.32\text{Å}$.

BiF_3(YF$_3 \cdot r$, O4.12, SR40.134, 43.340) $a(20,40,88+84,112+24)=6.56;7.02;4.84\text{Å}=b_F(1.75; 1.85;1.25)=e_B(3.5;3.75;2.5)=c_C(7;7.5;5)=g_F(7;7.5;5)$.

BiF_5(UF$_5$, U1.5, SR37.176), $a(10,20,44+70,56+20)=6.58;4.23\text{Å}=b_{FU}(\sqrt{5};2/2)=e_B(\sqrt{10};2)=c_C(\sqrt{40};4)=g_F(\sqrt{40};4)$.

SF_6(OsF$_6$, B1.6, SR42.165), $a(12,16+84,28)=5.92\text{Å}=b_B(2)=c_B(4)=g_C(8)$.

SeF_6(OsF$_6$, 74Pie), $a(12,20,32+84,28)=5.99\text{Å}=b_B(2)=e_C(4)=c_B(4)=g_C(8)$.

$SeF_6 \cdot l(O......,73Pie)$

TeF_4(O4.16, SR33.170) contains $TeF_3F_{2/2}$ molecules displaying F_3 parallel to a_2, a_3. $a(24,40,72+112,64+32)=5.36;6.22;9.67\text{Å}=b_C(2.5;2.5;4)=e_{FU}(2.5\sqrt{2};2.5\sqrt{2};8/2)=c_B(5;5;8)=g_C(10;10;16)$. The difference $|a_1|-|a_2| \neq$ might come from Hund insertion in b.

TeF_6(OsF$_6$, 73Pie) $a(12,20,36+84,56)=6.82\text{Å}=b_{FU}(\sqrt{8};2.8/2)=e_C(4)=c_B(4)=g_C(8)$.

$TeF_6 \cdot l$(73Pie).

ClF_3(O4.12, SR16.165, drwibid) contains two spin compensations in Cl, and consists of planar T shaped ClF_3 molecules with $d_{ClF}=1.7\text{Å}$. Between different molecules $d_{ClF}=3.1\text{Å}$ so that the coordination is higher. $a(28,32+84,28)=8.82;6.09;4.52\text{Å}=b_F(\sqrt{8};4/2;\sqrt{2})=c_B(2\sqrt{8}; 4;2\sqrt{2})=g_C(4\sqrt{8};8;4\sqrt{2})$. If b is a subset of c then c is somewhat overoccupied. It must therefore be assumed that b is not under c. The fit of the atom sites to the binding is good.

Following 75Wel there is no explanation from the electron pair model for the form of the molecule.

BrF_3(Q2.6,SR21.202) is composed of planar T-shaped molecules just as ClF_3. $a(28,40, 64+84,32)=5.34;7.35;6.61Å=b_{FH}(2.6/3;3;3/2)=e_{CH}(5.2/3;3;3/2)$ $=c_{CH}(10.5/3;6;6/2)=g_{BH}$ $(21/3;6;6/2)$. Once more b is not a subset of e but b and e are subsets of c. $N^{At}_{S(c)}=47$ is not comparable with the value for ClF_3 because of a strongly different electron numbers of both phases.

BrF_5(Q2.10,SR21.202) is a filling homeotype of BrF_3. $a(28,40,64+140,48)=6.42;7.25; 7.85Å=b_{FH}(3/3;3.2/2;3)=e_{CH}(6/3;3.2/2;3)=c_{CH}(12/3;6.4/2;6)=g_{BH}(24/3;6.4/2;6)$. It appears remarkable that the binding is rotated as compared with that of BrF_3.

IF_5(N10.50,SR21.201,40.132) $a=15.16;6.86;18.20Å93.23°$.

IF_7(OsF$_6$,SR27.446), $a(14,20,36+49,32+28)=6.28Å=b_B(2)=e_B(\sqrt{8};2.8)=c_C(\sqrt{32};5.6)$ $=g_F(\sqrt{32};5.6)$.

$IF_7.1<153K$(Q2.14,SR27.446) consists of IF_7 molecules. $a(28,40,72+196,64+56)=6.14; 8.87;8.74Å=b_{FU}(\sqrt{10};3/2)=e_C(\sqrt{20};3)=c_C(\sqrt{80};6)=g_F(\sqrt{80};6)$.

KrF_2(T4.8,73Pie), $a(32,40,64+56,24)=6.53;5.83Å=b_C(\sqrt{10};3.2)=e_C(\sqrt{20};4.5)=$ $c_{FU}(\sqrt{40}; 9/2)=g_C(\sqrt{80};9)$. The stability of noble gas fluorides proves that spins near A^{18} elements may exist which are not internally compensated, in other words, in Kr element e.g. there must be besides $a=b_C(4)$ also $a=b_F(2)$ weakly present.

XeF_2(U1.2,SR28.73) contains linear FXeF molecules along a_3. $a(16,20,36+28,32+8)= 4.32;6.99Å=b_{FU}(2;4.5/2)=e_C(\sqrt{8};4.5)=c_{FU}(4;9/2)=g_C(\sqrt{32};9)$. It is clearly seen that the matrix element 4.5 warrants the collective property.

XeF_3(M4.12,SR28.74) contains linear XeF_2 and planar XeF_4 molecules. $a(32,40,72+84, 64+24)=6.64;7.33;6.40Å92.67°=b_{FU}(\sqrt{8};4.5/2)=e_C(4;4.5)=c_{FU}(\sqrt{32};9/2)=g_C(8;9)$. The binding is written for the quasi tetragonal cell a.

XeF_4(M2.8;SR28.75) is a B1 type packing for planar XeF_4 molecules. $a(16,20,36+56, 32+16)=5.05;5.92;5.77Å99.6°=b_{\tilde{B}}(2;2;2)=e_B(\sqrt{8};2.5)=c_B(4;4;4)=g_C(8;8;8)$. It might be that the commensurability element 2.5 causes the monoclinic deformation.

XeF_6.r(M8.48,SR37.354;73Pie, $a(64,80,144+336,128+96)=9.33;10.96;8.95Å91.9°=b_{FU}$ $(\sqrt{13};6/2)=e_C(\sqrt{26};6)=c_{FU}(\sqrt{52};12/2)=g_B(\sqrt{104};12)$. The striking phenomenon that the c correlation is fully occupied by $b+e+c$ electrons must be understood by the assumption that the correlation sides need not lie in the summit of the electron density of a band but may lie in its spur. The phenomenon is mitigated be one spin per Xe being internally compensated.

$XeF_6.1_1$(O16.96,73Pie).

$XeF_6.1_2$(F36.216,SR40.133).

$XeF_6.1_3$(M64.384,73Pie).

Concluding remarks

The high electronegativity of F causes that Lewis' rule of spin compensation holds quite good in fluorides. Where the oxidation number of the cation is smaller than the maximum oxidation number, there must be assumed internal spin compensation. This explains why elements with even number of valence electrons display preferentially even oxidation numbers, and elements with odd number of valence electrons display odd oxidation numbers. Were this rule is not fulfilled a mixture of oxidation numbers must be assumed. The fact that these exceptions are possible clearly shows that spin compensation is not the only cause of stability. An additional cause of stability is the spatial correlation of the electrons. This spatial correlation of the electrons may be uncovered by first analysing the spatial correlation of the valence electrons (64Sch). Such a kind of analysis soon shows that deeper shells of electrons are influential. This observation leads to the concept of a collective bonding type i.e., of a bonding type in which the lattice of the averaged b correlation (83Sch) is a sublattice of the averaged e or c correlation, the e correlation is a sublattice of c or g and c is a sublattice of g. Of course this is a model, i.e. an approximation to reality, but it contains more parameters than the model of ionic bond and the model of covalent bond. Therefore the electron correlations model allows to find bonding types where the earlier models met difficulties. Another advantage of the electron correlations model is its generality. It contains the ionic and covalent models in it while the earlier models do not contain the correlations model in them. Therefore earlier valence rules such as Lewis' rule or Zintl's rule may be expressed in terms of the correlations model i.e. they are compatible with it. While the ionic model is restricted to the ionic compounds and is barely valid in covalent phases or metallic phases, the correlations model is valid in all kinds of phases. It even tells why the bonding types are valid in certain homologic classes. For instance in $A^1 A_M^{17}$ phases the b electrons of A^1 are distributed over the whole a cell so that it may be said they go over to A^{17} i.e. they charge the A^{17} anions. Or in A^{14} phases, the b electrons form a b correlation of high commensurability to the F2 structure just as the "bonds" of the covalent model; of course there are also differences between the models. For instance the "bonds" of the covalent model of A^{14} form a bad spatial correlation since they interfere near the A^{14} core instead to avoid each other. Finally the generality of the correlations model is the reason why new stability rules may be formulated for instance the shear density of homeotypes of Cu_3Au is governed by electro dipoles generated by the b correlation at the minority component (64Sch). Or the theory of packing density (40Deh,61Par) is transformed, by taking the electron correlations into account, to the site number rules (86Sch) telling which influences cause a decrease of site number in a low correlation. Or the cause of the validity of Zintl's supply rule lies in the fact that the $A^{1..2}$ elements contribute essentially only their b electrons into the binding while the $A^{9..17}$ elements display a strong influence of their e, c, g electrons.

The real existence of the assumed correlations can be made probable by analyses like the above one. Therefore the continuation of such analyses appears desirable.

References

31Ewa   P.P. Ewald, C. Hermann: Strukturbericht, Vol. 1. Leipzig 1931 Akad. Verl. Ges.
        from Vol. 8: Structure Reports.
35Ket   A.A.: Ketelaar: Z. Krist. A92 (1935) 30–38
40Deh   U. Dehlinger, G.E.R. Schulze: Z. Krist. A102 (1940) 377
53Zal   A. Zalkin, D.H. Templeton: J. Amer. Chem. Soc. 75 (1953) 2453–2458
61Par   E. Parthé: Z. Krist. 115 (1961) 52–72
64Sch   K. Schubert: Kristallstr. zweikomp. Phasen, Berlin 1964, Springer V.
64Schä H. Schäfer, H.G. v. Schnering: Angew. Chem. 76 (1964) 833
65Man   M. Mansmann, Z. Krist. 122 (1965) 375–398
66Tho   R.E. Thomas, G.D. Brunton: Inorg. Chem. 5 (1966) 1937–1939
68Bab   D. Babel: Struct. Bonding 3 (1968) (Octahedral Fluoro complexes)
68Can   J.H. Canterford, R. Colton: Halides of the second and third row transition metals.
        London 1969, Wiley–Intersci.
69Col   R. Colton, J.H. Canterford: Halides of the first row transition metals.
        London 1969 Wiley–Intersci.
70Hop   R. Hoppe: Adv. Fluorine Chem. 6 (1970) 387
71Bau   W.H. Baur, A.A. Khan: Acta Cryst. B27 (1971) 2133–2139
71Mic   C.Michel, J.M. Moreau, W.J. James: Acta Cryst.B27 (1971) 501–503
72Win   J.M. Winfield: Fluorides, in MTP Internat. Rev. Sci., Inorg. Chem. Ser. 1 Vol. 5
73O'Do T.A. O'Donell in J.C. Bailar: Compr. Inorg. Chemistry Oxford 1973 Vol. 2.
73Pie   W. Pies, A. Weiß: Landolt–Börnstein III 7a Berlin 1973
73Sob   B.P. Sobolev, P.P. Federov: Kristallografija 18 (1973) 624–625
75Wel   A.F. Wells: Structural inorg. Chem. Oxford 1975 Clarendon Pr.
78Get   W. Gettmann, O. Greis: J. Sol. State Chem 26 (1978) 255–263
78Gre   O. Greis, D.J.M. Bevan: J. Sol. State Chem. 24 (1978) 113–114
79Has   J.M. Haschke in K.A. Gschneidner, L. Eying: Hb. Phys. Chem. of Rare Earths,
        Vol. 4, Amsterdam 1979
81Sim   A. Simon: Angew. Chem. Int. Ed. 20 (1981) 1–22
82Bau   W.H. Baur, G. Guggenheim, J.C. Liu: Acta Cryst. B38 (1982) 351–355
82Gre   O. Greis, J.M. Haschke in K.A. Gschneidner, L. Ering: Hb. Phys. Chem. Rare
        Earths Vol. 5 Amsterdam 1982 North Holland.
82Sch   K. Schubert: Comm. Math. Chem. 13 (1982) 55–74
83Sch   K. Schubert: Z. Krist. 165 (1983) 23–45
84Sch   K. Schubert: J. Sol. State Chem. 53 (1984) 246–252
86Sch   K. Schubert: Comm. Math. Chem. 19 (1986) 287–307
88Köh   J. Köhler, A. Simon, R. Hoppe: J. Less Comm. Metals 137 (1988) 333–341
89Sch   K. Schubert: On the bindings in the chemical elements, Energetic
        arguments for the LaF$_3$ structure, submitted.