

On the bindings in two-component oxides

III.  $A^{11...18}O_M$  phases

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

(Received: February 1988)

#### Summary

The stability of the oxides of  $B^{1...8}(=A^{11...18})$  elements may be interpreted energetically by spatial correlations of electrons when it is assumed that the valence electrons of the shell nsp of the B component form a lattice-like distributed correlation (b) of their own, with cell b, while the (n-1)d, (n-1)sp, and (n-2)d or f electrons of the B component together with the  $O2s^{2,4}$  electrons form a lattice-like core-tied correlation (g), with cell g, being in harmonic commensurability with b and with the crystal cell a. This interpretation amounts to a coherent crystal chemical systematics of the  $B^{1...8}O_M$  phases. The Lewis' rule of octet completion is effective although most Bnsp electrons and the  $O2s$  electrons are not in the same band. The electron spins not compensated in the O atoms enjoy compensation by Bnsp spins. However, the influences described by Lewis' rule are only a part of the bonding, the other parts being provided by the harmonies between the crystal cell a, the cell b, and the cell g. Therefore, phases having no integral oxidation number may become stable. Numerous stability phenomena and structural phenomena in  $B^{1...8}O_M$  phases not understood so far find an energetic explanation and criteria for stability and structures are sharpened. The present systematics suggests many new experiments.

## Introduction

Several new crystal chemical rules for inorganic phases could be formulated using the concepts of the plural correlations model (86Sch), a model contributing to the problem of dependence of stability on electron numbers (02Lew,26Hum). These new rules allowed an analysis of the bonding types (bindings) in the  $A^{1...10}_M$  phases (87Sch, a list of abbreviations used in the present study may be found there). The bindings afford arguments for the stability of compounds and for their structures. The mentioned interpretation of the  $A^{1...10}_M$  phases suggests to seek also an interpretation of  $B^{1...8}_M$  phases reviewed by 72Sam,74Raq,75Pie,82Tro,85Vil and others. A first problem to be solved in a binding analysis is the electron count, i.e. the finding of the numbers of electrons belonging to the various correlations. Electron shells having the same band energy frequently have a common correlation. In cases lacking a calculated bandstructure the electron count must be sought by trial and error; a count yielding good bindings is more probable than a count yielding no bindings. It was a remarkable result of the  $A^{1...10}_M$  binding analysis that here the O2sp electrons were not in correlation with the 3d electrons of an A3d element, but with the 3sp electrons. Following the plural correlations model, in an inorganic phase there must exist on the one hand a valence electron correlation which contributes a part to the bonding, and on the other hand a core electron correlation which must be in harmonic commensurability to the structure and to the valence electron correlation. Strikingly, fairly many electrons were found to take part in the core electron correlation, and this result will be corroborated in the present analysis. The inference of a binding analysis (86Sch) presupposes the knowledge of all incident crystal chemical rules.

Conventionally, the binding in an oxide is described by an oxidation state of the cation which indicates the number of electron pair bonds and the number of lone electron pairs at the cation. Certainly such a description may be understood as an electron spatial correlation proposal as each bond implies a spatial correlation of two electrons and as the localization of a lone pair is also a kind of spatial correlation. However, unfortunately all parts of this conventional spatial correlation proposal are independently correlated and this is far from reality. Actually all bonds and lone pairs are ingredients of an embracing common correlation implying all interactions between bonds and between lone pairs. This common correlation must be lattice-like as it exists in a crystal.

Another shortcoming of the conventional approach to the valence theory of

oxides lies in the electron count. The Lewis rule of octet completion (23Lew) suggests that essentially the valence electrons of the cations and anions are responsible for the bonding. This cannot be the case as there are strong indications for a participation of energetically lower electron shells in the bonding, for instance the site number rule (83Sch). Further confirmations for an extended electron count are contained the binding proposals below.

Most chemists are very faithful to the conventional valence theory. This should be understood as an indication for the importance of a valence model for the every day work of the chemist. The high amount of information in chemistry can become transparent only when the chemist has at hand a guide to the numerous stability rules and structural rules i.e. a systematics with which any fact may be compared. The knowledge of an efficient systematics gives the insight necessary for finding interesting experimental problems. The following binding analysis attempts to contribute to the systematics of the  $B^1 \dots 8 O_M$  phases. It should not be expected that the present coherent binding analysis of the  $B O_M$  phases can interpret all observed phases. The more complicated structures yield only less certain binding proposals and their consideration should therefore be postponed in the present analysis. Also it is clear that the binding proposals found below can be only a first approximation. In phases with Hund insertion (lone pairs) for instance the site of the insertion cannot yet be specified with certainty. Nevertheless, the following binding analysis uncovers numerous new interrelations making the stability problem more transparent.

#### $B^1 O_M$ phases

$Cu_2O.h(C4.2, cuprite, SR1.153, drawing ibid.)$  is a red coloured semiconductor having a higher melting temperature than Cu, decomposing with decreasing temperature at 650K(58Han) and exhibiting a Cu partial structure of the Cu type. Contrary to  $NiO.h(NaCl$  type) the O atoms are in tetrahedral interstices of the metal partial structure as the decreased  $Cu3sp$  radius and the increased  $Cu4s$  radius favour this. The mole fraction  $N'_O=0.33$  of the phase is caused by Lewis' rule (23Lew) requesting the electron spins of the b band ( $Cu4s$ ) to compensate the spins at O caused by Hund's rule (spin pairing, short range ordering of spins). The binding derived by the earlier described methods (86Sch) may be  $a(Cu_2O, N=4, 40, 44, 32)=4.27R=b_B(\sqrt{2}; 1.4)=g_B(4)$ . The electron numbers N are noted for b( $Cu4s$ ), e( $Cu3d$ ), c( $Cu3sp+O2sp$ ), and f( $Cu2sp$ ). The binding assumes 0.4 electrons per Cu excited from the e correlation to the b correlation because of the small energy distance of the b and e bands in Cu. The

excitation depresses the site number ratio  $N_{-S(g)}^{S(b)}$  (86Sch). The spin compensation of Lewis' rule, remarkably, is not spoiled by the excitation, as this generates together a +spin and a -spin. While in NiO the Ni3d electrons formed a correlation of their own, here the Cu3d electrons contribute together with the Cu3sp electrons and O2sp electrons to the ground correlation  $\underline{g}$ . The somewhat sudden transition of the 3d electrons from the separated property in NiO to the united property in Cu<sub>2</sub>O is presumably caused by the influence of Cu4s electrons pressing the  $\underline{g}$  electrons more together. It finds a conspicuous expression in the high gap of miscibility between Cu and Cu<sub>2</sub>O. There is no compulsory indication that the  $\underline{b}$  electrons go over to the anions, spin compensation appears possible also with a fairly uniformly distributed  $\underline{b}$  gas. Although the Cu partial structure of Cu<sub>2</sub>O is the same as that of Cu there is a considerable difference in  $\underline{g}^{-1}\underline{a}$  commensurability. In Cu apparently there is an independent  $\underline{e}_B$  correlation (87Sch2), while in Cu<sub>2</sub>O  $\underline{e}, \underline{c}$  and possibly  $\underline{f}$  are united to form a  $\underline{g}$  correlation. A further insight into the change of correlations is provided by some metastable suboxides of Cu.

Cu<sub>4</sub>O.m(08.2,84qua, drawing ibid.) is formed by annealing electrolytically thinned Cu sheet 2 min at 770K under 2.2 Pa air. It contains a Cu-partial structure of the Cu type with the commensurability  $\underline{a}=\underline{a}_{Cu}(\sqrt{2};1)$ . The two O per cell are in tetrahedral interstices, and the structure may be described by O<sub>F</sub>Cu<sub>F</sub>2, i.e. O is in a compressed F cell, and Cu is in a F cell which must be multiplied by 2 in the directions of the basal plane to be equal to O<sub>F</sub> there. The structure is orthorhombic although the  $\sqrt{2}$ F2 structure might be described in P $\bar{4}$ m2. This suggests that the observed orthorhombic symmetry must be caused by the binding  $\underline{a}(\text{Cu}_4\text{O.m}, N=8, 80, 76, 64)=5.94; 5.66; 4.02 \underline{a}=\underline{b}_B(\sqrt{(29/8)}; \sqrt{(29/8)}; 3.8/\sqrt{8})=\underline{g}_B(\sqrt{29}; \sqrt{29}; 3.8)$ . This binding is the binding of Cu<sub>2</sub>O slightly rotated around  $\underline{a}_3$ , until it falls into a new harmony (83Sch) neighbouring that of Cu<sub>2</sub>O. The  $\underline{g}$  binding is strained in say  $\underline{g}_1$  direction since a  $\underline{b}$  point lies in a quasi octahedron of  $\underline{g}_B$  with small distance in  $\underline{g}_1$  direction. As  $\underline{g}$  is twinned in  $\underline{a}$  ( $\underline{a}=\underline{g}_B(5, \bar{7}, 2, 0; \bar{7}, 5, 0, 0; 0, 0, 3.8)$ ), a strain of  $\underline{a}$  in  $\underline{a}_1$  direction is the observable result. The striking orthorhombic deformation of Cu<sub>4</sub>O.m is therefore a consequence of the binding.

Cu<sub>8</sub>O.m(08.1,84qua2, drawing ibid.) is obtained when electrolytically thinned Cu films are oxidized several days at room temperature in air. The Cu partial structure is once more of the Cu type with O in tetrahedral interstices so that the commensurability is  $\underline{a}=\underline{a}_{Cu}(1, -1, 0; 1, 1, 0; 0, 0, 2)$  and O has a Q lattice site centered on  $\underline{a}_2$ . Also Cu<sub>8</sub>O.m might be tetragonal if the symmetry of the Cu partial structure were decisive, but it is orthorhombic with space group Bmm2. Since the dependence of the atomic volume on the mole fraction



of 0 suggests the composition  $\text{Cu}_{10}\text{O}$  the binding analysis uses tentatively this composition:  $\underline{a}(\text{Cu}_{10}\text{O.m}, \underline{N}=20, 200, 172, 160)=5.47; 6.02; 9.34\text{\AA}=\underline{b}_C(\sqrt{5.2; 4})=\underline{g}_B(\sqrt{26; 26; 8})$  with the same reason for the orthorhombic deformation as in  $\text{Cu}_4\text{O}$ .

$\text{Cu}_{64}\text{O.m}(\text{Q64.1, 85Gua, drw ibid.})$  was obtained similarly as  $\text{Cu}_8\text{O}$  and was found to have the commensurability  $\underline{a}=\underline{a}_{\text{Cu}}(2, -2, 0; 2, 2, 0; 0, 04)$  and 0 in a Q site centered on  $\underline{a}_2$ . The binding may be  $\underline{a}(\text{Cu}_{64}\text{O.m}, \underline{N}=128, 1280, 1036, 1024)=9.74; 10.58; 16.20\text{\AA}=\underline{b}_C(\sqrt{20; 8/2})=\underline{g}_B(10; 16)$ . It allows the orthorhombic deformation of the Cu partial structure, but a participation of Cu2sp electrons appears questionable. In the Cu phase the  $\underline{e}_{\text{vc}}$  correlation of  $\text{Cu}_{64}\text{O}$  seems to be decomposed so that  $\underline{e}$  forms an independent correlation.

$\text{Cu}_8\text{O}_7(\text{U8.7, SR44.187, 78Dat, drw SR44.187})$  is known as a mineral. The Cu partial structure is D-homeotypic to Cu with the commensurability  $\underline{a}=\underline{a}_{\text{Cu}}(\sqrt{2; 2})$ , and the O are approximately in tetrahedral interstices so that  $\text{Cu}_8\text{O}_7$  is IL-homeotypic to PtS. The binding may be  $\underline{a}(\text{Cu}_8\text{O}_7, \underline{N}=16, 160, 212, 128)=5.82; 9.89\text{\AA}=\underline{b}_U(\sqrt{3.2; 3.6})=\underline{g}_B(\sqrt{29; 9})$ . The  $\underline{b}$  correlation accepts 0.4 d electrons per Cu as in  $\text{Cu}_2\text{O.h}$ . The commensurability  $\underline{a}=\underline{a}_{\text{PtS}}(2)$  is caused mainly by the rotated  $\underline{g}$  correlation. The I-homeotypism to PtS is presumably influenced by  $\underline{b}$ . The assumption of interaction of  $\text{Cu}^{++}$  ions (78Dat, 78O'Ke) is confirmed. A self-deformation of the binding is absent perhaps as  $\underline{g}^{-1}\underline{b}$  is not very good in all directions.

$\text{CuO}(\text{N2.2, tenorite, SR3.11, 35.207, 35Tun, 70\text{\AA}sb, drw 64Sch.196})$  forms black crystals D-homeotypic to PtS (64Sch) and the homeodesmism to  $\text{Cu}_8\text{O}_7$  suggests the binding, written for the cell corresponding to the matrix diagonal,  $\underline{a}(\text{CuO}, \underline{N}=4, 40, 56, 32)=4.68, 0, -0.85; 3.42; 5.06\text{\AA}=\underline{b}_B(1.5; 1; 1.7)=\underline{g}_B(4.5; 3; 5)$ . The commensurability  $\underline{g}^{-1}\underline{b}=3$  is favourable and results in a self-straining of the binding in  $\underline{a}_2$  direction. The commensurability element  $(\underline{g}^{-1}\underline{a})_{33}=5$  introduces electric dipoles at the atoms which may cause the monoclinic deformation.

$\text{Ag}_2\text{O}(\text{Cu}_2\text{O, SR1.222})$  is blue black and isodesmic to  $\text{Cu}_2\text{O}$  with  $\underline{a}(\text{Ag}_2\text{O}, \underline{N}=4, 40, 44, 40)=4.74\text{\AA}=\underline{b}_B(\sqrt{2; 1.4})=\underline{g}_B(4)$ . At elevated pressures was found  $\text{Ag}_2\text{O.p}(\text{Cd I}_2, \text{SR28.344})$  yielding the binding  $\underline{a}(\text{Ag}_2\text{O.p}, \underline{N}=2, 20, 22, 20)=\text{H}3.07; 4.94\text{\AA}=\underline{b}_{\text{UH}}(1; 2.2/3)=\underline{g}_{\text{BH}}(2; 15.5/3)$ . Apparently the pressure improves the occupancy of  $\underline{g}$ . The stacking of Ag layers parallel to the basal plane follows the rules of 84Sch.

$\text{AgO}(\text{CuO, SR24.327})$  is black, but the cell differs somewhat from  $\underline{a}(\text{CuO})$ :  $\underline{a}(\text{AgO}, \underline{N}=4, 40, 56, 40)=5.49, 0, -1.76; 3.47; 5.58\text{\AA}=\underline{b}_B(1.6, 1; 1.7)=\underline{g}_B(4.7; 3; 5)$ . The commensurability  $\underline{g}^{-1}\underline{b}$  is conserved as compared with  $\text{CuO}$ , but the  $\underline{a}$  cell requires a slightly different  $\underline{g}^{-1}\underline{a}$ .

$\text{Au}_2\text{O}_3(\text{S4.6, SR45.220})$  is prepared by hydro-thermal synthesis (76Sch) 35d

275°C 0.3kbar. It has an Au partial structure remotely homeotypic to the Pt partial structure of PtO. Also the oxygen coordination to Au is quadratic. The binding might be tentatively  $\underline{a}(\text{Au}_2\text{O}_3, \underline{N}=16, 160, 272, 272)=12.83; 10.52; 3.84\bar{A} = \underline{b}_{\underline{B}}(4; 3.3; 1) = \underline{g}_{\underline{B}}(12; 10; 3)$ . The binding proposal is formed only on electron distance analogy with  $\text{Ag}_2\text{O}$ , and can therefore be not more than a first trial.

Under the bindings occurring in  $\text{B}^{10}\text{O}_M$  are  $\text{BB}/8$  (in  $\text{Cu}_2\text{O}$ ) with the site number ratio  $\underline{N}_{\underline{S}(\underline{b})}^{(\underline{S}(\underline{b}))} = 22.6$ ,  $\text{UB3}$  (in  $\text{Cu}_8\text{O}_7$ ) with  $\underline{N}_{\underline{S}(\underline{g})}^{(\underline{S}(\underline{b}))} = 22.0$  and  $\text{BB3}$  (in  $\text{CuO}$ ) with  $\underline{N}_{\underline{S}(\underline{g})}^{(\underline{S}(\underline{b}))} = 27$ . The best harmony in  $\text{BB3}$  causes  $\text{CuO}$  to be the most stable intermediate phase in  $\text{CuO}_M$ .

### $\text{B}^{20}\text{O}_M$ phases

$\text{ZnO.r}(\text{H2.2, SR1.78})$  obeys Lewis' rule and has a Zn partial structure of the Mg type with O in tetrahedral interstices, while in  $\text{ZnO.p}(\text{NaCl, SR27.475})$  the O are in octahedral interstices presumably as the pressure makes mainly the Zn atoms smaller. From the binding in  $\text{NiO.h}$  (87Sch) may be inferred  $\underline{a}(\text{ZnO.p, } \underline{N}=8, 40, 56, 32)=4.28\bar{A} = \underline{b}_{\underline{C}}(2) = \underline{g}_{\underline{B}}(4)$ . Contrary to  $\text{Cu}_2\text{O}$  there are no d electrons excited as there are more b electrons present. The  $\text{O}2\text{sp}$  electrons are assumed in c so that g is fully occupied. A self-deformation of the binding is not found because of binding twinning in a. At normal pressure, in  $\text{ZnO.r}$  a higher site number of g is aspired. This is possible by admitting instead of 12  $\underline{g}_{\text{BH}}$  chains parallel to  $\underline{a}_3$  now 13 chains (83Sch):  $\underline{a}(\text{ZnO.r, } \underline{N}=4, 20, 28, 16)=\text{H3.25; 5.21}\bar{A} = \underline{b}_{\underline{CH}}(\sqrt{1.1; 4/3}) = \underline{g}_{\text{BH}}(\sqrt{4.3; 16/3})$ . The commensurability element  $(\underline{g}^{-1}\underline{a})_{33} \approx 5$  favours the Mg type stacking of Zn following the rules of 84Sch.  $\text{ZnO.r}$  is a Lewis phase, the  $\text{Zn}4\text{s}^2$  electrons may compensate the spin of the  $\text{O}2\text{s}^2\text{p}^4$  electrons although these electrons are not in the same correlation.

$\text{ZnO}_2.\text{i}(\text{FeS}_2.\text{h, SR23.348})$  is stabilized by  $\text{H}_2\text{O}$  and may have a  $\text{CB2}$  binding in a somewhat different commensurability  $\underline{a}(\text{ZnO}_2.\text{i, } \underline{N}=8, 40, 80, 32)=4.87\bar{A} = \underline{b}_{\underline{C}}(\sqrt{5; 2}) = \underline{g}_{\underline{B}}(\sqrt{20; 4})$ . It has been reported (59Van) that the impurity is  $\text{H}_2\text{O}$ , this would stronger fill the g correlation.

$\text{CdO}(\text{NaCl, SR1.120})$  will be isodesmic to  $\text{ZnO.p}$ :  $\underline{a}(\text{CdO, } \underline{N}=8, 40, 56, 40)=4.695\bar{A} = \underline{b}_{\underline{C}}(2) = \underline{g}_{\underline{B}}(4)$ . The slight overfilling of the g correlation must cause some stoichiometric defect. In fact O lacunae have been found (74Rao, 71Str). Additional g sites may also be formed by a deformation of g in conjunction with g twinning.

$\text{CdO}_2.\text{i}(\text{FeS}_2.\text{h, SR21.237, 23.348})$  is not an exact peroxide. The content in  $\text{H}_2\text{O}$  is less than in  $\text{ZnO}_2.\text{i}$  because of the participation of the  $\text{Cd}3\text{d}$  electrons which might take part in the g correlation.

$\text{HgO}(04.4, \text{SR20.267, drw SR20.267})$  follows Lewis' rule and is I-homeotypic to  $\text{CdO}$  with the commensurability  $\underline{a} = \underline{a}_{\text{CdO}}(\sqrt{2; 1; 1/\sqrt{2}})$ . The binding will be  $\underline{a}(\text{HgO, } \underline{N}=$

8,40,56,56)=6.61;5.52;3.52 $\bar{A}$ = $\underline{b}_A(2\sqrt{2};2\sqrt{2})=\underline{g}_B(4\sqrt{2};4.8;2\sqrt{2})$ . From the full occupation of the binding of ZnO.p follows that the binding of this phase is not possible for HgO because of the participation of the Hg4f<sup>14</sup> electrons in  $\underline{g}$ . The heterotypism of the binding of HgO to that of CdO lies in the commensurability element  $(\underline{g}^{-1}\underline{a})_{22}=4.8$  which introduces an I-homeotypism into HgO. The correlation displays self-deformation because of the harmony  $\underline{g}^{-1}\underline{b}=(2)$ .

HgO.m(HgS,H3.3,SR22.303,drw.64Sch.206) is formed from an aqueous solution and transforms at 200°C irreversibly to HgO(04.4). The binding may be  $\underline{a}(\text{Hg } 0.m, \underline{N}=6,30,42,42)=\text{H}3.58;8.68\bar{A}=\underline{b}_{CH}(1;6/3)=\underline{g}_{UH}(\sqrt{12};10/2)$ . The  $\underline{g}_{UH}$  correlation gives more sites than a  $\underline{g}_{BH}$  correlation with corresponding commensurability. The so called peroxides have not exactly been proven to be two-component phases, their preparation method (SR23.348) suggests OH content. They are HgO<sub>2</sub>.i<sub>1</sub>(R3.6,SR23.348) and HgO<sub>2</sub>.i<sub>2</sub>(04.8,SR23.349). The following bindings are probable  $\underline{a}(\text{HgO}_2.i_1, \underline{N}=18,90,180,126)=\text{H}6.70;8.21\bar{A}=\underline{b}_{CH}(2;6/3)=\underline{g}_{BH}(4;24/3)$ , the little overoccupation of  $\underline{g}$  may be compensated by O lacunae, and  $\underline{a}(\text{HgO}_2.i_2, \underline{N}=8,40,80,56)=6.08;6.01;4.80\bar{A}=\underline{b}_C(2.5;2)=\underline{g}_B(5;4)$  with .88 occupancy of  $\underline{g}$ .

In B<sub>2</sub>O<sub>M</sub> phases the CB2 binding predominates with the site number ratio  $\frac{N_S(b)}{N_S(g)}=16$ .

### B<sub>3</sub>O<sub>M</sub> phases

B<sub>6</sub>O(H24.4,75Pie) allows the binding  $\underline{a}(\text{B}_6\text{O}, \underline{N}=96,56)=\text{H}5.40;12.34\bar{A}=\underline{b}_H(\sqrt{12};8)=\underline{c}_{CH}(\sqrt{12};20/3)$ . B<sub>2</sub>O.hp(H36.18,75Pie) is compatible with  $\underline{a}(\text{B}_2\text{O.hp}, \underline{N}=216,108)=\text{H}7.98;9.09\bar{A}=\underline{b}_{UH}(\sqrt{27};8/2)=\underline{c}_{CH}(\sqrt{27};15/3)$ .

B<sub>2</sub>O<sub>3</sub>(H6.9,SR33.258,drwSR33.259) is the Lewis phase of B<sub>0M</sub>. It is colourless and contains B<sub>3/2</sub> triangles. It yields the binding  $\underline{a}(\text{B}_2\text{O}_3, \underline{N}=72,30)=\text{H}4.34;8.34\bar{A}=\underline{b}_{BH}(2;18/3)=\underline{c}_{FH}(4;9/3)$ . The  $\underline{c}$  correlation does not provide spin compensation so that a p modification is probable. B<sub>2</sub>O<sub>3</sub>.p(Q4.6;SR33.259,drwSR33.261) contains B<sub>0</sub><sub>1/2+3/3</sub> tetrahedra, the binding may be  $\underline{a}(\text{B}_2\text{O}_3.p, \underline{N}=96,40)=4.61;7.80;4.13\bar{A}=\underline{b}_A(3.3;5/3)=\underline{c}_B(3.3;5/3)$ .

Al<sub>2</sub>O<sub>3</sub>(R4.6,corundum,SR1.240,25Pau,drw64Sch.198), a colourless high melting Lewis phase, is homeotypic and homeodesmic to MgO(NaCl) but with an O partial structure of the Mg type. The binding may be  $\underline{a}(\text{Al}_2\text{O}_3, \underline{N}=36,204)=\text{H}4.76;12.99\bar{A}=\underline{b}_{CH}(\sqrt{3};12/3)=\underline{c}_{HH}(\sqrt{12};9)$ . H' is a filled H correlation, occupied to .95 and the commensurability element 9 favours following 84Sch an Mg type stacking of the O-layers. Unfortunately H' is not an isometric type but it may be understood as a substitute of a strained  $\underline{c}_C$  correlation.

Al<sub>2</sub>O<sub>3</sub>.m(httpFe<sub>3</sub>O<sub>4</sub>,γ,SR3.338,35Häg,drw64Sch.344) is formed by annealing Al(OH)<sub>3</sub> at 1200K; it has an O partial structure of the Cu type and is homeotypic and

isodesmic to  $\text{MgO}$ ,  $\underline{a}(\text{Al}_{21.3}\text{O}_{32}, \underline{m}, \underline{N}=64, 363)=7.91\text{\AA}=\underline{b}_C(4)=\underline{c}_C(8)$ , and the occupancy of  $\underline{c}$  is only .71, which may cause the metastability. Here also  $\text{Na}_2\text{Al}_{22}\text{O}_{34}(\text{H}2.22.34, \text{SR}2.41)$  should be mentioned which was erroneously named  $\beta\text{-Al}_2\text{O}_3$ . Numerous additional impurity homeotypes of  $\text{Al}_2\text{O}_3$  are known (see 75Pie).

$\text{Ga}_2\text{O}_3.r(\text{Al}_2\text{O}_3, \text{SR}1.242, 32.257)$  is compatible with the binding  $\underline{a}(\text{Ga}_2\text{O}_3, \underline{r}, \underline{N}=36, 120, 204, 96)=\text{H}4.98; 13.43\text{\AA}=\underline{b}_{\text{CH}}(\sqrt{3}; 12/3)=\underline{e}_{\text{BH}}(\sqrt{12}; 45/3)$ . Following this binding proposal  $\text{Ga}_2\text{O}_3.r$  is homeodesmic to  $\text{Al}_2\text{O}_3$ . The discussion of  $\text{Ga}_2\text{O}_3.h(\text{N}4.6, \text{SR}24.319)$  will be postponed here.

$\text{In}_2\text{O}_3.r(\text{MnFeO}_3, \text{B}16.24, \text{SR}24.331, 31.120, \text{drw}64\text{Sch}, 231)$  is a yellow Lewis phase and is LI-hemeotypic to  $\text{CaF}_2$  with the commensurability  $\underline{a}=\underline{a}_{\text{CaF}_2}(2)$ . The binding may be  $\underline{a}(\text{In}_2\text{O}_3, \underline{r}, \underline{N}=96, 320, 544, 320)=10.12\text{\AA}=\underline{b}_{\text{FU}}(4; 6/2)=\underline{g}_C(\sqrt{128}; 11)$ ,  $\underline{b}_{\text{F}}$  does not contain spin compensation but  $\underline{g}_C$  provides a good spin compensation. The site number ratio  $\underline{N}_{\text{S}}^{\text{S}}(\underline{b})/\underline{N}_{\text{S}}(\underline{g})$  approximates the favourable value 16. The loose packing of  $\underline{g}$  suggests the stability of a high pressure phase.

$\text{In}_2\text{O}_3.p(\text{Al}_2\text{O}_3, \text{SR}32.260)$  has the binding  $\underline{a}(\text{In}_2\text{O}_3, \underline{p}, \underline{N}=36, 120, 204, 120)=\text{H}5.49; 14.51\text{\AA}=\underline{b}_{\text{CH}}(\sqrt{3}; 11.2/3)=\underline{g}_{\text{BH}}(\sqrt{12}; 48/3)$  which favours the O layer stacking of the Mg type (84Sch) and needs a little absorption of  $\underline{b}$  electrons by O. The p phase has a higher  $\underline{g}$ -density than the r phase, but its  $\underline{g}$ -occupancy curiously is slightly lower.

$\text{Ti}_2\text{O}(\text{R}4.2, \text{SR}37.220, 75\text{Pie})$ , a sub-oxide becomes stable as the many core electrons of Ti provide additional bonding energy. The binding may be  $\underline{a}(\text{Ti}_2\text{O}, \underline{N}=36, 120, 132, 168)=\text{H}3.52; 37.45\text{\AA}=\underline{b}_{\text{H}}(\sqrt{2.3}; 16)=\underline{g}_{\text{CH}}(\sqrt{7}; 69/3)$ .

$\text{Ti}_4\text{O}_3(\text{M}8.6, 75\text{Pie})$  shall be discussed later.

$\text{Ti}_2\text{O}_3(\text{MnFeO}_3, \text{SR}17.374, 33.262)$   $\underline{a}=10.54\text{\AA}$  is isotypic-isodesmic to  $\text{In}_2\text{O}_3.r$ .

$\text{Ti}_2\text{O}_3.p(\text{Al}_2\text{O}_3, \text{SR}34.239)$   $\underline{a}=\text{H}5.75; 14.85$  is isotypic-isodesmic to  $\text{In}_2\text{O}_3.p$ . In  $\text{B}^3\text{O}_\text{M}$  phases once more the CB2 binding is prominent.

#### $\text{B}^4\text{O}_\text{M}$ phases

In the series of Lewis phases  $\text{Li}_2\text{O}, \text{BeO}, \text{B}_2\text{O}_3, \text{CO}_2$  the valence electron concentration increases and therefore (64Sch.169) the atomic volume increases and the boiling temperature decreases. The phases of  $\text{CO}_\text{M}$  and  $\text{NO}_\text{M}$  and  $\text{OF}_\text{M}$  have molecular structures, the bindings are governed by molecular correlations packed together forming only a weak lattice-like correlation.

$\text{CO.1}_1(\text{H}2.2, \text{SR}3.245)$  is a Mg type packing of CO molecules,  $\underline{a}(\text{CO.1}_1, \underline{N}=20, 8)=\text{H}4.1; 6.8\text{\AA}=\underline{b}_{\text{CH}}(\sqrt{3}; 7/3)$ . When the  $\underline{b}$  layers parallel to  $\underline{a}_1, \underline{a}_2$  are smeared out in the  $\underline{a}_1, \underline{a}_2$  direction then electro-dipoles are generated which favour the Mg type stacking.

$\text{CO.1}_2(\text{C}4.4, \text{SR}2.13)$  is a Cu type packing of CO molecules,  $\underline{a}(\text{CO.1}_2, \underline{N}=40, 16)=$

$5.66\bar{A}=b_c(4)$ . Perhaps the  $\underline{c}$  electrons are contained in the  $\underline{b}$  correlation.

$CO_{2.1}(FeS_{2.1}, SR1.150, 226, 46.228)$  displays linear OCO molecules.  $\underline{a}(CO_{2.1}, N=64, 24)=5.62\bar{A}=b_c(4)=c_F(4)$ .

The molecular structures are in  $B^4O_M$  limited to B2sp elements because of the higher core electron concentration of the B3sp, B4sp and B5sp elements causing a more compact structure.

$SiO_{2.2}(1743...1978K, cristobalite, F2.4, SR1.169, 39.338, 25Wyc, 73Pea, drw64Sch. 200)$  may be prepared by annealing quartz glass at 1830K. It has a Si partial structure of the Si type with 0 near two Si. The loose packing of the structure is an intermediary example between a close packed structure and a molecular structure. The binding may be  $\underline{a}(SiO_{2.2}, N=32, 160)=7.13\bar{A}=b_F(2)=c_F(4)$  yielding the occupancies 100 and .62. Because of this looseness closer packed three component homeotypes become stable like  $KAlO_2$  (SR3.430),  $RbAlO_2$ ,  $CsAlO_2$  (SR29.318). Although the  $c_F$  type is not favourable because of missing spin compensation it may be accepted here with respect to the high equilibrium temperature. In a filled cell octant  $\underline{a}'=\underline{a}(1/2)$  there are 32  $\underline{c}$ -sites and 36  $\underline{c}$ -electrons, therefore  $\underline{c}$  sites in an empty neighbouring  $\underline{a}'$  are partly occupied and forbid  $SiO_2$  to enter there. The correlation  $b_F$  is well compatible with the Si partial structure and the 0 sites appear to be chosen for good spin compensation. It is conceivable that such a loosely packed phase may transform into metastable structures by annealing below 500K, for instance  $SiO_{2.2}m(T4.8, SR3.25, drw64Sch. 200)$  is I-homeotypic to  $SiO_{2.2}$  and will be homeodesmic to  $SiO_{2.2}$ :  $\underline{a}(SiO_{2.2}m, N=16, 80)=4.97; 6.92\bar{A}=b_c(\sqrt{8}/4)=c_{FH}(4; 8/2)$ .

$SiO_{2.1}(1140...1743K, H4.8, tridymite, SR1.203, drwSR1.171)$  is S-homeotypic to  $h_2$  and may have the binding  $\underline{a}(SiO_{2.1}, N=16, 80)=H5.03; 8.22\bar{A}=b_{FH}(2; 4/3)=c_{UH}(4; 9/2)$ . Here  $c_{UH}$  has a better spin ordering than  $c_F$  and favours the changed stacking. The binding analysis of  $SiO_{2.1}m(N24.48, SR24.462)$  should be postponed here.

$SiO_{2.2}r_2(848...1143K, H3.6, SR1.166)$   $\underline{a}=H5.04; 5.46\bar{A}$  will be isodesmic with  $SiO_{2.2}r_1(H3.6, quartz, SR3.21, 30.420, 35Wei, drw64Sch. 200)$ . Both structures contain  $SiO_{4/2}$  tetrahedra like  $h_2$  and  $h_1$ . But the Si partial structure is no longer S-homeotypic to Si, rather Si is in  $\underline{a}_3$  direction supported invariably by two Si. The binding may be  $\underline{a}(SiO_{2.2}r_1, N=12, 60)=H4.91; 5.40\bar{A}=b_{UH}(2; 3/2)=c_{UH}(4; 6/2)$ . The commensurabilities in the  $\underline{a}_1, \underline{a}_2$  plane are as in  $h_2$  and  $h_1$  but in  $\underline{a}_3$  direction the stacking of the electron layers has changed to improve the spin compensation. There has not been attained much improvement of correlation occupancy so that p- and i- heterotypism is possible.

$SiO_{2.2}p_1(N8.16, SR23.340, 59Zol, drwSR23.340)$  is pseudo hexagonal and contains

$\text{SiO}_{4/2}$  tetrahedra forming rings in the  $\underline{a}_1, \underline{a}_2$  plane. The binding may be described in the pseudohexagonal cell  $\underline{a}(\text{SiO}_2.p_1, N=64, 224)=H7.17; 12.38 \text{ \AA}=b_{\underline{UH}}(3; 7/2)=c_{\underline{H}}(6; 10)$ . The occupancy of  $\underline{b}$  is 1.00 while the occupation of  $\underline{c}$  is .62.

$\left\{ \begin{array}{l} \text{SiO}_2.p_2(\text{TiO}_2.r, T2.4, \text{SR}27.675, 62\text{Sti}, \text{drw}64\text{Sch.}275) \text{ is built with } \text{SiO}_{6/3} \text{ octahedra, } \\ \underline{a}(\text{SiO}_2.p_2, N=8, 40)=4.18; 2.67 \text{ \AA}=b_{\underline{FU}}(2; 1.8)=c_{\underline{C}}(4; 2.6). \end{array} \right.$  0.8  $\underline{b}$  electrons per cell descend to the  $\underline{c}$  correlation, therefore  $\underline{b}$  is full and the occupancy of  $\underline{c}$  is .98.

$\text{SiO}_2.i_1(T12.24, \text{SR}23.338, 59\text{Shr}, \text{drwSR}23.339)$  is formed in water at 720K and 1kbar. It contains  $\text{SiO}_{4/2}$  spirals along  $\underline{a}_3$ . The binding may be  $\underline{a}(\text{SiO}_2.i_1, N=48, 240)=7.46; 8.61 \text{ \AA}=b_{\underline{B}}(\sqrt{8}; 3.2)=c_{\underline{B}}(\sqrt{32}; 65)$ . The occupancy of  $\underline{c}$  would be .58.

$\text{SiO}_2.i_2(\text{SiS}_2.p_2, 4, \text{SR}18.361, \text{drw}64\text{Sch.}207)$  was formed in presence of Si and 1kbar  $\text{O}_2$  at 1650K. It is built with  $\text{SiO}_{4/2}$  tetrahedra. The binding may be  $\underline{a}(\text{SiO}_2.i_2, N=16, 80)=4.72; 8.36; 5.16 \text{ \AA}=b_{\underline{U}}(2; 4; 2)=c_{\underline{C}}(4; 7; 4)$ .

$\text{GeO}_{0..1.3}(\text{F}2.(0..2.6), \text{SR}2.262, 18.158, 32\text{Gol})$  needs confirmation since insertion of O into  $\text{Ge}^{\wedge}(\text{Si type})$  appears not very probable, as the  $\underline{c}$  correlation of Ge ( $\underline{a}=b_{\underline{F}}(2)=c_{\underline{B}}(4)$ ) is already filled to 0.62.

$\text{GeO}_2.r(\text{TiO}_2.r, \text{SR}20.263, 56\text{Bau})$  is isotypic to  $\text{SiO}_2.p_2$  and yields  $\underline{a}(\text{GeO}_2.r, N=8, 20, 40, 16)=4.40; 2.86 \text{ \AA}=b_{\underline{FU}}(2; 1.8)=g_{\underline{B}}(4; 2.6)$ . Few  $\underline{b}$  electrons are absorbed by O although the  $\underline{g}$  correlation appears to be highly filled. A band calculation of  $\text{GeO}_2(87\text{Sva})$  showed that the  $\text{Ge}3\text{spd}$  and the  $\text{O}2\text{p}$  electrons have approximately the same energy while the  $\text{O}2\text{s}$  electrons have a lower and the  $\text{Ge}4\text{s}$  electrons a higher energy. Therefore the present trial results are compatible with the band calculations, as electrons with the same energy interact strongly i.e. display a common spatial correlation.

$\text{GeO}_2.h(\text{SiO}_2.r, \text{SR}2.262, 28\text{Zac})$  is formed at  $T > 1320\text{K}$  and yields  $\underline{a}(\text{GeO}_2.h, N=12, 30, 60)=H4.99; 5.65 \text{ \AA}=b_{\underline{UH}}(2; 3/2)=g_{\underline{UH}}(4; 6/2)$ . The occupation of  $\underline{b}$  is 1.00 but  $\underline{g}$  has also an occupancy of 0.94. This suggests that the  $\text{Ge}2\text{sp}$  electrons cannot be essential in the binding of  $\text{GeO}_2.h$ .

$\text{SnO}(\text{PbO}, T2.2, \text{SR}11.238, 41\text{Moo}, \text{drw}64\text{Sch.}201)$  is a blue black suboxide and shows a Sn partial structure of a compressed F1 type with O in tetrahedral interstices forming layers parallel  $\underline{a}_1, \underline{a}_2$ . It yields  $\underline{a}(\text{SnO}, N=8, 20, 28, 20)=3.80; 4.83 \text{ \AA}=b_{\underline{B}}(\sqrt{2.5}; 2)=g_{\underline{B}}(\sqrt{10}; 4)$ . This binding should be compared with  $\underline{a}(\text{ZnS.r}, \text{F}1.1, N=32, 40, 64)=b_{\underline{F}}(2)=c_{\underline{B}}(4)$  being not possible for SnO because of  $\underline{b}$  and  $\underline{g}$ . The commensurability element  $\sqrt{10}$  favours the layered structure as it does not yield easy twinning of the binding relative to  $\underline{a}$  in all directions. The  $\text{Sn}5\text{s}^2$  electrons form a so called lone pair being within the  $\underline{b}$  correlation (41Moo). It may be that the arrangement of the lone pairs in a layer parallel to  $\underline{a}_1, \underline{a}_2$  also favours the T2.2 type, but this lone pair arrangement does not announce

that SnO.p is possible, while the partial occupation of  $\underline{g}$  in SnO immediately suggests the existence of SnO.p. As compared with  $\text{GeO}_2(\text{TiO}_2.\text{r})$  the  $\text{Sn}3d^{10}$  electrons favour a closer packing of the Sn.

SnO.p(17kbar,02:2,SR34.239) displays a Sn partial structure of the Cu type. The O are not in layers as in SnO.r but approximately in octahedral interstices. The binding conforms to the rule of site numbers  $\underline{a}(\text{SnO.p}, \underline{N}=8, 20, 28, 20)=3.83; 3.61; 4.30 \text{ \AA} = \underline{b}_B(16; 1.5; 1.75) = \underline{g}_B(3.2; 3; 3.5)$ . The  $\underline{g}$  correlation is now fully occupied at the expense of integral commensurability elements. These should generate a weak superstructure. The binding analysis of the red SnO.m(08.8,SR26.360,drw76Hul)  $\underline{a}=5.10; 5.72, 11.12 \text{ \AA}$  and of  $\text{Sn}_3\text{O}_4(\text{Z}, \text{SR}32, 509)$  shall be postponed.

$\text{SnO}_2(\text{TiO}_2.\text{r}, \text{SR}20.263)$  is a colourless Lewis phase being closely homeodesmic to  $\text{GeO}_2.\text{r}$ ,  $\underline{a}(\text{SnO}_2, \underline{N}=8, 20, 40, 20)=4.74; 3.19 \text{ \AA} = \underline{b}_{\text{FU}}(2; 2/2) = \underline{g}_B(4; 2.7)$ . The  $\text{Sn}3d^{10}$  electrons make the  $\underline{g}_B$  correlation necessary.

$\text{PbO.h}(04.4, \text{SR}26.360, 61\text{Lec}, \text{drwSR}26.361)$  is yellow and has a Pb partial structure of the Cu type with O near the centres of octahedral interstices. It yields the binding  $\underline{a}(\text{PbO.h}, \underline{N}=16, 40, 56, 56)=5.49; 4.78; 5.89 \text{ \AA} = \underline{b}_B(\sqrt{5}; 2) = \underline{g}_B(\sqrt{20}; 4)$ . The BB2 binding shows self-deformation (87Sch).

$\text{PbO.r}(\text{T}2.2, \text{SR}1.89, 26.360, 24\text{Dic})$  is red and isotypic-isodesmic to SnO with  $\underline{a}(\text{PbO.r}, \underline{N}=8, 20, 28, 28)=3.98; 5.02 \text{ \AA} = \underline{b}_B(\sqrt{2.5}; 2) = \underline{g}_B(\sqrt{10}; 4)$ . Curiously, this binding does not display self-deformation, perhaps at the lower temperature some  $\underline{b}$  electrons descend into the  $\underline{g}$  correlation so that  $\underline{b}$  has in fact a less good commensurability. For instance a kind of domain structure develops which destroys self-deformation.

$\text{Pb}_3\text{O}_4(\text{T}12.16, \text{minium}, \text{SR}11.240, 43\text{Bys}, \text{drw}64\text{Sch}, 201, \text{SR}11.241)$  is red and homeotypic to  $\text{PbO}_2(\text{TiO}_2.\text{r})$ . The binding may be  $\underline{a}(\text{Pb}_3\text{O}_4, \underline{N}=48, 120, 192, 168)=8.82; 6.57 \text{ \AA} = \underline{b}_B(3.5; 2.5) = \underline{g}_B(7; 5)$ . An advantage against PbO may be the commensurability without roots. A low temperature phase  $\text{Pb}_3\text{O}_4.1(012.16, \text{SR}41.212, 75\text{Gav}, \text{drwSR}41.213)$  may be caused by the self-deformation (87Sch) of the BB2 binding.  $\underline{a}(\text{Pb}_3\text{O}_4.1, \underline{N}=48, 120, 192, 168)=9.12; 8.47; 6.57 \text{ \AA} = \underline{b}_B(3.5; 3.5; 2.5) = \underline{g}_B(7; 7; 5)$ . The short BB2 deformation is intermediary between cubic BB2 and long  $\hat{\text{B}}\hat{\text{B}}2$ . The phases  $\text{PbO}_1.41.1.54(08.11, \text{SR}11.243)$ ,  $\text{Pb}_2\text{O}_3(\text{M}8.12, \text{SR}40.300)$  and  $\text{PbO}_1.55.1.66(\text{M}48.78, \text{SR}11.244)$  are homeotypic to  $\text{CaF}_2$  and their discussion shall be postponed here.

$\text{PbO}_2(\text{TiO}_2.\text{r}, \text{SR}2.222, 27.477)$  is brown and splits easily O, it allows  $\underline{a}(\text{PbO}_2, \underline{N}=8, 20, 40, 28)=4.96; 3.38 \text{ \AA} = \underline{b}_{\text{FU}}(\sqrt{4.25}; 2) = \underline{g}_B(\sqrt{17}; 28)$  similar to SnO<sub>2</sub>. The phase  $\text{PbO}_2.\text{p}(\text{CaF}_2, 75\text{Pie}, 68\text{Syo})$  permits the twinned binding  $\underline{a}(\text{PbO}_2.\text{p}, \underline{N}=16, 40, 80, 56)=5.35 \text{ \AA} = \underline{b}_{\text{FU}}(\sqrt{5}; 3.2/2) = \underline{g}_B(\sqrt{20}; 4.5)$  so that  $\underline{g}$  is occupied to .92.

Suboxides prefer BB2 while  $\text{F}_{\text{U}}\text{B}2$  predominates for the Lewis phases in  $\text{B}^*\text{O}_{\text{II}}$ .

For  $\text{SiO}_M$  the missing core electrons provide a lower  $\underline{c}$  occupancy.

### $\text{B}^5\text{O}_M$ phases

$\text{N}_2\text{O}(\text{CO}_2, \text{SR}26.344)$  shows linear NON molecules. The octets of N are completed and the phase is isodesmic to  $\text{CO}_2$ :  $\underline{a}(\text{N}_2\text{O}, \underline{N}=64, 24)=5.67\text{\AA}=\underline{b}_C(4)=\underline{c}_F(4)$ .

$\text{N}_2\text{O}_2(\text{M}4, 4, \text{SR}15.172, 17.370)$  consideration <sup>may be</sup> postponed.

$\text{N}_2\text{O}_3(\text{U}32.48, \text{SR}17.371)$  may have the tentative binding  $\underline{a}(\text{N}_2\text{O}_3, \underline{N}=896, 320)=16.40; 8.86\text{\AA}=\underline{b}_B(10; 5)=\underline{c}_A(20; 10)$ .

$\text{NO}_2(\text{B}6.12, \text{SR}12.146, \text{drw } 64\text{Sch.}202)$  is built of  $\text{N}_2\text{O}_4$  molecules.  $\underline{a}(\text{NO}_2, \underline{N}=204, 72)=7.77\text{\AA}=\underline{b}_C(\sqrt{34}; 6)=\underline{c}_C(\sqrt{68}; 8)$  is a tentative possibility.

$\text{N}_2\text{O}_5(\text{H}4.10, \text{SR}13.230, \text{drw } 64\text{Sch.}203)$ , a very hygroscopic phase, is built of  $\text{NO}_2^+$  and  $\text{NO}_3^-$  molecules. The binding may be  $\underline{a}(\text{N}_2\text{O}_5, \underline{N}=80, 28)=\text{H}5.45; 6.66\text{\AA}=\underline{b}_H(4; 5)=\underline{c}_{\text{CH}}(4; 12/3)$ .

$\text{P}_2\text{O}_5, \text{r}(\text{S}4.10, \text{SR}8.143, \text{drw } 64\text{Sch.}203)$  is built of  $\text{PO}_{1+3/2}$  tetrahedra similar as  $\text{SiO}_2$ . The binding might be  $\underline{a}(\text{P}_2\text{O}_5, \underline{r}, \underline{N}=80, 368)=16.30; 8.14; 5.26\text{\AA}=\underline{b}_C(8; 4; 2.5)=\underline{c}_C(16; 8; 5)$ . The  $\underline{c}$  correlation is occupied to .57.

Numerous other P-oxides shall not be considered here.

$\text{As}_2\text{O}_3, \text{r}(\text{Sb}_2\text{O}_3, \text{r}, \text{F}8.12, \text{SR}2.315, \text{drw } \text{SR}1.245, 240)$  contains an As partial structure of the Cu type with O near the tetrahedral interstices, it is homeotypic to  $\text{In}_2\text{O}_3$  with the commensurability  $\underline{a}=\underline{a}_{\text{In}_2\text{O}_3}(1)$ . The binding may be  $\underline{a}(\text{As}_2\text{O}_3, \underline{r}, \underline{N}=160, 320, 544, 256)=11.07\text{\AA}=\underline{b}_C(\sqrt{32}; 5.5)=\underline{g}_C(\sqrt{128}; 11)$ , it must be twinned. The homeotypism  $\text{In}_2\text{O}_3(\text{MnFeO}_3) \rightarrow \text{Sb}_2\text{O}_3, \text{r}$  comes from the homeodesmism  $\underline{b}_F \rightarrow \underline{b}_C$ . The lone pair of As is not explicitly described in the binding proposal, but the CC2 binding is certainly an important stability argument.

$\text{As}_2\text{O}_3, \text{h}(\text{T} > 383\text{K}, \text{M}8.12, \text{SR}15.193)$  has a greater density than r and the binding may have a smaller site number  $\underline{a}(\text{As}_2\text{O}_3, \text{h}, \underline{N}=40, 80, 136, 64)=5.25, 0, -0.30; 12.87; 4.53\text{\AA}=\underline{b}_B(2; 5; 2)=\underline{g}_B(4; 10; 4)$ . The occupancy of  $\underline{g}$  is .88 while it was in r only .80. The monoclinic deformation is not accounted for.

$\text{As}_2\text{O}_3(\text{O}8.16, \text{SR}46.229)$  contains  $\text{AsO}_6$  and  $\text{AsO}_4$  coordinations. The binding may be  $\underline{a}(\text{As}_2\text{O}_3, \underline{N}=40, 80, 160, 64)=8.60; 7.27; 5.24\text{\AA}=\underline{b}_C(3\sqrt{2}; 2.5\sqrt{2}; 27)=\underline{g}_C(6/2; 5\sqrt{2}; 5.3)$ . Once more the CC2 binding occurs.

$\text{As}_2\text{O}_5, \text{h}(\text{T}8.20, \text{SR}45.216, 79\text{Jan})$  contains infinite As-ribbons in  $\underline{a}_3$  direction, the two As near the axis of the ribbon are in  $\text{AsO}_{6/2}$  while the two As far from the axis are in  $\text{AsO}_{4/2}$ . It yields the binding  $\underline{a}(\text{As}_2\text{O}_5, \text{h}, \underline{N}=40, 80, 184, 64)=8.57; 4.64\text{\AA}=\underline{b}_C(\sqrt{18}; 2.3)=\underline{g}_C(\sqrt{72}; 4.6)$ . Surprisingly the commensurabilities in  $\underline{a}_3$  direction are not integral, this is an example for the rule that for stability a harmony in two directions is already sufficient. The  $\underline{b}$  correlation is practically fully occupied, but  $\underline{g}_C$  is practically fully occupied too. This appears



hard to accept for the channels around the  $4_2$  axes. However, there are several possibilities to remove the difficulty. For instance it might be assumed that the  $f$  electrons, or the  $O2s^2$  electrons do not take part in the  $g$  correlation and this may be partly occupied. Such a problem may be attacked when more such bindings are known.

$As_2O_5$ .r(08.20,SR44.183,78Jan,drw SR44.184) becomes stable below 578K and is D-homeotypic to h. The deformation will be caused by Hund insertion or ordering of spins. How important such phenomena are may be assessed from the cell deformation  $\underline{a}=8.65;8.45;4.63\text{\AA}$ .

$Sb_2O_3$ .r(F8.12,senarmontite,SR9.165,drw SR1.245,2.40) is isotypic-isodesmic to  $As_2O_3$ .r.  $\underline{a}(Sb_2O_3.r,\underline{N}=160,320,544,320)=11.15\text{\AA}=\underline{b}_C(\sqrt{32;5.5})=\underline{g}_C(\sqrt{128;11})$ , the spins of O are compensated with the spins of the  $Sb5p^3$  electrons, while the  $Sb5s^2$  spins are to be assumed to compensate themselves.

$Sb_2O_3$ .h(I>846K,08.12,valentinite,SR14.34,40.175,38Bue,drw 64Sch.204) has a higher density than r. The Sb partial structure of r undergoes a DIS-homeotypism. The binding may be  $\underline{a}(Sb_2O_3.h,\underline{N}=40,80,136,80)=4.92;12.46;5.42\text{\AA}=\underline{b}_B(2;5;2)=\underline{g}_B(4;10;4)$ . It may be assumed that the higher temperature favours a more uniformly distributed correlation. The closer packed B type causes the increase of density, the BB2 binding allows self-deformation to BB2 and the commensurability element  $(\underline{b}^{-1}\underline{a})_{22}=5$  favours the shearing (see 64Sch).

$SbO_2$ (08.16,SR6.114,41.214;43.174,drw SR41.214) has the Sb no more in a close packing and contains  $SbO_{4/2+2/3}$  and  $SbO_{4/3}$  coordination, it is heterotypic to  $AsO_2$ . The binding may be  $\underline{a}(SbO_2,\underline{N}=40,80,160,80)=5.44;4.81;11.76\text{\AA}=\underline{b}_B(2;2;5)=\underline{g}_B(4;4;10)$ , the phase is therefore heterotypic -isodesmic to  $Sb_2O_3$ .h. It appears remarkable that  $\underline{b}$  and  $\underline{g}$  are with 1.00 occupied.

$Sb_6O_{13}$ (F6.13,SR38.241,drw SR2.59) has a Sb partial structure of the Cu type with lacunae and the O in tetrahedral holes also displaying lacunae. The phase is therefore L-homeotypic to  $Sb_2O_3$ .r or to pyrochlor  $Ca_2Ta_2O_7$ (F4.4.14, SR2.60). The binding will be  $\underline{a}(Sb_6O_{13},\underline{N}=120,240,504,240)=10.30\text{\AA}=\underline{b}_C(5)=\underline{g}_C(10)$ . The tight fit of the binding explains why both components cannot show full occupation of their sites.

$Sb_2O_5$ (N4.10,SR45.217,79aJan,drw 79Jan) was prepared from  $SbO_2$  in presence of  $H_2O$  by an anneal 36h,873K,2kbar $O_2$ . It is isotypic to  $Nb_2O_5$ .r(64Lav,drw 72Pet.64) and contains an O partial structure of the Mg type with Sb in octahedral holes. For the binding analysis the cell  $\underline{a}=12.65,0;-1.30;4.78;5.27\text{\AA}$  is transformed into  $\underline{a}'=\underline{a}(1,0,0;0,1,0;2,0,1)$  containing hexagonal O layers in the  $\underline{a}'_1,\underline{a}'_2$  plane. Then the binding may be  $\underline{a}'(Sb_2O_5,\underline{N}=40,80,184,80)=14.55,0,2.95;4.78;4.56\text{\AA}=\underline{b}_{CH}(5;2/2;4/3)=\underline{g}_{CH}(10;4/2;9/3)$ . If  $\underline{g}_C$  were not compressed

i.e.  $\underline{a}' = \underline{g}_{CH}(10;4/2;8/3)$ , the number of  $\underline{g}$  sites would be 320 while 344 electrons are offered. The compression  $\check{CH}$  is fairly easy and probably  $\underline{b}_{CH}$  is also compressed to preserve the favourable harmony. The commensurability  $(\underline{g}^{-1}\underline{a})_{33}=9/3$  is favourable for the Mg type stacking in the 0 partial structure. The strong monoclinic form expressed by  $\underline{a}'_{13}=2.95\text{\AA}$  will have to do with the Sb distribution.

$\text{BiO}(\text{Rl.1,SR30.446})$  was obtained by oxidation of Bi films on NaCl. Also  $\text{Bi}_4\text{O}_5(\text{T8.10,SR37.221})$  and  $\text{Bi}_3\text{O}_4(\text{U6.8,75Pie})$  have been found in films and their consideration shall be postponed.

$\text{Bi}_2\text{O}_3.\text{h}(\text{F1.}(1.5),\delta,\text{SR44.342,78Har})$  is formed at 1002K from  $\text{Bi}_2\text{O}_3.\text{r}$  and melts at 1097K. It contains statistically distributed 0-lacunae, the 0 sites of the ionic conductor being distant from the centres of the tetrahedral interstices (78Har). h is therefore homeotypic to  $\text{Sb}_2\text{O}_3.\text{r}$ . It is also homeodesmic:  $\underline{a}(\text{Bi}_2\text{O}_3.\text{h},\underline{N}=20,40,68,56)=5.67\text{\AA}=\underline{b}_C(\sqrt{8;3})=\underline{g}_C(\sqrt{32;6})$ . The binding must be twinned, its probability is confirmed by the transformation into the next phase. The occupancy of  $\underline{g}$  is .85.

$\text{Bi}_2\text{O}_3.\text{m}(\text{T8.12},\beta,\text{SR44.342,72Aur,drw 78Har})$  forms at 923K from h and transforms to r at 920 to 773K. It is IL-homeotypic to  $\text{CaF}_2$  and permits the binding  $\underline{a}(\text{Bi}_2\text{O}_3.\text{m},\underline{N}=40,80,136,112)=7.74;5.73\text{\AA}=\underline{b}_C(4;3)=\underline{g}_C(8;6)$ . The number of  $\underline{g}$  sites is occupied once more to .85, this will be a reason for the metastability. The I-homeotypism is caused by  $(\underline{b}^{-1}\underline{a})_{33}=3$  introducing electro dipoles at the atoms, forcing the atoms out of their ideal position.

$\text{Bi}_2\text{O}_3.\text{r}(\text{M8.12},\alpha,\text{SR8.124,35.210,44.342,41Sil})^{\text{drw 78Har}}$  consists of yellow needles and transforms at 1002K to  $\text{Bi}_2\text{O}_3.\text{h}$ . The Bi and 0 form layers along  $\underline{a}_2.\underline{a}_3$ , alternating in  $\underline{a}_1$  direction.  $\underline{a}(\text{Bi}_2\text{O}_3.\text{r},\underline{N}=40,80,136,112)=5.38;8.17;-2.29,0,7.51\text{\AA}=\underline{b}_C(2.7;4;4)=\underline{g}_C(5.5;8;8)$ . As compared with  $\text{Bi}_2\text{O}_3.\text{m}$  the integral commensurability in  $\underline{a}_3(\text{m})$  has been given up to attain a higher occupancy .93 of  $\underline{g}$ . The position of the  $\text{Bi6s}^2$  lone pair was suggested by 70Mal (see also 78Har) from the atom sites. It appears probable that 8  $\underline{b}$  electrons per  $\underline{a}$  cell are in Hund insertion and thus deform  $\underline{b}_C$ .

$\text{Bi}_{13}\text{O}_{20}.\text{m}(\text{B13.20},\gamma,\text{Bi}_2\text{O}_3,\text{SR44.342,78Har,drw})$  is stabilized easily by impurities. The structure was first analysed for  $\text{GeBi}_{12}\text{O}_{20}(\text{SR32.292,67Abr})$  and for  $\text{FeBi}_{25}\text{O}_{40}.\text{ZnBi}_{38}\text{O}_{60}(\text{SR41.229,75Cra})$ . The binding may be  $\underline{a}(\text{Bi}_{13}\text{O}_{20},\underline{N}=130,260,448,364)=10.27\text{\AA}=\underline{b}_C(\sqrt{26;5.1})=\underline{g}_C(\sqrt{104;10.2})$ . The  $\underline{g}$  correlation is a little over-occupied, this might explain the little 0 deficiency (78Har) and the easy stabilisation by third elements. If it is assumed that the  $\text{O}2\text{s}^2$  electrons do not take part in  $\underline{g}$  then the binding might even be  $\underline{a}(\text{Bi}_{13}\text{O}_{20},\underline{N}=130,260,368,364)=\underline{b}_C(5)=\underline{g}_C(10)$  as the  $\underline{c}$  correlation frequently accepts few  $\underline{b}$  electrons.

With respect to the electron count  $N(\text{GeBi}_{12}\text{O}_{20})=128,260,448,336$  giving 1044 electrons in the  $\underline{g}$  correlation the non appearance of the  $02s^2$  electrons is necessary for the simple binding. On the other hand the non appearance of the  $02s^2$  electrons would not spoil the previous binding proposals as the  $\underline{g}$  correlation frequently shows partial occupation.

A two component oxide with  $\text{Bi}^{5+}$  is not known, but an example of such a three component oxide is  $\text{KBiO}_3$  (SR11.445,48Zem). It is isotypic to  $\text{KSbO}_3$  (C12.12.36,SR11.443,40Spi,drw SR11.444) containing  $\text{SbO}_6$  octahedra united to  $0_{4/2}\text{SbO}_2\text{SbO}_{4/2}$  molecules sharing corners. The binding may be  $\underline{a}(\text{KSbO}_3, N=12,60,120,408,120)=9.60\text{\AA}=\underline{b}_{\text{FU}}(2;3/2)=\underline{b}'_{\text{C}}(4)=\underline{g}_{\text{B}}(8)$ . The K4s electrons form  $\underline{b}$  and the Sb5sp electrons form  $\underline{b}'$ .  $\underline{g}$  is occupied only to .63.

In  $\text{B}^5_0\text{M}$  phases CC2 and BB2 bindings are predominant.

### $\text{B}^6_0\text{M}$ phases

$\text{SO}_2$  (Q2.4,SR16.223,drw ibid,64Sch.205) has the melting temperature  $T=198\text{K}$  and is a quasi cubic Cu type packing of  $\text{SO}_2$  molecules. It yields the binding  $\underline{a}(\text{SO}_2, N=24,80)=6.07; 5.94; 6.14\text{\AA}=\underline{b}_{\text{C}}(3)=\underline{c}_{\text{C}}(6)$ . While  $\underline{b}$  is occupied with .89, for  $\underline{c}$  comes only an occupancy of .37. It must be concluded that the  $\underline{b}$  electrons influence the packing of the molecules.

$\text{SO}_3$  (O12.36,SR8.148,41Wes,drw SR8.148,64Sch.205) melts at 290K. It is conventionally called  $\beta$  as  $\text{SO}_3 \cdot i_1, \alpha$  and  $\text{SO}_3 \cdot i_2, \beta$  have a lower vapour pressure (73Bai). Three  $\text{SO}_{2+2/1}$  tetrahedra form molecules packed in  $\beta$  manner with commensurability  $\underline{a}=\underline{a}_{\beta}(\sqrt{2};\sqrt{2};1)$ . The binding may be  $\underline{a}(\text{SO}_3, N=72,312)=10.7; 12.3; 5.3\text{\AA}=\underline{b}_{\text{C}}(5;6;2.5)=\underline{c}_{\text{C}}(10;12;5)$ . It exhibits a nearly fully occupied  $\underline{b}$  correlation and a  $\underline{c}$  correlation with .52 occupancy. It must be concluded that the low  $\underline{c}$  occupancy causes the molecular character permitting a higher  $\underline{c}$  occupancy in the molecule.

In  $\text{SO}_3 \cdot i_1$  and  $\text{SO}_3 \cdot i_2$  (M4.12,SR18.367)  $\text{SO}_4$  tetrahedra form chains. The binding analysis will be postponed.

$\text{SeO}_2$  (T8.16,SR5.4,46,37Cu1,drw 64Sch.206) is colourless and very loosely built. A Se atom is coordinated with  $0_{2/2}$  and  $0_1$ . The binding may be  $\underline{a}(\text{SeO}_2, N=48,80,160,64)=8.37; 5.06\text{\AA}=\underline{b}_{\text{C}}(\sqrt{20};2.7)=\underline{g}_{\text{C}}(\sqrt{80};5.4)$ . It is seen that  $\underline{b}$  is occupied to only .89. Probably  $(\underline{b}^4 \underline{a})_{33}=2.5$  and 8 or 16 electrons per cell are in Hund insertion and deform  $\underline{b}_{\text{C}}$ .

$\text{Se}_2\text{O}_5$  (M8.20,SR46.230) may be considered later.

$\text{SeO}_3$  (T8.24,SR30.306,65Mij,drw SR30.307) contains  $\text{SeO}_{2+2/2}$  coordinations adding up to two rings per cell. The binding comes as  $\underline{a}(\text{SeO}_3, N=48,80,208,64)=9.64; 5.28\text{\AA}=\underline{b}_{\text{C}}(5;2.75)=\underline{g}_{\text{C}}(10;5.5)$ . A good fit of the  $\underline{b}$  correlation to the ring

molecule may be observed. Also the vapour contains  $(\text{SeO}_3)_4$  rings (SR30.307), it may be conjectured therefore that in the molecule a similar spatial correlation is present. Since 6 electrons per Se cannot have the same spin it is concluded that there must exist a more complicated spin-spatial correlation. It is not the ambition of this study to make proposals for it.

$\text{TeO}_2(\text{T}4.8, \alpha, \text{SR}26.362, 33.263, 61\text{aLec}, \text{drw ibid}, 68\text{Lin})$  is colourless and I-homeotypic to  $\text{TiO}_2$ .r. The binding may be  $\underline{a}(\text{TeO}_2, \alpha, \underline{N}=8+16, 40, 80, 40)=4.81$ ;  $7.62\text{\AA}=\underline{b}_C(\sqrt{5}; 3.5)=\underline{g}_B(\sqrt{20}; 7)$ . The  $\underline{b}$  correlation is of the C type with Hund insertion ('). The  $\underline{g}$  correlation is occupied with 57, this corresponds to the site number rule. The fact that B and C are in good commensurability suggests the expectation that at low temperature or high pressure a phase with self-deformation becomes stable. This has indeed been found.

$\text{TeO}_2\text{-p}_1, >9\text{kbar}(\text{O}4.8, \text{SR}42.234, 75\text{Wor})$  is D-homeotypic to  $\text{TeO}_2$  and closely homeodesmic:  $\underline{a}(\text{TeO}_2\text{-p}, \underline{N}=24, 40, 80, 40)=4.61; 4.86; 7.53\text{\AA}=\underline{b}_C(\sqrt{5}; 3.5)=\underline{g}_B(\sqrt{20}; 7)$ , B is contracted in  $\underline{a}_1$  direction.

$\text{TeO}_2\text{-p}_2, 30\dots 80\text{kbar}(\text{O}2.4, 66\text{Kab})$  is homeotypic to  $\text{p}_1$  and may have the binding  $\underline{a}(\text{TeO}_2\text{-p}_2, \underline{N}=12, 20, 40, 20)=4.22; 4.84; 3.67\text{\AA}=\underline{b}_B(2; 2; 1.75)=\underline{g}_B(4; 4; 3.5)$ .

$\text{TeO}_2(\text{O}8.16, \text{tellurite}, \text{SR}32.261, 67\text{Bey}, \text{drw } 67\text{Bey})$  displays all Te in one site set with a coordination  $\text{TeO}_{4/2}$ . The binding may be  $\underline{a}(\text{TeO}_2, \text{O}8.16, \underline{N}=48, 80, 160, 80)=5.46; 5.61; 12.04\text{\AA}=\underline{b}_B(\sqrt{5}; 5)=\underline{g}_B(\sqrt{20}; 10)$ . When  $(\underline{b}^{-1}\underline{a})_{33}=4.8$  then  $\underline{b}$  would be fully occupied and the binding would exhibit a slight strain.

$\text{Te}_4\text{O}_9(\text{R}8.18, \text{SR}41.215, 75\text{Lin})$  contains  $\text{TeO}_6$  and  $\text{TeO}_4$  coordination.  $\underline{a}(\text{Te}_4\text{O}_9, \underline{N}=144, 240, 516, 240)=\text{H}9.32; 14.49\text{\AA}=\underline{b}_{\text{BH}}(\sqrt{7}; 20/3)=\underline{g}_{\text{BH}}(\sqrt{28}; 40/3)$ .

$\text{Te}_2\text{O}_5(\text{M}4.10, \text{SR}39.207, 73\text{Lin})$  consideration shall be postponed.

$\text{TeO}_3(\text{V}F_3, \text{R}2.6, \text{SR}33.262, 68\text{Dum})$  permits the binding  $\underline{a}(\text{TeO}_3, \underline{N}=36, 60, 156, 60)=\text{H}4.90; 13.02\text{\AA}=\underline{b}_{\text{CH}}(\sqrt{3}; 12)=\underline{g}_{\text{CH}}(\sqrt{12}; 24/3)$ . The higher dilution of Te favours the transition from the BB2 binding to CC2.

$\text{PoO}_2(\text{CaF}_2, \text{SR}18.366)$  was obtained by heating  $\text{Po}+\text{O}_2$  at  $T=550\text{K}$  for some hours. The binding may be  $\underline{a}(\text{PoO}_2, \underline{N}=24, 40, 80, 56)=5.69\text{\AA}=\underline{b}_C(\sqrt{8}; 2.8)=\underline{g}_C(\sqrt{32}; 5.6)$  and  $\underline{g}$  is occupied to .98.

$\text{PoO}_2(\text{T}\dots, \text{SR}18.269, 366)$  decomposes in few days. The binding may be  $\underline{a}(\text{PoO}_2, \text{T}, \underline{N}=?)=5.45; 8.36\text{\AA}=\underline{b}_B(\sqrt{5}; 3.5)=\underline{g}_B(\sqrt{20}; 7)$ . This binding suggests that the cell is only a subcell.

### $\text{B}^7\text{O}_M$ phases

$\text{Cl}_2\text{O}_7(\text{N}4.14, 87\text{Sim})$  melts at K and is built of  $\text{Cl}_2\text{O}_7$  molecules. The  $x_2$  parameters of Cl are approximately  $\pm 1/10, \pm 4/10$ . Since  $\text{P}_2\text{O}_5$ .r and  $\text{SO}_3(\text{g})$  permit a

CC2 binding, this may be expected for  $Cl_2O_7$ . It is found  $\underline{a}(Cl_2O_7, N=56, 148) = 13.69; 4.62; 8.74 \text{ \AA}; 90; 111.81; 90^0 = \underline{b}_C(6, 0; 4; 0, 2.5, 0; 4, 0, 2) = \underline{c}_C(12, 0, -8; 0, 5, 0; 8, 0, 4)$ . The  $\underline{b}$  cell is strongly deformed. This may have to do with spin ordering.

$I_2O_5$  (M8.20, SR35.208, 70Se1, drw 73Ba1) melts at 553K and is hygroscopic.  $QIOIO_2$  molecules are linked by I-O bonds so that layers parallel  $\underline{a}_1, \underline{a}_2$  are formed. The binding written for the diagonal cell may be  $\underline{a}(I_2O_5, N=56, 80, 148, 80) = 11.04, 0, -2.40; 5.06; 7.77 \text{ \AA} = \underline{b}_B(4.5; 2; 3) = \underline{g}_B(9; 4; 6)$ . Two  $\underline{b}$  electrons per cell descend to  $\underline{g}$ . The occupancy of  $\underline{g}$  is 0.71. The commensurability element  $(\underline{b}^{-1}\underline{a})_{33} = 3$  generates electro dipoles favouring the monoclinic symmetry.

### $B^8O_M$ phases

$XeO_3$  (04.12, SR28.130) is obtained by hydrolysis of  $XeF_4$  and evaporation.  $XeO_3$  molecules are in a  $\underline{B}1$  packing with  $\underline{a} = \underline{a}_{\underline{B}1}(1; 2; 1)$ . The binding may be  $\underline{a}(XeO_3, N=32, 40, 104, 40) = 6.16; 8.12, 5.23 \text{ \AA} = \underline{b}_C(3; 4; 2.5) = \underline{g}_C(6; 8; 5)$ . Probably  $1/2$   $\underline{b}$  electron per molecule descends to the  $\underline{g}$  correlation. The  $\underline{g}$  correlation is occupied to .77, this should be compared with .95 in  $TeO_3$  and .64 in  $SeO_3$ .

### Discussion

Frequently some difficulty is found in the assumption of a lattice-like correlation of electrons (86Bus). It is maintained that electron density measurements and quantum theory would show that at normal electron densities there is no lattice-like correlation of the valence electrons. However, it is well-known that electron density is not an indicator of spatial correlation (80Sch) and that electron spatial correlation plays a decisive role in atoms and molecules (02Lew, 27Hei, 76Hur, 84Fu1). The above critique does not come true therefore and it remains admissible and desirable to study indications for the occurrence of spatial correlations <sup>of electrons</sup> in crystals. Meanwhile these indications have become numerous and therefore invite to further investigate which crystal chemical rules may be connected with electron spatial correlation. This trial and error method may be supported by band calculations, but since there are not enough calculations available the trial method is at present the prevail- ing method of analysis.

Some doubt on the present approach may come from the high numbers of electrons involved in the  $\underline{g}$  correlation as they might not reproduce the experimentally known electron densities. This doubt follows from the misunderstanding that the lattice-like correlations are sharp electron lattices (86Bus). They have not this property, rather they are more or less slight modifications of a pair density derived from an ideal density matrix without correlation. A

hot plasma has a very small correlation, the cooler it becomes the more correlation it will exhibit. When for instance a f electron is relatively seldom far from its atom core it nevertheless may be in a correlation to the more peripheral electrons. At any case the assumption of the participation of f electrons in the g correlation is an energetical argument for the frequently observed heterotypism of heavy phases with lighter homologues. It must be considered as a crystal chemical rule requiring further investigation.

A question sometimes raised is, for what we need crystal chemical systematics when the quantitative energy calculation is rather advanced. On the one hand the small energy differences governing phase stability are not yet mastered by the calculations. On the other hand the theory of mixtures e.g. requires a crystal chemical systematics to complete the system of phase energies needed for the calculation of phase diagrams. Furthermore the so called "feeling" of the chemist consists mainly in the knowledge of some systematics, it runs along the rules of valence models.

The above systematics is not far from the presently accepted valence theory. The assumption of a distributed b correlation and a core tied g correlation corresponds to the earlier model that the b electrons go over to the O atoms to form negatively charged anions. Nevertheless, the early model implicitly suggests that the b electrons and the O2sp electrons might form a common band, the valence band. This appears not to be the case. The b electrons and the O2sp electrons have so different an energy that they must belong to different lattice-like correlations. The b electrons form an independent distributed correlation and the O2sp electrons belong to the core tied g correlation which is also sustained by the core electrons of the B atoms, and this assumption results in numerous surprising and plausible stability arguments.

The above discussed phases invariably show that the collective b correlation seeks harmony with a and g, and at such mole fractions  $N_O$  where it finds harmony a phase becomes stable. An example of a harmonic binding is CC2 i.e. b is of the C-type and g is of the C type and the cell  $g_C$  must be multiplied with 2 to be equal to  $b_C$ . Another example is BB2, displaying the conspicuous phenomenon of self-deformation.

The assumption of charged anions in oxides should therefore be used with caution, it mixes in the view of the present model electrons of different bands (or correlations) into one concept and becomes by this internal difficulty problematical. This may be a reason why a discussion of the oxides going beyond Lewis' rule did not become satisfactory in the past. Instead of

charged anions the various correlations and their harmonies deserve an increased attention, and indeed provide a helpful insight into various problems:

Why are suboxides of Cu metastable at oxygen mole fractions  $N_{\text{O}} < 0.33$ ? By decreasing  $N_{\text{O}}$  from the value 0.33 the occupancy of  $\underline{g}$  is decreased so that the  $\underline{g}$  correlations seek changed commensurabilities lying between the commensurability in Cu and that in  $\text{Cu}_2\text{O}$ . In fact there exist geometrically such intermediary harmonic correlations, and these determine mole fractions for suboxides.

Why has  $\text{HgO}(04.4)$  not a NaCl type of structure like  $\text{CdO}$ ? The heterotypism  $\text{CdO}(\text{NaCl})\text{-HgO}(04.4)$  may be understood as a confirmation for the assumption of the participation of  $\text{Hg}4f$  electrons in the binding.

Why is  $\text{Al}_2\text{O}_3.m(\text{htpFe}_3\text{O}_4)$  a homeotype of  $\text{MgO}$  only a metastable phase? The occupancy of  $\underline{c}$  is only .71 while in  $\text{Al}_2\text{O}_3$  it is .95. The low occupancy of the  $\underline{c}$  correlation is energetically expensive.

Why has  $\text{SiO}_2$  essentially three stable phases  $h_2, h_1,$  and  $r_1$ ? The binding of  $h_2, \text{FF}_2$ , may have a good spin compensation from  $\underline{b}$  to  $\underline{c}$  following Lewis' rule but the spin compensation within  $\underline{c}$  and within  $\underline{b}$  is not good. The transition  $\text{F} \rightarrow \underline{U}_H$  is an improvement of the internal spin compensation. It occurs first in  $\underline{c}$  as there are more  $\underline{c}$  electrons than  $\underline{b}$  electrons. This change causes the transition  $h_2 \rightarrow h_1$ . Although the  $\underline{b}$  electrons have to compensate the spins at 0 there is also a possibility to improve the spin compensation within  $\underline{b}$ . This is grossly described by the change  $\underline{b}_F \rightarrow \underline{b}_{U_H}$  and causes the transition  $h_1 \rightarrow r_1$ .

Why is  $\text{Bi}_2\text{O}_3.m$  formed when  $\text{Bi}_2\text{O}_3.h$  is cooled and only after heating  $\text{Bi}_2\text{O}_3.m$  goes over into  $\text{Bi}_2\text{O}_3.r$ ? All three phases contain the CC2 binding. In  $h$  it is a little compressed, in  $m$  it is relaxed and in  $r$  it probably contains localized Hund insertion i.e. localized lone pairs.

Why is the so called synthetic  $\text{TeO}_2(\text{T}4.8)$  not isotypic with  $\text{MoO}_2$ ? Already the axial ratio of  $\text{TeO}_2$  shows that there must be a different binding in  $\text{MoO}_2$  and  $\text{TeO}_2(\text{T}4.8)$ . Following the Lewis rule alone, there should be in both compounds one lone pair, but according to the present model the number of electrons in Hund insertion is more variable and must be inferred from the crystal structure.

Why is  $\text{I}_2\text{O}_5$  a molecular structure? The Lewis phase has a high  $\underline{b}$  electron concentration. In the chemical neighbourhood of  $\text{I}_2\text{O}_5$  the CC2 and BB2 bindings are especially probable. Since the  $\underline{g}$  correlation is not highly occupied there are ranges in the crystal without  $\underline{g}$  electrons and ranges with fully occupied  $\underline{g}$  correlation. The latter are the molecules and the first describe the interstices between the molecules.

The present analysis uncovers various crystal chemical rules which may be expressed in terms of the plural correlations model. Some of the rules are formulated in 86Sch, however, not all rules have been formulated explicitly for brevity. A careful reading of the analysis and various cross comparisons will result in finding additional rules being useful in the further binding analysis by increasing the determination of the analysis.

The inference of the bindings is only a preliminary result of the proposed valence model. The numerous assumptions on the influence of the bindings on the structure have to be confirmed by energy calculations. When for instance an I-homeotypism is said to be caused by the binding, then actual energy calculations have to prove that in fact the I-homeotypic structure has a lower energy than the more symmetric structure. Such calculations cannot start from the electron density in the well-known Madelung manner since the electro fields are caused by the correlations. All integrations have to involve in fact the six dimensional space of the spatial correlations. The problem of such energy calculations for correlation proposals is established by the binding analysis. The circumstance that in the present approximation the kinetic energy is disregarded is a feature common with the electrostatic theory of Born and Madelung which was of high utility in crystal chemistry. The more quantitative aspects of  $\lambda^a$  correlations model may be approached after it has been made probable that the correlations really exist. This can be done by finding conspicuous examples of coincidence of observation with expectation, i.e. by an extension of the interpretations over large classes of intermediate phases. This is a contribution of crystal chemical systematics to the solution of the stability problem.

Another unsolved problem of the present approach is the unsettled consideration of spin. The proposed correlations mostly permit a general spin compensation but do not afford spin structures of more specific nature like the lone pairs. This is connected with the simplification that the spatial correlation is composed of lattices. Future improvements of the model have to replace this simplification by modified assumptions.

#### Acknowledgement

The author thanks Prof. A.Simon for the access to data on  $\text{Cl}_2\text{O}_7$  prior to publication.



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