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On the bindings in ABe_M phases

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Abstract

A collective binding is described by a single averaged correlation g and allows therefore a simplified argument for stability. The averaged valence electron correlation b is generally a sublattice of g. It appears that the b(Be) electrons are in correlation with the $c(A^{1..3})$ electrons lying below $b(A^{1..3})$ or with the $c(A^{4..10})$ electrons lying above $c(A^{4..10})$. This distinction explains why in $A^{1..3}$ Be_M mixtures the minimum mole fraction of stable intermediate phases is $N^{\prime}_{Be}=0.8$, for $N^{\prime}_{Be}<0.8$ the distance d(Be2sp) is strained by the Be-dilution and falls out of correlation with $c(A^{1..3})$. The small b contribution of Be causes that the Be partial structure of a Be-rich ABe_M phase is homeotypic to a close packing in which two or more Be are replaced by one $A^{1..3}$ (multiple replacement structures). These structures are not possible in AB_M or AC_M phases because of the larger b contribution of B or C. The various multiple replacement structures are chosen as to give an energetically favourable commensurability of an appropriate g correlation to the crystal cell a. The Be-poor phases are homeotypic or isotypic to corresponding borides. The assumption that electrons below c (f electrons) take part in g is necessary. It allows for instance in CuBe(CsCl) the binding $a=g_F(2)$ and yields thus a simple interpretation of $Cu_{1.4}Be_{0.6}$.h(W) by a compression of g_F to g_B. Similarly the nonstoichiometry of $Cu_{0.75}Be_{2.25}(MgCu_2)$ finds an easy explanation.

Introduction

The equilibrium chemistry of two component phases containing Be is based on the description of composition and structure of the stable compounds (58Han,65Hau,67Pea, 71Eck,73Fer,73Gir,79Ald,85Vil). Additionally an indication of the energetic causes is desirable for these compounds (64Sch,73Eve,79Ald,82Sch1) by attributing a bonding type (binding) to each phase; the last references should be consulted for earlier literature.

The search for bindings in AC_M, AN_M, AO_M phases (88Sch) with the plural correlations model (83,86Sch) has revealed that a *collective* binding may be assumed in which valence electrons b and core electrons c obey the same lattice g of the averaged correlation (83Sch). This assumption simplifies the binding analysis. However, not only the b and c electrons may take part in g but also the f electrons belonging to shells below the c shell. When the distance of the summit of the f shell is quite near to the atomic centre then the spur of this shell will have a correlative influence on the other electrons (see 83Sch Fig.1).

The atoms certainly are deeply organized by spatial correlation of electrons and these correlations are fused together to form the electron correlation in the solid. This binding, a phenomenon existing independently on whether it is found or not, shall be sought.

The small number of valence electrons of Be causes that Be rich intermediate phases mostly exhibit a close packed Be partial structure in which the A component replaces two or more Be (multiple replacement structures, 64Sch). Such structures are not possible for borides or carbides because the numerous valence electrons do not permit a close packing. For the explanation of binding equations symbols see 83,86,88Sch.

Analysis

Be.h(W,SR23.45), $a(4,4)=2.55\text{Å}=b_F(1)=c_C(2)$ or $g_{FU}(2;2.8/2)$, $N_{oc}(g)=0.72$

Be.r(Mg,H2,SR1.40,23.46), $a(4,4)=\text{H}2.29;3.58\text{Å}=g_H(\sqrt{3};3)$, $N_{oc}(g)=0.89$. This binding is compressed in a_3 direction for spin compensation. It explains the under ideal axial ratio $|a_3|/|a_1|=1.57$ and the + − type of stacking (84Sch). Furthermore it suggests a low temperature phase which might be caused by untwinning of the binding.

$LiBe_M$ has no intermediate phase (nip), phase diagram 77Mof (phd77Mof).

$NaBe_M$(nip, phd 77Mof).

KBe_M (nip, 65Ell), a phase "KBe_2(MgCu$_2$,65Ell)" must be doubted because of atomic radius ratio.

$RbBe_M$ (nip,85Vil), $CsBe_M$(nip,85Vil).

$MgBe_{13}$(NaZn$_{13}$,F2.26,SR27.68,drw 64Sch.219) is a CsCl structure of Mg and Be_{13} icosahedra. The observed commensurability $a=a_{CsCl}(2)$ instead of $a=a_{CsCl}(1)$ allows an improved spatial fit of the Be_{13}. The sequence of the symbols in the chemical formula is chosen since the large Mg plays as minority component a cationic role. The electron count $Mg^{2\cdot8\cdot2}Be_{13}^{2\cdot2}$ suggests the binding proposal $a(16,272,224)=10.17\text{Å}=b_B(2)=g_C(8)$. The collective correlation $g=b\sim c\sim f$ does not necessarily cause a uniform electron density as may be concluded from the example 83Sch Fig.1. $MgBe_{13}$ is isodesmic with Na.r(W), $a=4.29\text{Å}=b_B(1)=g_C(4)$ (82Sch2). Phases with mole fractions $N_{Be}<0.93$ are not formed because the distance d(Be2sp) which expands in diluted Be does no longer fit to d(Mg2sp). All $NaZn_{13}$ isotypes with Be have $a\approx10.3\text{Å}$. Therefore, A^1 elements may be cations in AZn_{13} or ACd_{13} but not in ABe_{13}.

$CaBe_{13}$(NaZn$_{13}$,MgBe$_{13}$,SR27.68), $a(16,272,272)=10.31\text{Å}=g_B(8)$. The g_B correlation is only filled near the Ca atoms and fits well to $a_{Ca(F1)}(8,32,32)=5.59\text{Å}=g_B(4)$ (82Sch2).

$SrBe_{13}$(NaZn$_{13}$,MgBe$_{13}$,SR29.105), $a(16,272,288)=10.16\text{Å}=g_B(5)$.

$BaBe_{13}$(NaZn$_{13}$,MgBe$_{13}$,71Eck), $a(16,272,288)=10.49\text{Å}=g_B(5)$.

$ScBe_5$(CaZn$_5$,H1.5,SR29.105,drw 64Sch.165) consists of alternating close packed layers "$ScBe_2$" and "LBe_3" (L=lacuna), and may therefore be considered as a Be.r structure in which Sc replaces three Be (multiple replacement,64Sch) incidently causing some Be shifts. $a(3,18,18)=\text{H}4.55;3.50\text{Å}=b_H(2;1.5)=g_H(4;3)$. The H correlation is htpc to B1 but less favourable for spin compensation.

Sc_2Be_{17}(Th_2Ni_{17},H4.34,85Vil), a(12,100,100)=H7.61;7.50Å=g_{BH}(4;18/3).

$ScBe_{13}$($NaZn_{13}$,SR27.70), a(24,272,288)=10.10Å=g_B(8), $N_{oc}(g)$=0.55.

YBe_{13}($NaZn_{13}$,SR27.71), a(24,272,288)=10.25Å=g_B(8).

$LaBe_{13}$($NaZn_{13}$,SR27.71), a(24,272,272)=10.45Å=g_B(8). In $LaBe_{13}$ more f electrons may take part in g, and this presumably destabilizes "$LaBe_5$($CaZn_5$)".

In $TiBe_M$ the distance d(Ti3d) becomes comparable with d(Be2sp) (83Sch). Therefore, the electron count is changed to $Ti^{1.8}Be_M^{2.0}$.

TiBe.m(CsCl,85Vil), a(6,10,8)=2.94Å=$g_{\hat{C}}$(√8;3). Alternatively the binding a=g_F(2) could be chosen which would explain by its low occupancy ($N_{oc}(g)$=0.75) the metastability. The F correlation does not provide a good spin compensation. This may be considered as an indication for the weak influence of the Ti2sp electrons on the binding. If the influence disappeared completely the binding might be assumed as a=g_B(2).

$TiBe_2$($MgCu_2$,F2.4,drw 64Sch.158) displays a Be_{F1} site with the commensurability a=a_{F1}(2). In the Be_{F1} site 16 Be per a are replaced by 8 Ti so that the structure is a double replacement structure. a(64,96,64)=6.45Å=$b_{\hat{C}}'$(4)=g_F(4) with occupancy $N_{oc}(g)$=0.88. It becomes clear that the binding cannot be replaced by a=g_B(4) because of the number 96 of e electrons. The binding will be nearly fully occupied in $NbBe_2$($MgCu_2$) and in $TaBe_2$($MgCu_6$) even overoccupied.

$TiBe_3$($NbBe_3$,R3.9,SR26.59,drw 64Sch.168)cmp, is composed of three $MgZn_2$ elements and three $CaZn_5$ elements. a(36+54,72+54,72)=H4.49;21.32Å=g_{FH}(4;24/3). While the occupancy g was $N_{oc}(g)$=0.88 in $TiBe_2$, it is 0.75 in $TiBe_3$ corresponding to the smaller Ti content.

Ti_2Be_{17}(Nb_2Be_{17},R2.17,SR26.59,drw SR23.48) cmp 1700°C, has Nb atoms in ±0.0.16 etc. (hexagonal coordinates) each surrounded by 3 Be hexagons just as in $CaZn_5$. a(126, 150,48)=H7.39, 10.79Å=b_{FH}(4;7/3)=g_{BH}(4;28/3). The less close packed g_{BH} binding corresponds to the lower b concentration, $N_{oc}(g)$=0.72.

$Ti_{1.8}Be_{17}$(Th_2Ni_{17},H4.34,SR26.59) is htpc to $CaZn_5$ with a=a_{CaZn_5}(√3;2). a(82,97, 29)=H7.36;7.30Å=b_{FH}(4;5/3)=$g_{\hat{B}H}$(4;18/3), $N_{oc}(g)$=0.72.

$TiBe_{12}$($ThMn_{12}$,U1.12,SR26.59,drw 64Sch.167) is a $CaZn_5$ structure with half of the Ca replaced by Zn_2. a=a_{CaZn_5}(−1,0,1;1,0,1;0,2,0). The Zn essentially lie in a U1 lattice which has 32 sites for a, being occupied by 24 Be. One Ti replaces therefore effectively 4 Be. a(56,64,16)=7.35;4.19Å=$g_{\hat{B}}$(√32;3), $N_{oc}(g)$=0.71. The $g_{\hat{B}}$ correlation is a g_F correlation with an improved spin compensation. The occupancy is $N_{oc}(g)$=0.71. In "$TiBe_{13}$($NaZn_{13}$)" the binding a(32,272,272)=g_B(8) would yield $N_{oc}(g)$=0.56. It may be assumed that such a low occupancy is not tolerated for "$TiBe_{13}$" since the distance d(Ti3d) has decreased too much as compared with $ScBe_{13}$.

$ZrBe_2$(AlB $_2$,SR18.54) may be considered as a fourfold replacement structure. A look to the atomic volumes of the components (64Sch.34) reveals that a double replacement structure as in $TiBe_2$ or $NbBe_2$ is not possible here. a(8,12,10)=H3.82; 3.24Å=g_{BH}(2;8/3). The correlation is not g_F as in $TiBe_2$ but g_B because the phase is more voluminous. The

occupancy is $N_{oc}(g)=0.94$ because the f electrons compress the crystal. The commensurability of g in the hexagonal basal plane may be described as $a=g_H(\sqrt{12};3)$. When more Be is introduced into the cell g must seek a commensurability richer in sites.

$ZrBe_5$(CaZn$_5$,ScBe$_5$,SR23.51), $a(14,18,10)$=H4.56,3.49Å=$g_H(4;3)$, $N_{oc}(g)=0.88$. Instead of seeking a new commensurability, a g plane may be puckered.

Zr_2Be_{17}(Nb_2Be_{17},Ti_2Be_{17},SR23.51,51.20), $a(126,150,60)$=H7.54,11.02Å=$g_{BH}(4;29/3)$, $N_{oc}(g)=0.72$.

$ZrBe_{13}$($NaZn_{13}$,$MgBe_{13}$,SR26.60), $a(240,272,80)=10.04$Å$=g_B(8)$, $N_{oc}(g)=0.58$. The strong decrease of the occupancy with the mole fraction N_{Be} suggests that $a=g_C(8)$ bears the $b\sim c$ correlation, while f locally fills the C cubes.

HfBe.m(TlI,85Vil), a(24,40,56)=3.34;10.00;3.72Å=$g_{\hat{B}}(\sqrt{8};7.5)$.

$HfBe_2$($AlBe_2$,$ZrBe_2$,SR26.60), $a(8,12,14)$=H3.79;3.20Å=$g_{BH}(2;8.3/3)$. The binding appears to be slightly overoccupied, see $TaBe_M$.

$HfBe_5$($CaZn_5$,$ScBe_5$,SR26.59), $a(14,18,14)$=H4.53;3.47Å=$g_H(4;3)$.

Hf_2Be_{17}(Nb_2Be_{17},R2.17,Ti_2Be_{17},SR26.56) cmp 1860° C, $a(126,150,84)$=H7.49;10.93Å=$g_{BH}(4;28/3)$.

$Hf_{1.8}Be_{17}$(Th_2Ni_{14},$Ti_{1.8}Be_{17}$,SR26.56), $a(82,97,50)$=H7.44;7.38Å=$g_{BH}(4;20/3)$.

$Hf_{1.4}Be_{17}$(U_2Zn_{17},SR26.59,71Eck) needs confirmation. The three phases are homeodesmic.

$HfBe_{13}$($NaZn_{13}$,$MgBe_{13}$,SR26.58), $a(240,272,112)=10.01$Å$=g_B(8)$.

VBe_2($MgZn_2$,H4.8,SR4.240,drw 64Sch.161) is a stacking htp of $MgCu_2$(F2.4). Double layers consisting of a puckered Mg_2Zn net and a plane LZn_3 net (L=lacuna) are stacked in + – sequence (Zhdanov symbol). If the LZn_3 net is considered as a part of a close packed Zn site net, then two Mg replace 4 Zn. $a(20+16,32+16,32)$=H4.39;7.14Å= $g_{\hat{F}H}(4;9/3)$. The number of sites is $N_{S(g)}/a=144$ and the number of electrons $N_{b\sim e\sim c\sim f}/a=116$. It must therefore be assumed that contrary to the heavier homologues $NbBe_2$($MgCu_2$) and $TaBe_2$ ($MgCu_2$) the phase $TiBe_2$ accepts a lower occupancy of g (rule of correlation site numbers, 83,86Sch). The strain of F_H is caused by a PtCu-type spin-ordering. The stacking sequence is favoured by electro dipoles in g_3 direction alternating with the double layers (84Sch).

VBe_{12}($ThMn_{12}$,$TiBe_{12}$,SR21.48), $a(58,64,16)$=7.28;4.21Å=$g_{\hat{B}}(\sqrt{32};3)$. If the +spin electrons are counted 10+48+8+24+8=98 then the g_C part of g_B is overfilled. It must be inferred therefore that only 4 electrons per V may have the same spin in slight violation of Hund's rule. The strain of $g_{\hat{B}}$ may be caused by the deviation of Be_{U1} from Be_{B1}.

Nb_3Be_2(U_3Si_2,T6.4,SR24.59,drw 64Sch.252) is homeotypic to W with $a=a_W(2;1)$ and two W are replaced by Be_2. $a(38,56,60)$=6.49;3.35Å=$g_B(\sqrt{29};2.8)$, $N_{oc}(g)=0.95$.

$NbBe_2$($MgCu_2$,$TiBe_2$,SR23.49), $a(72,96,80)$=6.54Å=$g_F(4)$. This binding has an occupancy of $N_{oc}(g)=0.97$ and in $TaBe_2$ even =1.1. It may be assumed that within Ta the g_F correlation is filled to g_C.

$NbBe_3$(R3.9,$TiBe_3$,SR23.49), $a(99,126,90)$=4.56;21.05Å=$g_{\hat{F}H}(4;23/3)$.

Nb_2Be_{17}(R2.17,Ti_2Be_{17},SR23.47), $a(132,150,60)$=H7.41;10.84Å=$g_{BH}(4;28/3)$.

$NbBe_{12}$(ThMn$_{12}$,TiBe$_{12}$,SR21.48), a(58,64,20)=7.38;4.26Å=$g_B(\sqrt{32};3)$. The $NaZn_{13}$ type does no longer become stable since the d(Nb4d) distance is too small.

$Ta_3Be(CaAl_2,SR30.117)$ is the Be-poorest phase up to now, the high electron density of Ta prevents the Be-electrons from expanding and falling out of the b correlation. a(48,72,112)=6.00;4.90Å=$g_B(5;4)$. The binding appears highly overoccupied, four f electrons per Ta must find room elsewhere.

Ta_3Be_2(U_3Si_2,Nb_3Be_2,SR26.60), a(38,56,84)=6.50;3.31Å=$g_B(\sqrt{29};2.8)$. The binding is overoccupied.

$TaBe_2$($MgCu_2$,$TiBe_2$,SR26.40), a(72,96,112)=6.51Å=$g_F(4)$, overoccupied.

$TaBe_3$($NbBe_3$,$TiBe_3$,SR26.59), a(99,126,126)=H4.53;20.95Å=$g_{FH}(4;24/3)$. This binding is no longer overoccupied.

Ta_2Be_{17}(Nb_2Be_{17},Ti_2Be_{17},SR26.59), a(132,150,84)=H7.39;10.74Å=$g_{BH}(4;28/3)$.

$TaBe_{12}$(ThMn$_{12}$,TiBe$_{12}$,SR21.48), a(58,64,28)=7.33;4.27Å=$g_B(\sqrt{32};3)$. The overoccupation was finished in the last three phases because of the low occupancy of the Ta poor phases. The earlier overoccupation may be only apparent. It is to be expected for a shell which is quite near to the core since in this case electrons less frequently occupy their correlation site.

$CrBe_2$($MgZn_2$,VBe_2,SR20.46), a(40,48,32)=H4.26;6.98Å=$g_{FH}(4;9/3)$.

$CrBe_{12}$(ThMn$_{12}$,TiBe$_{12}$,SR21.48), a(60,64,16)=7.23;4.17Å=$g_B(\sqrt{32};3)$.

Mo_3Be(Cr_3Si,C6.2,SR24.60,drw 64Sch.150), a(40,52,60)=4.89Å=$g_B(\sqrt{20};4)$. It is clear that this binding must be twinned. $N_{oc}(g)$=0.95.

$MoBe_2$($MgZn_2$,VBe_2,SR15.22), a(40,48,40)=H4.43;7.34Å=$g_{FH}(4;9/3)$. $N_{oc}(g)$=0.89.

$MoBe_{12}$(ThMn$_{12}$,TiBe$_{12}$,SR21.48,51.19), a(60,64,20)=7.27;4.23Å=$g_B(\sqrt{32};3)$. $N_{oc}(g)$=0.75.

$MoBe_{22}$($ZrZn_{22}$,F2.44,SR27.70,drw 72Pea.688) contains Mo in a diamond site and Be forming a 16 vertex polyhedron (Friauf–polyhedron) built from a truncated tetrahedron by the site net named (g) in the space group with 4 equilateral hexagons capped by 6 icosceles triangles uniting in a point of a (d) site set. The coordination around the Be(d) atoms is formed by two hexagons of neighbouring Friauf-polyhedra forming a hexagonal prism. a(400,416,80)=11.63Å=$g_B(9)$ leading to $N_{oc}(g)$=0.61.

WBe_2($MgZn_2$,VBe_2,SR4.240), a(40,48,56)=H4.45;7.29Å=$g_{FH}(4;9/3)$, $N_{oc}(g)$=1.00.

WBe_{12}(ThMn$_{12}$,TiBe$_{12}$,SR21.48), a(60,64,28)=7.36;4.22Å=$g_B(\sqrt{32};3)$, $N_{oc}(g)$=0.79.

WBe_{22}($ZrZn_{22}$,$MoBe_{22}$,SR27.70), a(400,416,112)=11.63Å=$g_B(9)$, $N_{oc}(g)$=0.64.

$MnBe_2$($MgZn_2$,VBe_2,SR23.47), a(44,48,32)=H4.24;6.92Å=$g_{FH}(4;9/3)$, $N_{oc}(g)$=0.86.

$MnBe_5$($PdBe_5$,SR21.49), a(68,72,32)=5.91Å=$g_F(4)$, $N_{oc}(g)$=0.67.

$MnBe_{12}$(ThMn$_{12}$,TiBe$_{12}$,SR21.48), a(62,64,16)=7.30;4.26Å=$g_B(\sqrt{32};3)$, $N_{oc}(g)$=0.74.

$TcBe_{12}$(ThMn$_{12}$,TiBe$_{12}$,Acta Cryst. 10.1957.768).

$TcBe_{22}$($ZrZn_{22}$,$MoBe_{22}$,73Fer).

$ReBe_2$($MgZn_2$,VBe_2,SR4.240), a(44,48,56)=H4.35;7.10Å=$g_{FH}(4;9/3)$. The binding is slightly overfilled, see $TaBe_M$.

$Re_{0.92}Be_{16}$(F(0.2),4,SR51.19), $a(38.5,39.5,14)=5.88Å=b_{FU}(\sqrt{10};4.5/2)=c_{FU}(\sqrt{10};4.5/2)=g_B(\sqrt{20};4.5)$.

$ReBe_{22}$(ZrZn$_{22}$,MoBe$_{22}$,SR27.71), $a(408,416,112)=11.56Å=g_B(9)$.

Fe_3Be(Fe$_3$Si,see 79Ald), $a=5.61Å$.

$FeBe_2$(MgZn$_2$,VBe$_2$,SR12.24) cmp 1480°C, phd 58Han, $a(48,48,32)$=H4.19;6.81Å=$g_{FH}(4;9/3)$. The deformation is so strong that also g_{UH} could be assumed, however, g_{FH} easliy yields the stacking + −. The occupancy is $N_{oc}(g)=0.89$.

$FeBe_5$(PdBe$_5$,F1.5,SR12.24) has a $MgCu_2$ structure with half of the Mg atoms replaced by Cu. $a(72,72,32)=5.85Å=g_F(4)$, $N_{oc}(g)=0.69$. The phase is said to be ferromagnetic below 75K (79Ald).

$FeBe_{6.6}$(RhBe$_{6.6}$,H(2.4).(15.3),SR35.29) is htpc to $CaZn_5$ with $a=a_{CaZn_5}(1;3)$. $a(50,50,19)=4.14;10.72Å=g_{FH}(4;12/3)$. $N_{oc}(g)=0.62$.

"$FeBe_{12}$(ThMn$_{12}$,SR21.48)" was not confirmed (70Joh).

Ru_2Be_3(B,71Eck), $a=11.42Å$. See critique of 73Fer.

$RuBe_2$(MgZn$_2$,VBe$_2$,71Eck), a=H5.96;9.18Å, needs confirmation since the cell is not compatible with $a(ReBe_2)$, see critique of Ferro.

Ru_3Be_{10}(B,71Eck), $a=11.03Å$, is perhaps identical with Ru_3Be_{17}.

Ru_3Be_{17}(B12.68,SR27.74) displays a similar coordination as Mo in $MoBe_{22}$. $a(464,464,240)=11.34Å=g_B(9)$. $N_{oc}(g)=0.80$.

Ru_2Be_{17}(H,73Fer,SR38.160), a=H4.20;10.90Å.

Os_3Be_{17}(Ru$_3$Be$_{17}$,SR27.70), $a(464,464,336)=11.34Å=g_B(9)$.

Os_2Be_{17}(H,73Fer,SR38.160), a=4.22;10.95Å.

$OsBe_{12}$(M,85Vil).

Co_3Be.h, phd 77Mof.

CoBe(CsCl,SR4.240) cmp 1420°C, $a(11,10,8)=2.59Å=g_F(2)$. This collective binding may be resolved into $a=b_F(1)=e_C(2)=c_C^+(2)=c_C^-(2)=f_C(2)$ where c^+,c^- have different spin.

$CoBe_3$.h(Be rich border of CoBe).

$CoBe_3$.r(H24.74,77Ald), a=H8.38;13.77Å.

$CoBe_5$(PdBe$_5$,85Vil), $a(76,72,32)=5.85Å=g_F(4)$, tentative.

$CoBe_5$(F,77Ald), $a=15.25Å$, needs confirmation, see 79Ald.

$CoBe_{6.6}$(RhBe$_{6.6}$,FeBe$_{6.6}$,H(2.4).(15.3),SR35.29), $a(52,50,20)$=H4.11;10.66Å=$g_{FH}(4;12/3)$.

$CoBe_9$(htpc Cu_5Zn_8,77Ald), $a=7.61Å$.

$CoBe_{12}$(ThMn$_{12}$,SR21.48) was not confirmed by 70Joh,77Ald.

RhBe(CsCl,85Vil), $a(11,10,10)=2.74Å=g_F(2)$.

$RhBe_2$(IrBe$_2$?,SR4.240).

$RhBe_{6.6}$(H(2.4).(15.3),FeBe$_{6.6}$,SR35.29,38.160), $a(52,50,24)$=H4.19;10.89Å=$g_{FH}(4;12/3)$.

$IrBe_2$(complex, SR4.240).

$IrBe_{6.6}$(RhBe$_{6.6}$,FeBe$_{6.6}$,SR35.29), a(52,50,34)=H4.20;10.84Å=g_{FH}(4;12/3). See also SR38.160.

NiBe(CsCl,SR9.32), a(12,10,8)=2.62Å=g_F(2), phd58Han.

Ni_5Be_{21}(Dhtp Cu_5Zn_8,SR3.617;9.32), a(184,164,80)=7.60Å. This early assumption should be replaced by $NiBe_5$, $NiBe_7$ (79Ald).

$NiBe_5$(F,79Ald), a=15.28Å (80Fri).

$NiBe_7$(Cu_5Zn_8,79Ald), a=7.61Å. Both phases should be confirmed. Assuming 52 atoms in the cell would yield Ni_6Be_{46}, a(152,140,48)=7.61Å=g_C(8), $N_{oc}(g)$=0.66. $NiBe_5$ might be isodesmic and the larger cell could be caused by Ni arrangement.

Pd_3Be

Pd_2Be

Pd_3Be_2

Pd_4Be_3.h

$Pd_{13}Be_{12}$ is doubted by 87Tan.

PdBe(CsCl,SR4.240),cmp, a(12,10,10)=2.82Å=g_H(2), $N_{oc}(g)$=1.0. It is conspicuous that "PtB(CsCl)" has not been found since 4f^4 electrons do not find a site.

$PdBe_5$(F1.5,$FeBe_5$,SR3.330), a(80,72,40)=5.99Å=$g_{\hat{F}}$(4), $N_{oc}(g)$=0.75. A phase "$PdBe_2$ ($MgCu_2$)" would have the electron numbers (112,96,80), not permitting stability with the proposed binding.

$PdBe_{12}$($ThMn_{12}$,$TiBe_{12}$,SR22.49), a(68,64,20)=7.27;4.25Å=g_B(√32;3.3), $N_{oc}(g)$=0.71. The structure was not stable in A^8Be_M and A^9Be_M, perhaps the binding is no longer strained.

$Pt_{15}Be$(H768.51?,SR27.322) is a replacement htp of Cu, a( )=H22.13;27.12Å.

Pt_5Be_{21}(Dhtp Cu_5Zn_8,SR4.240).

$PtBe_5$($PdBe_5$,SR22.49), a(80,72,56)=5.98Å=g_F(4). A phase "$PtBe_2$($MgCu_2$)" would have the electron numbers (112,96,112), not compatible with $a=g_F$(4).

$PtBe_{12}$($ThMn_{12}$,$TiBe_{12}$,SR22.49), a(68,64,28)=7.24;4.25Å=$g_{\hat{B}}$(√32;3).

$Cu_{14}Be_{69}$.h(W,SR3.588), a(2.6,15.2,11,11)=2.80Å=g_B(√8;2.8). The phase is homeodesmic to CuBe.

CuBe(CsCl,SR3.589), a(1,12,10,8)=2.70Å=g_F(2). It is easily seen that "AgBe(CsCl)" or "AuBe(CsCl)" are not possible with that binding.

CuBe.m_1(T1.1,71Eck), a(1,12,10,8)=2.79;2.54Å=$g_{\hat{B}}$(√8;3.9/2). This phase has a favourable composition and a full occupation.

CuBe.m_2(M1.1,71Eck).

$Cu_{0.75}Be_{2.25}$($MgCu_2$,SR22.5), a(42,96,48,48)=6.00Å=g_F(4). The phase "$CuBe_2$ ($MgCu_2$)" would have the electron number 40+112+64+64=280 and would therefore not allow the favourable g_F binding. For a presumable phase $CuBe_3$(Mg) see 79Ald.

Ag_2Be_3.h(phd,58Han), not confirmed, see 79Ald.

$Ag_{0.75}Be_{2.25}$($MgCu_2$,SR4.240), a(42,96,48,60)=6.30Å=g_F(4).

$AuBe_{12}$(ThMn$_{12}$,TiBe$_{12}$,SR22.49), a(50,68,16,20)=7.28;4.25Å=g_B(√32;3). The phase was not confirmed, see 79Ald.

Au_2Be(O12.4,SR22.48), a(12,128,104,168)=7.49;10.42;3.01Å=g_B(7;10;3) phd. 78Han.

Au_2Be(MoSi$_2$,U2.1,SR22.48,drw 64Sch.313), a(8,44,32,56)=2.93;9.79Å=g_B(√8;9). The strain of the subcell is explained by the binding, $N_{oc}(g)$=0.97.

Au_4Be_3.h.

AuBe(FeSi,C4.4,SR22.48,drw 64Sch.308), a(12,48,32,56)=4.67Å=g_B(√20;4), $N_{oc}(g)$=0.93.

$Au_{0.75}Be_{2.25}$(MgCu$_2$,SR22.48), a(42,96,48,84)=6.32Å=g_F(4;9/2), $N_{oc}(g)$=0.94.

$AuBe_5$(PdBe$_5$,SR3.330,22.48), a(44,80,32,56)=6.10Å=g_B(4), $N_{oc}(g)$=0.83.

$AuBe_{12}$(ThMn$_{12}$,TiBe$_{12}$,SR22.49), a(50,68,16,28)=7.24;4.25Å=g_B(√32;3.3), $N_{oc}(g)$=0.76.

The following phases are more inorganic in character since Be has cationic property expressed by the stability of Lewis phases. They are considered here to have a more complete insight into the chemical properties of Be.

$BeZn_M$(nip,65Ell). "BeZn(CsCl)" might yield the binding a(4,12,8,8)=g_F(2). The instability of this phase suggests that the Zn2sp shell falls out of the binding.

$BeCd_M$(nip,65Ell), $BeHg_M$(nip,58Han).

Be_4B(T8.2,SR27.65,drw ibid.) is lacuna htpc to Be.h. a(22,20)=3.37;7.05Å=g_C(√8;6), $N_{oc}(g)$=0.88. For additional remarks see: Bindings in AB_M phases.

Be_2B.h(CaF$_2$,SR26.57), a(28,24)=4.66Å=g_C(4), $N_{oc}(g)$=0.81.

Be_2B_3(T24.36?,73Ste), a(156,120)=7.25;8.46Å=g_C(√40;7.5), $N_{oc}(g)$=0.92.

BeB_3(H27.82), BeB_6(T28.168), BeB_{12}(T4.48), see AB_M phases.

$BeAl_M$(nip,58Han), BGa_M(nip,65Ell), BIn_M(nip,65Ell),$BeTl_M$

Be_2C(CaF$_2$,SR3.20), a(32,24)=4.34Å=g_C(4), $N_{oc}(g)$=0.88.

BeC_2 not solved, see AC_M.

$BeSi_M$(nip,58Han), $BeGe_M$(nip,77Mof), $BeSn_M$(nip,65Ell), $BePb_M$.

Be_3N_2.h(H6.4,SR34.29) is a Lewis phase with N close packing stacked by + + − − and containing Be in tetragonal interstices. a(32,20)=12.84;9.69Å=g_{CH}(2;17/3). A g correlation smeared in a_1,a_2 direction favours the observed stacking (84Sch), $N_{oc}(g)$=0.76.

Be_3N_2.r(MnFeO$_3$,B24.16,SR38.120,drw 64Sch.231) is a CaF_2 structure with F-lacunae. The commensurability a=a_{CaF_2}(2) has electrostatic advantages. a(256,160)=8.15Å=g_C(8). $N_{oc}(g)$=0.81 obeying the occupancy rule (86Sch).

Be_3P_2(U48.32,SR41.31,drw ibid.) is htpc to CaF_2, a=a_{CaF_2}(2;4). a(512,704)=10.22; 20.39Å=g_B(8;15). $N_{oc}(g)$=0.63. BeP_2(85Vil).

$BeAs_M$ a compound appears possible, (65Ell). $BeAs_2$(85Vil).

$Be_{13}Sb$(NaZn$_{13}$,MgBe$_{13}$,SR43.13), a(248,288,64)=10.05Å=g_B(8), $N_{oc}(g)$=0.59.

Be_3Sb_2(64Shu), $BeSb_2$(htpc C,85Vil), a=5.88Å.

$BeBi_M$(nip,77Mof).

The BeA_M[16..17] phases are reviewed in 73Gir.

BeO.h(T4.4,SR30.304) has an O_{rutile} site set with Be in tetrahedral interstices. a(32.8)=4.75;2.74Å=$g_C(\sqrt{20};2.5)$, $N_{oc}(g)$=0.80.

BeO.r(ZnO,H2.2,SR20.261,drw SR1.78) obeys Lewis' rule of compensation of spins near O by spins near Be. a(16.4)=H2.70;4.38=$g_{CH}(\sqrt{3};7/3)$, $N_{oc}(g)$=0.95. In both phases it has been assumed that the O1s^2 electrons do not take part in the g correlation.

BeS(ZnS,F1.1,SR20.49), a(32,40)=4.86Å=$b_F(2)=g_B(4)$.

BeSe(ZnS,SR1.134), a(32,40,32)=5.14Å=$b_F(2)=g_B(4)$.

BeTe(ZnS,SR1.134), a(32,40,32)=5.63Å=$b_F(2)=g_B(4)$. The Te3d^{10} electrons can take part at most only partly.

BePo(ZnS,SR24.218), a(32,40,32)=5.84Å=$b_F(2)=g_B(4)$.

BeF_2.h_2(SiO_2.h_2,F2.4,SR20.216,drw 64Sch.200), a(128,32)=6.78Å=$g_F(4)$, $N_{oc}(g)$=0.62. The low occupancy is caused by the loose packing of the atoms.

BeF_2.h_2m(SiO_2.h_2m,T8.16,73Pie,drw 64Sch.200), is I-homeotypic to h_2. a(128,48)=6.61;6.75Å=$g_{FU}(\sqrt{29};8/2)$, $N_{oc}(g)$=0.76.

BeF_2.h_1(O64.128,73Pie) is perhaps stabilized by impurities (73Pie).

BeF_2.r_2(SiO_2.r_2,H3.6,SR16.167,drw 64Sch.200), a(48,18)=H4.74;5.15Å=g_{UH}(4;6/2), $N_{oc}(g)$=0.69. Since the binding of h_2 has a bad spin compensation, the phase transforms to r_2 having a good spin compensation.

BeF_2(SiO_2.r_1,73Pie) is I-homeotypic to r_2, and presumably idmc.

$BeCl_2$.h(O,73Pie), a=16.08;14.48;10.10Å.

$BeCl_2$.r(SiS_2,P2.4,SR16.183,drw 64Sch.207) is a Cl_{F1} structure with Be in tetrahedral interstices. a(64,72)=9.86;5.36;5.26Å=$b_{FU}(3;8/2)=g_C(\sqrt{18};8)$.

$BeBr_2$(SiS_2,$BeCl_2$.r,SR28.300), a(64,88,64)=10.32;5.52;5.54Å=$g_B(\sqrt{18};8)$. The participation of the Br3sp electrons (c correlation) allows $b\sim e$ to have more electrons than $b\sim c$ in $BeCl_2$.r.

BeI_2.h(O32.64,SR21.216) is htpc to SiS_2.

BeI_2.r(T4.8,SR21.216), a(64,88,64)=6.12;10.63Å=$g_B(\sqrt{20};8)$, $N_{oc}(g)$=0.68. Further phases see 73Pie.

For three component phases containing Be see 71Eck, 73Pie, 79Ald, 85Vil.

Discussion

The junction of the electron correlations within the atoms to a correlation within the crystal results in a chord and the energy is low in a harmonic chord yielding integral number commensurability elements between the crystal cell a and the correlation cell g. Since the bindings obey rules, they provide a better understanding of the features of chemical equilibrium. The understanding consists in answers to numerous unpretending questions as for example:

Why do the mixtures A^1Be_M not contain A^1Be_{13}($NaZn_{13}$) phases? The Be component allows only a lattice constant of 10Å and this is too small for the larger A^1 atoms.

Why do the mixtures A^2Be_M not contain phases with mole fractions N_{Be}<13/14? If

the Be component is more diluted in the A^2 component then the distance d(Be2sp) becomes longer so that the Be2sp electrons fall out of the correlation with the core electron of A^2.

Why has $ScBe_5(CaZn_5)$ only two layers parallel to the hexagonal basal plane? The binding causes momentary electrical dipole vectors in a_3 direction, alternating in sign with increasing layer number. These vectors cause that neighbouring layers repel each other while next neighbouring layers attract each other.

Why is $TiBe_2$ based on a F1 close packing and not on H2 like Be.r? The Ti atom contributes 20 electrons into the g correlation but Be only 4. The valence electron concentration is therefore increased by the addition of Ti. While in the close packed layers of Be.r there was the commensurability $a=g_H(\sqrt{3})$ in $TiBe_2$ it is $a=g_H(\sqrt{2})$. The electron concentration in $TiBe_2$ has a value favouring a g_F correlation, the commensurability of which to a favours the F1 packing.

Why is $VBe_2(MgZn_2)$ of a hexagonal double replacement structure? The double replacement structures are composed of double layers V_2Be + LBe_3 (L=lacuna). In VBe_2 there are two double layers. Since V contributes more electrons than Ti and since the occupancy of g in VBe_2 may be smaller than in $NbBe_2(MgCu_2)$ there are 9 g layers parallel to the hexagonal basal plane. They favour the + − type stacking of the double layers (84Sch).

Why becomes the big $MoBe_{22}(ZrZn_{22})$ stable? Mo has a g contribution of 24 electrons and there are 48 Mo4 d electrons in the cell. They may be accommodated by $a=b_B(3)$ but not in the binding of $MgBe_{13}$: $a=g_C(8)$. The b correlation is a sublattice of $a=g_B(9)$ leading to the reasonable $N_{oc}(g)=0.61$.

Why is $MnBe_5(PdBe_5)$ stable? The phase $MnBe_2$ has the $MgZn_2$ type instead of the $MnCu_2$ type since the g concentration is too high for the binding of $TiBe_2(MgCu_2)$. The $PdBe_5$ type is formed from the $MgCu_2$ type by replacing 4 minority atoms by a majority atom. Therefore the $PdBe_5$ type becomes possible.

Why has $FeBe_2$ the highest melting temperature in $FeBe_M$? It has the highest occupancy of the $FeBe_M$ phases.

Why is RhBe(CsCl) stable but not "IrBe(CsCl)"? The simple binding $a=g_F(2)$ is highly occupied in RhBe but would be overoccupied in "IrBe".

Why is "$PtBe_2(MgCu_2)$" not stable although the atomic radius ratio is favourable? The binding $a=g_F(4)$ would be overfilled.

Why has CuBe(CsCl) a neighbouring phase $Cu_{1.4}Be_{0.6}$·h(W)? The bindings $a=g_F(2)$ and $a=g_B(\sqrt{8};2.8)$ are homeotypic.

The ease of the answers to the plain questions confirms the utility of the plural correlations model as a valence model for beryllium compounds.

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