

On the bindings in two-component oxides

I. $A^1 \dots^5 O_M$ phases

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Bonding types (bindings) / Oxides, two component / Spatial correlation

(Received: January 1988)

Abstract

An interpretation of $A^1 \dots^5 O_M$ phases ($A^1 \dots^5 = \text{Li} \dots \text{V}$ homologous class) by bonding types (bindings) may be obtained under the assumption that the O_{2sp} electrons take part in the c correlation of the filled peripheral $A(n-1)sp$ shells, while the A_n s electrons populate the b correlation, and the $A(n-1)d$ electrons the e correlation. Even $A(n-2)d$ or f electrons seem to take part in the binding (f correlation). Because of the small bonding contribution of the $A(n-1)sp$ noble gas shell the site number ratio in A^1 elements is $N/S(b) = 32$. This large value is decreased by the bonding of entering O atoms and reaches a minimum near the mole fraction $N_O = 0.33$. Bindings like CB_2 and CC_3 or BB_3 are possible in $A^1 O_M$ phases. For $A^2 O_M$ phases CC_2 and CB_2 bindings prevail. In $A^3 O_M$ phases a united bve correlation may be assumed which forms BB_2 or once more CC_2 bindings. In $A^4 O_1$ phases the union bve \cup cvf $=$ g causes constitutional vacancies (lacunae). The union means that bve electrons and cvf electrons together approximate a common lattice as they are concentrated in different ranges around the atoms. The proposed bindings interpret phenomena like cluster formation in A^1 suboxides, peroxides with A^2 elements, the $MnFeO_3$ (B16.24) type in A^3 oxides, the occurrence of suboxides in $A^4 O_M$, the tritypism of ZrO_2 , the Magnéli phases in $A^5 O_M$, etc.

Note : Abbreviations used in the plural correlations model

\underline{a}_{ik} =crystal cell, \underline{a}_{i1} =first elementary translation of the crystal, etc.
 A^n =chemical element of homologic class n, $A^{1...5}$ =set of homologic classes of Li...V
 $A3d=M$ -line of the periodic system, $A4d=N$ -line, $A5d=O$ -line
 \underline{b} =(cell of) valence electron spatial correlation, $\underline{b}'=\underline{b} \vee \underline{e}$
 $(\underline{b} \vee \underline{c})$ =united correlation of the valence electrons and the core electrons
 B =body centered cubic Bravais lattice
 $B^1=A^{11}$ etc., $B16.24$ =type designation, see 64,83Sch
 \underline{c} =correlation of the peripheral core electrons, $\underline{c}'=\underline{c} \vee \underline{f}$, c =cubically stacked layer
 C =cubic primitive Bravais lattice
 CH =cubic primitive lattice in hexagonal aspect
 $CC2$ =binding symbol, \underline{b} is of the C-type, \underline{c} is of the C-type, $(\underline{c}^{-1}\underline{b})_{11}=2$
 d =atomic state with angular momentum 2
 \underline{d}_e =electron distance in the \underline{e} correlation
 D =deformation homeotypism
 drw =drawing
 \underline{e} =correlation of the first peripheral d electrons,
 \underline{f} =correlation of the second peripheral d or f electrons
 F =face centered cubic Bravais lattice, filling homeotypism
 $F_H=F$ in hexagonal aspect
 $F_U=F$ in tetragonal aspect
 \underline{g} =united ground correlation $=\underline{b} \vee \underline{e} \vee \underline{c} \vee \underline{f}$ in $A^{6...10}$ oxides
 h =high temperature phase, htp =homeotype of, h =hexagonally stacked layer
 H =hexagonal Bravais lattice, in a correlation $\underline{b}_1^H = \underline{b}_3^H$ (isometric property)
 i =phase stabilized by impurity, first matrix index
 I =homeotypism by inhomogeneous deformation=displacive homeotypism
 k =second matrix index
 \underline{k} =shear plane direction
 K =Kelvin
 \underline{K}' =commensurability matrix used in a foregoing equation

l=low temperature phase

\underline{l} =shear length

L=lacuna homeotypism, lacuna=constitutional vacancy

μ_B =Bohr's magneton

m=metastable phase

M=monoclinic Bravais lattice

\underline{M} =undetermined mole number used to designate a chemical mixture

n= integral number, main quantum number

N=monoclinic one face centered Bravais lattice

\underline{N} =electron number per \underline{a} cell in the correlations $\underline{b}, \underline{e}, \underline{c}, \underline{f}$

\underline{N}_2' =mole fraction of the second component

O=orthorhombic primitive Bravais lattice, O=oxygen

p=high pressure phase, p=atomic state with angular momentum 1

P=orthorhombic body centered Bravais lattice

Q=one face centered orthorhombic Bravais lattice

r=room temperature phase

R=rhombohedral Bravais cell (generally assumed in hexagonal aspect)

s=atomic state with zero angular momentum

\underline{s} =shear vector

S=orthorhombic all faces centered, S= shear homeotypism, S=site

SR2.25=Structure Reports vol.2 p.25

T=tetragonal primitive Bravais lattice

\underline{T} =temperature

U=tetr. body cent. Bravais lattice, in a correlation having isometr.prop.

Z=triclinic Bravais lattice

'=Hund insertion in a correlation type

$\wedge \vee$ =strained or compressed cell type (direction of strain is the main axis)

\vee =union of correlations

(;)=linear numerical notation of a matrix, semicolon separating matrix lines

$|\underline{a}_1|$ =modulus of the vector \underline{a}_1

Introduction

It is an early problem of crystal chemistry to find for every phase a bonding type (binding) providing a crystal structure systematics with an energetical background. Although the knowledge of bindings does not yield exact energy values, it allows to recognize whether or not a structure is energetically favourable, a binding is therefore a qualitative stability argument. The search for a probable binding is a kind of structure determination since each binding (also a conventional one) implies an electron pair density matrix (56Löw) which may be reduced to a pair density function for the purpose of a valence model (64,83Sch). The data for a binding determination are crystal structures, crystal chemical rules, electron numbers, energetical requirements, etc. Because of the wealth of crystal chemical data and rules, the binding determination is not so ~~underdetermined~~ as it might seem at first sight, an application to the broad structural knowledge readily rules out proposals and models being remote from reality. However, an earlier binding proposal may violate rules which have been found later. Such a binding proposal should be modified in the light of the new understanding.

Although the oxides play an important role in the valence theory and although they have been, because of technological interest, intensively studied physically (74Rao), the problem of their bindings needs further study. New rules for the bindings have been found by using the concept of a two electron reduced density matrix in a vigorously simplified form (plural correlations model 86Sch2). Therefore several conventional binding proposals should be revised drawing more attention to the spatial correlation of the electrons. The following binding analysis (86Sch2) of oxides yields proposals for the electron correlations. These should be considered by constructing diagrams of electron distance \underline{d} over mole fraction \underline{N}_O (drawn below only for A^{10}_M for brevity) examining to what extent the rules (86Sch2) are fulfilled. Consulting earlier articles on the model cited in 86Sch2, may be helpful to readers raising unanswered objections. As always in systematic chemistry, cross-comparisons improve the understanding

of the interpretation. For the reading of this article a parallel use of 75Pie may be convenient.

While earlier valence models paid attention mainly to electron charges and bonds, the plural correlations model considers lattice-like spatial correlations of electrons in the various energy bands. For two different correlations b and c in a crystal two kinds of coexistence are conceivable. Either the less dense correlation is inserted into the denser correlation so that the electrons of both correlations are as far distant from one another as possible, or the correlations are united to b+c and extend like shells around the atoms. Instead of "united" or "inserted" also the terms collective or localized may be used. It seems that the insertion is only chosen when c is highly enough occupied and it is the task of the binding analysis to find a probable model for a given phase.

The new binding proposals generally do not supplant the earlier views, they merely supply them, since also in a defective model truth may be contained. For instance the Lewis spin compensation is contained in the present model because only correlations are admitted which allow good spin neighbouring. Also the influences of atomic radii (72Pea) and of atomic charges (75Hop) are not neglected. The wording of the new model may be somewhat shifted to facilitate the necessary reflections, but the valuable contents of the earlier models will be widely conserved. The bindings found are not final, they are open to improvement just as they improve the earlier bindings. However, the missing definitiveness of the proposals is no reason to disregard them, the study of new models is indispensable.

Various abbreviations used below are explained in the Note above.

A¹O_M phases

In the systems LiO_M, NaO_M and KO_M suboxides do not occur since for the stabilization of these compounds d or f electrons are necessary providing an additional bonding energy. Therefore the first phases in these mixtures are the Lewis

phases permitting full compensation of the O atom electron spins, caused by Hund's rule, by spins of the cations.

$\text{Li}_2\text{O}(\text{CaF}_2, \text{F1.2,SR3.283,drw64Sch p.231})$ is a white coloured phase melting above 2000K. It obeys Zintl's supply rule since the anion occupies the site set of a noble gas. The difference of the valence electron distances in Li and O (83Sch) causes that the \underline{b} correlation contains only $\text{Li}2s$ electrons while the $\text{O}2sp$ electrons perhaps together with the $\text{Li}1s^2$ electrons are in the \underline{c} correlation so that the binding may be proposed $\underline{a}(\underline{N}=8,40)=4.61\text{\AA}=\underline{b}_{\underline{c}}(2)=\underline{c}_{\underline{c}}(4)$, where $\underline{N}=8,40$ are the numbers of electrons per crystal cell \underline{a} , and $\underline{b}_{\underline{c}}, \underline{c}_{\underline{c}}$ are the cubic primitive cells of the $\underline{b}, \underline{c}$ correlations. This proposal equals just the classical model when it is assumed that \underline{b} and \underline{c} form a united correlation $(\underline{b} \vee \underline{c})$. In this case every O is in fact surrounded by 8 $\underline{b} \vee \underline{c}$ electrons although $\underline{b} \vee \underline{c}$ is not fully occupied. Since the $\text{Li}2s^1$ electrons compensate the electron spins of the O atoms they are named valence electrons or unpaired electrons, however, they are in the \underline{b} correlation while the $\text{O}2sp$ electrons are in the \underline{c} correlation. The distance $\underline{d}_b(\text{Li}_2\text{O})$ is essentially smaller than $\underline{d}_b(\text{Li})$ because of the additional bonding introduced by the O atoms (Fig.1). The low occupancy of the above binding may be the cause for the stability of a rhombohedral phase with $a=90.16^\circ$:

$$\text{Li}_2\text{O}(\text{R8.4,SR46.228}), \underline{a}(\underline{N}=24,120)=\text{H}6.53; 7.96\text{\AA}=\underline{b}_{\text{CH}}(2;6/3)=\underline{c}_{\text{CH}}(4;9/3)$$

allowing full occupation of $\underline{b} \vee \underline{c}$.

$\text{LiO}(\text{H4.4,SR21.233})$ is less stable than Li_2O as judged from the melting temperature 700K (75Pie). The spin compensation is here partly between the O atoms so that ions O_2^{2-} are formed (peroxide ions). These have their molecule axis parallel to \underline{a}_3 and form a site set of the Mg type with Li in octahedral and triangular holes. The chemical formula is not written Li_2O_2 , since other structural phenomena also caused by lower correlations are not described either by the chemical formula (for instance the ferromagnetism). $\underline{a}(\underline{N}=4,8+24)=\text{H}3.14, 7.60\text{\AA}=\underline{b}_{\text{CH}}(1;6/3)=\underline{c}_{\text{CH}}(2;9/3)$ allowing full occupation of $\underline{b} \vee \underline{c}$. The underoccupation of \underline{b} is indicative for a united correlation. The binding explains also the remarkable homeotypism of the cells of $\text{Li}_2\text{O}(\text{R})$ and LiO . Furthermore the matrix element 9/3

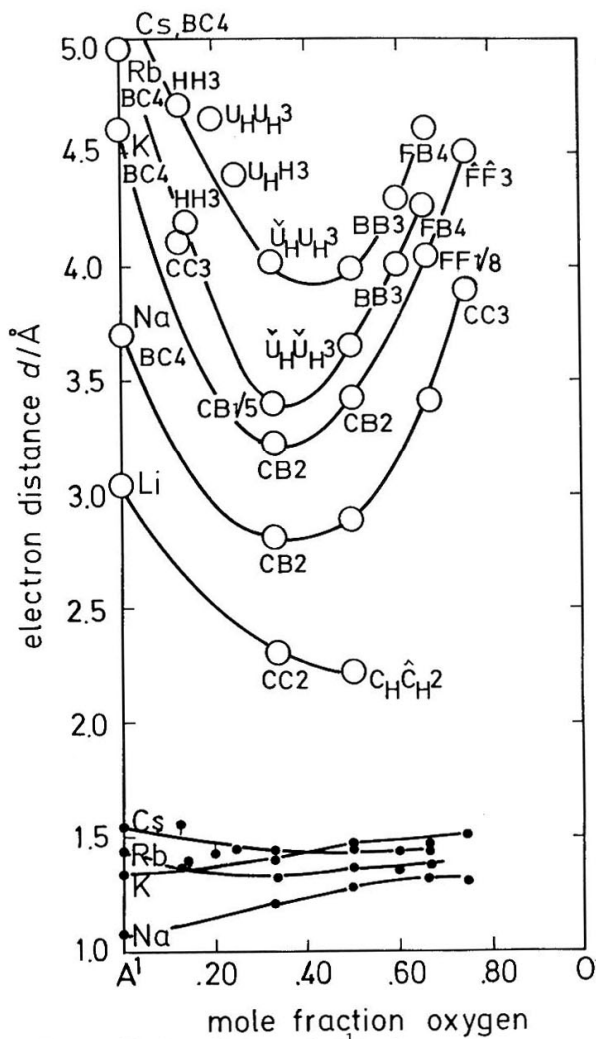


Fig. 1 Electron distances in A_1O_M phases

favours the Mg type packing of the O_2 following the rules of 84Sch.

$LiO_2.l(0...,75Pie), \underline{a}=5.91;4.94;4.38\text{\AA}$ needs further analysis.

$Na(W,SR1.33)$ may have the binding $\underline{a}(N=2,16)=4.29\text{\AA}=\underline{b}_B(1)=\underline{c}_C(4)$ (74Sch). The site number ratio $\underline{N}_{S(C)}^{S(b)}/\underline{N}_{S(C)}=32$ is large as the $Na2sp$ shell is a weakly bonding noble gas shell and the single $Na3s^1$ electron cannot provide much more bonding. The ratio will be strongly lowered in the subsequent oxide but the ratio decrease is stopped near the mole fraction $\underline{N}'_O=0.33$ (Fig.1). Since the electron distance \underline{d}_C is fairly independent on \underline{N}'_O (Fig.1), the site number decrease causes a decrease of volume per Na explaining by means of the virial theorem the high reactivity between Na and water.

$Na_2O(CaF_2,SR3.283)$ cannot be completely isodesmic with Li_2O because of the $Na2sp$ electrons. It appears suggestive that the $Na2sp$ electrons and the $O2sp$ electrons form a common \underline{c} correlation. The electron distance \underline{d}_C must be intermediary between $\underline{d}(Na2sp)$ and $\underline{d}(O2sp)$ (see83Sch) so that $\underline{a}(N=8,64+24)=5.56\text{\AA}=\underline{b}_C(2)=\underline{c}_B(4)$. This binding is homeotypic to that of Li_2O , but the similarity to the classical Lewis binding has decreased since the O atoms are essentially surrounded by 6 electrons. This heterodesmism to Li_2O corresponds to the heterotypism of the subsequent peroxides. The CB2 binding should be generally self-deformed but the union between \underline{b} and \underline{c} may suppress the phenomenon. The partial occupation of $\underline{b}^v\underline{c}$ corresponds to the partial occupation of \underline{c} in Na. The bindings for the remaining $NaO_{\underline{M}}$ phases are more tentative but fit well to the $\underline{d}_{\underline{b},\underline{c}}(\underline{N}'_O)$ relation (Fig.1).

$NaO.r(H6.6,SR21.234)$ is homeotypic to NiAs with Na in As sites and with the commensurability $\underline{a}=\underline{a}_{NiAs}(\sqrt{3};1)$. The Ni sites occupied by O undergo an I-homeotypism by the peroxide ion formation required by spin compensation between two O atoms. The binding may be $\underline{a}(N=6,84)=H6.21;4.47\text{\AA}=\underline{b}_{UH}(2;2/2)=\underline{c}_{CH}^v(\sqrt{12};8/3)$. The \underline{b} correlation is somewhat underoccupied, perhaps \underline{b} electrons are contributed by \underline{c} . The matrix element $(\underline{c}^{-1}\underline{a})_{33}=8/3 \times 3$ favours the observed Mg type stacking of Na, and the \underline{c}_{UH}^v correlation allows good spin compensation. Two additional phases $NaO.h(SR26.348)$ and $NaO.m(SR26.348)$ are not yet well enough known to

allow binding analysis.

$\text{NaO}_2 \cdot r(\underline{T} > 223\text{K}, \text{C4.8}, \text{SR17.380})$ is homeotypic to $\text{FeS}_2 \cdot h$ with rotational disorder of O_2 . $\underline{a}(\underline{N}=4,80)=5.49\text{\AA}=\underline{b}_C(\sqrt{2.6};1.5)=\underline{c}_B(\sqrt{13};3.6)$. The binding of a somewhat artificial CB/5 type is compatible with $\underline{b} \cdot \underline{c}$ union. At $192 < \underline{T} < 223\text{K}$ $\text{NaO}_2 \cdot 1_1(\text{FeS}_2 \cdot h)$ isodesmic to r has been found and at $43 < \underline{T} < 192\text{K}$ $\text{NaO}_2 \cdot 1_2(02.4, \text{FeS}_2 \cdot r, \text{SR17.380})$ with the tentative binding $\underline{a}(\underline{N}=2,40)=4.26;5.57;3.44\text{\AA}=\underline{b}_C(1.5;2;1)=\underline{c}_B(3;4;2)$. The \underline{c} correlation is strained by \underline{b} and few electrons are excited to \underline{b} . Presumably the \underline{c} correlation has a better commensurability to the cell than in r .

$\text{NaO}_3(\text{U7.21}, \text{SR29.416}, 27.482)$ the sodium "ozonide" is coloured dark red and might have the binding $\underline{a}(\underline{N}=14,364)=11.65;7.66\text{\AA}=\underline{b}_C(3;2)=\underline{c}_C(9;6)$. Unfortunately the atom sites appear to be not yet well-known. The low occupancy of \underline{c} may have to do with the paramagnetic susceptibility (75Ebs) caused by uncompensated spins.

$\text{K}(\text{W}, \text{SR1.34})$, $\underline{a}(\underline{N}=2,16)=5.32\text{\AA}=\underline{b}_B(1)=\underline{c}_C(4)$.

$\text{K}_2\text{O} \cdot r(\text{CaF}_2, \text{F1.2}, \text{SR3.283})$ is a colourless phase isodesmic with Na_2O , $\underline{a}(\underline{N}=8,88)=6.44\text{\AA}=\underline{b}_C(2)=\underline{c}_B(4)$.

$\text{K}_2\text{O} \cdot h_1(\text{C48.24}, 75\text{Pie})$ and $\text{K}_2\text{O} \cdot h_2(\text{R48.24}, 75\text{Pie})$ may be caused by a temperature dependent \underline{b} contribution and should be discussed when they are better known.

$\text{KO}(\text{Q4.4}, \text{SR21.235})$ formed by thermal decomposition of K_2O , is homeotypic to CaF_2 with O_2 replacing Ca. Since the O_2 molecules alternate in direction the structure becomes orthorhombic. $\underline{a}(\underline{N}=8,112)=6.74;7.00;6.48\text{\AA}=\underline{b}_C(2)=\underline{c}_B(4)$. Once more the homeotypism of $\text{K}_2\text{O} \cdot r$ and KO is remarkable.

$\text{KO}_2 \cdot r(\text{CaC}_2, \text{U1.2}, \text{SR19.351}, \text{drw 64Schp222})$ is an ordered NaCl type structure of K and O_2 . The binding may be $\underline{a}(\underline{N}=2,40)=4.03;6.70\text{\AA}=\underline{b}_{\text{FU}}(1;2)=\underline{c}_{\text{FU}}(\sqrt{8};6/2)$, it has the site number ratio $\underline{N}_{\text{S}(\underline{c})}^{\text{S}(\underline{b})}=24$ between 16 of CB2 and 27 of FF3 (see below).

$\text{KO}_2 \cdot h(\text{NaCl}, \text{SR16.213})$ $\underline{a}=6.09\text{\AA}$ is homeodesmic to r .

$\text{KO}_2 \cdot 1_1(\text{SR42.231})$ and $\text{KO}_2 \cdot 1_2(\text{N2.4}, \text{SR42.231})$ shall not be discussed here since the structures are not well enough known.

$\text{KO}_3(\text{U4.12}, \text{SR28.118})$ the "ozonide" is homeotypic to CsCl with O_3 in Cl sites and $\underline{a}=\underline{a}_{\text{CsCl}}(2)$. The binding may be $\underline{a}(\underline{N}=8,208)=8.60;7.08\text{\AA}=\underline{b}_{\text{FU}}(2;2/2)=\underline{c}_{\text{FU}}(6;6/2)$. The FF3 binding has not a good spin compensation, the little strain in \underline{a}_3

direction provides a better spin compensation in the (001) plane. Remarkably $\underline{b}\underline{v}\underline{c}$ is fully occupied.

In $\text{RbO}_{\underline{M}}$ and $\text{CsO}_{\underline{M}}$ suboxides become stable (79Simon) since the numerous core electrons of Rb and Cs provide additional metal-metal bonding as compared with $\text{NaO}_{\underline{M}}$ and $\text{KO}_{\underline{M}}$.

$\text{Rb}(\underline{W}, \text{SR1.747})$ may have the binding $\underline{a}(\underline{N}=2,16,20)=5.70\text{\AA}=\underline{b}_{\underline{B}}(1)=\underline{c}_{\underline{C}}'(4)$ where $\underline{c}'=\underline{c}\underline{v}\underline{f}$. The site number of the \underline{c}' correlation is so large that the additional \underline{f} electrons (Rb3d) may easily take part in the C type correlation. The occupancy of $\underline{b}\underline{v}\underline{c}\underline{v}\underline{f}=\underline{g}$ is 0.6.

$\text{Rb}_{6.33}\text{O.m}(\text{F38.6,SR44.182,78Dei,drw ibid.})$ is formed by quenching a melt $\text{Rb}_{\sim 8}\text{O}$ from room temperature to 123K and subsequent heating to 140K. It contains Rb-icosahedra, and the binding may be $\underline{a}(\underline{N}=152,1360,1520)=23.15\text{\AA}=\underline{b}_{\underline{C}}(\sqrt{32};5.6)=\underline{c}_{\underline{C}}'(3/\sqrt{32};17)$. The rare CC3 binding provides 4896 sites with 0.62 occupancy and must be twinned in \underline{a} . The $\underline{c}_{\underline{C}}'$ correlation of Rb is conserved while $\underline{b}_{\underline{B}}$ is changed to $\underline{b}_{\underline{C}}$ yielding the lower site number ratio $\underline{N}_{\underline{S}(\underline{c}')}^{\underline{S}(\underline{b})}=27$. The next suboxide becomes stable since its HH3 binding is homeotypic to the CC3 binding of $\text{Rb}_{6.33}\text{O.m}$.

$\text{Rb}_6\text{O.l}(\text{H24.4,SR42.231,79Sim,drw ibid.p.89})$ is formed peritectoidally from $\text{Rb}+\text{Rb}_9\text{O}_2$ at 265K (79Sim). The structure displays a close packed Rb partial structure with stacking sequence ABCBACBC=ccchccch, and commensurability $\underline{a}_{\text{Rb60}}=\underline{a}_{\text{FH}}(\sqrt{3};8/3)$. The \underline{O} are in octahedral interstices. The binding might be $\underline{a}(\underline{N}=24,216,240)=\text{H8.39;}'\longrightarrow 30.47\text{\AA}=\underline{b}_{\underline{H}}(2;7.3)=\underline{c}_{\underline{H}}'(6;22)$. The \underline{g} correlation is occupied with 0.61 just as in Rb, but the site number ratio $\underline{N}_{\underline{S}(\underline{c})}^{\underline{S}(\underline{b})}$ has dropped from 32 in Rb to 27 as the \underline{O} atoms contract the volume per Rb from 92.6 in Rb to 77.4\AA^3 . The low occupation of \underline{c}' favours formation of clusters in the range of which the occupancy of \underline{c}' is higher. The decrease of $\underline{d}_{\underline{b}}$ will continue up to the Lewis phase Rb_2O . If the number of $\sim 7 \underline{b}_{\underline{H}}$ layers is compared with the number of 8 Rb layers parallel to the basal plane then two sign changes of electrical dipole vector in \underline{a}_3 direction, generated by the \underline{b} correlation, occur. These two changes correspond to the two h values in the stacking symbol ccchccch, so that the rule of stacking (84Sch) is fulfilled. The little deviation of the \underline{b} layer

number of 7.3 instead of 7 leads to stacking defects which are so remote from one another that they escape the structural analysis. In Rb_6O several Rb remain without a contact to an O atom. This is no more so in the next phase. Unfortunately the spin compensation in the H correlation is not good. However, if $(\underline{b}^{-1}\underline{a})_{33}$ has the exact value 7 then a better spin ordering becomes possible as the electron distances near \underline{a}_3 become longer than those near $\underline{a}_1, \underline{a}_2$.

Rb_9O_2 (M18.4, SR43.172, drw ibid, 79Sim) forms peritectically at $T=308\text{K}$ (79Sim), has a close packed Rb partial structure of the ABABCBCAC type and is composed of Rb_9O_2 clusters. The quasi hexagonal $\underline{a}_1, \underline{a}_2$ plane contains 6Rb per cell and there are 3 such layers per \underline{a}_3 axis. The binding is, as in $\text{Rb}_{6.33}\text{O}$ and Rb_6O of the rare three-factorial type $\underline{a}(N=18, 168, 180)=8.35, 0, -2.93; 14.02; 11.31\text{\AA}=\underline{b}_{\text{UH}}(2; 2, -0.7; 2, 2, -0.7; 0, 0, 3/2)=\underline{c}'_{\text{UH}}(6, -6, -2; 6, 6, -2; 0, 0, 9/2)$. There are 24 \underline{b} sites per \underline{a} cell, so that 6 electrons must be excited. There are 648 \underline{c}' sites per \underline{a} cell, so that \underline{c}' has an occupancy of 0.54. A result of the low occupancy of \underline{g} is just as in Rb_6O the cluster or molecule formation. Within the molecule the \underline{g} correlation is better occupied since high occupancy is energetically favourable. Possibly the matrix elements $(\underline{b}^{-1}\underline{a})_{33}$ and $((\underline{c}')^{-1}\underline{a})_{33}$ are somewhat smaller to provide a higher occupancy.

$\text{Rb}_2\text{O.r}(\text{CaF}_2, \text{SR7.85})$ has $\underline{a}(N=8, 88, 80)=6.76\text{\AA}=\underline{b}_{\text{C}}(2)=\underline{c}'_{\text{B}}(\sqrt{20}; 4.5)$. The \underline{g} correlation is nearly fully occupied and must be twinned. The high occupation of \underline{g} is the cause for the sharp increase of $\underline{d}_{\text{b}}(N_0^-)$ (Fig.1). Since \underline{c}' electrons may be excited to the \underline{b} correlation the stability of h phases appears conceivable.

$\text{Rb}_2\text{O.h}_1(\text{C48.24, 75Pie})$ is not yet well-known structurally. The binding might be tentatively $\underline{a}(\text{---} N=48, 528, 480)=12.44\text{\AA}=\underline{b}_{\text{C}}(\sqrt{13}; 3.6)=\underline{c}'_{\text{B}}(\sqrt{65}; 8)$, it could be of the inserted type. The analysis of $\text{Rb}_2\text{O.h}_2(\text{R48, 24, 75Pie})$ must be postponed.

$\text{RbO.r}(\text{P2.2, SR21.236})$ is D-homeotypic to CaF_2 with O_2 on Ca sites, all O_2 being parallel contrary to K0. The binding might be $\underline{a}(N=4, 56, 40)=4.20; 7.08; 5.98\text{\AA}=\underline{b}_{\text{UH}}(1; \sqrt{3}; 2/2)=\underline{c}'_{\text{UH}}(3; 3\sqrt{3}; 6/2)$. The $\underline{b}\underline{c}'$ correlation has a good commensurability to \underline{a} .

Rb_2O_3 (B8.12, SR8.150, drw 64Sch.224) exhibits a Rb site being I-homeotypic to

B1 with inserted O_2 . $a(N=16,272,160)=9.32\bar{A}=b_B(2)=c'_B(6)$. It might be that b is inserted into c' , but the cubic symmetry does not admit self deformation. Another possibility would be lacunae in the Rb site set.

$RbO_2 \cdot r(CaC_2, U1.2, SR7.84, drw 64Sch.222)$ may have the binding $a(N=2,40,20)=4.26; 7.03\bar{A}=b_{F\bar{U}}(1;2)=c'_B(\sqrt[3]{8};4)$. c'_B is strained to yield a better $(c')^{-1}b$ commensurability. The g correlation is nearly full.

$Cs_7O(H21.3, SR42.232, drw 79Sim.91)$ contains on the one hand $Cs_{11}O_3$ molecules formed by three $Cs_{2/3+2/2+2}O$ octahedra having common faces, and on the other Cs atoms which are not coordinated to O atoms. The structure is not compatible with a closest packed Cs partial structure, the heterotypism to RbO_M must come from the possible occupation of Cs4f orbitals or from atomic radius. $a(N=21,186,210)=H16.24; 9.15\bar{A}=b_H(\sqrt[3]{12};2)=c'_H(3/12;6)$. The site number ratio has decreased from $N_{S(c'f)}^{S(b)}=32$ in Cs to 27 in Cs_7O .

$Cs_4O(048.12, SR42.232, drw 76Sim)$ may be understood as a Mg type stacking in a_1 direction of $Cs_{11}O_3$ having Cs atoms in octahedral holes as in the NiAs type. $a(N=48,456,480)=16.83; 20.57; 12.40\bar{A}=b_{UH}(4/2; \sqrt[3]{21}; \sqrt[3]{7})=c'_H(11/2; \sqrt[3]{189}; \sqrt[3]{63})$ is a tentative binding providing $N_{S(c')}^{S(b)}=24$.

$Cs_{11}O_3(M44.12, SR43.173)$ should be analysed later.

$Cs_3O(H6.2, SR20.260)$ has a Cs site I-homeotypic to Mg with $a=a_{Mg}(\sqrt[3]{3};1)$ and with O in octahedral interstices forming chains along a_3 . $a(N=6,60,60)=H8.78; 7.52\bar{A}=b_{UH}(2;2/2)=c'_H(6;5)$. It is surprising that the channels along a_3 being not filled with atoms are partly filled with g sites. It must be assumed that many g electrons are excited to the b correlation and require therefore a U_HU_3 binding.

$Cs_2O(CdCl_2, R2.1, SR20.260, drw SR1.742)$, the Lewis phase, has a Cs site of the Cu type with O in octahedral interstices so that each second layer of interstices parallel to a_1, a_2 (H cell) is filled. $a(N=6,66,60)=H4.26; 18.99\bar{A}=b_{UH}^Y(1;6/2)=c'_{UH}(3;15/2)$. b is filled and favours the observed Cs stacking. The close packed Cs site set fits better to the strong metal-metal bonding than the Cl site set of Rb in Rb_2O .

$\text{CsO}(\text{RbO}, \text{P2.2}, \text{SR21.236})$ is a D-homeotype of CaF_2 with O_2 in Ca site. $\underline{a}(\underline{N}=4, 56, 40)=4.32; 7.52; 6.43 \underline{R}=\underline{b}_{\text{UH}}(1; \sqrt{3}; 2/2)=\underline{c}'_{\text{UH}}(3; 3/\sqrt{3}; 6/2)$. The $\underline{b}_{\text{UH}}$ correlation has in the $\underline{a}_1, \underline{a}_2$ plane the 3-commensurability to the \underline{c}' correlation, leading to $\underline{N}_{\text{S}(\underline{c}')}^{\text{S}(\underline{b})}=27$. Between Cs_2O and CsO the decrease of $\underline{N}_{\text{S}(\underline{c}')}^{\text{S}(\underline{b})}$ with increasing mole fraction \underline{N}_0 goes over into an increase.

$\text{Cs}_2\text{O}_3(\text{Rb}_2\text{O}_3, \text{B8.12}, \text{SR8.150})$ suggests that the Cs6s electrons are inserted into \underline{c}' . $\underline{a}(\underline{N}=16, 272, 160)=9.88 \underline{R}=\underline{b}_{\text{B}}(2)=\underline{c}'_{\text{B}}(6)$. Another assumption could be that vacancies are in the Cs site set.

$\text{CsO}_2(\text{CaC}_2, \text{U1.2}, \text{SR7.85}, \text{drw 64Sch.222})$ is D-homeotypic to NaCl with O_2 in Cl sites. $\underline{a}(\underline{N}=2, 40, 20)=4.43; 7.20 \underline{R}=\underline{b}_{\text{FU}}(1; 2/2)=\underline{c}'_{\text{B}}(\sqrt{8}; 4)$. The site number ratio reaches here the value $\underline{N}_{\text{S}(\underline{c}')}^{\text{S}(\underline{b})}=32$. The consideration of the dependence of $\underline{N}_{\text{S}(\underline{c}')}^{\text{S}(\underline{b})}$ on \underline{N}_0 shows that the value begins to increase when \underline{g} is fully occupied.

$\text{CsO}_3(\text{U5.15?}, \text{SR31.257})$, $\underline{a}=9.73; 8.76 \underline{R}$, binding model cannot yet predict structure.

The alkali oxides apparently contain a \underline{b} band which is only occupied by $\text{A}^{1\text{ns}}_1$ electrons. The $\text{O}2\text{sp}$ electrons accommodate in the \underline{c} band which is also populated by the $\text{A}^1(\text{n-1})\text{sp}$ electrons. Since the O atoms exhibit two uncompensated spins, the Lewis phases A^1_2O become stable in which, using for instance a CB2 binding, all \underline{b} electrons are used for spin compensation. In RbO_M and CsO_M , between A^1 and A^1_2O , suboxides are stabilized by the strong additional bonding provided by the A^13d and A^14d electrons. Here the bonding afforded by the O atoms causes for instance in a HH3 binding an occupation of $\underline{c}'=\underline{c}_{\text{f}}$ greater than in A^1 , the contraction being completed at $\underline{N}_0=0.33$, i.e. in the Lewis phases. The existence of uniform electron spatial correlations in the A^1 suboxides describes well the metallic bonding assumed by 79Simon, while the clusters are an expression for the low occupation of \underline{c}_{f} caused by the weak bonding of $\text{A}^1(\text{n-1})\text{sp}$. For $\underline{N}_0>0.33$ the spins of the O atoms can no longer be fully compensated by \underline{b} electrons so that peroxides and ozonides are formed in which spin compensation occurs partly between O atoms, causing O_2 and O_3 ions in the crystal structures. The stabilizing energy comes here from appropriate harmonies between $\underline{a}, \underline{b}, \underline{c}, \underline{f}$. It appears that \underline{b} and \underline{c}_{f} mostly form a united correlation $\underline{b}\underline{c}_{\text{f}}=\underline{g}$, the ground

correlation, exhibiting a unified lattice-like property of the bonding which is presumably of influence without strongly modifying the partial correlations. The decreased \underline{b} concentration for higher N_0 results in the formation of XX_3 bindings ($X=C, B, F$, etc.) barely occurring in non-alkali oxides. Therefore the A^1O_M phases with exception of Lewis phases are quite specific, i.e. their structures occur rarely in non-alkali mixtures.

A^2O_M phases

$BeO.r(ZnO, H2.2, SR20.261, drw SR1.78)$ obeys Lewis' rule of compensation of the spins near O atoms by the spins near Be atoms. $\underline{a}(N=4, 12+4)=H2.70; 4.38\bar{A}=b_{CH}(\sqrt{0.75; 3.5/3})=c_{CH}(\sqrt{3; 7/3})$. The \underline{b} correlation would be overoccupied. This suggests that \underline{b} is in reality united with \underline{c} . When the \underline{c} layers parallel to $\underline{a}_1, \underline{a}_2$ are smeared out in the $\underline{a}_1, \underline{a}_2$ plane then electro dipoles in \underline{a}_3 direction are formed at the atoms which favour the Mg type stacking of the components (84Sch). At elevated temperatures the O core electrons tend to enter \underline{b}^*c .

$BeO.h(T4.4, SR30.304)$ has an O site set DI-homeotypic to Cu with Be in tetrahedral interstices, it is DI-homeotypic to $BeO.r$. $\underline{a}(N=8, 24+8)=4.75; 2.74\bar{A}=b_c(\sqrt{5; 1.25})=c_c(\sqrt{20; 2.5})$. \underline{b} causes the DI-homeotypism of the O site set to Cu. The CC2 binding allows also here a united \underline{b}^*c correlation, but the occupation is lower than in r .

$Mg(H2, SR1.40, 23.176)$ displays a closest packing of atoms and is compatible with the binding $\underline{a}(N=4, 16)=H3.21; 5.21\bar{A}=b_{CH}(1; 4/3)=c_{CH}(2; 9/3)$. While in Na the site number ratio $\frac{N/S(b)}{S(c)}$ was 32 it is here 9 so that the $\underline{d}_{\underline{b}}$ contraction by oxygen mole fraction increase must be smaller than in A^1O_M phases. The small deformation of c_{CH} yields the matrix element $(c^{-1}a)_{33}=9/3$ causing the Mg type stacking sequence following the stacking rule (84Sch). With respect to the low occupation of \underline{c} the binding will be of the united type. The compression of c_{CH} is presumably necessary to achieve a smooth decrease of \underline{c} sites per atom as compared with Na. Since the presence of O decreases the \underline{c} site number per atom, in the next intermediate phase a CC2 binding is to be expected.

MgO(NaCl,SR21.485) is a colourless Lewis phase and melts at 3070K. $\underline{a}(\underline{N}=8,56)=4.21\text{\AA}=\underline{b}_C(2)=\underline{c}_C(4)$. The CC2 binding was quite rare in A^1O_M because of the small \underline{b} contribution. The united binding $\underline{a}=\underline{g}_C(4)$ is a perfect description of the classical binding proposal assuming the octet of the anions completed by the valence electrons of the cation. However, in other phases obeying Lewis' rule there is no octet completion because the CC2 binding is not probable. Only spin compensation is present which does not need a C type correlation but is possible in other correlations as well. In Na_2O for instance a CB2 binding is assumed providing good spin compensation in the case of a united $(\underline{b}^{\vee}\underline{c})_B$ correlation. Therefore spin compensation should be considered as the basis of Lewis' rule, not octet completion.

$MgO_2(FeS_2.h,SR23.348,drw64Sch.347)$ was prepared by reaction $MgO+85\%H_2O_2$. $\underline{a}(\underline{N}=8,80)=4.84\text{\AA}=\underline{b}_C(\sqrt[5]{5};2.2)=\underline{c}_C(\sqrt[5]{20};4.5)$. The united binding $\underline{a}=\underline{g}_C(\sqrt[5]{20};4.5)$ is nearly fully occupied. The binding $\underline{a}=\underline{b}_C(2)=\underline{c}_C(4)$ would not give an argument for the I-homeotypism of MgO_2 to CaF_2 .

$MgO_4(R_{75Pie})$, $\underline{a}=\underline{H}11.44;12.58\text{\AA}$, discussion is postponed.

$CaO(NaCl,SR11.220)$ $\underline{a}(\underline{N}=8,56,32)=4.81\text{\AA}=\underline{b}_C(2)=\underline{c}_B(4;3)$.

$CaO_2(CaC_2,U1.2,SR20.262)$ $\underline{a}(\underline{N}=4,40,16)=3.56;5.96\text{\AA}=\underline{b}_C(\sqrt[5]{2};2)=\underline{c}_B(\sqrt[5]{8};4)$. The strain of \underline{a} is here not caused by self deformation since probably the correlations are united, it is caused by the O_2 dumb-bells.

$SrO(NaCl,SR1.73)$ $\underline{a}(\underline{N}=8,56,40)=5.16\text{\AA}=\underline{b}_C(2)=\underline{c}_B(4;3.2.5)$,

$SrO_2(CaC_2,SR20.452)$ $\underline{a}(\underline{N}=4,40,20)=3.57;6.62\text{\AA}=\underline{b}_C(\sqrt[5]{2};2)=\underline{c}_B(\sqrt[5]{8};4)$,

$BaO(NaCl,SR19.487)$ $\underline{a}=5.54\text{\AA}$, isodesmic to SrO ,

$BaO_2(CaC_2,SR18.367)$ $\underline{a}=3.81;6.84\text{\AA}$, isodesmic to SrO_2 , CB2.

In BeO_M the CC2 binding is applied to phases with few electrons. In MgO_M the CC2 binding prevails and in heavier mixtures the CB2 binding replaces CC2 because of the participation of \underline{f} electrons in the binding. Union of correlations is possible.

A^3O_M phases

ScO(NaCl,SR29.128) is a grey powder obtained by reduction of Sc_2O_3 with Si, it contains therefore presumably some Si impurity. Since the \underline{e} correlation of the Sc3d electrons enters here, the binding may be $\underline{a}(\underline{N}=4,8,56)=4.45\bar{R}=b_F(1)=\underline{e}_C(2)=\underline{c}_C(4)$. Here \underline{e} could be united with \underline{c} while \underline{b} remains independent. In this case there is no reason for the formation of constitutional vacancies (lacunae).

$\text{Sc}_2\text{O}_3(\text{MnFeO}_3, \text{B16.24, SR1.262, 26.350, drw64Sch.231})$ is a white Lewis phase melting at 2740K. The O are in a part of the tetrahedral interstices of a Sc(F1) site set. As compared with MgO , the A atoms are therefore quasi hexahedrally surrounded by O atoms, $\underline{a}(\underline{N}=32+64,544+256)=9.85\bar{R}=\underline{e}'_B(4)=\underline{c}'_B(8;7)$. The filling of Sc(F1) with more O than in ScO results in the change $(\underline{c}\underline{v}\underline{f})_C \rightarrow (\underline{c}\underline{v}\underline{f})_B = \underline{c}'_B$. The doubling of the lattice constant of ScO in Sc_2O_3 must be caused by the electrostatic moments introduced by the partial filling of the fluorine sites of CaF_2 by O atoms.

$\text{Sc}_2\text{O}_3.p(\text{Sm}_2\text{O}_3, \text{N6.9, 75Pie})$ shall not be considered here.

"Y0(NaCl)" is not stable as the $\text{Y}3d^{10}$ electrons cannot be accommodated in the $\underline{a}=\underline{c}_C(4)$ correlation of ScO.

$\text{Y}_2\text{O}_3.r(\text{MnFeO}_3, \text{SR1.263, 30.309, the so called "C-form" of lanthanon resquioxides, see 75Pie p.69})$ is homologous to Sc_2O_3 : $\underline{a}(\underline{N}=96,544+320)=10.60\bar{R}=\underline{e}'_B(4)=\underline{c}'_B(8;7.5)$, there are 960 g sites for 960 electrons.

$\text{Y}_2\text{O}_3.h_1(\text{Sm}_2\text{O}_3, \text{N6.9, 75Pie, "B-form" of } \text{Ln}_2\text{O}_3)$ will not be discussed here.

$\text{Y}_2\text{O}_3.h_2(\text{La}_2\text{O}_3.h_1, \text{H2.3, 75Pie, "A-form", drw64Sch.229})$ is identical with the Mg_3Sb_2 type. O is in $\hat{\text{C}}_{\text{H}}1$ while Y displays an Mg type site set. As compared with $\text{Y}_2\text{O}_3.r$, the Y atoms remain in a close packing while the O atoms go from a partially occupied undistorted Cl site into a fully occupied strained Cl site. $\underline{a}(\underline{N}=6,34+20)=\text{H}3.6; 5.8\bar{R}=\underline{e}'_{\text{BH}}(1;7.5/3)=\underline{c}'_{\text{BH}}(2;15/3)$. The correlations may be united $\underline{b}\underline{v}\underline{e}\underline{c}\underline{v}\underline{f}=\underline{g}_{\text{BH}}$ and are then fully occupied. The less good commensurability $((\underline{b}\underline{v}\underline{e})^{-1}\underline{a})_{33}=7.5/3$ causes transition into B16.24 at lower temperatures.

$\text{Y}_2\text{O}_3.h_3(\text{Nd}_2\text{O}_3.h_2, \text{H2.3, 75Pie, "H-form" of } \text{Ln}_2\text{O}_3, \text{ see SR} \hat{45.220})$ has more statistically distributed atom sites, $\underline{a}=3.81; 6.09\bar{R}$. For "X-form" see $\text{La}_2\text{O}_3.h_2$.

$\text{La}_2\text{O}_3.r(\text{MnFeO}_3, \text{B16.24, SR7.101, "C-form"})$ $\underline{a}(\text{La}_2\text{O}_3.r, \underline{N}=96,544,320)=11.36\bar{R}=\underline{e}'_B(4)=\underline{c}'_B(8;7.5)$

$$e'_B(4)=c'_B(8;7.5).$$

$La_2O_3 \cdot h_1(H2.3, SR1.744, 17.386, "A\text{-form}"), \quad \underline{a}(N=6, 34, 20)=H3.84; 6.13\text{\AA}=$
 $\underline{b}_{BH}(1;7.5/3)=(\underline{e}^v c)_{BH}(2;15/3).$ The $\underline{e}^v c$ correlation favours the Mg type stacking of La (84Sch).

$La_2O_3 \cdot h_2(Nd_2O_3 \cdot h_2, SR30.309, "H\text{-form}"),$ has La and O statistically distributed on incompletely occupied sites (65Mül). $\underline{a}=H4.06; 6.43\text{\AA}$, the phase is isodesmic to h_1 .

$La_2O_3 \cdot h_3(FhtpW, B1.(1.5), SR45.220, "X\text{-form}" \text{ of } Ln_2O_3),$ has statistically distributed O sites. $\underline{a}(N=6, 34, 20)=4.51\text{\AA}=\underline{e}'_C(2)=\underline{c}'_C(4).$ An excitation might fill $\underline{b}^v e$. The binding may be understood as $\underline{a}=\underline{g}_C(4).$ The strong thermal dilatation favours the CC2 binding against the BB2 binding of the above phases.

Peroxides with A^3 elements would have the composition $A^3_2(O_2)_3=A^3O_3$ and are therefore too anion-rich. In the following mixtures too, peroxides and ozonides are not to be expected. While in A^2O_M CC2 was frequent, here BB2 is the main bonding type. Since in A^2O_M as well as in A^3O_M the united binding is found, the \underline{B}_c correlation provides for the same commensurability more electron sites.

A^4O_M phases

For the mixture TiO_M (recent assessment 87Mur) bindings were proposed (85Sch) which will be somewhat modified here to fit better to the above assumptions. The binding $\underline{a}(Ti.h)=\underline{b}_B(1)=\underline{e}_C(2)=\underline{f}_F(2)$ has in collective form $\underline{a}=\underline{g}_{FF}(\sqrt{8}; 3.4/2)$ the occupancy $\underline{N}^{fs}_g=0.88$. The strain \hat{F} is necessary to provide spin compensation. At lower temperatures the occupancy will be higher:

$Ti.r(Mg, SR1.53), \underline{a}=H2.95; 4.68\text{\AA}=\underline{g}_{CH}(2; 6.5/3),$ or $\underline{a}(1; 2)=\underline{g}_{CH}(2; 13/3), \underline{N}^{fs}_g=0.92.$
 The following suboxides are F-homeotypes of $Ti.r$ with O in octahedral holes. Note the increase of $|\underline{a}_2|/|\underline{a}_1|$.

$$Ti_6O(H12.2, SR31.259), \underline{a}(N=48+108)(\sqrt{3}; 1)^{-1}=H2.97; 9.48\text{\AA}=\underline{g}_{CH}(2; 14/3), \underline{N}^{fs}_g=0.93.$$

$$Ti_3O(H12.4, SR27.484), \underline{a}(N=48+120)(\sqrt{3}; 1)^{-1}=H2.97; 9.53\text{\AA}=\underline{g}_{CH}(2; 15/3), \underline{N}^{fs}_g=0.93.$$

$Ti_2O_{0.8}(CdI_2, SR27.484), \underline{a}(N=8+21)(1; 2)=H2.96; 9.70\text{\AA}=\underline{g}_{CH}(2; 16/3), \underline{N}^{fs}_g=0.91.$ Here \underline{g}_{CH} is no longer strained so that the Ti site set might be transformed to the

Cu type. However, because of the stoichiometry an intermediary phase becomes stable.

$\text{Ti}_2\text{O}(\text{LhtpCoSn}, \text{H}3.3, \text{SR}23.330, 59\text{Now}, \text{drw}64\text{Sch}.310)$ is found below 1310K, and the hexagonal Ti layers have no longer in \underline{a}_3 direction the support number 3, but 1. The binding might be $\underline{a}(\underline{N}=12, 33)=\text{H}4.99; 2.88\hat{\text{R}}=\underline{e}_{\text{BH}}^1(\sqrt{3}; 5/3)=\underline{c}_{\text{CH}}(\sqrt{12}; 5/3)$ or $\underline{a}=\underline{g}_{\text{CH}}(\sqrt{12}; 5/3)$. It suggests that the number of atoms per cell is higher than assumed.

$\text{TiO.h}(\text{LhtpNaCl}, \text{SR}7.87)$ has an atomic occupation $\underline{N}_{\text{At}}^{\text{S}}=0.85(39\text{Ehr})$. $\underline{a}(\underline{N}=13.6, 47.6)=4.18\hat{\text{R}}=\underline{g}_{\text{C}}(4), \underline{N}_{\underline{g}}^{\text{Sg}}=0.96$. The problem of lacunae in TiO , VO , and NbO has been discussed on the basis of atomic clusters (64Schä, 81Sim) and of the band model (84And, 84Schw). These interpretations did not yield an electron count like that above, appearing necessary for the understanding of the phenomenon. At lower temperatures L-ordering homeotypes of TiO.h have been found.

$\text{TiO.r}(\underline{N}5.5, \text{SR}32.254, \text{drw}76\text{Eyr})$ will be isodesmic to TiO.h .

$\text{Ti}_4\text{O}_5(\text{U}4.5, 75\text{Pie}, 68\text{Wat})$, $\underline{a}(\underline{N}=32, 124)=6.59; 4.17\hat{\text{R}}=\underline{g}_{\text{C}}(\sqrt{40}; 4), \underline{N}_{\underline{g}}^{\text{S}}=0.97$. The further decrease of Ti content changes the commensurability and spoils the Cutype O-site set.

$\text{Ti}_2\text{O}_3.\text{r}(\text{Al}_2\text{O}_3, \text{R}4.6, \text{SR}27.484, \text{drw}64\text{Sch}.198)$ is dark violet, melts at 2110K, and has an O site set of the Mg type. $\underline{a}(\underline{N}=48, 204)=\text{H}5.15; 13.64\hat{\text{R}}=\underline{g}_{\text{CH}}^{\wedge}(\sqrt{12}; 21/3), \underline{N}_{\underline{g}}^{\text{S}}=1.00$. The phase is semi-conducting (SR43.175, 77Ric) and 7 \underline{g} layers parallel $\underline{a}_1, \underline{a}_2$ to \underline{a}_3 per 2 O layers favour (84Sch) the Mg type of the O site set. Near 410K a strong increase of $\{\underline{a}_3 \mid \sqrt{3}\} \underline{a}_1$ from 1.523 at 300K to 1.572 at 868K (74Rao) occurs, increasing the \underline{g} site number and allowing metallic electro conductivity.

$\text{Ti}_3\text{O}_5.\text{r}(\underline{N}6.10, \text{SR}23.335, \text{drw}64\text{Sch}.275)$ is L-homeotypic to NaCl with $\underline{a}=\underline{a}_{\text{TiO.h}}$ ($\sqrt{5}; 1$) and allows $\underline{a}(\underline{N}=48, 216)=9.75; 3.80; -0.26, 0, 9.44\hat{\text{R}}=\underline{g}_{\text{C}}(\sqrt{80}; 3.6), \underline{N}_{\underline{g}}^{\text{S}}=0.92$.

$\text{Ti}_4\text{O}_7.\text{r}(\text{Zl}6.28, \text{SR}37.222)$ opens a series of shear homeotypes of TiO_2 (see below), $\text{Ti}_{n\text{O}_{2n-1, 4 \leq n \leq 10}}$ (Magnéli phases, 56And, 60And, 77Mar, 73Mar). The shear is described by coordinates of the cell $\underline{a}_{\text{TiO}_2.\text{r}}^1$. A shear plane \underline{k} divides the crystal into two halves. The shear vector $\underline{s}=[0\bar{1}1]'/2$ acts on the half crystal on the positive side of \underline{k} . It reproduces approximately the O site set,

and may condense the Ti site set. The shear length $l = \frac{[00n]}{k(2)}$ should not lie in \underline{k} , and determines the distance of the second shear plane, Λ from the first Λ before the crystal on the positive side of $k(2)$ is sheared. It may be shown that $(121)'[0\bar{1}1]_Z$ $[00n]'$ leads to the chemical formula Ti_nO_{2n-1} . For $n > 10$ a shear plane $\underline{k} = (132)'$ was found and $16 \leq n \leq 36$ (71Bur). Ti_4O_7 has $\underline{N} = 9.1, 42.3$ so that $\underline{N}/\underline{S} = 0.89$ in the binding noted now for $TiO_2.r$.

$TiO_2.r(T2.4)$, rutile, SR20.263, drw64Sch.275) is a Lewis phase and LDI-homeotypic to NaCl (see also 59Gra, 61Bau, 82Gon, 87Res). $\underline{a}(\underline{N}=8, 40) = 4.59; 2.96 \text{ \AA} = \underline{g}_C(\sqrt{20}; 2.9)$, $\underline{N}_{OC}^g = 0.83$. The low occupation ratio provokes ^{the} compressive crystallographic shears mentioned above. Besides $TiO_2.r$ two metastable phases occur.

$TiO_2.m_1(U2.4)$, anatase, SR38, 241, drw64Sch.275) is obtained by 900°C calcination of hydrated TiO_2 , it is L-homeotypic to NaCl with $\underline{a} = \underline{a}_{NaCl}(1; 2)$. $\underline{a}(\underline{N}=16, 80) = 3.79; 9.51 \text{ \AA} = \underline{g}_C(\sqrt{13}; 9)$, $\underline{N}_{\Lambda}^S = 0.82$. The result that \underline{g} is not filled corresponds to the finding (74Rao) that P^{5+} and S^{6+} stabilize m_1 . Perhaps $TiO_2(H_2O)_M$ contains a stable U2.4 phase.

$TiO_2.m_2(08.16)$, brookite, SR23.343) is S-homeotypic to $FeS_2.h$. $\underline{a}(\underline{N}=32, 160) = 9.18; 5.46; 5.14 \text{ \AA} = \underline{g}_C(\sqrt{26}; 9)$. Here also stabilizers may exist.

$TiO_2.p(PbO_2.m, 04.8)$, SR32.255) contains an O site set of the Mg type, $\underline{a} = \underline{a}_{Mg}(0, 2, -2; 0, 2, 2; 1, 0, 0)$ with Ti in octahedral holes. $\underline{a}(\underline{N}=16, 80) = 4.52; 5.50; 4.94 \text{ \AA} = \underline{g}_{CH}(8/3; 4; 4/2)$, allowing the participation of $Ti2sp$ electrons.

$Zr_3O.h(H2.(0.7))$, SR17.252, 24.202) is homogeneously connected with $Zr.r(65E11)$. $\underline{a}(\underline{N}=8, 20+20) = H3.25; 5.19 \text{ \AA} = \underline{g}_{BH}(2; 13/3)$, $\underline{N}_{\underline{g}}^S = 0.92$. Low temperature phases are:

$Zr_3O_{0.8}(H18.5)$, SR33.119), $\underline{a}(\underline{N}=72, 174+180) = 5.63; 15.59 \text{ \AA} = \underline{g}_{BH}(\sqrt{12}; 38/3)$, $\underline{N}_{\underline{g}}^S = 0.93$.

$Zr_3O(H36.12, 75Pie)$, $\underline{a}(\underline{N}=144, 360+360)(1; 0.5)^{-1} = H5.63; 15.60 \text{ \AA} = \underline{g}_{BH}(\sqrt{12}; 39)$, $\underline{N}_{\underline{g}}^S = 0.92$.

$Zr_3O_{1.1}(H6.2)$, SR33.118), $\underline{a}(\underline{N}=24, 61, 60) = H5.63; 5.19 \text{ \AA} = \underline{g}_{BH}(\sqrt{12}; 13.3/3)$, $\underline{N}_{\underline{g}}^S = 0.91$.

$Zr_2O(H50.24, 75Pie)$ needs further elaboration.

$ZrO.i(NaCl)$, SR18.253) could not be prepared by heating $Zr+ZrO_2$. $\underline{a}(\underline{N}=16, 56, 40) = 4.60 \text{ \AA} = \underline{g}_B(4)$, $\underline{N}_{\underline{g}}^S = 0.88$. The low $\underline{N}_{\underline{g}}^{S(g)}$ requires impurities for stabilization.

$ZrO_2.h_2(CaF_2)$, SR27.480) is a Lewis phase stable for $2560 < T < 2980K$. $\underline{a}(\underline{N}=16, 80, 40) = 5.26 \text{ \AA} = \underline{e}_B'(2) = \underline{c}_B'(4)$. The well fitting binding causes the high thermal stability.

Only the localized binding is possible.

$ZrO_2 \cdot h_1$ (DhtpCaF₂, SR27.480) is stable for 1360 < T < 2560 K. \underline{a} (N=8, 40, 20)=3.64; 5.27 Å = $\underline{e}_B^1(\sqrt{2}; 2) = \underline{c}_B^1(\sqrt{8}; 4)$. Since \underline{e}^1 needs no spin compensation, self deformation must occur. Because \underline{c}^1 is not fully occupied, $ZrO_2 \cdot r$ is formed. For $ZrO_2 \cdot h_1$ an electronic structure has been calculated. But since the exchange-correlation was described by a one electron potential the self-deformation of a BB2 correlation was not uncovered.

$ZrO_2 \cdot r$ (M4.8, baddeleyite, SR23.342, 30.307, drw64Sch.278) forms thin plates. \underline{a} (16, 80, 40)=5.07; 5.20; -0.82, 0, 5.31 Å = $\underline{e}_B^1(3.75/2; 2; 2) = \underline{c}_B^1(3.75; 4; 4)$. \underline{e}^1 is overoccupied with 1 electron per \underline{a} cell. The monoclinic deformation improves the commensurability (\underline{c}^1)⁻¹ \underline{a} . The two different 0 layers parallel to (100) correspond to the half integral property of the commensurability in [100] direction.

$ZrO_2 \cdot p$ (0 4.8, 75Pie), \underline{a} (N=16, 120)=5.07; 5.11; 5.27 Å = $\underline{g}_B^1(4; 4.25)$. Probably the pressure has transformed the localized binding into a collective one.

Hf₆O₉ (H18.3, 72Hir), \underline{a} (N=72, 162+252)=H5.55; 15.30 Å = $\underline{g}_{BH}^1(\sqrt{12}; 42/3)$, $N_Q^S = 0.96$.

Hf₆O₁₁ (Ti₆O, H12.2, 72Hir), $\underline{a} = \underline{a}_{Hf \cdot r}(\sqrt{3}; 2)$, homeodesmic to Hf₆O₉.

HfO₂ · h (CaF₂, SR30.450), \underline{a} (N=16, 80+56)=5.30 Å = $\underline{e}_B^1(2) = \underline{c}_B^1(4)$. The \underline{c}^1 correlation is strongly overoccupied by 8 electrons. Perhaps these are depressed into a lower correlation. This phenomenon presents a serious problem.

HfO₂ · h₁ (ZrO₂ · h₁, SR19.362), $\underline{a} = 5.14; 5.25$ Å, homeodesmic to ZrO₂ · h₁.

HfO₂ · r (ZrO₂ · r, SR23.342), $\underline{a} = 5.12; 5.17; 5.29$ Å, β = 99.18°, hdm ZrO₂ · r.

HfO₂ · p (ZrO₂ · p, 75Pie), $\underline{a} = 5.01; 5.06; 5.22$ Å, hdm ZrO₂ · p.

While all TiO_M phases yield collective bindings, in ZrO₂ and HfO₂ localized bindings emerge because of the numerous electrons in the f correlation below the \underline{c} correlation.

A⁵O_M phases

The bindings proposed (86Sch) for VO_M shall be somewhat modified to fit better to the above assumptions.

V(W, SR26.257), \underline{a} (N=2, 8, 16)=3.02 Å = $\underline{b}_B^1(1) = \underline{e}_C^1(2) = \underline{c}_F^1(2)$ (82Sch). This binding is of the localized type although the low occupation of \underline{c} suggests a collective binding $\underline{a} = \underline{g}_{FU}^1(\sqrt{8}; 3.5/2)$, $N_Q^S = 0.93$. The collective binding is homeotypic to that of Ti.h, see above, and may repeat as $\underline{a}_{Cr \cdot h} = \underline{g}_{FU}^1(\sqrt{8}; 3.58/2)$ and $\underline{a}_{Cr \cdot r}(T28)$ (N=168,

224)=2.88;40.3 \bar{R} = $\underline{g}_{\text{FU}}(\sqrt{8};50/2)$ having an even integral value only at 14($\underline{a}_{\text{Cr.r.}}\rangle_3$. These relations suggest that in $\text{A}^{4..5}$ suboxides at low temperatures fine neutron diffraction details may be hidden.

$\text{V}_8\text{O}(\text{Tl}92.24,74\text{Gu},76\text{Ga})$ is a F-homeotype of V with 0 in quasi octahedral holes and $\underline{a}=\underline{a}_{\text{V}}(4;6)$. The binding may be $\underline{a}(\underline{N}=960,1680)=12.39;17.96\bar{R}=\underline{g}_{\text{FU}}(4\sqrt{8};6\times 3.67/2)$ with $\underline{N}_{\underline{g}}^{\text{S}}=0.94$.

$\text{V}_{16}\text{O}_3(\text{U}32.6,\text{SR}39.210)$ is stable up to 1942K(71Al) with $\underline{a}=\underline{a}_{\text{V}}(4;2)$. $\underline{a}(\underline{N}=320,584)=11.96;6.60\bar{R}=\underline{g}_{\text{FU}}(4\sqrt{8};2\times 3.75/2)$, $\underline{N}_{\underline{g}}^{\text{S}}=0.94$. Conspicuously $2|\underline{a}_3|/|\underline{a}_1|=1.1$ i.e. although $\underline{g}_{\text{FU}}$ is strained \underline{a} is also strained to provide a good spin compensation.

$\text{V}_7\text{O}_4(\text{N}7.4,75\text{Pie},71\text{Cam},\text{drw}71\text{Cam})$ is stable below 1380K and $\underline{a}=\underline{a}_{\text{V}}'(3,0,1,0,1,0;-1,0,2)=9.52;2.95;7.77\bar{R},\beta=90.67^\circ$. The binding may be $\underline{a}_{\text{V}}'(\underline{N}=70,160,\underline{N}'=10,22.8)=2.97;3.56\bar{R}=\underline{g}_{\text{FU}}(\sqrt{8};4)$.

$\text{VO}(\text{LhtpNaCl},\text{SR}18.258)$ has 0.84 of the sites occupied (65Str,830pp.78). $\underline{a}(\underline{N}=16.8,47)=4.09\bar{R}=\underline{g}_{\text{C}}(4)$, the binding of MgO. The number of lacunae in the range of homogeneity is independent on $\underline{N}_{\underline{O}}$. A pressure 50kbar reduces the number of lacunae only by 10% (74Rao).

$\text{VO}_{1,17}(\text{U}...,70\text{And}),\underline{a}=26.08;8.30\bar{R}$ needs further elaboration.

$\text{V}_{13}\text{O}_{16}(\text{U}26.32,70\text{And})$ has an O site set of a full Cu type and $\underline{a}=\underline{a}_{\text{VO}}(\sqrt{8};2)$. $\underline{a}(\underline{N}=260,800)=11.72;8.25\bar{R}=\underline{g}_{\text{C}}(4\sqrt{8};4\times 2)$, the binding is somewhat overoccupied.

$\text{V}_2\text{O}_3.\text{r}(\text{Al}_2\text{O}_3,\text{R}4.6,\text{SR}18.377,\text{drw}64\text{Sch.198})$ is isotypic to $\text{Ti}_2\text{O}_3.\text{r}$. $\underline{a}(\underline{N}=60,204)=44.95$; $\underline{a}_{\text{CH}}=\underline{g}_{\text{CH}}(\sqrt{12};22/3)$, $\underline{N}_{\text{OC}}=1.00$. V_2O_3 is a semiconductor for $\text{T}<151\text{K}$ (74Rao).

$\text{V}_3\text{O}_5(\text{N}6.10,\text{SR}23.337,42.235)$ is homeotypic to $\text{V}_2\text{O}_3.\text{r}$. Discussion is postponed.

$\text{V}_4\text{O}_7(\text{Z}8.14,\text{SR}38.241,39.209)$ is closely homeotypic to Ti_4O_7 and opens the shear homeotype series $\text{V}_{n2n-1}, 4\leq n\leq 8$ (Magnéli phases, references see 86Sch). Phases with $n=4,5,6,8$ undergo metal-insulator transitions (73Kac).

$\text{VO}_2.\text{h}(\text{TiO}_2.\text{r},\text{T}2.4,\text{SR}26.352,\text{drw}64\text{Sch.275})$ may have the binding $\underline{a}(\underline{N}=10,40)=4.53;2.87\bar{R}=\underline{g}_{\text{C}}(\sqrt{20};2.8)$. $\underline{N}_{\underline{g}}^{\text{S}}=0.89$ makes possible the above shear homeotypes.

$\text{VO}_2.\text{r}(\text{MoO}_2,\text{M}4.8,\text{SR}20.264,\text{drw}64\text{Sch.277})$ is I-homeotypic to $\text{VO}_2.\text{h}$ with $\underline{a}=\underline{a}_{\text{h}}(1,0,0;0,1,0;-1,0,2)$. $\underline{a}(\underline{N}=20,80)=4.53;4.52;-2.90,0,5.74\bar{R}=\underline{e}_{\text{B}}'(2;2.5)=\underline{c}_{\text{C}}(4;5)$ as written for the quasi tetragonal cell. Apparently, the \underline{g} correlation of h has precipitated

the $\underline{e}'=\underline{b}\underline{v}\underline{e}$ correlation and the new correlations, choose a new commensurability. The value $N_{\underline{e}}^S=1.0$ corresponds to the insulator property of $V_{0.2}\cdot r(74\text{Rao}, 85\text{Edw})$. The I-homeotypism to h is favoured by $(\underline{c}^{-1}\underline{a})_{33}=5$. The following three phases shall only $\underline{b}\underline{e}$ briefly noted, since they must be homeodesmic to V_2O_5 below.

$V_6O_{13}(N6.13, SR11.296; 37.223, \text{drwSR11.297})$ is a double shear homeotype of ReO_3 (see below) to be described relative to $\underline{a}'_{\text{ReO}_3}$. The first shear is $(001)'[0, 1, -1]'/2[002]'$ and the second $(100)'[-1, 0, -1]'/2[300]'$. A double shear system is more favourable than a simple shear system since the shear planes repelling one another bear a condensation of electron density.

$V_4O_9(016.36, SR35.202, \text{drw70Wil}, \text{see also } 77\text{Gry})$ is homeotypic to V_6O_{13} .

$V_3O_7(N18.42, SR40.177, \text{drw ibid})$ is homeotypic to V_4O_9 .

$V_2O_5(04.10, SR26.353, \text{drw64Sch.278}, \text{change the quality of the atoms in } \pm 1/3, 1/2)$ is a yellow orange Lewis phase melting at 949K. The structure follows from a ReO_3 structure by the 0 expelling shear system $(100)'[-1, 1, 0]'/2[200]'$. The binding may be $\underline{a}(\underline{N}=20, 92)=11.51; 3.56; 4.37\text{\AA}=\underline{g}_C(10; 3; 4)$. The number of 10 \underline{g} layers perpendicular to \underline{a}_1 causes with the 6 atomic layers the sequence of dipole vectors $++--$ which may favour the shears. The following three component phases are homeotypic.

$V_{1.4}\text{Mo}_{0.6}O_5(\text{Nb}_2O_5\cdot m_R, N2.5, SR32.273, \text{drw70Mag.156})$ is D-homeotypic to V_2O_5 . $\underline{a}(\underline{N}=21.2, 92, 34)=11.81, 0, 0.04; 3.65; 4.17\text{\AA}=\underline{g}_C(11; \sqrt{13})$. The binding is slightly overoccupied. The rotation of \underline{g} indicated by $\sqrt{13}$ may cause the monoclinicity.

$V_2\text{MoO}_8(N3.8, SR31.145, \text{drw70Mag.157})$ displays $\underline{a}=\underline{a}_{\text{ReO}_3}(5; 1; 1)$ and yields $\underline{a}(\underline{N}=32, 144, 20)=13.40; 0, -0.02; 3.63; 4.12\text{\AA}=\underline{g}_C(18; \sqrt{13}), N_{\underline{g}}^S=0.84$, see also Nb_3O_7F below.

$\text{Nb}(W, SR1.56)$ $\underline{a}(\underline{N}=10, 16+20)=3.30\text{\AA}=\underline{g}_B(\sqrt{8}; 2.9), N_{\underline{g}}^S=0.99$ The early suboxides are F-homeotypic to Nb, the supercell being caused by the distribution of O atoms.

$\text{Nb}_6O(T128.21, 67\text{Ste}), \underline{a}(\underline{N}/64=10, 18, 20)^{-1}=3.38; 3.23\text{\AA}=\underline{g}_B(\sqrt{8}; 3), N_{\underline{g}}^S=1.0$.

$\text{Nb}_4O(T8.2, 67\text{Ste}), \underline{a}(2; 1)^{-1}(\underline{N}=10, 19, 20)=3.33; 3.33\text{\AA}=\underline{g}_B(\sqrt{8}; 3.25), N_{\underline{g}}^S=0.94$.

$\text{Nb}_2O(T12.6, 67\text{Ste})$ has a cell needing confirmation (75Pie). $\underline{a}(2; 1.5)^{-1}(10, 22, 20)=3.32; 3.21\text{\AA}=\underline{g}_B(\sqrt{8}; 3.33), N_{\underline{g}}^S=0.97$. More compression of B would lead to the U correlation not allowing spin compensation. Therefore a jump of the crystal axial

ratio leads to the next phase.

$\text{NbO}(\text{C}3.3, \text{SR}8.123)$, $\underline{a}(\underline{N}=15, 42, 30)=4.21 \text{\AA}=\underline{g}_{\text{Fu}}^{\text{S}}(4; 6/2)$, $\underline{N}_{\underline{g}}^{\text{S}}=0.91$. The somewhat low occupation suggests that slightly more than Nb_3O_3 are in the cell. This might be related to a supercell $\underline{a}'=\underline{a}_{\text{NbO}}(3)$ reported by 67Ste. Other interpretations for NbO have been advanced by 64Schä, 81Sim, 84And, 84Schw.

$\text{Nb}_2\text{O}_3(\text{H}4.6, 75\text{Pie})$ needs confirmation.

$\text{NbO}_2\cdot\text{h}(\text{TiO}_2\cdot\text{r}, \text{SR}1.158, \text{drw}64\text{Sch}.275)$ is isotypic but probably not isodesmic to $\text{VO}_2\cdot\text{h}$ as is suggested by the fact that $\text{VO}_2\cdot\text{r}$ is heterotypic to $\text{NbO}_2\cdot\text{r}$. $\underline{a}(\underline{N}=10, 40, 20)=4.84; 3.01 \text{\AA}=\underline{g}_{\text{B}}^{\text{S}}(4; 2.5)$, $\underline{N}_{\underline{g}}^{\text{S}}=0.87$, the phase is a metallic conductor (80E11).

$\text{NbO}_2\cdot\text{r}(\text{U}16.32, \text{SR}27.478, 43.175, 45.218)$ is I-homeotypic to $\text{NbO}_2\cdot\text{h}$ with $\underline{a}=\underline{a}_{\text{h}}(\sqrt{8}; 2)$. The binding may be $\underline{a}(\underline{N}=160, 640, 320)=13.70; 5.98 \text{\AA}=\underline{e}'(\sqrt{32}; 2.5)=\underline{c}_{\text{B}}'(\sqrt{128}; 5)$. The \underline{e}' and the \underline{c}' correlation are fully occupied, therefore the binding must be localized. It must be said that the \underline{f} correlation which is also localized is not fully occupied. Since it does not much contribute to conductivity, $\text{NbO}_2\cdot\text{r}$ is a semiconductor (80E11). The subsequent phases are shear homeotypes of ReO_3 .

$\text{NbO}_2\text{F}(\text{ReO}_3, \text{C}1.3, \text{SR}20.223, \text{drw}64\text{Sch}.278)$ is a Lewis phase with Nb octahedrally coordinated by O and F. $\underline{a}(\underline{N}=5, 27, 10)=3.90 \text{\AA}=\underline{g}_{\text{C}}(\sqrt{13}; 3.6)$. The binding $\underline{a}=\underline{g}_{\text{C}}(3)$ was not acceptable because of the monoclinic $\text{Nb}_2\text{O}_5\cdot\text{m}_R(\text{N}2.5)$, see below. Since \underline{g}_{C} is not fully occupied there exists a tendency towards compressive shears (70Wad, 76Eyr). The shears are described in $\underline{a}'_{\text{ReO}_3}$. The shear vector $\underline{s}=[1, 0, -1]'/2$ expels atoms of the sites $\text{O}[\underline{00}\frac{1}{2}, \frac{1}{2}\underline{00}]'$ and condenses $\text{O}[\underline{0}\frac{1}{2}\underline{0}]'$, $\text{Re}[\underline{000}]'$. The vector is applied to the atoms on the positive side of the shear plane $\underline{k}=(001)'$ and changes the condensed site set by the volume $(\underline{s}, \underline{k})\text{det } \underline{a}$. The shear distance $\underline{l}=[\underline{00n}]'$ measured before the second shear is made, determines the shear system, the super cell $\underline{a}=\underline{a}'(1, 1, 2n-1)$ and the composition $\text{Nb}_n\text{O}_{3n-1}$. The slab determined by two ^{successive} shear planes has at its surface an increased \underline{g} electron density. The level of the slab is given by the $\underline{x}_1(\text{Nb})$ coordinate. Because of the repulsion of the shear planes, structures with two orthogonal shear systems \underline{n}' , \underline{n} are stable which contain columns (Fig.2). Structures with three shear systems are not

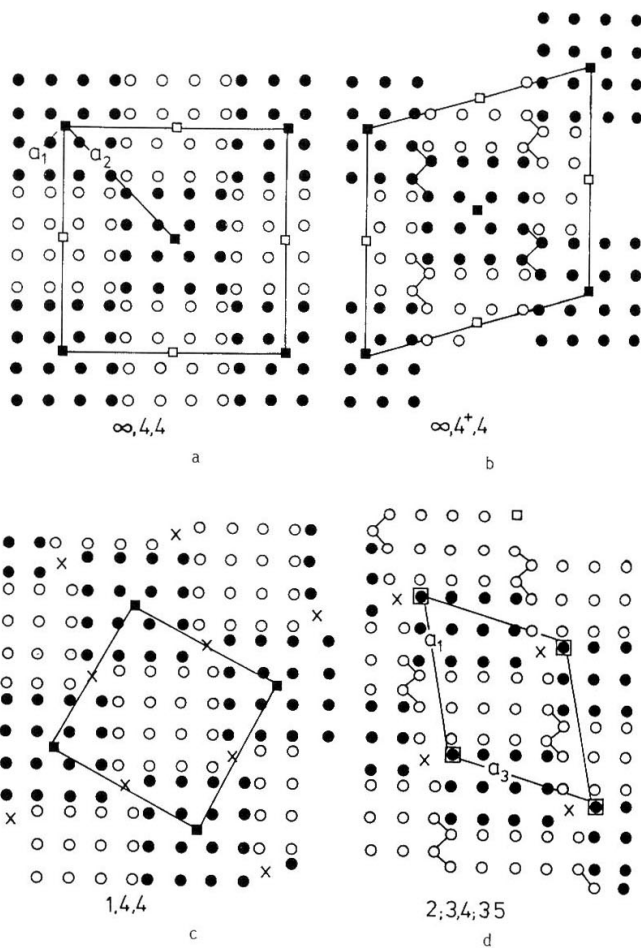


Fig.2 A-atom array in shear homeotypes of ReO_3

(a) $\infty, 4, 4$: $\text{Nb}_2\text{O}_5 \cdot m_M$ (U16.40), (b) $\infty, 4^+, 4$: $\text{Nb}_2\text{O}_5 \cdot m_N$ (N16.40)

(c) $1, 4, 4$: $\text{Nb}_{14}\text{W}_3\text{O}_{44}$ (U17.44), (d) $2; 3, 4; 3, 5$: $\text{Nb}_2\text{O}_5 \cdot h_H$ (M28.70)

squares=possible origins, full circle:A in $\underline{x}_1, \underline{x}_2, 0$

open circle A in $\underline{x}_1, \underline{x}_2, 0.5$, cross A in tetrahedral 0-coordination.

formed because of the binding of $\text{Nb}_2\text{O}_5\text{F}(\text{Cl.3})$. To mitigate the high electron density at the column edge, a volume conserving shear component indicated by + in the second shear system \underline{n}' (Fig.2b) may decrease the energy. A stronger mechanism is the introduction of empty channels parallel to the column edges (Fig.2c). The number of columns per channel is described by the conjunction number \underline{p} (65Rot4) operating after \underline{n}' .

$\text{Nb}_2\text{O}_5\cdot\text{m}_R(\text{N}2.5,66\text{Gru},\text{drw}70\text{Wad})$ is a metastable Lewis phase named R by 66Gru to distinguish several $\text{Nb}_2\text{O}_5\cdot\text{m}$ phases. The structure is generated by $(001)'\{1,0,-1\}'/2[002]'$ from ReO_3 and classified by $\underline{p}\underline{n}'\underline{n}=\infty 2$. $\underline{a}(\underline{N}=20,92,40)=3.98;3.83;-0.05,0,12.79\text{\AA}=\underline{e}_C'(\sqrt{3}.25;6)=\underline{c}_C'(\sqrt{13};2)$ or $\underline{a}=\underline{g}_C(\sqrt{13};2)$. The interaction of the shear with the binding will cause the N-symmetry.

$\text{Nb}_2\text{O}_5\cdot\text{m}_P(\text{U}4.10,65\text{Pet})$ is obtained in form of plates by heating $\text{Nb}_2\text{O}_5\cdot\text{m}_R$ 20h1025K. The cell $\underline{a}_P=3.90;25.43\text{\AA}=\underline{a}_R(1;1;2)$ may yield an improved electrostatic multipole compensation as compared with \underline{a}_R .

$\text{Nb}_3\text{O}_7\text{F}(\text{Q}3.8,\text{SR}29.270,\text{drw ibid.})$ is a Lewis phase of the class $\underline{p}\underline{n}'\underline{n}=\infty 3$. $\underline{a}(\underline{N}=30,146,60)=3.83;3.93;20.67\text{\AA}=\underline{g}_C(\sqrt{13};19)$.

" $\text{Nb}_4\text{O}_9\text{F}_2(\infty 4)$ " conjectured by 70Wad appears less probable since for a larger shear length the ionization of the shear plane increases and this is energetically unfavourable. Also the range of the correlation is finite and forbids too long shear lengths (64Sch.100).

$\text{Nb}_2\text{O}_5\cdot\text{m}_R(\text{U}16.40,\text{SR}35.209,\text{drw}70\text{Wad})$ is S-homeotypic to ReO_3 of the type $\underline{p},\underline{n}',\underline{n}=\infty 4,4$ (Fig.2a) the character M was used by 41Bra to indicate the occurrence of m_M at medium annealing temperatures (3h1200K,70Mer). From Fig.2a it is seen that $\underline{a}_{\text{mM}}(\sqrt{2};1)=\underline{a}'_{\text{ReO}_3}(7;1)$, hence the binding may be $\underline{a}(\underline{N}=160,736+320)(\sqrt{2};1)=20.44;3.83\text{\AA}(\sqrt{2};1)=\underline{e}_C'(\sqrt{174}.25;1.75)=\underline{c}_C'(\sqrt{697};3.5)$, $\underline{N}_g^S=0.99$. The commensurability element $\sqrt{13}=\sqrt{(9+4)}$ yielding for $\text{m}_M \sqrt{(21^2+14^2)}=\sqrt{637}$ has been tentatively replaced by $\sqrt{(21^2+16^2)}=\sqrt{697}$ to obtain a good occupation, similarly as in R instead of $3\times 3.6=10.8$ the commensurability element 12 had to be chosen. The metastability of m_M caused by the unfavourable column edges has the consequence that m_M always exhibits a high defect density (70Mer).

$\sqrt{\text{Nb}_2\text{O}_5 \cdot m_N}(\text{N}4.10, \text{SR}32.257, \text{drw}70\text{Wad. } 13, \text{Fig.}2\text{b})$ is of the type $p, n, n = 4^+4$ where + indicates an additive volume-conserving shear component. Instead of $(010)'[0-11]'/2[040]', (100)'[-101]'/2[400]'$ as in m_M , it is chosen $(010)'[-2-11]'/2[040]', (100)'[-101]'/2[400]'$. The volume conserving shear component -2 dissects the column edges of high electron density into two edges of lower electron density (Fig.2). The phase m_N will be closely homeodesmic to m_M .

$\text{TiNb}_2\text{O}_7(\text{N}3.6.21, \text{SR}26.382, \text{drw}70\text{Wad. } \odot 18)$ is a Lewis phase of the type $\infty 3^+3$.

$\text{Ti}_2\text{Nb}_{10}\text{O}_{29}(\text{N}12.29, \text{SR}26.382, \text{drw}70\text{Wad. } \odot 18)$ is of the type $\infty 4^+3$.

$\text{Nb}_{12}\text{O}_{29}(\text{N}24.58, \text{SR}31.122)$ not obeying Lewis' rule is (66Nor) homeotypic to $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$.

$\text{Ti}_2\text{Nb}_{10}\text{O}_{29}(\text{Q}24.58, \text{SR}26.382, \text{drw}70\text{Wad. } \odot 19, \text{SR}26.385)$ is of the type $\infty 4^+3$ where the volume conserving vector alternates and thus causes orthorhombic symmetry.

$\text{Nb}_{12}\text{O}_{29}(\text{Q}24.58, \text{SR}28.123)$ is homeotypic to $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}(\text{Q}24.58)$. The volume conserving shear is associated with the larger shear length since the highly charged column edges which are nearer together must in first line be weakened. The above given formulae for ∞n phases superpose (65 Rot~~h~~) in the case $\infty 4^+3$ so that the composition is $\text{Nb}_{3 \cdot 4} \text{O}_{3 \cdot 3 \cdot 4 - 3 - 4} = \text{Nb}_{12}\text{O}_{29}$ and the elementary cell $\underline{a} = \underline{a}' \text{ReO}_3$ (6-1;8-1;1). The binding may be $\underline{a}(\underline{N}=240;1080;480)=28.90;3.84;20.72 \text{\AA} = \underline{e}_C'(13.5;1.8;9.5) = \underline{c}_C'(27;3.6;19), \underline{N}_g^S = 0.97$. As a rule, on \underline{n} atom layers perpendicular to \underline{a}_1 or \underline{a}_3 there come $2\underline{n}-1$ \underline{c}' -layers.

A further reduction of the energy of the column edges in $\text{Nb}_2\text{O}_5 \cdot m_M$ may be achieved by introducing a quasi shear using the vector $\underline{s} = [010]'$ on the positive sides of a step surface which causes volume conservation at the part of the surface parallel to $(100)'$ and volume gain at the part of the surface parallel to $(010)'$. The volume gain consists in empty tubes along \underline{a}_3' into which 4 0 forming a tetrahedron must be filled in per \underline{a}_3' to complete the violated 0 octahedra around each Nb and furthermore one A atom to compensate for the newly introduced 0 atoms. The type may also be formed directly from $\infty 44$ by rotating each column around \underline{a}_3' by a certain angle, and may be named $p, n, n=1,4,4$. The

composition of the $\underline{p}, \underline{n}', \underline{n}$ type must be $A_{\underline{p}\underline{n}'+1}^0 3\underline{p}\underline{n}'\underline{n}-\underline{p}(\underline{n}'-\underline{n})+4$ (65Roth, Wadsley 2). This type has been found on the Lewis-section $\text{Nb}_2\text{O}_5(\text{WO}_3)_M$ (65Rot3).

$\text{Nb}_{14}\text{W}_3\text{O}_{44}$ (U17.44, SR30.340) is of the 1,4,4 type, some of the W statistically replace Nb of the parent phase $\infty, 4, 4$, but all tetrahedrally surrounded atoms are W atoms as the W need a lower coordination because of their higher \underline{e}' electron contribution. $\underline{a}(\underline{N}=176, 800, 364)=21.02; 3.82 \underline{x}=\underline{e}'_B(10; 1.8)=\underline{c}'_B(20; 3.6)$. It might be that the small W-content causes the B type of \underline{c}' . A union $\underline{g}=\underline{e}'\vee\underline{c}'\vee\underline{f}$ is possible. The range of mole fractions apart from the Lewis section appears to be unknown so far. The following homeotypes may be mentioned.

$\text{Nb}_9\text{PO}_{25}$ (U9.1.25, SR30.338, drw ibid.) $\underline{p}, \underline{n}', \underline{n}=1, 3, 3$.

$\text{VNb}_9\text{O}_{25}(\text{Nb}_9\text{PO}_{25}, 65\text{Rot1}), \text{Nb}_9\text{AsO}_{25}(\text{Nb}_9\text{PO}_{25}, 65\text{Rot1})$.

$\text{Nb}_{12}\text{WO}_{33}$ (N12.1.33, SR30.342, 65Rot2) $\underline{p}, \underline{n}', \underline{n}=1, 3, 4$.

$\text{Nb}_{16}\text{W}_5\text{O}_{55}$ (N20.1.55, SR30.342, 65Rot2) $\underline{p}, \underline{n}', \underline{n}=1, 4, 5$.

$\text{Nb}_{18}\text{W}_8\text{O}_{69}$ (U25.1.69, SR30.342, 65Rot2) $\underline{p}, \underline{n}', \underline{n}=1, 5, 5$.

Higher $\underline{n}'\underline{n}$ values expected by 75Eyr are improbable because of the finite range of the \underline{e}' correlation.

$\text{Nb}_{25}\text{O}_{62}(\text{TiNb}_{24}\text{O}_{62}(\text{SR30.338}), \text{N25.62, SR31.285, drwSR30.340})$ has the 2,4,3 type. \underline{p} increases the O content while \underline{n}' decreases it.

$\text{Nb}_{31}\text{O}_{77}\text{F}$ (N31.78, SR31.123, drw70Wad, 23) has a 2,3,5 type and has following the Roth-Wadsley formula the composition $A_{2 \times 3 \times 5 + 1} B_{3 \times 2 \times 3 \times 5 - 2(3+5)} + 4$ where B replaces O and F.

$\text{Nb}_2\text{O}_5 \cdot \text{h}_H$ (M28.70, SR29.305, drwSR29.307) was named H by 41Bra as it is the high temperature phase of Nb_2O_5 . It has the type 2;3,4;3,5 i.e. it contains two different column types (Fig.2d). As compared with $\infty, 4, 4$ the shear density is essentially increased (decreasing the O content) and the tetrahedral site density is increased (increasing the O content). The binding analysis should be postponed, but two homeotypes may be mentioned.

$\text{Nb}_{22}\text{O}_{54}$ (M22.54, 66Nor2, drw70Wad, 21) has a 2;3,3;4,2 type.

$\text{Nb}_{34}\text{O}_{48}\text{F}_2$ (see 70Wad) has a 2;3,5;6,2 type. It appears remarkable that the phase of Nb_2O_5 stable at room temperature does no longer belong to the S-homeotypes of ReO_3 .

$\text{Nb}_2\text{O}_5\cdot r_B(\text{N}4.10, 64\text{Lav}, 72\text{Pet})$ is prepared by transport reaction at 900K, and was named B because of its blade-like ideomorphism. It has an Mg type site set for O with Nb in octahedral holes, and therefore an essentially higher density than $\text{Nb}_2\text{O}_5\cdot h(66\text{Sch})$. The binding analysis shall be postponed for r_B and also for $\text{Nb}_2\text{O}_5\cdot \text{ph}_T(\text{O}17.42, \text{SR}41.217)$.

Ta(W, SR1.57, 15.129), $\underline{a}(\underline{N}=10, 16, 28)=3.30\text{\AA}=\underline{g}_B(3)$, $\underline{N}_g^{\prime S}=1.00$. The participation of the Ta4f electrons results in a small electron distance $\underline{d}_g=0.95\text{\AA}$. The first suboxides are F-homeotypic to Ta with O in octahedral holes, and fit to a useful relation of the atomic volume V_{At} to the mole fraction \underline{N}_O (66Ste).

Ta₁₂O(T96.8, 78Mil), $\underline{a}(4;3)^{-1}(\underline{N}=10, 17, 28)=3.34; 3.30\text{\AA}=\underline{g}_B(\sqrt{9.3;3})$, $\underline{N}_g^{\prime S}=0.98$. Note, $9.3 \cdot 16 = 149 = 10^2 + 7^2$, is a harmony of the basal plane.

Ta₆O(Nb₆O, T128.21, 67Ste, 79Hör), $\underline{a}(4)^{-1}(\underline{N}=10, 18, 28)=3.36; 3.26\text{\AA}=\underline{g}_B(\sqrt{9.6;3})$, $\underline{N}_g^{\prime S(g)}=0.97$. Note $9.6 = (12^2 + 3^2)/16$.

Ta₄O(O4.1, SR18.254), $\underline{a}(2;1;1)^{-1}(\underline{N}=10, 19, 28)=3.59; 3.27; 3.20\text{\AA}=\underline{g}_B(3.25;3;3)$, $\underline{N}_g^{\prime S}=0.97$.

Ta₃₂O(B64.18, SR31.251), $\underline{a}(4)^{-1}(\underline{N}=10, 19.4, 28)=3.35\text{\AA}=\underline{g}_B(\sqrt{9.6;3;13})$, $\underline{N}_g^{\prime S}=0.97$.

Ta₂O(B8.4, SR30.312), $\underline{a}(2)^{-1}(\underline{N}=10, 22, 28)=3.34\text{\AA}=\underline{g}_B(\sqrt{10;3;13})$, $\underline{N}_g^{\prime S}=0.96$.

TaO_{0.85}(Lhtp NaCl, SR18.257, 75Pie), $\underline{a}(\underline{N}=20, 52.4, 56)=4.44\text{\AA}=\underline{g}_B(4)$, $\underline{N}_g^{\prime S}=1.00$.

TaO_{1.6}(O40.64, SR38.243, 248) needs further elaboration.

TaO₂·h(TiO₂·r, SR18.257), $\underline{a}(\underline{N}=10, 40, 28)=4.71; 3.07\text{\AA}=\underline{g}_B(\sqrt{18;27})$, $\underline{N}_g^{\prime S}=0.81$.

TaO₂·r(U16.32, SR32.262), $\underline{a}(\underline{N}=160, 640, 448)=13.32; 6.2\text{\AA}=\underline{e}_B^{\prime}(\sqrt{32;2.5})=\underline{c}_B^{\prime}(\sqrt{128;5})$.

Apparently \underline{e}^{\prime} is precipitated from \underline{g} of the h phase.

Ta₂O₅·h(N6.15, pseudoU6.15, SR37.223) has the Ta partly 6-coordinated by O and partly 7-coordinated in a pentagonal bipyramide, $\underline{a}(\underline{N}=60, 276+168)=3.81; 35.97\text{\AA}=\underline{e}_B^{\prime}(\sqrt{2.5;13})=\underline{c}_B^{\prime}(\sqrt{10;26})$. The \underline{c}_B^{\prime} correlation is assumed to be strongly strained to obtain high occupation of the united correlations. If $(\underline{c}^{-1}\underline{a})_{33}=25.5$ the monoclinic deformation could be accounted for.

Ta₂O₅·r(O22.55, SR37.243, drw70Rot, SR37.243) is a member of homeotypic structures found closely together on the Lewis section Ta₂O₅(WO₃)_M(70Rot). These structures have the cell $\underline{a}=6.2; n3.4; 3.9\text{\AA}$ and contain 6 coordinated Ta(octahedra) and 7 coordinated Ta (pentagonal dipyrramids) with main axis of the polyhedra

parallel to \underline{a}_3 . Each pentagon shares two edges with other pentagons. This permits waves along \underline{a}_2 with amplitudes in \underline{a}_1 direction. In the extremal points of the waves the density of A atoms is increased. $\underline{a}(N=110,506+308)=6.20;40.29;3.89\text{\AA}$
 $= \underline{e}_B(2.5;16.5;1.5)=\underline{c}_B^I(5;33;3)$. Since the number of electrons is $N_g=924$ and the number of \underline{c}' sites $N_{S(\underline{c}')}=990$ a united correlation appears possible. It remains to be shown how the $\text{Ta}_2\text{O}_5\text{W}_{0.3}\text{M}_{0.3}$ phases are related to the binding of Ta_2O_5 .r.

Discussion

The investigation of the correlative distribution of electrons in inorganic phases stands in its beginning at present so that improvements certainly must be envisaged. Nevertheless, the rules found so far by the plural correlations model recommend themselves as a promising approach towards a systematic crystal chemistry. The insights provided by this branch of chemistry suggest numerous experimental problems the solution of which will promote our understanding of stability.

At first sight some questions may arise which should be briefly considered.

How is a union of say \underline{b} and \underline{c} possible when the distances \underline{d}_b and \underline{d}_c are quite different? Considering as example $\text{MgO}(\text{NaCl})$, it is clear that a correlation $\underline{a}=\underline{c}_C(4)$ may exist which is fully occupied near the Mg atoms, but only partially occupied near the O. The insertion of one \underline{b} electron into the lacunae of \underline{c} near O is easy but the second \underline{b} electron must be shifted from its position prescribed by $\underline{a}=\underline{b}_C(2)$. The deformation of the \underline{b} correlation although costly provides the remarkable gain by the formation of \underline{g}_C . Since the \underline{b} electrons belong to a band of their own it appears justified to consider the \underline{b} correlation as a proper part of the binding. However, from the simple binding of MgO it cannot be inferred that all Lewis phases have a \underline{c}_C and a \underline{b}_C correlation. Therefore the rigid concept of octet completion should be replaced by the more flexible notion of spin compensation. Since the \underline{g}_C correlation may be occupied by + and - spins following the NaCl type, in the binding of MgO full spin compensation is possible, as it is requested by Lewis' rule.

In the present analysis the change from a united (collective) correlation to an inserted (localized) correlation has been a helpful notion. As the example of $\text{VO}_2 \cdot \text{h} \rightarrow \text{VO}_2 \cdot \text{r}$ shows, this change may cause a so-called metal-insulator transition (74Rae,83Pet,85Edw). Following 71Goo (see also 84Hon) the transformation $\text{h} \rightarrow \text{r}$ is a "cooperative atomic displacement" causing a "band \rightarrow homopolar bond" transition in the following way. In h there is a band of d orbitals having the principal radial extension parallel to the unique crystallographic axis. This band, yielding metallic conductivity in h , splits in r into two bands so that conductivity is stopped and the covalent bonds between two V are formed.

In the present interpretation the d electrons ($\underline{\text{b}}\underline{\text{v}}\underline{\text{e}}$) are at high temperatures in a united correlation together with the $\underline{\text{c}}$ correlation of the $\text{V}3\text{sp}+02\text{sp}$ electrons. It is named $\underline{\text{g}}=\underline{\text{b}}\underline{\text{v}}\underline{\text{e}}\underline{\text{v}}\underline{\text{c}}$, and is not fully occupied i.e. metallic conductive. At the transformation temperature $\underline{\text{b}}\underline{\text{v}}\underline{\text{e}}$ is precipitated from $\underline{\text{g}}$. Both new correlations seek new commensurabilities and both are completely filled so that metallic conductivity is no longer possible. Furthermore the new commensurability causes the I-homeotypism $\text{h} \rightarrow \text{r}$.

It is not surprising that both models are related. To the bands correspond the correlations, to the splitting corresponds the precipitation, to the covalent bonds correspond the commensurabilities. However, the new model is founded upon simpler and earlier concepts: The correlation is a kind of structure, the precipitation is an old experience and the commensurability is an extension of the concept of harmony. Moreover, the simplicity of the new model allows a more comprehensive and more coherent energetical interpretation of the stability of all oxide phases ^{just} as it is desired by the chemist.

Following the chemistry of actinides it is ^{clear} λ that electrons below the peripheral $\text{A}(n-1)\text{sp}$ electrons, like the $\text{Cs}4\text{d}^{10}$ electrons, should take part in the binding. A valence model should provide a reason for the frequently observed heterotypism of $\text{A}3\text{d}$ and $\text{A}4\text{d}$ compounds as for instance $\text{KO}_{\underline{\text{M}}}$ and $\text{RbO}_{\underline{\text{M}}}$ phases. The participation of the low electrons is also satisfactory since in the low electron shells must be a considerable correlation which will influence

the higher shells. The plural correlations model attempts to contribute to the investigation of these relations. It may be conjectured that a systematic crystal chemistry^{of oxides} without regard to the low electrons will not be successful.

The foregoing examples confirm that there is a demand for a further development of the valence theory. The assumptions that an A atom may display different valence numbers depending on composition is merely a mapping of observed compositions into the octet completion rule, the valence number is ^{as} assumed^{to} fulfil Lewis' rule, but it is not made clear why the various valence numbers are stable. What is needed is an independent stability argument. Such an argument has so far neither been advanced by the^{otherwise} useful consideration of atomic radii or charges nor by the^{otherwise} important analysis of the energy bands nor by the calculation of the density functional. However, it is provided in the present model by the rule of harmony of electron correlations with the crystal structure.

Acknowledgement

The author wishes to thank Dr.W.Mader, Stuttgart and Profs.W.Petter, Zürich, M.Rühle, H.G.v.Schnering, Stuttgart, A.Simon, Stuttgart, for valuable informations.

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