ON THE BINDING IN TWO-COMPONENT FLUORIDES

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Summary

A systematical consideration of two-component fluorides is worked out on
the basis of spatial correlation of the electrons, and gives numerous
interesting interpretations of facts not understood before. The old ques-
tion of the ionic lattice theory, why the NaCl type for instance of NaF
is preferred to the CsCl type contrary to the expectation from ionic radii,
is answered by the remark that the binding of the NaCl type permits a
greater average valence electron distance than the binding of the CsCl
type. The compound $MgF_2(TiO_2.r$ type) is found to be homeodesmic to
NaF(NaCl), and it may also be considered as topologically homeotypic to a
vacancy homeotype of NaCl. In $TiF_3(VF_3$type) may be expected that the 3sp
electrons of Ti leave the $\underline{c}$ correlation with the result that the $\underline{c}_c$corre-
lation transforms to a $\underline{c}_F$ correlation which is quite persistent in the
following compounds. This is confirmed by the homeotypism of many subse-
quent compounds to the ReO_3 type, and by the sequence of binding BF2, CF2
for instance in the mixture $NbF_{\underline{M}}$, while FF2 cannot be stable. In Nb_2F_5
Hund insertion appears to support Nb - cluster formation.
The deformation-homeotypism of CrF_2 to $TiO_2.r$ is found to be a consequence
of the commensurability rule. The shear homeotypism of HgF(U2.2) to NaCl
may be explained in the same manner as the shears in homeotypes of Cu_3Au.
The deformation homeotypism of TIF.r to NaCl follows immediately from the
FUHT2 binding. In SbF_3 having a C'C2 binding, clear indications of Hund
insertion are found. Many further interpretations confirm that the two-

correlations model gives a helpful insight into the valence problem of fluorides.

Introduction

The experience that the analysis of the probable spatial correlations in twocomponent oxides [1] gave illuminating interpretations for many structural phenomena , suggests to try an analysis also for two-component fluorides. Clearly the fluorides are, with respect to bonding, quite opposed to metallic phases, for which the two correlations model had been devised; therefore the validity of this model for fluorides might appear questionable. However, in fluorides there must exist a spatial correlation of the valence electrons (b correlation) and a spatial correlation of the peripheral core electrons (c correlation) and these correlations may be assumed,just as in metallic phases, as lattice like and commensurable to the crystal cell a and to one another [2]. Also in earlier analyses indications for the influence of spatial correlations of electrons in fluorides have been found [3].

The fluorides have been carefully reviewed by Pies and Weiß [4], and this listing is of great help in systematical work. Reference is made in the following TABLE 1, preferredly to Structure Reports A [5] (although unfortunately they are not free from omissions) as these reports are supposedly at hand in most structural laboratories. It is well known that F has a great electronegativity so that its compounds are strongly ionic, and F induces the greatest oxidation numbers in cationic components as compared with other halogen anions. The fact that fluorides have often structures different from chlorides, bromides, and iodides, is caused by the fact that the F core has only two peripheral core electrons while Cl has 8 and Br, I have 10. As has been shown repeatedly [1,2,3], for an analysis of the bonding type (binding) an assumption on the electron count is necessary. From a binding proposal the electron count may be retrieved by applying the rule of full occupation of the b correlation [2]. It is found unexpectedly that the analysis affords interpretations which are probable with respect to the rules of the two-correlations model, when it is proposed that the valence electrons of F populate the c correlation while the peripheral electrons of A elements populate partly the b correlation and partly the c correlation. This assumption had been confirmed previous-

ly for oxides [1], therefore the analysis of the binding in oxides gives
good advice for the analysis of the binding in flourides. (Also the nomen-
clature used in [1] shall be followed here)

The above surprising electron count implies, that the Lewis phenomenon
of octet completion is also possible when the completing electrons belong
to another correlation than the valence electrons of the anions. In fact,
when an electron "goes over to the anion" it is yet admissible that it is
correlated to electrons of other cations. Even more surprising is the
possibility of Hund insertion, which appears to imply that the spin of a d
electron is not quenched only when it is in Hund insertion. However, these
interesting problems are not the subject of this inquiry, the question here
is, whether the phenomenon of spatial correlation of electrons may be
used for an interpretation and classification of our knowledge on crystal
structures. When the answer is affirmative then new empirical structural
rules must emerge, and there must appear some parallelism between data and
model. It should not be expected that all the binding proposals are final,
so that they hold all in the future development of the model.On the contra-
ry it must be expected that sets of proposals based on some assumption
which was falsified is to be changed somewhat. In reality there are so
many examples of parallelism between the proposals and experimental facts
that the general approach appears truly rewarding.

It might be questioned whether the finding of a low-energy bonding type
(binding) for stable phases has some explanatory value. But every valence
model attempts to find bonding types forming a variety smaller than the
chemical compounds and affording thus a classification of compound.
Certainly the crystal structure gives also a classification of compounds,
but this could be only the geometrical part of a solution of the valence
problem as it does not make appropriate use of the electron numbers. The
two-correlations model utilizes the electron numbers and relates them to
the structures by the electron spatial correlations, it is therefore a
phenomenological valence model. The phenomenological valence theory has un-
covered many rules unknown before, and explained many unsolved structural
phenomena, therefore it is an admissible and necessary method of investi-
gation.

Analysis

The fluorides of the alcali elements (A^1) obey the Lewis octet rule, and exclusively the compounds $A_1^1F_1$ become stable (see TABLE 1); their structures obey Zintl's supply rule: the A^1 atom supplies to F one electron and the anions form a partial structure isotypic to Ne. If a uniform valence electron gas is expected (electron count $A^{1,8}F_M^{7,2}$), the binding for the NaCl structures A^1F might be assumed as $\underline{a}=\underline{b}_F(2)=\underline{c}_C(4)$ (for matrix symbols see [2]). However, when the electron count $Na^{1,8}F_M^{0,7}$ is supposed then the homeotypic binding $\underline{a}=\underline{b}_F(1)=\underline{c}_C(4)$ appears probable (the use of character F in two meanings should not confuse the reader, if necessary Fl might be written for fluorine). Although the valence electron of Na does not belong to the $\underline{c}$ correlation, which contains the valence electrons of F, the octet completion remains possible [1]. For the high pressure $A^1F.p$ phases of the CsCl(C1.1) type like KF.p (for phase and type description see [2,3]) a CB2 binding is probable (TAbLE 1). For KF following the electrostatic lattice theory the CsCl type is expected (see [3]) but the NaCl type (being stabilized really) is preferred by the present binding since it allows an electron distance $\underline{d}_b$ which is nearer to the distance in the element K(W type) than the $\underline{d}_b$ in the CsCl type. The CsCl type has a closer packed $\underline{c}$ correlation than the NaCl type and is therefore stabilized by pressure. - By analogy to the suboxides of Rb and Cs a stabilization of subfluorides might be possible.

The structures of BeF_2 are reported to be isotypic to structures of SiO_2 (see [1]). This supports the assumption of an electron count like $Be^{2,2}F_7^{7,2}$. For $MgF_2(TiO_2.r)$ and the following phases an electron count like $Mg^{2,8}F_2^{0,7}$ is probable. Although the octet completion is fulfilled in MgF_2, Zintl's supply rule is not fulfilled, as the anions are not in a Cu type partial structure. But the rule of the ionic lattice theory is fulfilled that the smallest cation is 4-coordinated, the greater 6-coordinated ($TiO_2.r$ type of MgF_2) and the greatest 8-coordinated (CaF_2 in F1.2 type) by anions. While CaF_2 is a L-homeotype of CsCl (L=lacuna) the $TiO_2.r$ type is only topologically homeotypic to a L-homeotype of NaCl. Considering a NaCl representative like NaF with the $\underline{c}$ correlation $\underline{a}=\underline{c}_C(4)$ the strong compression of the cell leading to the cell of $MgF_2(TiO_2.r)$ may transform the commensurability of the correlation to $\underline{a}=\underline{c}_C(\sqrt{20};3)$ so that the number of $\underline{c}$ places per cell is reduced from 64 in NaF to 60 in MgF. Such a decrease is to be expected from the decrease in Mg content caused by the octet rule. The small decrease of

number of places per cell in $\underline{b}$ correlation $N_{p''}^{/C}$=3.75 may be removed by a little Hund insertion in the $\underline{b}$ correlation. Therefore the F'C4 binding of MgF_2 is essentially the same as the FC4 binding of NaF. Also the CB2 binding of CaF_2 is the same as that of KF.p(CsCl) and $Ca_{1-M}Y_MF_{2+M}$(SR44.324). At elevated pressures CaF_2.p($PbCl_2$, 04.8, drawing [3] p.322) becomes stable. The $PbCl_2$ type is a RDI-homeotype of Cu (R = replacement, D = homogeneous, I = inhomogeneous deformation) and this is compatible with its stabilisation under pressure. A binding of the kind UC3 being homeotypic to the below CC3 binding appears to obey the rules. A binding with similar commensurability to $\underline{a}$ was found in $CaSn_3$(Cu_3Au, SR3.638,15.25) $\underline{a}$=4.74A=$\underline{b}_F$(3/2)=$\underline{c}_B$(·) .

Similar to the mixtures A^2F_M in A^3F_M (M = undetermined mole number) only the octet completed compounds have been found, but in A^4F_M subfluorides occur. The phase ScF_3.r(R.3) has been doubted [7] while ScF_3.h(ReO_3) is confirmed [7,8] . The CF2 binding of ReO_3 appears not probable for ScF_3 as $\underline{d}_b$ would become somewhat great, but the homeotypic FF2 binding fits well.

The homeotypism of TiF_3 (VF_3 type) to TaF_3(ReO_3) consists in a small rotation around $\underline{a}_3$ of the TiF_6 octahedra (described by an x-parameter of the F position) conserving the common corners; the value of x is a function of the axial ratio [10]. The greatest rotation is reached in PdF_3(SR21.206) (see [3] p.283). Just as $CaTiO_3$ is a filling homeotype of ReO_3 the phase $LiTaO_3$(SR32.312) is a filling homeotype of VF_3 which fits together with further isotypes to the x-$|\underline{a}_3|$/$|\underline{a}_1|$ relation [10]. The binding is discussed below. Several T^4F_M structures require further refinement, the binding analysis may be postponed to avoid uncertain proposals.

For VF_2(TiO_2.r) the binding $\underline{a}$=$\underline{b}_C$($\sqrt{2}$;1)=$\underline{c}_B$($\sqrt{10}$;2.1) could be assumed, but it is known [4,14] that at low temperatures a magnetic structure appears. This probably corresponds to Hund insertion which occurs preferredly in a $\underline{c}_F$ correlation. Therefore the FF3 binding (TAB. 1) is considered probable, which has $N_{p''}^{/V}$=22$\underline{c}$ places per V atom. The transition of the F'C4 binding of MgF_2 to the FF3 binding of VF_2 corresponds to the transition of the FC4 binding of NaF to the FF2 binding of TiO.h [1]. The fact that CaF_2 with its CB2 binding has $N_{p''}^{/Ca}$=32, conforms to the rule of place numbers [2] that a heavier compound needs less $\underline{c}$ places, also CaF_2 has many $\underline{c}$ correlation places as the Ca atom is so great. VF_3(R2.6) has no magnetic ordering (SR22.232). The structure is homeotypic to ReO_3

(see [3] p.283), in ReO_3 there is a CF2 binding [1] and this holds in VF_3 also; the heterotypism to ReO_3 is perhaps caused by some Hund insertion. Hund insertion certainly is responsible for the persistency of the VF_3 type up to PdF_3. While VF_4 is not yet analysed well enough, $VF_5(\supset 8.40)$ displays clearly the homeotypism to ReO_3 or NaCl. Conventionally it is described by infinite zigzag chains of V in $\underline{a}_1$ direction where each F_6 octahedron has two common corners. This becomes necessary in the ReO_3 family by the composition 1:5. Such an array however could be achieved in very different ways, it is therefore important to state also the homeotypism to NaCl $\underline{a}_{VF5} = \underline{a}_{NaCl}(1,0,-1.5;0,4,0;1,0,1.5)$. Out of 48F places (calculate the determinant) 40 are occupied, i.e. 5/6, while in ReO_3 3/4 only, because of a higher electron offer for the $\underline{c}$ correlation in ReO_3. The fit of the $\underline{c}$ correlation is not very good; this must be taken as an indication of Hund insertion, as Hund insertion strongly deformes the fundamental correlation. The matrix element 6/2 of the $\underline{b}^{-1}\underline{a}$ commensurability must be responsible for the array of the V chains in a similar manner as the shear in the S-homeotypes of Cu_3Au was explained [3] (S=shear).

The phase Nb_2F_5(B6.15) is a lacuna-homeotype of NaCl with the commensurability $\underline{a}_{Nb2F5} = \underline{a}_{NaCl}(2)$ and there are 20 Nb-vacancies and 2 F-vacancies in the cell. As there are 12Nb in the cell the $\underline{b}$ correlation contains 16 electrons per cell when the electron contribution $Nb^{1.3,3.7}$ is assumed, and this permits the correlation $\underline{a} = \underline{b}_B(2)$ which is in good commensurability to the $\underline{a}$ cell, and yields with $F^{0,7}$ the number of 254.4 electrons per cell in the $\underline{c}$ correlation. This number indicates that a full occupation of the Cl partial structure of NaCl by fluorine is not possible, i.e. the expected $\underline{a} = \underline{c}_F(4)$ correlation does not allow in Nb_2F_5 a fully occupied fluorine partial structure. The easiest possibility for the ordering of the fluorine vacancies is in a B1 site as it is observed in fact. However, with the number 254 the $\underline{c}_F(4)$ correlation would be nearly fully occupied. As this is energetically not very favourable it must be assumed that several electrons are Hund inserted in the $\underline{c}_F(4)$ correlation. As Hund insertion fosteres the formation of metal clusters a disorder of F vacancies (like O vacancies in TiO.h(L-homeotype of NaCl)) is not possible; the Nb_6F_{15} arrangement could even exist in some solution, as the energetic favour of the binding may persist for stronger perturbations as they occur in the liquid. The anions will have also in solution partial Hund insertion; therefore these anions behave unsymmetrically and favour agglomerations in clusters [11,12]. The

centre of a cluster is a fluorine vacancy, the neighbouring Nb move onto
the vacancy because of $\underline{c}$ correlation, they are neutralized by fluorine
atoms and these put their Hund insertion on the cluster surface and stabi-
lize the cluster. In fact a Nb_6F_{15}cluster in solution is not known as yet
but the other B^7 elements form a multitude of clusters with Nb and Ta in
solutions.

NbF_4(SnF$_4$ type) also is a L-homeotype of NaCl, with a filled F partial
structure. It has the CF2 binding like $NbF_3.i(ReO_3)$. The full occupation
of the $\underline{c}$ correlation should not be taken too literally because of Hund
insertion. The matrix element 2 in the equation $\underline{a}_{NbF4}=\underline{a}_{NaCl}(1;2)$ is neces-
sary to have a close coordination of the F to the Nb.

Also NbF_5(MoF$_5$) is a L-homeotype of NaCl with a complete F partial struc-
ture. The array of the Nb causes a DI-homeotypism. NbF_5 is probably homeo-
desmic to NbF_4, it is a seperate phase because of the deformation homeo-
typism.

It may be summarized that all phases of the mixture NbF_M are L-homoeotypes
of NaCl. This corresponds to the fact that the stable intermediary phases
are limited to a fairly narrow range of composition (see TAB. 1). All phases
are stabilized by a $\underline{c}_F$ correlation. Fluorine vacancies occur only when
there are too many Nb atoms in the structure the $\underline{c}_F$ correlation having the
commensurability as in NbF_4. The array of the T atoms is not the most uni-
form one as T clusters are formed. This probably has to do with Hund in-
sertion of $\underline{c}$-electrons into $\underline{c}$ correlation. Also some interaction of the T
atoms may be present, but the Hund insertion would be an additional mecha-
nism which limits the uniform distribution of T atoms. At the point where
Hund insertion occurs at a fluorine atom the atom is only able to form a
van der Waals bond so that the distance to the next atom becomes greater.

The heterotypism TaF_3(ReO$_3$)-VF$_3$(R2.6) corresponds to the stability of
the ReO$_3$ type in ReO$_M$ but not in MnO$_M$; it is not yet clear why in TaF$_3$
there is one F vacancy per NaCl cell while in Nb_2F_5 there are only 0.25.
It might be conjectured that the heavy Ta atom discourages Hund insertion
at F atoms so that vacancy formation is favoured.

The phase CrF_2 is D-homeotypic to $TiO_2.r$ contrary to VF_2 and MnF_2 which
are isotypic. Comparison of the lattice constants of VF_2 and CrF_2 reveals
that the tetragonal axial ratio $|\underline{a}_3|/|\underline{a}_1|$ has increased considerably as it
is to be expected when the electron concentration increases while the commen-

surability of the correlation to the crystal is conserved in the basal
plane. The matrix element $(\underline{c}^{-1}\underline{a})_{33}$=3.8 (TABLE 1) may be idealized to 3.5 as
Hund insertion may strain the correlation. This matrix element gives a
whole number commensurability for the translation $2\underline{a}_3$, but there is neces-
sary also a shift of $\underline{a}_1/5 \cong 0.95\underline{a}_1/|\underline{a}_1|$Å (look at the $\underline{a}_1 \& \underline{a}_2$ mesh with inser-
ted √13 commensurability); the crystal distortion affords $2|\underline{a}_3|\cos\alpha_3$=0.79Å
which is in fair agreement with the expectation, as a greater accuracy can-
not be expected because of other interactions. It may therefore be said
that the two-correlations model gives by the commensurability rule an ex-
planation of the monoclinic D-homeotypism of CrF_2 to VF_2. To be shure the
commensurability requirement needs not be the only cause of the phenomenon,
Hund insertion may take further advantage of the deformation. This may be
seen from MoO_2 which is a different homeotype of TiO_2.r and reveals the
Hund insertion by shifts of Mo atoms. This shift might also be interpreted
by cluster forming forces, therefore Hund insertion may be considered as a
cluster forming agent.

At this occasion it may be remembered that the TiO_2.r type is topological-
ly related to a L-homeotype of NaCl. A strong tetragonal compression of a
NaCl structure homeodesmic to TiO.h may transform the correlation $\underline{a}_{TiO.h}$=$\underline{c}_F(2)$
[1] into $\underline{a}_{TiO2.r}$=$\underline{c}_{FU}(\sqrt{10};3/2)$ [1] so that the number of $\underline{c}$-places per cell is
reduced from N_{bh}^{C}=32 to 30 corresponding to the decrease in Ti content. Just
as there are heterodesmic subtypes of the NaCl type [1] also in the TiO_2.r
type hetereodesmic representatives occur; in $VF_2(TiO_2.r)$ for instance a FF3
binding with √13 commensurability appears possible. This possibility of he-
terodesmic isotypism may explain an irregular behaviour of the axial ratio
of TiO_2.r representatives [13]. The commensurability of the binding to the
elementary cell is in both cases oblique and to this property corresponds
the oblique character of the fluorine (or oxygen) sites.

Cr_2F_5(N4.10) is homeotypic to ReO_3 with the commensurability $\underline{a}_{Cr2F5}$
=$\underline{a}_{ReO3}(2,0,0;0,2,0;-1,0,2)$. The phase has in the approximately quadratic
mesh $0,x_2,x_3(0 \leq x; \leq 1)$ 4Cr distributed quadratically like the Re in $0,x_2,x_3$
of ReO_3. Only the Cr in 0,0,0 and 0,0,1/2 are coordinated by
$F(\pm\underline{a}_2/4,\ \pm(\underline{a}_1+\underline{a}_3/2)/4)$ and $F_{1/2}(\pm\underline{a}_3/4)$ so that there are octahedral chains
in $\underline{a}_3$ direction, and two Cr are only 2-coordinated by F. These Cr_4F_{10} lay-
ers are stacked up in such a manner that the two-coordinated Cr become
approximately 6 coordinated. The structural relation of Cr_2F_5 to NaCl is

therefore a LS-homeotypism (L=lacuna, S=shear). The determinant of the commensurability shows that in the cell there are 24 F places as compared with the ReO_3 type. The compression of the structure of Cr_2F_5 in $(\underline{a}_1+\underline{a}_3/2)$ direction causes that only 20 F are in the cell. The binding may be assumed as HTF2 which is closely homeotypic to CF2 of ReO_3 and CrF_3. The octet rule leads to the conventional formulation $Cr^{2+}Cr^{3+}F_5^{1-}$, but there is no indication of Cr clustering, which should be expected if there are remaining A atom valences. Since the $\underline{c}$-occupation ratio is $N_C^{/P"}=0.8$ the $\underline{c}$ correlation probably has not much Hund insertion and therefore clustering is not favoured.

The isotypism of $MoF_3(VF_3)$ and $MoF_5(NbF_5)$ with quasi homologous phases discussed earlier is satisfactory as the phases are dominated by the majority component F and the relative change of the electron contribution caused by the homologic changes of A atoms is relatively small. While the oxidation number 6 was not stabilized in CrF_M it occurs in $MoF_6(OsF_6)$. The room temperature phase MoF_6 displays rotational disorder of octahedral MoF_6 molecules (SR41.151) but the distance $\underline{d}(Mo-F)=1.8$Å points preferredly in $\underline{a}$ axis direction. Starting from the homeotypism to ReO_3 the 6 coordination of Mo by F is conserved and from the composition, common corners or edges are not allowed. Therefore there are no more chains or layers homeotypic to NaCl. When the approximate relation $a_{MoF6}=a_{ReO3}(\sqrt{2};1.5)$ is considered a $\underline{c}_B$ correlation becomes probable with respect to the CF2 binding of ReO_3. In $MoF_6.1(UF_6)$ the Mo are 6-coordinated by F but these atoms form a ABAC hexagonal close packed partial structure without lacunae. A very simple $\underline{c}_{FH}$ correlation emerges with the electron distance $2d_{\underline{c}}=\underline{d}_{F1}$ just as in ReO_3. But the $\underline{c}$ correlation is nearly fully occupied and the $\underline{d}_{\underline{c}}(MoF_6.1)$ is 6% greater than $\underline{d}_{\underline{c}}(MoF_6)$. This suggests strong Hund insertion at the F atoms, and the Hund insertion must also be responsible for the peculiar stacking sequence of the F1 layers parallel $\underline{a}_2$ and $\underline{a}_3$ along $\underline{a}_1$.

The WF_M phases are isodesmic to phases discussed earlier.

$MnF_2(TiO_2.r)$ is antiferomagnetic (SR15.359) so that it may be concluded that a $\underline{c}_F$ correlation contains Hund insertion. The binding may be described by the FF'3 bonding type. $MnF_2.p_1(PbO_2.m)$ has a Mg type partial structure of F with $\underline{a}=5.0;5.8;5.4$Å$=\underline{a}_{Mg}(0,2,-1;0,2,1;1,0,0)$ in the octahedral interstices of which the Mn are inserted. The stabilisation of three different high pressure phases probably has to do with change in electron count. Regarding

the uncertain electron count in Mn the binding analysis may be postponed.

The partial isotypism of TcF_M and ReF_M with A^6F_M is a consequence of the particular elctron count which leaves the b-electron contribution of the A atom essentially independent of a homologic change and which renderes the change of A electrons in the c correlation less important as there are so many electrons in it.

In all F_M phases the c_F correlation is found which must be understood more or less Hund inserted. In $FeF_2(TiO_2.r)$ the number of 2 valence electrons per cell requires a little deformation of b_F. Therefore it is satisfactory that Fe_2F_5 has been found which may have a undeformed FF3 binding. Since FF3 affords 27 c correlation places per b correlation place it is satisfactory that FeF_3 with a CF2 binding becomes stable which affords 32 c-places per b-place.

In the mixture RuF_M the phase $RuF_6(OsF_6$ type) displays a BB4 binding mentioned before which has 64 c places per b place. The $HFH\sqrt{12}$ binding of $RuF_6.1(UF_6)$ affords only 48 places as an increased Hund insertion decreases the apparent place number by increasing the average electron distance of the c_F correlation.

The $T^{9...10}F_M$ mixtures show mainly isotypes of phases discussed earlier. The binding of $PdF_3(htpVF_3)$ is an interesting homeotype of the VF_3 binding. The structure of $PdF_4(ThCl_4)$ is a remote I-homeotype of CaF_2 as a partial C1 structure of Fl is homeotypic to the fluorine partial structure in PdF_4. The FB4 binding is homeotypic to the CB2 binding of CaF_2.

For CuF(ZnS) following the electrostatic lattice theory a CsCl type is to be expected (see [3] p.42). The fact that instead the sphalerite structure is stabilized might indicate a change of electron count to $Cu^{1,10}F^{7,2}$ and a b correlation of the F type as in diamond. The c correlation takes a C type because of the few core electrons contributed by fluorine. To be shure for CuF also the binding of AgF might be possible but with respect to the B^nB^{8-n} phases (Grimm-Sommerfeld phases) the FC2 binding was preferred. In CuF_2 which has a monoclinically deformed $TiO_2.r$ structure the electron count of the TF_M phases is recovered and the explanation of the monoclinicity is as in CrF_2, not considering Hund insertion.

The brass like colored subfluoride $Ag_2F(CdI_2)$ probably has the prior electron count $Ag^{1,10}F_M^{0,7}$ in analogy to the alkali suboxides [1]. The

correlation $\underline{c}_{CH}^{\curvearrowright}$ is a hexagonally compressed CH correlation which belongs to the isometric lattices. The compression is necessary from the occupation rule and incidentally favours the hexagonal stacking. For AgF_2 contradictory results on the structure seem to be reported, so that the binding search should be postponed.

AuF_3(H6.18) crystallizes in space group $P6_122$ so that all Au are symmetrically equivalent. If the count $Au^{1,10}F_3^{0,7}$ is chosen a $\underline{c}_H$ correlation might be possible. In $ZnF_2(TiO_2.r)$ the undistorted $TiO_2.r$ type reappears. The remarkable phenomenon that the structure type is stable from VF_2 up to ZnF_2 and contains essentially the same $\underline{c}$ correlation is caused by the Hund insertion mainly at the T atoms. The strong increase of the number of $\underline{b}$ electrons per cell going from NiF_2 to ZnF_2 results in a change of the $\underline{b}_{FU}$ into a $\underline{b}_C$ correlation so that a CFU2 binding is formed. The phase $ZnF_2.p_1$(T4.8) is D-homeotypic to $ZnF_2.r$ with the commensurability $\underline{a}_{p1}=\underline{a}_r(1;2)$.

$CdF_2(CaF_2)$ permits a twinned CFU2 binding with a relatively rare commensurability to the crystal which will be more comprehensible after comparison with the binding of HgF_2. It becomes apparent here that a simple commensurability $\underline{b}^{-1}\underline{c}$ of the $\underline{b}$ correlation to the $\underline{c}$ correlation is more important than a simple $\underline{b}^{-1}\underline{a}$ commensurability. The fact that Hund insertion at Cd is not necessary does not mean that it is not present. It appears that in $CdF_2.p(PbCl_2)$ full Hund insertion at Cd is necessary.

The subfluoride HgF(HgCl,U2.2) is a DS-homeotype of NaCl (D=deformation, S=shear) with the commensurability $\underline{a}_{HgF}=\underline{a}_{NaCl}(1/\!\sqrt{2};2)$ (see [3] p.191). Starting from the FC4 binding of NaF leads to a HH2 binding (see TABLE 1) affording the place numbers per cell $N_{p',p''}^{/C}$=10,80 which are to be compared with the electron numbers $N_{V,C}^{/C}$=8,68. The place numbers account for the wellknown valence electron contribution of Hg which exceeds 2 and for the increased number of core electrons as compared to NaF. The axial ratio is borne out well by the binding and the shears follow a rule found in S-homeotypes of Cu_3Au[3], that the dipole array generated by the commensurability of the electron correlation causes the shear system in the structure. It must be concluded that HgF is stabilized by the energetic favour of the HH2 binding and that forces within the structure generate the mercurous ion Hg_2^{2+}. From the ionic lattice theory it is somewhat surprising

that the dipol interaction is so strong as to introduce shears into a NaCl
type structure. But the fact that $\underline{b}$ correlation and $\underline{c}$ correlation take
part in the generation of the shears shows that the whole binding favours
this homeotypism. Also the existence of the Hg_2^{2+} ion in aqueous or other
solutions appears to indicate that there is some "covalent bond" which
favours the Hg_2^{2+} molecule ion. However, since the two-correlations model
is a new form to argue on covalent bonding, there is no real contradic-
tion between the interpretations; the spatial correlation of the $\underline{b}$ and
$\underline{c}$ electrons around Hg_2^{2+} will be similar in the HgF crystal and in its
solution; an increased association of anions and cations might exist and
also the OH^{1-} ions may be similar as the F^{1-} ion. As the compounds HgCl,
HgBr, HgI are isotypic to HgF (see SR1.237,239) it is quite clear that
in melts containing B^7 anions also the Hg_2^{2+} ion will appear when some
of these compounds are solved remembering that a melt is essentially a
crystal which has lost its shear stiffness. From these reasons it becomes
apparent that the above interpretation is the first explanation of the
remarkable homeotypism NaCl-HgCl; the "covalent bond" in Hg_2^{2+} is only
another wording for the observation of the HgCl structure but not a con-
sistent relation to electronic data. Also on the instability of AgF and
its homologues falls a new light as the binding $\underline{a}=c_{HT}(4)$ could substitute
$\underline{a}=\underline{c}_c,(4)$. Using $\underline{d}_c(HgF)$ for the interpretation of HgF_2 leads to a CFU2
binding which is homeotypic to the HH2 binding, and which must be twinned
in the crystal.

The phase $B_2F_4 \cdot 1(M4.8)$ not obeying octet completion melts at -56 °C,
it is a molecular structure. Probable strong Hund insertion makes the
analysis of the binding difficult so that it should be postponed.

$AlF_3 \cdot h(htpReO_3)$ has completed anions but Zintl's rule is not followed
as F is not in a noble gas structure. Nevertheless the structure is homeo-
typic to NaCl and a FF2 binding comes which was for instance also found in
in $TiO \cdot h(LhtpNaCl)$. As both correlations are not fully occupied it appears
reasonable that a tetragonally compressed homeotype $AlF_3 \cdot \gamma$ occurs in which
there are less places for the $\underline{c}$ correlation while the binding remains FF2.
The really stable phase $AlF_3(VF_3)$ is homeodesmic to VF_3, and GaF_3, InF_3
are isodesmic to AlF_3.

In $TlF \cdot h(U1.1)$ a D-homeotype of NaCl appears. As the electron count is

$Tl^{3,10}F^{0,7}$ the NaCl type cell is tetragonally strained and to this strained cell fits a c_{HT} correlation like as in HgF, but a HH2 binding is not possible because of the greater valence electron contribution of Tl; the stability of b_{FU} instead of b_{HT} spoils the formation of shears as in HgF. As the c_{HT} correlation is only pseudo tetragonal it is gratifying that TlF.r is orthorhombically deformed.

SiF_4.1(B1.4) melts at -90 °C, it is a molecular crystal in which according to the completion rule every Si is surrounded by a regular tetrahedron of F atoms. A binding $\underline{a}=\underline{b}_C(2)=\underline{c}_C,(4)$ assumes that 4 electrons of the $\underline{c}$ correlation at every Si are in Hund insertion. A binding $\underline{a}=\underline{b}_F(2)=\underline{c}_C,(4)$ would admit that the $\underline{b}$ correlation is only occupied to 0.25. This assumption would deny full $\underline{b}$-occupation and is therefore less probable.

GeF_2.r(04.8) is composed of (Ge)F2$F_{0.5}$ triangles in the plane $(\underline{a}_2 \& \underline{a}_3)$ (similar as $PbCl_2$) where the binding $F_{0.5}$ atoms form nearly straight lines along $\underline{a}_2$. There is a I-homeotypism to PbF_2 (I=inhomogeneous deformation) with the commensurability $\underline{a}_{GeF2}=\underline{a}_{PbCl2}(1)$, but as the axial ratios of GeF_2.r and PbF_2.r are quite different the bindings cannot be in the same commensurability. Curiously two different commensurabilities of a FF2 binding are possible: $\underline{a}=\underline{b}_{FH}(2;2;4/3)=\underline{c}_{FH}(4;4;8/3)$ and $\underline{a}=\underline{b}_{FU}(2.5/2;2;3.25)$ $=\underline{c}_{FU}(5/2;4;6.5)$. Decision between the two may be postponed. The cell of GeF_2.h is to be doubted as it gives too great a volume, it has been considered by the authors as tentative.

While SnF_2.h and SnF_2.r have fairly great cells, the simple SnF_4(U1.4) consists of a fully occupied F1 partial structure of fluorine with Sn in octahedral holes and the commensurability $\underline{a}=\underline{a}_{NaCl}(1;2)$. This structure occurred also for NbF_4 with the binding $\underline{a}=\underline{b}_C(1;2)=\underline{c}_F(2;4)$, but in present case a FF'2 binding must be assumed or a FB $\sqrt{8}$ binding, which is homeotypic.

In PbF_2.h the CaF_2 type reappears, the $\underline{c}_B(4)$ of CaF_2 is conserved but the $\underline{b}_C(2)$ of CaF_2 is transformed into $\underline{b}_B(2)$. The fact that in PbF_2.h the $\underline{c}$ correlation is only partly occupied leads to the stabilisation of PbF_2.r($PbCl_2$) which is DI-homeotypic to Cu. A $\underline{c}_{FU}(5;3;8/2)$ correlation conserves the electron distance of PbF_2.h, and a F'F2 binding becomes possible.

SbF_3(Q2.6) is pseudo tetragonal and a remarkable homeotype of CaF_2

with the commensurability $\underline{a}=\underline{a}_{CaF2}(\sqrt{2};1)$. In the fluorine partial structure
of SbF_3 4 atoms per cell are missing and in the Sb partial structure also.
The quadratic $\underline{c}$ net in the basal plane corresponds to the quadratic $\underline{c}_B$ net
in SnF_4, but the open packing of the fluorine nets suggests $\underline{c}_c(\sqrt{32};4)$ with
128 places to be compared with 124 $\underline{c}$ electrons. The $\underline{b}$ correlation may be
assumed as $\underline{b}_c(\sqrt{8};2)$ affording 16 places to be compared with 20 valence
electrons of the Sb atoms. This is only possible when 1 valence electron
per Sb is in Hund insertion, a number which must be considered as plausible.
The high occupation of the $\underline{c}$ correlation explains the fluorine vacancies.
Evidently the Hund insertion at the cation has a distorting influence on
the structure: near the Sb atom there are two directions of van der Waals
bond, i.e. two directions with missing close fluorine coordination, so
that here a localized Hund insertion may be assumed. It may therefore be
said that the C'C2 binding stabilizes the oxidation number Sb^{3+}.

$BiF_3(YF_3)$ has a quasi tetragonal structure which yields $\underline{c}_{FU}(5;5;5/2)$
fitting well to the Bi position; in a FF2 binding come only 15.5 places
for the $\underline{b}$ electrons in $Bi^{5,10}F_3^{0,7}$, so that Hund insertion of one $\underline{b}$ elec-
tron per Bi is to be expected. It should be noted that the Bi position is
similar to the Br position in BrF_3. $BiF_5(UF_5)$ has six-coordinated Bi with
common F in $\underline{a}_3$ direction. A CHT2 binding appears possible.

$SF_6(OsF_6)$ melts at 210 K (73PW) and is a molecular phase. A $b_c,(2)$
correlation might be possible, with two electrons per S atom Hund inserted.
The $\underline{c}_B(4)$ correlation is the same as in OsF_6. A crystal phase stable at
room temperature although very reactive is TeF_4. The F partial structure
is I-homeotypic to Mg. To find the binding is difficult as $\underline{b}$-correlation
and $\underline{c}$-correlation are susceptible of Hund insertion, and as the fundamental
correlation is strongly deformed by the insertion it becomes more difficult
to find it. Therefore the FF2 binding assumption of TAB.1 must remain ten-
tative.

The phase ClF_3(04.12, drawing SR16.166) has a molecular structure. All
Cl are symmetrically equivalent and have in the distance 1.7 Å 3F forming
a T while the closest distance of Cl to a F of another molecule is $d_{F,Cl}=$
3.1 Å; for the electron count $Cl^{7,8}F_3^{0,7}$ the number of electrons per cell
is $N_{V,C}^{/C}$=28,116, a good binding could be the common FB2 type (TABLE 1),
yielding here the place numbers $N_{p'p''}^{/C}$=32,128. Inserting this binding into
$\underline{a}$ shows that all atoms are in a $\underline{c}$ cube and only the cubes of bound F share

faces with the cubes of Cl. It appears remarkable that the Cl position is DI-homeotypic to Cu and has approximately the same commensurability to the c_B correlation as Si to its c_B correlation. The assymmetry enters as 3F per Cl are stuffed into the cell, the octahedral interstices contain 3F and this results in a strong inhomogeneous deformation and increase of number of substructure cells per cell.

In BrF_3(Q2.6) also T-shaped molecules exist. A simple binding proposal is difficulty to be found as the Hund insertion strongly deforms the a, b, c cells. The above mentioned homeotypism to $BiF_3(YF_3)$ suggests a F'F2 binding with approximately 3 b electrons per Br Hund inserted. BrF_5(Q2.10) is a filling homeotype of BrF_3(Q2.6). The uniform increase of a_2 and a_3 suggests the tranformation of c_{FU} into c_B while b_{FU} remains the same. Once more it becomes apparent that the two-correlations model may stabilize a phase by fairly simple changes in the binding, here by the transition $c_{FU} \rightarrow c_B$.

The phase XeF_2(U1.2) contains linear symmetrical molecules directed along the tetrad axis. The Xe partial structure is D-homeotypic to Xe(Cu) a=6.20 Å, therefore the b correlation will be near to $b_C(\sqrt{8};4.5)$. The F atoms are pairwise in the octahedral interstices and for the c correlation could come $c_{HT}(4;6.5/2)$. Unfortunately the distance d_c=1.1 Å is too small. Therefore $a=b_C(\sqrt{6.5};4)=c_C(\sqrt{13};6)$ might be acceptable, and this proposal holds also for XeF_3. It should be appreciated that $CC\sqrt{2}$ is a filling homeotype of FUC2. For XeF_4 a change of the binding is found which has the advantage to be compatible with the monoclinic symmetry, as the matrix element $(\underline{b}^{-1}\underline{a})_{33}$=2.5 gives in the monoclinic case a better commensurability.

Concluding Remarks

The conventional valence explanation for SbF_3 e.g. says, the oxidation number 3 of Sb is realized; this is a formal rule without energetic evidence. Contrary, the two-correlations model says: the phase belongs to the C'C2 binding; this has an immediate energetic sense. The present model succeeds in finding energetic valence arguments for a simple reason. The older crystal chemical models considered in first line the surroundings of an atom as they started from the assumption of a short range of the chemical

forces (bonds). The two-correlations model on the other side concluded from the finding of great elementary cells that the chemical interactions have a range of the order 50 Å [3] , it therefore considers mainly long range homeotypisms like commensurabilities, homogeneous deformations, shears, chain shears, distributed inhomogeneous deformations and distributed partial occupation. These long range homeotypisms are caused by long range chemical forces which may be described by lattice like spatial correlations of electrons. The result of the new points of view is a phenomenological valence theory which permits to discuss mixtures (e.g. two component systems) and also sets of mixtures as a whole. This is not yet common in crystal chemistry, but it is desirable as only by complete argumentations a coherent understanding of solids may be developed.

It might be argued that a unified description and explanation of the structural principles of fluorides on the basis of all conventional phenomenological valence arguments (F ions completed, mostly whole number oxidation number accepted, remaining electrons of T atoms form cluster bonds) gives a comparable result as the present model. But this is not so. When for instance a phase NbO (homeotypic to NaCl) is formed, why should "NbF" be impossible? Simons diagram [12] (plotting the phases by the parameters: number of B atoms and number of cluster electrons per T atom) states that "NbF" does not exist, but this is once more a statement of fact. The present analysis immediately says that the FF2 binding of NbO would require for "NbF" so many vacancies that the structure is no more stable. Only when the F content is increased, for instance to Nb_2F_5 a NaCl homoetype becomes stable; to be sure a FF2 binding is no more possible as there are no more enough b electrons, but BF2 would also be a favourable binding. Further decrease in Nb content leads to the CF2 binding which entails the phase $NbF_4(SnF_4)$. It is seen by these examples that the two-correlations model offers valence arguments which are not yet presented by the conventional arguments. Therefore the two-correlations model affords supplementary necessary valence arguments.

The discussion of the structural and electronic commensurabilities opens a promising field of structural chemistry which is far from being exhausted at present.

TABLE 1: Bindings in two-component fluorides

LiF(NaCl,SR1.73)4.03A=bF(2)
NaF(NaCl,SR1.73)4.63A=bF(1)=cC(4)
KF(NaCl,SR1.73)5.34A=idm NaF
KF.p(CsCl,73PW)3.06A=bC(1)=cB(2)
RbF(NaCl,SR1.73)5.63A=idm NaF
RbF.p(CsCl,SR27.425)3.27A
CsF(NaCl,SR1.73)6.02A=idm NaF
CsF.p(CsCl,73PW)3.39A

BeF2.h2(SiO2.h2,F2.4,SR20.216)6.79A=bB(4)=cC8   N=128,48
BeF2.h2m(SiO2.h2m,73PW)6.61;6.75A
BeF2.h1(O64,73PW)
BeF2.γ(SiO2.r2,SR16.167)H4.74;5.15A=bF'H(3;4/3)cFH(√27;7/3)N=48,18
BeF2.β(SiO2β,SR16.167)
BeF2.25-217°C(SiO2.α,SR16.167)
MgF2(TiO2.r,T2.4,SR1.158)4.65;3.12A=bF'U(√2.5,1.5/2)=cC(√20;3)   N=4,44
CaF2(F1.2,SR1.148)5.46A=bC(2)=cB(4)   N=8,88
CaF2.mp(PbCl2,O4.8,73PW)3.581;5.959;7.009A=bU(1;2;2)=cC(3;5;6)
SrF2(CaF2,SR1.150)5.79A=idm CaF2
SrF2.mp(PbCl2,SR31.243)3.789;6.306;7.428A=idm CaF2.mp
BaF2(CaF2,SR1.150)6.20A=idm CaF2
BaF2.mp(PbCl2,SR31.243)4.035;6.705;7.911A=idm CaF2.mp
RaF2(CaF2,SR4.8)6.38A=idm CaF2

ScF3.h(ReO3,SR23.288)4.010A=bF(1)=cF(2)
ScF3.r(R1.3,SR7.12)H5.667;7.017A
YF3.h(LaF3,SR17.328)H7.13;8.45A   N=6,138
YF3.r(O4.12,SR17.328)6.353;6.850;4.393A=bHT(2.5;2.5;2/2)=cFU(5;5;4.7/2)   N=12.116
LaF3(H6.18,SR31.84)H7.185;7.351A   =cCH(4;10/3)

TiF3(VF3,H6.18,SR18.351)H5.44;13.61A=CH(1;6/3)=cFH(4;12/3) N=6,144
TiF4(cubic,73 PW   )8.238A
ZrF2(O4.8,73PW)4.09;491;6.56A
ZrF3(htpReO3,73PW)3.96A
ZrF4.h(N6.24,SR12.168,29.260)M126.15°11.71;9.89;7.67A
ZrF4.r(M52.208,SR29.439)M106.25°15.82;13.73;15.11A
ZrF4.i(F2.8,73PW)7.88A
HfF4(T7.28,73PW)7.85;7.67A
HfF4(N6.24,SR12.168)126.08°11.70;9.86;7.64A

VF2(TiO2.r,73PW)4.80;3.24A=bFU(√1.5;1,1/2)=cFU(√13;3.4/2)   N=2,36
V2F5(∞T,73PW)htpVF2
VF3(R2.6,SR15.145)H5.170;13.40A=bCH(1;6/3)=cFH(4;12/3)   N=6,150
VF4(Q4.16,73PW)9.35;5.33;5.16A
VF5(O8.40,SR34.172)5.40;16.72;7.53A=bC(√2;6/2;2)=cFU(4;16/2;6)   N=8,312
Nb2F5(B6.15,SR30.261)8.19A=bB(2)=cF(4)   N=12,258
NbF3.i(ReO3,SR20.223,73PW)3.90A=bC(1)=cF(2)
NbF4(SnF4,U1.4,73PW)4.083;8.161A=bC(1;2)=cF(2;4)   N=2,64
NbF5(MoF5,N4.20,SR29.258)M96.1°9.26;14.43;5.12A
TaF3(ReO3,SR15.147)3.901A=bC(1)=cF(2)   N=1.26
TaF5(MoF5,SR29.258)M96.3°9.64;14.45;5.12A=idm NbF5

CrF2(CuF2,M2.4,SR21.204)M96.52°4.732;4.718;3.505A=bFU(√1.5;1.1/2)cFU(√13;3.8/2)
Cr2F5(N4.10,SR29.255)6.425;7.540;-4.375,0,7.440A=bHT(2/2;2;2)cF(7/2;4;4)
CrF3(VF3,SR21.204)H4.989;13.219AbCH(1;6.5)=cFH(4;13/3)
CrF5(VF5,SR28.296)5.5;7.4;16.3A=idm VF5
MoF3(VF3,SR24.274)H5.208;14.409A=hdm CrF3
MoF5(N4.20SR27.445)M94.35°9.61;14.22;5.16A=idm NbF5
MoF6(OsF6,B1.6,SR41.151)6.23A=bB(1)=cB(4)   N=2,94
MoF6.1(UF6,O4.24,SR41.151)9.61;8.75;5.07A=bH(2;√3;1)=cFH(8/3;6;4/2)   N=4,188
WF5(MoF5,73PW)M94.6°9.61;14.26;5.32A=idm NbF5
WF6(OsF6,73PW)6.28A=idm MoF6
WF6.1(UF6,SR41.152)9.68;8.81;5.09A=idm MoF6.1

MnF2(TiO2.r,SR18.348,15.359)4.873;3310A=bFU(√1.5;1.1/2)=cFU(√13;3.5/2) N=2,40
MnF2.p1>20kb(PbO2.m,SR28.72,30.449)4.960;5.830;5. A
MnF2.p2>50kb(T4.8,SR30.449)5.20;4.97A=bFU(√2;2/2)=cFU(4;5.3/2) N=4,80
MnF2.p3>80kb(PbCl2,73PW)3.323;5.560;6.454A
MnF3(N6.18,htp VF3,SR21.207)M92.74°8.904;5.037;13.448A N=12,324
TcF5(VF5,73PW)5.76;7.75;17.01A=idm VF5
TcF6(OsF6,73PW)6.16A=idm MoF6 N=2,96
TcF6.1(UF6,73PW)9.55;8.74;5.02A=idm MoF6.1 N=4,192
ReF4(T24.96,73PW)10.12;15.95A
ReF5(VF5,73PW)5.70;17.23;7.67A=idm VF5
ReF6(OsF6,73PW)6.26A=idmMoF6
ReF6.1(UF6,73PW)9.61;8.76;5.06A=idm MoF6.1
ReF7(OsF6,73PW)6.26A

FeF2(TiO2.r,SR18.348,17.327)4.697;3.309A=bFU(√1.45;1.1/2)=cFU(√13;3.6/2)N=2.42
Fe2F5(T12.30,73PW)8.05;9.56A=bFU(2;3.3/2)=cFU(6;10/2) N=12,282
FeF3(VF3,SR21.206)H5.196;13.33A=idm VF3 N=6,168
RuF3(VF3,SR21.206)H4.966;13.76A=idm VF3
RuF5(M8.40,SR29.260)M99.83°12.47;10.01;5.42A
RuF6(OsF6,73PW)6.11A=idm OsF6
RuF6.1(UF6,73PW)9.44;8.59;4.98A=idm MoF6.1
OsF5(RuF5,SR37.177)M99.5°5.53;9;91;12.59A
OsF6(B1.6,SR22.233)6.23A=bB(1)=cB(4) N=2,98
OsF6.1(UF6,73PW)9.59;8.75;5.04A=idm MoF6.1

CoF2(TiO2.r.SR21.209)4.695;3.180A=bFUK"/3=cFU(√13;3.5/2) N=2,44
CoF2.p(htpGaF2,73PW)4.91A
CoF3(VF3,SR21.206)H5.035;13.22A=idmVF3
RhF3(PdF3,SR21.206)H4.875;13.58A=idm PdF3
RhF5(RuF5,SR39.138)M100.42°12.338;9.917;5.517A
RhF6.h(OsF6,73PW)6.13A=idm MoF6
RhF6(UF6,73PW)9.40;8.54;4.96A=idm MoF6.1
IrF3(PdF3,SR21.207)H4.930;13.830A
IrF5(RuF5,73PW)M99.8°12.5;10.0;5.40A
IrF6(OsF6,SR22.233)6.23A
IrF6.1(UF6,73PW)9.58;8.73;5.04A

NiF2(TiO2.r,SR21.209)4.651;3.084A=idmCoF2 N=2,46
NiF2.1(htpTiO2.r,73PW)4.648;4647;3.074A
NiF2.p(htpCaF2,73PW) 4.84A
PdF2(TiO,2.r,SR22.233)4.956;3.389A=bFU(√1.4;0.8/2)=cFU(√13;3.5/2) N=2,48
PdF3(R2.6,SR21.207)H5.009;14.13A=bCH(1;7/3)=cFH(√13;12.5/3) N=6,180
PdF4(ThCl4,U2.8,73PW)6.585;5.835A=bFU(√25;1)=cB(√20;4) N=4,148
PtF4(M4.16,73PW)M92.02°6.68;6.68;5.71A
PtF6(OsF6,SR26.301)6.209A
PtF6.1(UF6,SR26.301)9.55;8.71;5.03A

CuF(ZnS,SR3.7,but see 18.350)4.264A=bF(2)=cC(4)
CuF2(M2.4,SR21.205)4.59,0,0.386;4.54;3.298A=bB(√1.4;0.8)=cFU(√13;3.7/2)N=2,48
Ag2F(CdI2,SR31.83)H2.996;5.691A=bUH(1;2)=cC(√3;9/3) N=2,27
AgF(NaCl,SR1.73)4.93A=bF(1)=cC'(4) N=4,68
AgF2(CuF2,SR37.178)M96.8°4.61;4.59;3.40A=idm CuF2
AgF2(O4.8,SR37.178)5.073;5.529;5.813A

AuF3(H6.18,SR32.155)H5.149;16.26A=bČH(1;6.5/3)=CH(4;13) N=6,186

ZnF2(TiO2.r,SR21.209)4.703;3.134A=bC(√3.25;1.23)=cF'U(√13;3/2) N=4,48
ZnF2.p1(MnF2.p2,T4.8,73PW)4.908;4.658A=bC(2)=cFU(4;5.4/2) N=8,96
ZnF2.p2(ZrO2.r,73PW)
ZnF2.pm(PbO2.m,SR28.72)4.683;5.658;5.166A
CdF2(CaF2,SR15.144)5.388A=bC(√4.25;2.1)=cFU(√17;≈6/2) N=8,96
CdF2.p(PbC12,73PW)3.368;5.690;6.730A=   =cFU(2.5;6/2;5) N=8,96
HgF(HgCl,U2.2,SR20.214)3.66;10.90A=bHT(√2;5/2)=cHT(√8;10/2) N=8,68
HgF2(CaF2,SR3.20)5.537A=bC(√4.5;2.1)=cFU(√18;6/2) N=8,96

B2F4.1(M4.8,SR22.230)M102.5°5.49;6.53;483A
AlF3.h(htpReO3.SR18.440)3.58A=bF(1)=cF(2) N=3,29
AlF3.γ(T2.6,73PW)3.54;6.00A=bF(1;3.5/2)=cF(2;7/2)
AlF3(htpVF3SR3.40)H4.9?12.48A=bH(2;5)=cFH(4;12/3) N=18,174
GaF3(VF3,SR23.289)H5.00;12.97A=idm AlF3 N=18,186
InF3(VF3,SR31.260)H5.419;14.43A=idm AlF3
TlF.h(htpNaCl;U1.1,SR33.171)3.771;6.115A=bFU(√2;3/2)=cHT(√8;5/2) N=6,34
TlF.r(S1.1,SR3.9,40131)5.495;6.080;5.180A=BFU(2;3/2;2)=cHT(4;5/2;4)N=12,68
Tl2F3(CaTiO3,73PW)4.604A=bB(1.5)=cB(3) N=6,41
TlF2(htpCaF2,O8.16,73PW)8.348;8228;6.262A N=24.192
TlF3(O4.12,SR38.194)5.825;7.024;4.851A N=12,124

SiF4.1(B1.4,SR2.37,18.353)5.46A=bC(2)=cC'(4) N=8,72
GeF2.h(M4.8,73PW)M116.0°7.55;8.58;4.87A?
GeF2.r(O4.8,SR31.82)4.682;5.178;8.312A=bFH(2;2;4/3)=cFH(4;4;8/3) N=16,96
Ge5F12(M10.24.SR39.137)M93.03°7.96 9;7.590;8.536A
SnF2.h(N8.16,SR27.430,42.163,45.143)M109.5°13.46;4.92;13.86A
SnF2.r(O16.32,73PW)15.42;4.78;10.28A
SnF4(U1.4,SR27.442)4.04;7.93A=bF(1;2)=cB(√8;5.5) N=8,76
PbF2.h(CaF2,SR15.145)5.939A=bB(2)=cB(4) N=16,96
PbF2.r(PbC12,SR15.145)6.441;3.897;7.648A=bFU(2.5;1.5;4/2)=cFU(5;3;8/2)N=16,96
PbF4(SnF4,SR27.442)4.24;8.03A=idmSnF4 N=8,76

N2F4(F;73PW)24.95A
SbF3(Q2.6;SR9.152,35.147)7.26;7.46;4.95A=bC'(√8;2)=cC(√32;4) N=20,124
SbF5(N8.40,SR37.353,   )M94.0°19.00;14.10;529A
BiF3(YF3,73PW)6.563;7.021;4.845A=bF'U(2.5;2.5;2.5/2)=cFU(5;5;5/2)N=20.124
BiF5(UF5,U1.5,SR37.176)6.581;4.229A=bC(√6.25;1.6)=cHT(5;3.7/2) N=10,90

SF6((OsF6,SR42.165)5.915A=bC'(2)=cB(4) N=12,100
SeF6(OsF6,73PW)5.99A=idm SF6
SeF6.1(O,73PW)10.66;9.85;4.62A
TeF4(O4.16,SR33.170)5.36;622;9.67A=bF'U(2;2;4/2)=cF'U(4;4;8/2) N=24,152
TeF6(OsF6,73PW)6.82A=idm SF6 N=12,104
TeF6.1(,73PW)

ClF3.1(O4.12,SR16.165)8.82;6.09;4.52A=bF(√8;2;√2)=cBK'(2) N=28,116
BrF3(Q2.6,SR21.202)5.34;7.35;6.61A=bF'U(2.7/2;25;2.5)=cFUK'(2) N=28,124
BrF5(Q2.10,SR21.202)6.422;7.245;7.846A=bFU(3/2;2.5;2.5)=cB(4;5;5)
IF5(N10.50,SR21.201,40.132)M93.23°15.16;6.86;18.20A
IF7(OsF6,SR27.446)6.28A
IF7.1(Q2.14,SR27.446)614;8.87;8.74A

KrF2(T4.8,73PW)6.533;5.831A N=32,88
XeF2(U1.2,SR28,73)4.315;6.990A=bC(√6.5;4)=cC(√13;6)
XeF3(M2.6,SR28.74)M92.67°6.64;7.33;6.40A=bC(√13;4)=cC(√26;6) N=16.72
XeF4(M2.8,SR28.75)M99.6°5.050;5.922;5.771A=bB(√8;2.5)=cF(√8;2.5)
XeF6(M8.48,SR37.354), XeF6.11(O16.96), .12(M64.384), .13(F36.216,SR40.133)

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