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On the bindings in two-component oxides
II. $A^{6\ldots10}O_{\underline{M}}$ phases

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Summary

The bindings in $A^{6\ldots10}$ metal oxides may be described by harmonic commensurabilities between the spatial correlation of the peripheral $\hat{s}p^6$ electrons of the metal and the valence electrons of oxygen on the one side and the peripheral d electrons of the metal on the other. The harmony is described by integral commensurability matrix elements. Between $VO_{\underline{M}}$ and $MnO_{\underline{M}}$ a change in binding occurs. Whereas in TiO and VO a collective correlation $(\underline{b}\vee\underline{e}\vee\underline{c})_C$ may be formed and causes an atomic occupancy of 0.85, in MnO the number of constitutional vacancies (lacunae) would become too great so that the $\underline{c}_C$ correlation is replaced by $\underline{c}_B$. Besides a $\underline{b}'=\underline{b}\vee\underline{e}$ correlation is found being trapped by the $\underline{c}$ correlation. Another change in the electron count is found between A3d, A4d and A5d elements. While there are few indications of a participation of the A2sp electrons in the binding of A3d oxides, in A4d or A5d oxides the participation of the A3d or A4f electrons in the $\underline{c}$ correlation appears suggestive. This participation, favoured by the high compliance of 3d or 4f electrons, must be considered as a cause of the frequently occurring heterotypism between A3d, A4d, and A5d oxides. The high compliance of the d or f electrons describes the generally accepted metal-metal interactions in $AO_{\underline{M}}$ phases. Numerous structural phenomena in $A^{6\ldots10}O_{\underline{M}}$ phases, not understood so far, may be explained by demonstrating that they obey crystal chemical rules formulated by the concepts of the plural correlations model.

Introduction

An energetical interpretation of the transition metal oxides, reviewed by 74Rao, 75Pie, 74Til, 76Eyr, 81Eyr, 81Che presupposes assumptions on the band structures reported and referenced by 71Goo and 74Rao. An inference of the electron spatial correlations within and between the bands (86aSch) might provide a test for the compatibility of the proposed band structures with the experimental results since the energy of the correlations has an influence on the bands.

In part 1 of this analysis (87Sch2) it was found that an interpretation of the two-component oxides is possible when for instance the Ti3sp electrons are in a common c correlation with the O2sp electrons while the Ti3d^4 electrons are in the b∘e correlation. In TiO_M phases the e' and c correlation form a united or collective correlation g=e'∘c , i.e. e' and c conform approximately to one and the same lattice g of the averaged correlation (86aSch). If the occupation of the collective correlation becomes too high then the e' correlation will be precipitated from the g correlation i.e. it forms a correlation of its own and does no longer take part in a e'∘c correlation. As an example the phases TiO.h, VO, and MnO of the NaCl type may be considered.

TiO.h(Lhtp NaCl, SR7.87) has the atomic occupancy $N_{At}^{/S(At)}$=0.85. Using the count $Ti_{3.4}^{4,8}O_{3.4}^{0,6}$ yields a(N=13.6,47.6)=4.18Å=$e'_B(2)$=$c_C(4)$=$g_C(4)$. The e' correlation provides electro conductivity while the g correlation causes the lacunae. This binding is compatible with earlier band assumptions (71Goo p. 230,249) and has the collective property.

While VO(LhtpNaCl) is (86bSch) essentially isodesmic to TiO.h, and also a metallic conductor (74Rao), there is no stable "CrO" and the green MnO(NaCl) is an insulator (74Rao p.2). Because of this property a g correlation like that in TiO.h is not probable in MnO and the e correlation of TiO.h becomes more localized relative to the correlation around the O atoms and the correlation of the Mn3sp electrons around the Mn atoms. A cause for such an abrupt transition from the collective to the localized correlation type shall be proposed in the following analysis of the bindings.

The above model allows a binding analysis utilizing the crystal chemical rules collected in it. The surprising phenomenon that

there are still many crystal chemical rules to be uncovered comes from the fact that the search for rules has been based so far on somewhat narrow concepts for the bindings in oxides, while the plural correlations model employs more general concepts like spatial correlations instead of bonds, or consideration of more electrons responsible for bonding than only the valence electrons. The enlarged electron count opens the idea of harmony playing a role in crystal chemistry. This provides a selection principle for conceivable bindings. The bonding is no longer an intuitive concept, but rather the two-electron reduced density matrix, as prescribed by quantum chemistry (56Löw), vigorously simplified for use in the systematics of crystal chemical data (see 86aSch for references).

The reader of the following analysis may study the binding formulae by drawing the correlations for comparison with the crystal structure and then checking to what extent the rules (86Sch2) are fulfilled. Two coexisting correlation lattices should always be so arranged that they are as far apart from one another as possible . This electron model may be imagined to fluctuate in the crystal, although of course, the density matrix indicated by the proposal is time-independent. Consulting referenced earlier articles may be helpful to readers with unanswered objections. The mental presence of the rules of the model is indispensable for own attempts to make a binding analysis.

For abbreviations and symbols see the Appendix of 87Sch2.

A^6O_M phases

While many suboxides have been found in TiO_M and VO_M , in CrO_M the intermediate phase poorest in O is Cr_2O_3.h. The cause for this remarkable difference must be the increased $\underline{e}'=\underline{b}^{v}\underline{e}$ electron contribution of Cr which prevents a collective spatial correlation of the electrons to be formed as in V_8O etc. Nevertheless in Cr_2O_3.h the binding may be of the collective type and the following proposal will admit this:

The phase Cr_2O_3.h(Al_2O_3,R4.6,SR2.310,23Dav,drawing 64Sch p.198) may correspond following a binding analysis (86aSch) to the binding

$\underline{a}$(Cr$_2$O$_3$.h,N= 72,204)=H4.96;13.59Å=$\underline{e}'_{BH}$($\sqrt{125}$;22/3)= $\underline{c}_{\hat{C}H}$($\sqrt{13}$;22/3).

The $\underline{e}'$ correlation may be united with the $\underline{c}$

correlation so that the binding is collective. The 22 $\underline{e}$ layers parallel to $\underline{a}_1,\underline{a}_2$ indicate a reason for the antiferromagnetism (74Rao,SR13.227), as in the B_H type the neighbouring $\underline{e}$ layers may have different spin and $\underline{e}$-lacunae represent a magnetic moment. Also they provide a cause for the Mg type of the O partial structure following the rules of 84Sch. Cr_2O_3.r(SR13.227) is D-homeotypic to Cr_2O_3.h.

CrO_2(TiO_2.r,T2.4,SR9.148,43Mic) is ferromagnetic and allows the binding

$\underline{a}(CrO_2,\underline{N}=\frown 12,40\quad)=4.42;2.92\mathring{A}=\underline{e}_B(\sqrt{5};1.5)=\underline{c}_C(\sqrt{20};3)$.

The rotated commensurability of $\underline{e},\underline{c}$ to $\underline{a}$ fits well to the observed oxygen sites. The site number $\underline{N}^{/a}_{S(\underline{e})}=15$ suggests that there are three $\underline{e}$ lacunae per cell while $4\mu_B$ have been observed (74Rao), hence 1 $\underline{e}$ electron goes to $\underline{c}$. The assumption $\underline{a}=(\underline{e}^{\vee}\frown\underline{c})_C(\sqrt{20};3)$ appears possible as the ferromagnetism requires unoccupied sites (87Sch) being available here. $\underline{a}=\underline{e}_C(\sqrt{10};2)=\underline{c}'_C(\sqrt{20};3)$ would not provide an appropriate number of $\underline{e}$ sites. Therefore, if the electron count is taken as $Cr^{0,6,8}\frown O_2^{0,0,6}$ then the binding might be as proposed. It appears that the $O1s^2$ electrons are not in $\underline{c}$.

$CrO_{1.98}$(T4.8,SR17.389,53Ari) was said to be doubtful (SR17.389) but might be homeotypic to ReO_2.h.

Cr_5O_{12}.p(O20.48,SR30.304,65Wil) contains a Cu type O partial structure with the commensurability $\underline{a}=\underline{a}_{Cu}(3;2;2)$. It allows the binding

$\underline{a}(Cr_5O_{12},\underline{N}=\frown 120,448\quad)=12.04;8.21;8.18\mathring{A}=\underline{e}_{FU}(8/2;4)=\underline{c}_C(12;8)$.

While CrO_2(TiO_2.r) has a BC2 binding, Cr_5O_{12} has a F_UC2 binding. (Perhaps the C type correlation becomes $\underline{a}=(\frown\underline{c}^{\vee}\underline{f})_{FU}(16;8)$ so that the binding would be of the FF2 type) A binding even poorer in $\underline{e}$ electrons than F_UC2 might be the CC2 binding, but the observed phase suggests the homeotypic HH2 binding.

The Lewis phase CrO_3(Q2.6,SR35.206,50Bys,70Ste) has the Cr atoms tetrahedrally coordinated by O as the uniform distribution of the d electrons leaves a smaller cation radius for Cr than in CrO_2 where the Cr were octahedrally coordinated by O. The Cr form zigzag chains along $\underline{a}_3$ in the $\underline{a}_2,\underline{a}_3$ plane which are intermediary between a three dimensional framework and a molecular structure. The binding may be assumed as

$\underline{a}(CrO_3,\underline{N}=24,104,32\ )=4.79;8.56;5.74\mathring{A}=\underline{e}_{HT}(2;4/2;2.5)=\underline{c}_{HT}(4;8/2;5)$.

The $\underline{e}$ correlation is fully occupied when it is assumed that $\underline{c}$ accepts 1 $\underline{e}$ electron per Cr which is less than the 6 electrons assumed by Lewis' rule. A filling of the nobel gas shell of O need not be assumed, as a compensation of spins generated by Hund's rule already fulfils Lewis' rule. The remarkable compliance

of the $\underline{e}$ correlation (Fig.1) is therefore a consequence of Lewis' rule, and the only new assumption is that the $\underline{e}$ correlation must be harmonic with the other correlations. A participation of Cr2sp electrons in the binding does not appear necessary because of the low Cr content.

In MoO_M (see 63Kih1) the instability of phases with small mole fraction $\underline{N}_O^-$ is even more pronounced than in CrO_M as Mo is heavier than Cr and therefore repels the Mo4d electrons more vigorously into localisation.

The phase with smallest $\underline{N}_O^-$ is MoO_2(M4.8,SR11.261,32.259,47Mag,drawing 64Sch p.277) being an I-homeotype of TiO_2.r in which the A atoms along $\underline{a}_3(TiO_2.r)$ form pairs. The binding may be proposed for the quasi tetragonal diagonal part of $\underline{a}$ as

$\underline{a}(MoO_2,\underline{N}=24,80,40)=5.583,0,-2.694;4.843;4.825Å=\underline{e}_B(\sqrt{5};2.5)=\underline{c}'_C(\sqrt{20};5)$.

The $\underline{e}$ correlation is nearly fully occupied. Apparently the Mo3d electrons do not all take part in the binding. The commensurability element $(\underline{c}^{-1}\underline{a})_{33}=5$ is the cause for the Mo atom displacements in $\underline{a}_1$ direction since the 5 electron sites on $\underline{a}_1$ favour a pair formation of 2 Mo sites on $\underline{a}_1$. The heterotypism to $CrO_2(TiO_2.r)$ fulfils the rule (86 Sch1) that the heavier phase has less $\underline{c}$ sites. It is to be assumed that the decrease of the axial ratio $|\underline{a}_3|/|\underline{a}_1|$ of TiO_2.r-isotypes on the number of d electrons per A-atom (57Mar) is caused by that rule.

A series of phases between MoO_2 and MoO_3 was represented in a phase diagram (SR23.358,59Kih).

The phase Mo_4O_{11}.h(O16.44,SR28.126,48aMag,drawingSR11.292) is homeotypic to ReO_3(C1.3,drawing 64Sch p.278) in displaying ReO_3 type layers separated by thinner layers with MoO_4 coordination. These thinner layers are a means of decreasing $\underline{N}_O^-$ as compared with MoO_3. Quite tentatively the binding may be proposed as

$\underline{a}(Mo_4O_{11}.h,\underline{N}=96,392,128)=24.49;5.46;6.75Å=\underline{e}_B(9;2;2.5)=\underline{c}'_B(18;4;5)$.

This is a binding isotypic to the BB2 binding of MoO_3 (see below) but the reason for the tilting of the binding to the ReO_3 layers is not yet clear.

The phase Mo_4O_{11}.r(M16.44,SR28.125) is homeotypic to Mo_4O_{11}.h.

The phase $Mo_{17}O_{47}$(O34.94,SR24.323,drawing 63aKih) is homeotypic to Mo_5O_{14} and it will also be homeodesmic to Mo_5O_{14}.

The phase Mo_5O_{14}(T160.448,SR29.308,drawing 63Kih,81Eyr p.359)(64Kih) has a subcell T40.112 in which four "pentagonal columns" (71Lun) are contained: A pentagon of O in the $\underline{a}_1,\underline{a}_2$ plane, centered by Mo, capped in $\pm\underline{a}_3$ direction by O, and sharing edges with five MoO_6 octahedra, is repeated in $\underline{a}_3$ direction so that the MoO_7 and MoO_6 double pyramids share corners. The pentagonal columns are connected with elements of the ReO_3 structure so that channels are formed with 3,4,5,6-gonal cross sections. The binding may be

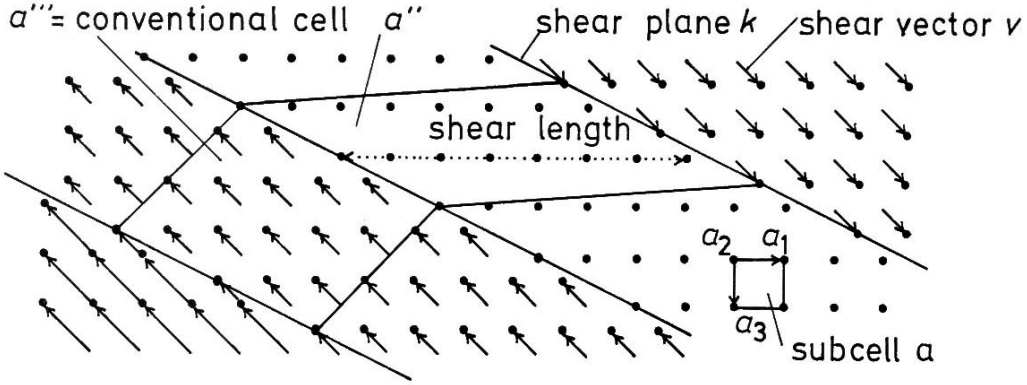

Fig. 2 Different cells of Mo_8O_{23}

$\underline{a}(Mo_5O_{14}$,T40.112,$\underline{N}$= ⌒ 240,992,400)=23.00;3.94Å=$\underline{e}_B^{\vee}(\sqrt{74};1.5)=\underline{g}_B^{\vee}(\sqrt{296};3)$.
If from the 112 O atoms per cell 40 capping O atoms are subtracted then 72 equatorial O atoms remain. This means that nearly every equatorial O may be approximately in a quasi octahedron of $\underline{e}$ sites. The remaining 40 MoO must be so distributed in the cell that their sites are compatible with the equatorial O sites and with the $\underline{e}$ correlation. The simplest distribution were attained when for every two equatorial O atoms one Mo were available so that 36 MoO had to be distributed (ReO_3 structure). However, there are 4 more MoO to be distributed, and these may be identified with the centres of the pentagonal columns. The installation of pentagonal columns is therefore a further method to decrease $\underline{N}_0^{\vee}$ in a ReO_3 type structure. If the 400 Mo3d electrons take part in the $\underline{b}^{\vee}\underline{c}$ correlation then 1392 electons are to be distributed on 296⌒×⌒6=1776 sites.

The phases Mo_8O_{23}(M16.46,SR11.293,17.397,48Mag,drawingSR11.294), Mo_9O_{26}.h (M18.52,SR11.294,48Mag,drawingSR11.295), and Mo_9O_{26}.r(Z36.104,SR23.358, phase diagram) are shear-homeotypic to ReO_3 and $WO_3.h_2$ obeying the formula Mo_nO_{3n-1}. The term "shear" suffers from confusion with the term "mechanical shear" (70Hyd) whence earlier the term "Verwerfung" had been used (55Sch). However, the term "crystallographic shear" has generally been accepted. The BB2 binding of $WO_3.h_2$ e.g. (see below) is exactly filled in the $\underline{e}$ correlation but underoccupied in the $\underline{c}^{\vee}\underline{f}$ correlation. This implies that a filling of an ideal $WO_3.h_2$ type phase "MoO_3" with more Mo atoms would be energetically favourable, more exactly, the filling of $\underline{c}^{\vee}\underline{f}$ is favourable as this correlation becomes more homogeneously occupied, while the filling of $\underline{e}$ is somewhat costly as this correlation is already filled and therefore requests $\underline{e}$ transfer to $\underline{b}$. Because of participation of Mo3d electrons in the core electron correlation the introduction of Mo atoms cannot occur statistically but must be made cooperatively. The cell $\underline{a}$ of ReO_3 with $\underline{a}_1$ pointing to the right and $\underline{a}_2$ perpendicularly to the drawing plane contains the partial structures $O(\frac{11}{22}0,0\frac{1\bar{1}}{22})$ and $O(\frac{1}{2}0\frac{1}{2})$,$Re(\frac{111}{222})$. The shear vector $\underline{v}=\frac{1}{2}0\frac{1}{2}$ changes the second partial structure (but reproduces the first of equatorial O atoms) and may therefore introduce a $\underline{N}_0^{\vee}$ change in the ReO_3 structure. The degree of Mo condensation for given $\underline{v}$ depends (1) on the direction $\underline{k}$ of the shear plane separating the sheared half from the unsheared half of the crystal and (2) on the shear length $\underline{l}$ (=$n\underline{a}_1$) measuring in $\underline{a}_1$ direction the distance of the shear planes. It has been shown (64Sch p.281) that $\underline{k}$=(101) and (001) (=(10∞)) are unfavourable as the Mo atoms become too much concentrated; $\underline{k}=(10\bar{3})$ has been observed for $W_{20}O_{58}$(SR13.235) and gives a stronger condensation than $\underline{k}=(10\bar{2})$ observed in the above phases (see 64Sch p.280); $\underline{k}=(10\bar{1})$ gives no

condensation. It is easily seen that the shear plane $(10\bar{2})$ subtracts one O atom per cell in the formula Mo_nO_{3n} so that the formula of the condensed phase is Mo_nO_{3n-1} (55Mag). The shear length $\underline{l}=n\underline{a}_1$ should not be too small in order to allow a relief of the tension in the $\underline{e}$ correlation, and not too long in order to stabilize $\underline{k}$. Following the above arguments the cell of Mo_8O_{23} should be $\underline{a}'=\underline{a}_{ReO3}(6.5,0,2;0,1,0;-0.5,0,1)$, but like as in $WO_3.h_2$ (see below) there are displacements of the Mo in $\underline{a}_2$ direction requesting $\underline{a}''=\underline{a}(6.5,0,4;0,1,0;-0.5,0,2)$(Fig.2). The conventional cell is $\underline{a}'''=\underline{a}(4,0,-2.5;0,1,0;2,0,2.5)=\underline{a}[(6.5,0,4;0,1,0;-0.5,0,2)+(-2.5,0,-6.5;0,0,0;2.5,0,0.5)]$ (see Fig.2,64Sch p. 280,SR11.294).

In order to assess the binding of Mo_8O_{23} it is appropriate to consider the diagonal part of the conventional cell obtained by suppressing the matrix element -4.65Å(see brief matrix notation 83Sch) in the following formula :

$\underline{a}(Mo_8O_{23},\underline{N}=\ 96,404,252)=16.14;4.04;-4.65\ ,0,13.40Å=\underline{e}_B(6;1.5;5)=\underline{c}'_B(12;3;10)$.

Six $\underline{e}$ electrons have been transferred to the $\underline{c}'$ correlation. When it is assumed that the $Mo3d^{10}$ electrons ($\underline{f}$) take part in $\underline{c}'_B$ the occupation becomes 91%. The so called non-stoichiometry of the Mo_8O_{23} phase is therefore a phenomenon which improves the core electron correlation at the expence of the spin equilibrium described by Lewis' rule. When instead of Mo atoms there were W atoms contributing $W4f^{14}$ electrons then the $\underline{c}'$ correlation were fully occupied or in some sense too highly filled. In fact it has been found (55Mag) that gradual substitution of Mo by W increases the shear length in the n,3n-1 homeotypic series. It is seen that the extensively discussed phenomenon of oxydic shear homeotypes (74Til,76Eyr,81Eyr,81Che) has its roots in the bonding. The bonding types (bindings) found in the present analysis indicate why the shear homeotypes of ReO_3 occur only in AO_M phases and not, for instance, in BO_M phases. The main reasons lie in the high compliance of the $\underline{e}$ correlation and in the energetical advantage of the BB2 binding. More on the energetics of shear homeotypes of ReO_3 is found in 76Til,78Igu.

The Lewis phase MoO_3(04.12,SR28.128,50And,63Kih,drawing 64Sch p.281) contains an O partial structure of the Cu type with zigzag Mo chains along $\underline{a}_3$ in the $\underline{a}_2,\underline{a}_3$ plane, the Mo being octahedrally coordinated by oxygen. The edge sharing of the MoO_6 octahedra corresponds to the cristallographic shear considered in Mo_8O_{23} for the case of $\underline{k}=(001)\overset{=(10\infty)}{\wedge}$(see64Sch p.281). However, MoO_3 is not a shear-homeotype of ReO_3 since it should then have the composition "Mo_2O_5" as was found in $Nb_2O_5.m$(N2.5,66Gru). The binding may be

$\underline{a}(MoO_3,\underline{N}=24,404,64)=3.96;13.86;3.70Å=\underline{e}_B(1;3.5\sqrt{2};\sqrt{2})=\underline{c}'_B(3;7\sqrt{2};\sqrt{8})$.

It appears conceivable that $Mo3d^{10}$ electrons ($\underline{f}$ correlation) take part in $\underline{c}$.

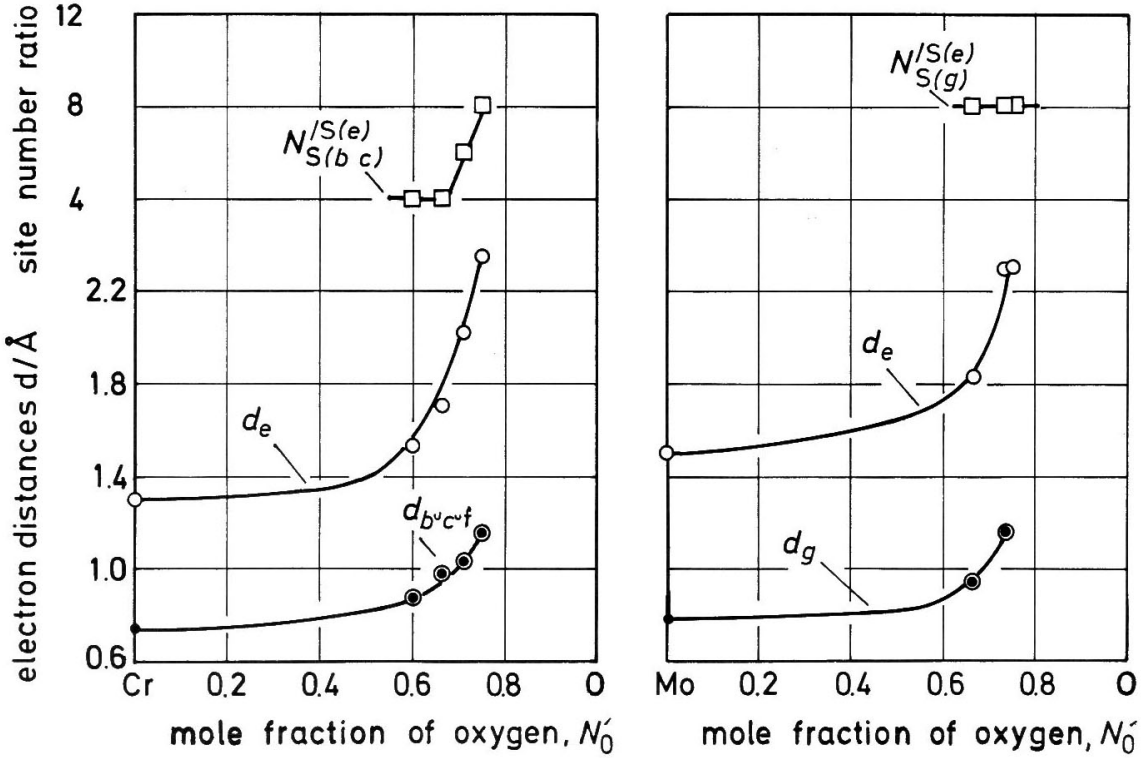

Fig. 1 Electron distances and site number ratio in $Cr\underline{O}_{\underline{M}}$ and $MoO_{\underline{M}}$ in dependence of $\underline{N}_O'$

A small overoccupation resulting from electron transfer $\underline{e}\rightarrow\underline{c}$ might cause the small deviation from the integral commensurability elements. The $\underline{f}$ participation would also explain why homeotypes of ReO_3 have not been found with 3d elements but only with 4d and 5d elements. Another indication for the probability of the above binding is the slight puckering in $\underline{a}_1$ direction of the Mo layers parallel to $\underline{a}_2,\underline{a}_3$. This is confirmative for the commensurability element $(\underline{c}'^{-1}\underline{a})_{11}=3$ as will be seen below in $WO_3.h_2$. If Mo were fully substituted by W then the number of electrons in the $\underline{g}$ correlation would be 184 because of the participation of $W4f^{14}$ electrons. Therefore the MoO_3 type is not possible for WO_3 as $\underline{c}'$ accepts only 168 electrons.

The phase $W_3O(Cr_3Si$,SR18.259) was doubted by 64Phi. Therefore the blue WO_2 (MoO_2,M4.8,SR11.262,45.219,47Mag) is the O-poorest intermediate phase. It is homeodesmic or practically isodesmic with MoO_2(M4.8)

$\underline{a}(WO_2,\underline{N}=$ 24,80,72)=5.56,0,-2.87;4.90;4.88$\overset{\circ}{A}$=$\underline{e}_B(\sqrt{5};2.5)=\underline{c}'_B(\sqrt{20};5)$.
The BB2 binding will be the cause for all intermediary phases in WO_M.

The phase $W_{20}O_{50}$(M20.50,SR17.399,53Mag) is homeotypic to the following phase .

The reddish violet $W_{18}O_{49}$(M18.49,SR12.185,49aMag,drawingSR12.187,80Eks)= $WO_{2.722}$ has the highest melting point of all WO_M phases and exists up to at least 2073K (69Shu). It is a homeotype of ReO_3 and has pentagonal columns. The binding might be (formulated for the diagonal cell)

$\underline{a}(W_{18}O_{49},\underline{N}=108,438,350$)=18.32,0,-5.94;3.79;12.72$\overset{\circ}{A}$=$\underline{e}_B(5\sqrt{2};1.5;3.5\sqrt{2})=\underline{c}'_B(10\sqrt{2};3;7\sqrt{2})$
The $\underline{e}$ correlation has only 105 sites so that 3 $\underline{e}$ electrons must go to $\underline{c}'$.
The number of $\underline{c}'$ sites per W is 46.7 while in $WO_3.h_2$ it will be 48. This is an indication for the compression of the structure in $W_{18}O_{49}$ relative to the binding.

$W_5O_{14}.i(Mo_5O_{14}$ without supercell,SR44.187,drawing 80Eks)=$WO_{2.80}$ is another structure with pentagonal columns.

$W_{24}O_{68}$(M24.68,drawing80Eks)=$WO_{2.83}$ is an intergrowth structure of pentagonal column layers and ReO_3.

Beginning with $WO_{2.83}$, S-homeotypes with shear plane $(10\bar{3})$ and shear length $12\leq n\leq 30$ have been found by electron microscopy (74Sun,76Sun and others). Examples for the more fully refined structures of these series are the following.

$W_{20}O_{58}$(M20.58,SR13.235,50Mag,53)=$WO_{2.90}$. This structure is described in the space group P2/m and has, therefore, no puckered $W\underline{a}_1,\underline{a}_3$ layers contrary to $W_{25}O_{73}$ and $WO_3.h_2$. Because of the binding it must be conjectured that an appropriate annealing of $W_{20}O_{58}$ leads to the puckering. In fact for $WO_{2.96}$ (see below) two phases r,h were found, with,(r), and without, (h), puckering (66Gel).

$W_{20}O_{59}$(M40.118,SR30.312,65Gad)=$WO_{2.95}$. It appears that the cell of this

phase is so similar to the cell of $W_{20}O_{58}$ that it must be assumed that there is some allowance for the O content and the formula W_nO_{3n-2} is not fully consistent with all the representatives of the $(10\bar{3})$S-structures.

$W_{25}O_{73}$(M50.146,SR42.237,76Sun)=$WO_{2.92}$,

$W_{25}O_{74}$.h(M25.74,75Pie,66Geb)=$WO_{2.96}$,

$W_{25}O_{74}$.r(M50.148,75Pie,66Geb)=$WO_{2.96}$,

$W_{25}O_{74}$.r has practically the same cell as $W_{25}O_{73}$, and since 76Sun did not find an additional O in the difference Fourier sythesis it must also be assumed that there is some allowance for the O content depending on preparation .

Above the composition $WO_{2.94}$ up to $WO_{3.00}$ the $(10\bar{2})$S-homeotypes of ReO_3 are stable (74Sun).

The yellow $WO_3.h_2$ (T2.6,SR16.229,52Keh,drawing 64Sch p.280), obeying Lewis' rule of octet completion of the anion, is DI-homeotypic to ReO_3 and permits the simple binding:

$\underline{a}(WO_3.h_2,\underline{N}=12,52,40)=5.27;3.92Å=\underline{e}_B(2;1.5)=\underline{c}'_B(4;3)$.

The D-homeotypism to ReO_3 is exactly explained by the commensurability of $\underline{c}'=\underline{c}\cdot\underline{f}$ to $\underline{a}$. The I-homeotypism of the W sites to the Re sites follows from $(\underline{c}'^{-1}\underline{a})_{33}=3$ causing an instability of W positions fixed according to the ReO_3 type. The BB2 binding does not suffer from self-deformation because the high temperature causes the deformation to be more uniformly distributed. It may be assumed that $W4f^{14}$ electrons take part in the $\underline{c}'$ correlation. The binding in ReO_3, noted below, necessitates $\underline{e}\rightarrow\underline{c}'$ transfer and is therefore twinned so that the crystal structure becomes simpler.

At 1010...600K the phase $WO_3.h_1$(04.12,SR15.191,21.232,43.176)with $\underline{a}$=7.34; 7.57;7.75Å is stable. A more accurate knowledge of this structure appears desirable. The stability of the phase may be interpreted by the remark that the BB2 binding is at sufficiently low temperatures <u>self-deforming</u> as the octahedral interstice of $\underline{c}'_B$ has only tetragonal point symmetry.

The phase $WO_3.r$(600...290K,M8.24,SR24.325,43.176,31.123,drawing 64Sch p.280) shows as compared with h_2 a displacive homeotypism of the W in the basal plane of h_2.

The phase $WO_3.l_1$(290...233K,Z8.24,SR24.325,44.186,78Die) is pseudo cubic with ReO_3 substructure. The W atoms form three long distances W-O in the O_6 octahedra. If it is assumed that the $O1s^2$ electrons do not take part in the $\underline{c}'_B$ correlation of $WO_3.h_2$ then there are per W atom 40 electrons and 48 sites in that correlation. This might contribute to the off-centre position of the W atom in the O_6 octahedron.

Discussion of $WO_3.l_2$(T<233K,M4.12,SR24.325,43.176) shall be postponed in the

present study.

In relation with WO_3 some ternary compounds (80Eks), homeotypic to $CaTiO_3$ (perovskite) a filling homeotype of ReO_3, should be briefly considered. The so called tungsten bronzes $Na_{0...0.1,0.4...0.9}WO_3$(C1.1.3,SR3.377,35Häg) displaying Na in cubooctahedral interstices show vivid colours depending on $\underline{N}_{Na}$. With the electron count $Na^{1,0,8,0}_{n}W^{0,6,8,14}O^{0,0,6,0}_{3}$ comes the binding proposal

$\underline{a}(Na_{0.9}WO_3,\underline{N}=1,6,34,14)=3.85\mathring{A}=\underline{b}_C(1)=\underline{e}_{\check{B}}(\sqrt{2};1.5)=\underline{c}'_{\check{B}}(\sqrt{8};3)$.

The binding must be twinned; the deformation $\check{B}$ comes from the self deformation of BB2; the stoichiometric defect of Na comes from the overfilling of the $\underline{c}''\underline{f}=\underline{c}'_B$ correlation. Analogously is found(SR15.329,51Mag)

$\underline{a}(Na_{0.32}WO_3,\underline{N}=0.6,12,60,28)=5.248;3.895\mathring{A}=\underline{b}_C(1;0.7)=\underline{e}_B(2;1.5)=\underline{c}'_B(4;3)$.

The homeodesmism to $WO_3.h_2$ was pointed out by 51Mag. The low $\underline{N}_{Na}$ probably degrades the $\check{B}\check{B}2$ binding to BB2. For $Na_{0.75}WO_3$ has been reported $\underline{a}(Na_{0.75}WO_3)=2\underline{a}(Na_{0.9}WO_3)$,SR24.326, as the Na are ordered.

The perovskites $Ca^{2,0,8}Ti^{0,4,8}O^{0,0,6}_{3}$(C1.1.3,SR1.300) may have the binding

$\underline{a}(CaTiO_3,\underline{N}=2,4,34)=3.8\mathring{A}=\underline{b}_B(1)=\underline{e}_{\check{B}}(\sqrt{2};1.5)=\underline{c}'_{\check{B}}(\sqrt{8};3)$.

It may be that $\underline{b}$ and $\underline{e}$ are united to a common correlation. The commensurability element $(\underline{c}'^{-1}\underline{a})_{33}=3$ has the tendency to cause atom shift in atom rows $\underline{a}_1$ just as in $WO_3.h_2$. Since the binding is twinned also $\underline{a}_2$ and $\underline{a}_3$ chains may be inhomogeneously deformed. The deformations occur at different temperatures as each transformation yields an energetic relaxation. In fact for $BaTiO_3$ it has been found (SR12.200) that below 183K the structure is rhombohedrally deformed, between 183 and 268K orthorhombically, between 268K and 393K tetragonally, and above 393K it is cubic (see SR12.202).

The tetragonal tungsten bronze $K_{0.6}WO_3$(T6.10.30,SR12.292,49Mag,drawing SR12.293) is homeotypic to $CaTiO_3$. Some K are enclosed in pentagonal prisms of oxygen while K lacunae become enclosed in trigonal O-prisms. With the electron count $K^{1,0,8}_{0.6}W^{0,6,8,14}O^{0,0,6}_{3}$ comes the binding

$\underline{a}(K_{0.6}WO_3,\underline{N}=6,60,308,140)=12.32;3.84\mathring{A}=\underline{b}_{FU}(\sqrt{5};1.4)=\underline{e}_{\check{B}}(\sqrt{20};1.5)=\underline{c}'_{\check{B}}(\sqrt{80};3)$.

In $Na_{0.9}WO_3$ the number of $\underline{e}$ sites per W was 6, so it is here.

Another homeotype is the hexagonal tungsten bronze $K_{0.3}WO_3$(H2.6.18,SR17.401, 53aMag,drawing 78Mag,80Eks), where the K are included in hexagonal O-prisms. The binding may be

$\underline{a}(K_{0.3}WO_3,\underline{N}=2,36,172,84)=H7.37;7.54\mathring{A}=\underline{b}_{CH}(1;2.5/3)=\underline{e}_{BH}(2;10/3)=\underline{c}'_{BH}(4;20/3)$.

The BB2 binding seems to apply here also. This assumption is confirmed by the existence of the so called intergrowth tungsten bronzes (76Hus) in which (110) layers of $WO_3.h_2$, several cells thick alternate with (100) layers of $K_{0.3}WO_3$,

one or two cells thick (see phase diagram and structures in 78Mag).

It is seen that all the tungsten bronzes are homeodesmic with $WO_3.h_2$ and arise from the favourable BB2 binding in various harmonies. The intergrowth tungsten bronzes only seemingly violate the phase concept. A careful equilibrium annealing should permit separation of different phases having extreemly similar composition.

A^7O_M phases

A binding analysis of MnO_M phases should be compatible with the bindings in Mn (87Sch):

Mn.h_3(W,SR18.210,N=2.4,11.6,16)3.08Å=$\underline{b}_B(\sqrt{1.25};1.1)=\underline{e}_{FU}(\sqrt{5};3.2/2)=\underline{c}_{FU}(\sqrt{5};3.2/2)$,

Mn.h_2(Cu,SR18.210,N=4,24,32)3.86Å=$\underline{b}_F(1)=\underline{e}_F(2)=\underline{c}_F(2)$,

Mn.h_1(C2O,SR2.3,N=16,124,160)6.31Å=$\underline{b}_B(2)=\underline{e}_B(4)=\underline{c}_U(4;5)$,

Mn.r(B2J,SR2.2,N=35,370,464)8.91Å=$\underline{b}_{FU}(\sqrt{8};4)=\underline{e}_{\check{B}}(\sqrt{32};6)=\underline{c}_C(8)$.

Just as in Fe, the oligotypism in Mn is caused by a temperature dependent $\underline{b}$ contribution. The phases Mn.h_2 and Mn.h_3 are closely homeodesmic to Fe.h_2 and Fe.h_3 (87aSch), but Mn.h_1 is heterodesmic to Fe.h_1 as in Mn.h_1 there are nearly no unoccupied $\underline{e}$ sites. Also the isotypism $\underline{e}=\underline{c}$ found in Fe does not occur in Mn.h_1 and Mn.r. Following Ekman's rule (31Ekm) the $\underline{b}$ band of Mn will be suppressed in MnO_M phases.

As in A^6O_M, no suboxides are formed in MnO_M. This also suggests that no the suboxides stabilizing $\underline{b}$ band populated by $Mn\overline{4s}^1$ is probable in the MnO_M phases and the electron count $Mn^{0,7,8}O_M^{6,0,2}$ might be tried. The band formed by the $O2s^2p^4$ electrons may be called the $\underline{o}$ band and the band formed by the $Mn3d^7$ electrons $\underline{e}$ band.

The phase MnO(NaCl,SR1.74,18.576) is the intermediate phase with smallest O content in MnO_M. When the binding is tentatively written $\underline{a}(\underline{N}=24,28,40)=\underline{o}_F(2)=\underline{e}_F(2)=\underline{c}_C(4)$ then the localized property of the correlation is not well expressed. It might therefore be tentatively written $\underline{a}(\underline{N}=24,28,40)=4.45Å=(\underline{o}^v\underline{e})_C(4)=\underline{c}_C(4)$ having an unfilled collective correlation. The most probable proposal appears to be:

$\underline{a}$(MnO ,$\underline{N}=$ 28,56,40)=4.45Å=$\underline{e}_F(2)=\underline{c}'_B(4)$

where $\underline{o}^v\underline{c}^f=\underline{c}'$. Instead of $\underline{a}=\underline{e}_F(2)$ perhaps $\underline{a}=\underline{e}_{HT}(\sqrt{8};3.3)$ might be chosen. On the other hand a binding $\underline{a}=\underline{o}_F(2)=(\underline{e}^v\underline{c})_C(4)$ would be impossible because of overoccupation of $\underline{e}^v\underline{c}$. Therefore the binding analysis of MnO suggests once more a $\underline{o}^v\underline{c}^v\underline{f}$ correlation independently from the binding analysis in A^6O_M with $Mn^{0,7,8,8}O_M^{0,6,2}$.

The phase MnO.p(T4.4,75Pie) is D-homeotypic to NaCl and allows

$\underline{a}$(MnO.p,$\underline{N}=$ 28,56,40)=4.36;4.27Å=$\underline{e}_{\hat{F}}(2;3.5/2)=\underline{c}'_B(4;3.9)$

where $\hat{F}$ is strained in $\underline{a}_3$ direction and $\check{B}$ compressed. The correlations deform

each other to attain a higher occupation of the $\underline{e}$ correlation. This proposal might be examined by studying $Mn_{1-\underline{N}}Fe_{\underline{N}}O.p$ in which the axial ratio $|\underline{a}_3|/|\underline{a}_1|$ should increase with $\underline{N}$.

Below 122K, the antiferromagnetic MnO.1(NiO.r,SR13.175) is found and the $\underline{e}$ correlation becomes more filled to $\underline{e}_{F'}$, and expands in $\underline{a}_3$ direction in order to avoid too many $\underline{e}$ sites:

$\underline{a}$(MnO.1,$\underline{N}$= 21,42,30)=H3.147;7.620Å=$\underline{e}_{F'H}$(2;5.5/3)=$\underline{c}'_{BH}$(2;24/3).

Since $(\underline{e}^{-1}\underline{a})_{33}\neq 6$ antiferromagnetism develops and the observation $\underline{a}_3^{magn}=2\underline{a}_3^{chem}$ (SR13.175) may be understood, as there are only 3 Mn layers in the cell which alternate in the magnetic moment.

The phase Mn_3O_4.h(T>1435K,Fe_3O_4,F6.8,SR13.412) permits the binding proposal

$\underline{a}$(Mn_3O_4,$\underline{N}$/8= 21,48,32)=8.64Å= $\underline{e}_C$($\sqrt{32}$;5.6)= $\underline{c}'_B$(8).

This binding is underoccupied in $\underline{e}$ and $\underline{c}'$ so that it will transform at lower temperatures.

Mn_3O_4.r(U6.8,DhtpFe$_3O_4$,SR26.407) may have the binding

$\underline{a}$(Mn_3O_4.r,$\underline{N}$= 84,192,128)=5.76;9.46Å=$\underline{e}_B$(3;5)=$\underline{c}'_C$(6;10).

The $\underline{e}_B$ correlation is somewhat underoccupied, this leads to magnetism. The $\underline{c}'$ correlation has an enlarged commensurability element 10 as the decrease in $|\underline{a}_1|$ causes increase in $|\underline{a}_3|$. If Fe_3O_4 is mixed to Mn_3O_4 the $\underline{e}$ concentration is increased so that because of $(\underline{e}^{-1}\underline{a})_{11}>3$ the ratio $|\underline{a}_3|/|\underline{a}_1|$ decreases (SR13.411). At the mole fraction $\underline{N}_{Fe3O4}$=0.25 a stationary value of $|\underline{a}_3|/|\underline{a}_1|$ appears to be reached, corresponding to a new correlation, and at $\underline{N}_{Fe3O4}$=0.40 the axial ratio becomes cubic.

If to Mn_2O_3 some Fe_2O_3 is mixed then the phase $MnFeO_3$(B16.24,bixbyite, drawing 64Sch p.231,SR2.38,37.225) becomes stable. The oxygen atoms are in a C1 partial structure containing lacunae. The binding may be

$\underline{a}$($MnFeO_3$,N= 240,544,352)=9.41Å=$\underline{e}_B$(5)=$\underline{c}'_C$(10).

The BC2 binding is an alternative to the FB2 binding and has the advantage of a better spin compensation in $\underline{e}$. Also the presence of 50% Fe becomes clear, as otherwise the $\underline{e}$ correlation would be under-occupied.

The pure Mn_2O_3.r(O32.48,SR32.256) is homeotypic to $MnFeO_3$ and may have the binding

$\underline{a}$(Mn_2O_3.r,$\underline{N}$=224,544,352)=9.412;9.418;9.423Å=$\underline{e}_B$(5;4.5)=$\underline{c}'_C$(10)

The commensurability element $(\underline{e}^{-1}\underline{a})_{33}$=4.5 introduces an I homeotypism leading to the D homeotypism.

The phase Mn_5O_8(N5.8,SR32.285) contains MnO_6 octahedra sharing edges and yields

$\underline{a}$(Mn_5O_8,$\underline{N}$=70,176,112)=9.76;5.72;-3.44,0,4.85Å=$\underline{e}_B$(5;3;2.5)=$\underline{c}'_C$(10;6;5).

The BC2 binding is no more distorted as in Mn_2O_3.

MnO_2 (TiO_2.r,T2.4,SR13.187,pyrolusite,drawing64Sch p.275) may have the binding

$\underline{a}(MnO_2,\underline{N}=\frown 14,40,24)=4.39;2.87\mathring{A}=\underline{e}_B(\sqrt{5};1.5)=\underline{c}'_C(\sqrt{20};3)$.

Presumably the $O1s^2$ electrons do not take part in the $\underline{c}'$ correlation. The nearly fully occupied $\underline{e}$ correlation might give an explanation for the shear homeotypes of MnO_2, for instance ramsdellite (SR13.188). A study of $Mn_{1-n}Fe_nO_2$ could help to examine the binding.

The red Lewis phase Mn_2O_7(M16.56,87Sim,drawing87Sim) has a melting temperature of 5.9°C and detonates on impact (87Sim). Just as in CrO_3 the metal is 4-coordinated by O because of the utilized high compliance of the $Mn3d^7$ electrons. The O atoms form a Cu type partial structure (87Sim) with the commensurability $\underline{a}=\underline{a}^{\perp}_{Cu}(1.5,0,-1;0,4,0;0.5,0,2)$. This leads to the binding

$\underline{a}(Mn_2O_7,\underline{N}=112,464,240)=6.80,0,-1.67;16.69;6.69\mathring{A}=\underline{e}_C(3,0,-2;8;1,0,4)=\underline{c}'_C\underline{K}'(2)$

where $\underline{K}'=\underline{e}^{-T}\underline{a}$. This CC2 binding presents a fully occupied $\underline{e}$ correlation. If Mn is assumed to be in a cube of $\underline{e}$ sites then it would have too many $\underline{e}$ sites around it. If two of the 8 $\underline{e}$ sites belong to two Mn atoms then only 14 $\underline{e}$ sites belong to two Mn. An analogous conclusion requires the MnO_4 tetrahedra to share an edge.

In TcO_M a phase Tc_2O_3(pseudocubic,SR29.322) was reported, homeotypic to the phase Mn_2O_3. A binding analysis could be made after the structure has been refined.

TcO_2(MoO_2,M4.8,75Pie,drawing64Sch p.277) will be homeodesmic to MnO_2

$\underline{a}(TcO_2,\underline{N}=\frown 28,80,48)=5.55,0,-2.97;4.85;4.77\mathring{A}=\underline{e}_B(\sqrt{5};5/2)=\underline{c}'_B(\sqrt{20};5)$.

The characteristic difference of the $\underline{a}^{\vee}\underline{c}^{\vee}\underline{f}$ site number as compared with MnO_2 leads to the simple commensurability element $(\underline{c}'^{-1}\underline{a})_{33}=5$ causing the Tc pairs along $\underline{a}_1$ and with them the I-homeotypism to TiO_2.r.

Tc_2O_7(O8.28,SR37.225, 71Kre) contains centro symmetric Tc_2O_7 molecules built of two TcO_4 tetrahedra sharing corners. The binding may be

$\underline{a}(Tc_2O_7,\underline{N}=\frown 56,232,120)=13.76;7.44;5.62\mathring{A}=\underline{e}_{\hat{B}}(5.5;3;1.7)=\underline{c}'_{\hat{B}}(11;6;7/2)$.

The $\hat{B}\hat{B}2$ binding is closer packed than the CC2 binding of Mn_2O_7 in agreement with the rule of participation of Tc3d electrons in the binding.

The ReO_M phases are contained in the narrow interval $0.67\leq\underline{N}'_O\leq 0.78$, as only the BB2 binding is favourable enough for phase formation.

ReO_2.h(O4.8,SR21.226,57Mag) is a shear homeotype of TiO_2.r with shear plane (010). It might be that additional electrons are excited to the $\underline{e}$ correlation

$\underline{a}(ReO_2$.h,$\underline{N}=28,80,72)=4.81;5.64;4,60\mathring{A}=\underline{e}_{\vee B}(\sqrt{5};3)=\underline{c}'_B(\sqrt{20};5.3)$.

The binding is formulated for the quasi tetragonal cell. The $\underline{e}$ correlation is a little compressed so that excited $\underline{e}$ electrons also find a site. The

commensurability element $(\underline{e}^{-1}\underline{a})_{33}$=3 causes the shear following the mechanism explained earlier for shear homeotypes of Cu_3Au (64Sch).

ReO_2.r(MoO_2, SR29.417, 51Zac) may have the binding

$\underline{a}(ReO_2.r,\underline{N}=\frown 28,80,72)=5.58,0,-2.87;4.81;4.79\mathring{A}=\underline{e}_B(\sqrt{5};5.2/2)=\underline{g}_B(\sqrt{20};5.2)$.

The binding is written here for the diagonal part of the cell and is homeotypic to the binding of ReO_2.h. The reason for the transformation must be sought in a descent of d electrons to the $\underline{c}'$ correlation. The matrix element $(\underline{e}^{-1}\underline{a})_{33}$ =5.2 indicates that in $A^{8..9}O_M$ only TiO_2.r isotypes are to be expected.

Re_2O_5(T8.20,75Pie,65Tri) allows the binding

$\underline{a}(Re_2O_5,\underline{N}=\quad 56,184,152)=5.80;12.87\mathring{A}=\underline{e}_C(\sqrt{8};6)=\underline{c}'_C(\sqrt{32};12)$.

The $\underline{e}$ correlation appears over-occupied, so that transfer $\underline{e}\rightarrow\underline{b}$ must be assumed. A participation of 4f electrons in the $(\underline{\ }^{\vee}\underline{c})_C$ correlation is possible.

$Re_{1.16}O_3$(H(2.3).6,SR38.244,72Jei) exhibits a O partial structure of the Mg type (commensurability $\underline{a}=\underline{a}_{Mg}(\sqrt{3};1)$) containing some Re in octahedral holes. It allows the binding

$\underline{a}(Re_{1.16}O_3,\underline{N}=16,55,44\quad)=H4.84;4.54\mathring{A}=\underline{e}^{\vee}_{CH}(\sqrt{3};4.5/3)=\underline{c}'^{\vee}_{CH}(\sqrt{12};9/3)$.

Less than 1 $\underline{e}$ electron descents to $\underline{o}$. The commensurability $((\underline{o}^{\vee}\underline{c}^{\vee}\underline{f})^{-1}\underline{a})_{33}$ favours the Mg stacking.

The red ReO_3(C1.3,SR2.31,32Mei,drawing 64Sch p.278) allows the twinned binding

$\underline{a}(ReO_3,\underline{N}=\frown 7,26,20)=3.75\mathring{A}=\underline{e}^{\vee}_B(\sqrt{2};1.5)=\underline{c}'^{\vee}_B(\sqrt{8};3)$.

The $\underline{e}$ correlation has only 6 sites per cell, consequently there is some electron transfer from $\underline{e}$ to $\underline{o}$. The $\underline{o}^{\vee}\underline{c}^{\vee}\underline{f}$ correlation is therefore higher occupied than in WO_3 and favours the compression and twinning causing the heterotypism to $WO_3.h_2$. If the ReO_3 type is changed to the $CaTiO_3$ (perovskite,SR1.300) type the occupancy becomes 83%. It appears probable that the $Ca4s^2$ electrons are in a $\underline{e}$ correlation with the $Ti3d^4$ electrons.

The Lewis phase Re_2O_7(O16.56,SR34.244,69Kre) is homeotypic with ReO_3 and allows the binding

$\underline{a}(Re_2O_7,\underline{N}=\frown 112,464,336)=12.51;15.20;5.45\mathring{A}=\underline{e}^{\wedge}_B(5;6;2)=\underline{c}'^{\wedge}_B(10;12;4)$.

The binding is slightly strained in $\underline{a}_3$ direction as it is to be expected by the self-deformation of the BB2 binding. As compared with Tc_2O_7 the strain of B is weaker.

A^8O_M phases

The FeO_M phases, being homeotypic with one another, are contained in the mole fraction range $0.5\leq\underline{N}'_O\leq 0.6$. This suggests that the phases are to some extent homeodesmic.

The phase $Fe_{0.9}O.h$(NaCl,wüstite,SR1.122,25Wyc) has a lower melting temperature than Fe_3O_4 and exhibits statistically distributed Fe-lacunae. Presumably at elevated temperatures Fe needs 9 $\underline{e}$ sites so that the phase becomes homeodesmic to MnO

$\underline{a}(Fe_{0.9}O,\underline{N}=\ 29,53,37)=4.31\mathring{A}=\underline{e}_F(2)=\underline{c}'_B(4)$.

Such a binding cannot occur in oxides with A4d and A5d components as in the heavier phases less $\underline{c}'$ sites per cell are probable.

Below the Néel temperature 198K $Fe_{0.9}O.h$ transforms to the low temperature (l) metastable (m) phase $Fe_{0.9}O.lm$(NiO,R1.1,SR17.424,53Wit) with the binding $\underline{a}(Fe_{0.9}O.lm,\underline{N}=\ \hat{\smile}\ 22,40,28)=H3.026;7.518\mathring{A}=\underline{e}_{\check{U}H}(2;7/2)=\underline{c}'_{BH}(2;24/3)$.

The $\check{U}_H$ correlation provides a better spin compensation than the F correlation. An unoccupied site in $\underline{e}_{\check{U}H}$ corresponds to an uncompensated spin of the $\underline{e}$ correlation (87Sch). In the $\check{U}_H$ correlation the spins are the same in $\underline{a}_1$ and $\underline{a}_2$ direction and in the $\underline{a}_3^{lm}$ direction the sequence of +-+-+- layers is to be assumed. Since there are lacunae in the $\underline{e}$ layers antiferromagnetism will occur. The direction of the spin which is empirically parallel to $\underline{a}_3$ (74Rao) is presumably determined by more subtle influences.

In Fe_3O_4(F6.8,$MgAl_2O_4$,magnetite,SR1.350,15Bra,drawing64Sch p.344) the $\underline{e}$ correlation will have lacunae so that magnetism becomes possible

$\underline{a}(Fe_3O_4,\underline{N}=192,384,256\ \ )=8.39\mathring{A}=\underline{e}_{\hat{F}}(\sqrt{32};7/2)=\ \ \underline{c}'_B(8)$.

The strained $e_{\hat{F}}$ correlation has 224 sites and therefore 32 lacunae per cell so that $4\mu_B$ per Fe_3O_4 are available. Fe_3O_4 is ferrimagnetic below the Néel temperature $\underline{T}_N$=860K (74Rao). The binding must be twinned to be compatible with the cubic symmetry. The $\hat{F}B2$ binding is homeotypic to the FB2 binding of $Fe_{0.9}O.h$. The uniform $\underline{e}$ correlation is the cause for the uniform Fe distribution. It is seen that the present formulation of the binding is closely related to the magnetic properties. However, since the main roots of the binding model lie in the crystal chemical data, these data are considered in first line, postponing a more strict analysis of the magnetic data. The tetragonal binding is a reason for a low temperature phase with lower symmetry.

At $\underline{T}$<119K $Fe_3O_4.l$(P6.8,SR22.301,58Ham) has been found with the tentative binding

$\underline{a}(Fe_3O_4.l,\underline{N}=96,192,128\ )=5.91;5.95;8.39\mathring{A}=\underline{e}_B(\sqrt{10};4.5)=\underline{c}'_C(\sqrt{40};9)$.

The twinning of the binding in Fe_3O_4 is lost. It might appear puzzling that the loss of twinning of the binding causes an orthorhombic cell (55Abr). However, the interaction of the binding with the structure may cause a displacive change of the atomic sites which may exclude the tetragonal symmetry.

The antiferromagnetic Fe_2O_3(Al_2O_3,R4.6, haematite,drawing64Sch p.198,

SR2.310,28Zac) has a Mg type O partial structure. Its commensurability to Mg is $\underline{a}=\underline{a}_{Mg}(\sqrt{3};3)$, and the following binding appears probable

$\underline{a}(Fe_2O_3,\underline{N}=$ 96,204,132)=H 5.03;13.75Å$=\underline{e}_{BH}(2;27/3)=\underline{c}'_{CH}(4;27/3)$.

The $\underline{e}_B$ correlation of Fe_3O_4 is conserved and the unoccupied sites in $\underline{e}$ cause the antiferromagnetism. The commensurability element $(\underline{e}^{-1}\underline{a})_{33}=9$ favours the Mg type stacking following an earlier rule (84Sch).

If Fe_3O_4 is oxidized at temperatures of $200^oC < T < 400^oC$ (58Han) a metastable phase $Fe_2O_3.m_1$(T64.96,γ,SR22.299) is formed exhibiting the commensurability $\underline{a}=\underline{a}_{Fe3O4}(1;3)$. This phase is homeodesmic to Fe_3O_4. The structure occurs also in $InS_{\underline{M}}$(85Göd) where the In lacunae occur following Lewis' rule.

The binding analysis of $Fe_2O_3.m_2$(M40.60,SR28.320) shall be postponed. The low melting temperature of Mn_2O_7 foreshadows that a "FeO_4" is not stable.

In the mixture $RuO_{\underline{M}}$ "RuO" or "Ru_2O_3" are not stable as the high electron density of Ru favours a localized instead of a collective $\underline{e}$ correlation of the O2sp electrons. The phase poorest in O is $RuO_2(TiO_2.r$,SR1.213) and it appears that in the electron count $Ru^{0,8,8,10}O_{\underline{M}}^{0,0,6}$, the $\underline{o}$ and $\underline{c}$ electrons are strongly interacting and the $\underline{e}$ electrons form a separate collective correlation. The binding may be

$\underline{a}(RuO_2,\underline{N}=$ 16,40,28)=4.49;3.11Å$=\underline{e}_B(\sqrt{5};1.5)=\underline{c}'_B(\sqrt{20};3)$.

One $\underline{e}$ electron per cell is contributed to the $\underline{b}$ correlation. The BB2 binding shows that a phase richer in O may be stable as a CC2 binding might follow on BB2.

In the Lewis phase $RuO_4(OsO_4$,N2.8,drw SR30.312,75Pie,65Uek) a O partial structure of the Cu type is filled in tetrahedral interstices by Ru, so that every O belongs to just one Ru. The low Ru content causes a large extension of $\underline{d}_{\underline{e}}$ so that the binding might become:

$\underline{a}^s(RuO_4,\underline{N}=$ 8,32,18)=4.25;4.49Å$=\underline{e}_C(2)=\underline{c}'_C(4)$.

The quasi tetragonal subcell $\underline{a}^s$ is used from which the true cell follows by $\underline{a}=\underline{a}^s(2,0,0;0,1,0;-1,0,2)$. The binding is of the CC2 type perhaps as near Ru even more electrons fill the correlation. This leads to electro dipoles at Ru which may cause the super cell.

The phases $OsO_2(TiO_2.r$, SR1.213) and OsO_4(N2.8,SR30.311) are isodesmic to the isotypes in $RuO_{\underline{M}}$.

$\underline{A^9O_{\underline{M}}}$ phases

CoO.r(NaCl,SR13.167,17.382,50Tom) is not known to have lacunae like $Fe_{0.9}O$, however, see 68Han. The binding may be:

$\underline{a}(CoO.r,\underline{N}=$ 36,56,40)=4.26Å$=\underline{e}_{\underline{F}}(2;4.5/2)=\underline{c}'_B(4)$.

The compression of $\underline{e}_F^{\vee}$ increasing the site number provides a better spin compensation than in $\underline{e}_F$. Furthermore a descent of $\underline{e}$ electrons to $\underline{h}$ may be assumed.

The r phase transforms at 286K to CoO.1(N1.1,75Pie,SR13.168), the cell is pseudotetragonal and this cell will be used to describe the binding

$\underline{a}$(CoO.1,$\underline{N}$=36,56,40)=4.26;4.21Å=$\underline{e}_F^{\vee}$(2;5)=$\underline{c}_B^{\prime}$(4).

By the compression once more additional sites are provided and the spin compensation is improved. Since the spin depends on which partial lattice of $\underline{e}_F^{\vee}$ the unoccupied site lies in, the phase CoO.1 is antiferromagnetic (74Rao).

The phase Co_3O_4(Fe_3O_4,F6.8,SR33.290) may be closely homeodesmic to Fe_3O_4

$\underline{a}$(Co_3O_4,$\underline{N}$= 216,384,256)=8.08Å=$\underline{e}_{FU}^{\wedge}$($\sqrt{32}$;7.5/2)=$\underline{c}_B^{\prime}$(8).

It must be assumed that 32×7.5=240 sites lead to 24 lacunae and therefore to $3\mu_B$ per Co_3O_4 (74Rao).

The phase Co_2O_3(75Pie)H4.64;5.75Å needs confirmation. However, at high pressure Co_2O_3.p(Al_2O_3,R4.6,71Che) was found of the same structure type with the binding

$\underline{a}$(Co_2O_3,$\underline{N}$=108,204,132)=4.89;13.34Å=$\underline{e}_{BH}$(2;27/3)=$\underline{c}_{CH}^{\prime}$(4;27/3).

The $\underline{d}_{\underline{e}}$ value of Co_2O_3 is too low as compared with that of Co_3O_4. This may have to do with the high pressure preparation.

Rh_2O_3.r(Al_2O_3,R4.6,SR2.310,27Lun) is isodesmic to Cr_2O_3, Fe_2O_3, and Co_2O_3

$\underline{a}$(Rh_2O_3.r,$\underline{N}$=108,204,156)=H5.13;13.85Å=$\underline{e}_{BH}$(2;27/3)=$\underline{c}_{CH}^{\prime}$(4;27/3).

The Rh3d electrons probably take part in this binding.

Above 1020K Rh_2O_3.h(O16.24,SR39.211,73Bie) is stable and allows

$\underline{a}$(Rh_2O_3.h,$\underline{N}$=144,272,208)5.15;5.44;14.70Å=$\underline{e}_F^{\vee}$($\sqrt{5}$;7)=$\underline{c}_B^{\prime}$($\sqrt{20}$;12).

The binding is homeotypic to the FB2 binding. The contraction of $\underline{e}_F$ is necessary to have good spin compensation in $\underline{e}$. The Rh3d electrons take part in $\underline{c}^{\prime}$.

Above 60kbar Rh_2O_3.p(O8.12,SR35.211) was found. The binding

$\underline{a}$(Rh_2O_3.p,$\underline{N}$=72,136,104)=5.17;5.38;7.24Å=$\underline{e}_F^{\vee}$($\sqrt{5}$;3.5)=$\underline{c}_B^{\prime}$($\sqrt{20}$;6)

is isotypic to that of h.

RhO_2(TiO_2.r,SR33.271) has the binding

$\underline{a}$(RhO_2,$\underline{N}$= 18,40,20)=4.49;3.09Å=$\underline{e}_B$($\sqrt{5}$;1.5)=$\underline{c}_C^{\prime}$($\sqrt{20}$;3)

and is isodesmic to RuO_2(TiO_2.r). The partial filling of $\underline{c}^{\prime}$ causes the quasihomologic isotypism.

IrO_2(TiO_2.r,SR1.158)4.49;3.15Å is isodesmic to RhO_2(TiO_2.r).

Lewis phases with $A^{9..10}$ are not stable since $\underline{d}_{\underline{e}}$ would become too long.

$\underline{A^{10}O_M}$ phases

NiO.h($\underline{T}$>470K,NaCl,SR11.254) melts near 2000K and may have the binding

$\underline{a}$(NiO.h,$\underline{N}$= 40,56,40)=4.20Å=$\underline{e}_F^{\vee}$(2;2.5)=$\underline{c}_B^{\prime}$(4).

It should be noted that the $\underline{e}$ correlation is as in Ni, but there is no $Ni4s^{0.6}$ band as the volume is increased by the insertion of O.

For $\underset{\sim}{T}$<450K one finds NiO.r(R1.1,SR11.254)

$\underline{a}$(NiO.r,$\underline{N}$=18,30,24,24)=H2.96;7.23Å=$\underline{e}^{\vee}_{UH}$(2;7/2)=$\underline{c}'_{BH}$(2;24/3).

The $\underline{e}$ correlation provides, presumably, a better spin compensation. The phase is also found with Ni lacunae $Ni_{3.7}O_4$(75Pie). This might explain the above defect in the $\underline{e}$ site number. Another spinel-like phase is $Ni_{28}O_{32}$(F7.8,75Pie) with:

$\underline{a}$(Ni_7O_8,$\underline{N}$= 280,146,288)=8.12Å=$\underline{e}_B$(5)=$\underline{c}'_C$(10).

The $\underline{e}_B$ correlation provides a good spin compensation.

The phase Ni_2O_3(Co_2O_3,H4.6,SR26.358,75Pie) needs confirmation.

Also the phase NiO_2(C ,SR15.177) a=4.62Å might need confirmation.

The phase PdO(PtS,T2.2,drw64Sch p.195,SR8.124) has a Pd partial structure of a strongly strained Cu type with O in tetrahedral holes. The binding may be

$\underline{a}$(PdO,$\underline{N}$= 20,28,24)=3.04;5.34Å=$\underline{e}_C$($\sqrt{5}$;4)=$\underline{c}'_C$($\sqrt{10}$;5.5).

The heterotypism to NiO.h is caused by a change of $\underline{e}^{-1}\underline{a}$ in the $\underline{a}_1\underline{a}_2$ plane, increasing the number of $\underline{c}'$ sites per PdO. This is required by the participation of the f electrons ($Pd3d^{10}$).

PtO(PtS,SR8.125)3.05;5.34Å is isodesmic to PdO and the participation of 4f electrons suggests that $O1s^2$ electrons do not take part in the $\underline{c}$ correlation.

Pt_3O_4(C6.8,SR33.270) has a Cl partial structure of O and the binding

$\underline{a}$(Pt_3O_4,$\underline{N}$= 60,96,84)=5.59Å=$\underline{e}_C$(4)=$\underline{c}'_C$($\sqrt{32}$;5.7).

The phase PtO_2(CdI_2,SR15.186,21.223) may have the binding

$\underline{a}$(PtO_2,$\underline{N}$= 10,20,14)=H3.10;4.19Å=$\underline{e}_H$(2;2.5)=$\underline{c}^{\vee}_{CH}$(2;9/3).

Unfortunately, the lattic data in the literature are somewhat different so that new measurements appear desirable. The value $(c^{-1}\underline{a})_{33}$=3 favours the Mg type stacking of the O.

The phase PtO_2.p($CaCl_2$,02.4,SR33.270) is D-homeotypic to TiO_2.r. The binding may be

$\underline{a}$(PtO_2.p,$\underline{N}$= 20,40,28)=4.49;4.54;3.14Å=$\underline{e}_C$($\sqrt{10}$;2.2)=$\underline{\ }_C$($\sqrt{20}$;3).

The orthorhombic deformation must come from the over-occupation of the ($\underline{o}^{\vee}\underline{c}^{\vee}\underline{f}$) =$\underline{c}'$ correlation.

Discussion

The above tentative analysis contributes towards confirming that fundamental energetical crystal chemistry is of a simple geometrical nature. A first assumption of the analysis is the lattice-like property of the various spatial correlations inferred from a multitude of obvious interpretations of structural phenomena using the plural correlations model (64,86Sch1). A regular distribution of bonds in a

crystal is similar to a lattice-like spatial correlation of electrons. However, a lattice-like correlation is more realistic since in crystals bonds cannot exist, as these would be disturbed by their mutual interaction. A second assumption of the analysis is the electron count which is found by trial and error. It appears as a characteristic result for the present phases, that the peripheral d electrons of the A component form a correlation of their own while the 2sp electrons of the oxygens are in a localized correlation united with the correlation of the nsp electrons of the And component. This assumption is compatible with Lewis' rule (23Lew) of octet completion of the oxygen atoms which may be interpreted by complete compensation of the spins at atoms generated by Hund's rule, and no longer by the filling of a noble gas shell of oxygen. The above two assumptions permit establishing a correspondence of bonding types (bindings) to most observed members of the $A^{6\ldots10}O_M$ class of phases. These bindings answer various questions referring to structure (and also magnetism) by showing that the phases obey remarkable crystal chemical rules, for instance:

Why does MoO_2 crystallize in a monoclinic superstructure of TiO_2.r?
The binding of MoO_2 causes the equidistant sites of A atoms along $\underline{a}_3$ (TiO_2.r) to be unstable and the atoms to condense in pairs, so that the array of these chains makes the structure monoclinic.

Why does CrO_2, being homologic to MoO_2, not crystallice in the MoO_2 type but in the TiO_2.r type?
There is a rule in crystal chemistry (83Sch) that in heavy compounds the number of $\underline{c}$ sites per atom is smaller than in light compounds, as the additional electrons in them provide additional bonding. Since the commensurability in the basal plane is conserved, the element $(\underline{c}^{-1}\underline{a})_{33}$ is increased in the homeotypism $MoO_2 \rightarrow CrO_2$ so that the commensurability is changed and the superstructure is lost.

Why is the shear plane $\underline{k}=(10\bar{2})$ in Mo_8O_{23} more favourable than $(10\bar{3})$, (001), (101)?
In the unfavourable cases the crowding of Mo atoms is stronger and therefore the costly deformation of the $\underline{e}$ correlation is larger.

Why is $WO_3.h_2$(T2.6) DI-homeotypic to ReO_3(C1.3) and not isotypic?
The occupation of $\underline{c}'$ is simpler in $WO_3.h_2$ than in ReO_3 so that the structure of $WO_3.h_2$ may be deformed, while the less simple occupation cannot deform the crystal and will be twinned so that a cubic cell is generated.

Why is VO an electric conductor and MnO an insulator?

In VO, e and c are collected to c. Therefore the V4s band is presumably populated. In MnO, e and c cannot be collected since too many e electrons are present. Therefore e is localized by c' and the Mn4s band is not populated.

Why is $Fe_{0.9}O$.h not stable at lower temperatures?
The e_F correlation does not provide a good spin compensation since the electron distances d_{++} are equal to d_{+-}.
What is the reason for the stability of Fe_3O_4?
The decrease of the e electron concentration as compared to $Fe_{0.9}O$.h suggests a $\hat{F}B2$ binding for Fe_3O_4.
Why does Fe_3O_4 become tetragonal at lower temperatures?
The binding of Fe_3O_4.h is twinned. At lower temperatures the twinning is lost so that the structure becomes tetragonal.
Why does $Fe_2O_3(Al_2O_3)$ have a Mg type partial structure of O while $Fe_{0.9}O$.h and Fe_3O_4 have a Cu type partial structure of O?
The e correlation becomes of the B_H type and the commensurability of e_{BH} to the crystal favours the Mg type.
Why is $RuO_4(OsO_4)$, a quasi cubic phase with Cu type O partial structure, stable?
The BB2 binding of $RuO_2(TiO_2.r)$ may be transformed to the favourable CC2 binding as the e electron concentration has decreased.
Why is $RuO_2(TiO_2.r)$ heterotypic to $TcO_2(MoO_2)$?
The higher e electron concentration of RuO_2 does not permit the MoO_2 type.
Why is PdO(PtS,T2.2) heterotypic to the homologic NiO.h?
PdO has less c' sites than NiO conforming to the rule that the lighter phase has more sites. The reason for this phenomenon lies in the high compliance of the Pd3d electrons providing additional bonding.

For all these phenomena, explanations from other valence models are missing. Therefore, before rejecting the plural correlations model, another explanation should be presented. It might appear not very certain that deep shells take part in the binding of the chemical compounds. However, the relations found should be considered as some kind of hidden Lewis or Hume-Rothery rules which may be verified by many examples and which are of interest since they lead to experimental questions making the empirical investigations more determined. Finally it should be concluded that the present analysis gives new answers to some old questions, unfortunately not to all, as it is based on an approximate model.

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Figure captions

Fig.1: Comparison of the binding diagrams CrO_M and MoO_M

Fig.2: Mo sites of Mo_7O_{24-1}(M16.46) and different cells

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