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ON THE BINDING IN $A^nA_{\underline{M}}^{1\cdots7}$ PHASES

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Summary

The crystal chemistry of $A^nA_{\underline{M}}^{1..6}$ phases is predominantly fairly monotonous: either no intermediate phases are formed as the energy of formation is too small; or Friauf-Laves phases and similar ones appear which represent a possibility of coalescence of components with different radius; or homologous miscibility occurs in which the mixed crystals have the same structure and binding as the components, and the difference of the atomic sizes is only of secondary importance. But in $A^nA_{\underline{M}}^{7}$-mixtures a sequence of complex phases, the Cr_3Si family, emerges (Raub's rule) which permits a binding interpretation explaining partly the remarkable structures and reversedly corroborating the necessity of an analysis of the spatial correlation of electrons for the crystal chemical systematics of metallic phases. The structures of the Cr_3Si family are not closest packed as follows from the support number of the primary layers and from the occurrence of shrinking homeotypisms in the family. In the binding this less close packing is expressed by a low occupation number of the $\underline{c}$ correlation indicating a weak interaction of the atom cores. The greater wealth of phases in $A^nA_{\underline{M}}^{7}$-mixtures is caused by the greater difference in the place number ratio of the components.

Introduction

The two-correlations model, a valence model for metallic phases, should be tested by application to as many phases as possible. In order to limit the labour of such an application only two-component phases are considered here and furthermore phases containing lanthanoids and actinoids are left out, as they contribute a more uniform crystal chemistry. Compounds with Li,Be,B,C,N, O,F are treated separately as the atomic core of these elements is quite different from the core of their heavier homologues.

Since a valence interpretation of intermediate phases intends to find rules describing the type of their chemical bonding, the alphabetical order of compounds used in many compilations of metallic phases (58Han,65Ell,67Pea,69Shu, 71Eck,73Don,77Mof,81Pow) is not satisfactory, a homologous ordering should be used, i.e. an ordering which permits a (more or less) easy comparison of compounds, the components of which are neighbouring in the periodic system of elements. The homologous classes of chemical elements should be named, as 71IUP requests, 1A, 2A, ...,1B ,... . However, the utilisation of these symbols for describing compound classes or mixture classes leads to misunderstandings; therefore it must be written $A^1,A^2,\ldots,B^1,\ldots$, and a confusion with ionic charges is not to be feared as these require a + or - sign added as requested by 71IUP. A homologous mixture class is then $A^2A^4_{\underline{M}}$ e.g. where $\underline{M}$ is an undetermined mole number; however, there is no $A^4A^2_{\underline{M}}$ mixture class, as this symbol is not compatible with the convention (see 64Sch) always to chose in $A^nA^{n'}_{\underline{M}}$ the order $n \leqq n'$. After the phase or mixture symbol there should follow (in brackets) a statement on the crystal structure type or the statement "nic" when no intermediate compound is formed or "tm" when two melts are observed or "bm" when broad marginal phases are found. The structure type is described by the prototype formula, i.e. by the formula of the phase earliest found to belong to the type. For the prototype phase itself the A.J.C.Wilson-Laves structure indication is noted which is utilized also by 81Pow. To be sure the form used here is a little improved (64Sch) in order to permit an easy calculation of numbers of electrons per crystal cell $\underline{a}$. Since the type nomenclature must also be applied to describe bindings (80Sch) i.e. $\underline{b}$-electron correlation type and $\underline{c}$-electron correlation type and their commensurabilities to $\underline{a}$, it is essential that the nomenclature is concise. Therefore a similar later nomenclature (67Pea) substituting the old Structure Reports type description is not appropriate for the present purpose, it is doubly as long in the letters, where it should be brief and too short in the numbers as to permit easy calculation of electron numbers.

The statement on structure type should be referenced, the simplest reference being to Structure Reports^ (SR). The elementary cell *a* of a phase, which is the starting point of its binding analysis, is described in an abbreviated matrix form (82aSch) which immediately may be equalized to the product of cell and commensurability of the *b*-electron correlation and to the product of cell and commensurability of the *c*-electron correlation. One more abbreviation has been used in the commensurability matrices in dropping their rotatory part (82aSch) which may easily be reconstructed from the data given.

In order to facilitate the examination of a binding the numbers *N* of *b* and *c* electrons per cell are sometimes noted. Additional information is provided by the reference to a phase diagram (phd) in the reports of 58Han, 65Ell, 69Shu and 77Mof cited as HA, E, S, M. The phase diagram helps in fact to understand the bonding, for instance a high and congruent melting point (cmp) of a phase indicates a favourable bonding type by the commensurability rule (82aSch).

The analysis of the binding in $A^nA_M^{1..6}$ compounds remains somewhat inconclusive because of the paucity of the intermediate phases which hinders the distance assessment. However, in $A^nA_M^7$ alloys the sequence of structures expressed by Raub's rule (see $A^5A_M^7$) offers the possibility to determine a probable electron count affording the opportunity to find structural arguments for the different and complex members of the Cr_3Si family. The resulting electron counting for instance of $Mn.r^{2.16,13}$ discloses that such a counting may differ appreciably from $Mn^{1,14}$ as assumed for many MnB_M^n phases. The uncertainty in electron count implies an uncertainty in electron distances which renders more difficult and uncertain the finding of the probable binding. It therefore cannot be excluded that here and there improvements of bindings remain probable. However, fundamental findings like the possible incommensurability of correlations in one direction very probably will remain unchanged.

$A^1A_M^1$ phases. The alloys between alkali elements are examples for mixtures of homologous components. Since the isotypism and isodesmism of homologous components is probable, also uninterrupted mixed crystals are probable (see TABLE A1A1M) or, when the atomic radii are too different, no intermediate compounds are formed. An exception of these mixed crystal mixtures is NaK_M with Na_2K ($MgZn_2$,H4.8,drawing 64Sch p.161) which displays an alternation or coalescence of hexagonal close packed layers having 3 or 4 places per *a* mesh, where the greater atom (K,Mg) which always enters the 3-place layer expels one smaller atom from the neighbouring 4-place layer, and is therefore shifted somewhat out of its layer. Three frequent shear hometypes $MgCu_2$(F2.4), $MgZn_2$(H4.8) and $MgNi_3$(H8.16) have been discribed by Friauf 1927 and Laves 1935 and are sometimes named after these authors. However, the homeotypic family of the 3,4 coalescence structures is more extended comprising $CaCu_5$(H1.5,SR11.59), $ThMn_{12}$(U1.12,SR16.113),$NbBe_3$(R3.9,SR23.49) and many more (see 64Sch or 67Pea). While the 3,4 coalescence is clearly caused by the difference of the atomic radii of the components the main problem lies in the question why just the $MgZn_2$ shear homeotype is chosen by the Na_2K phase. The answer requires some statement on the bonding, in the simplest case a specification of a bonding type (binding). To find the binding the electron correlations in the marginal phases Na(Wtype) and K(W) must be considered. The correlation $\underline{a}_{Na}=\underline{b}_B(1)$ has already been found by Wigner and Seitz 1933 and the correlation $\underline{a}=\underline{c}_C(4)$ is easily established by comparison with the crystal structures of B^{ε} elements (74Sch). Using the electron distances following from this binding for Na and K the $\tilde{U}H\not{H}13$ binding of TABLE A1A1M becomes probable where $\tilde{U}H$ is a UH stacking with the layer distance $\underline{d}/\sqrt{2}$, $\underline{d}$=distance in the layer; more binding symbols see 82bSch. It is compatible with the $MgZn_2$ type and would give to the $MgCu_2$ type a higher energy since the 6 atom layers perpendicular to $\underline{a}_3$ generate with the 10 $\underline{c}$ layers a system of electrical dipoles which probably favours the $MgZn_2$ type.

$\underline{A^1A^2_M\text{ phases.}}$ The mixtures of this class do not have homologous components so that uninterrupted mixed crystals are not probable. The great difference in atom radii and the weak interaction of the cores prevents miscibility even in the melt. The structures in the mixture $NaBa_{\underline{M}}$ are not yet known well enough to allow a binding analysis.

$\underline{A^2A^2_M\text{ phases.}}$ The stability of $Mg_2Ca(MgZn_2)$ indicates that the difference in atomic radii does not permit in all mixtures continuous solubility, which may be expected from the homology of the components. The $\tilde{C}HUH3$ binding of Mg_2Ca should be considered as a first trial. The mixture $MgSr_{\underline{M}}$ is an example for a mixture of homologous components which forms several intermediate phases. The valence electron concentration does not change with the mole fraction but the volume difference of the components is so great that the place number ratio $\underline{N}^{/P'}_{P''}$ (82bSch) shows considerable change in the mixture. $Mg_{17}Sr_2(Th_2Ni_{17}$,H4.34) is homeotypic to $CaCu_5$ with the commensurability $\underline{a}=\underline{a}_{CaCu5}(\sqrt{3};2)$; the great atom is sometimes replaced by a dumbbell of small atoms with axis parallel to $\underline{a}_3$, the binding might be HFH2. It is seen from the TABLE A2A2M that $\underline{N}^{/P'}_{P''}$ increases with increasing mole fraction $\underline{N}'_{Sr}$, as the volume of Sr is greater than that of Mg. For the remaining phases more analysis appears necessary.

A1A1M

Na2K(MgZn2,SR9.120)H7.50;12.29A=bŨH(√3;4/2)=cH(√39;10) phdHA N=12,96
NaRbM(nic) phdHA KRbM(W) phdHA Na2Cs(H8.4,see HA) phdHA
KCsM(W)
K2Cs(,J.Phys.Chem.So142.1981.23) phdHA
RbCsM(W) phdHA

A1A2M

NaMgM(nic,tm)phd M KMgM(nic,tm)phd M RbMgM(nic,tm)phd M CsMgM(nic,tm)phd M
NaCaM(nic,tm)phdHA KCaM(nic,tm)phd M RbCaM(nic,tm)phd M CsCaM(nic,tm)phd M
NaSrM(nic) phd S KSrM(nic,tm)phd M RbSrM(nic,tm)phd M CsSrM(nic,tm)phd M
Na12Ba(Naturw.44.1957.535)
Na6Ba(ibid)
Na4Ba(tetr.,SR29.104,see SR30.117)9.16;17.28A phdS
NaBa(orth.,SR29.104)4.26;5.88;9.65A
KBa(nic,tm)phd M RbBaM(nic,tm)phd M CsBaM(nic,tm)phd M

A2A2M

Mg2Ca(MgZn2,SR5.53)H6.23;10.12A=bC̃H(√3;8/3)=cUH(√27;10/2) N=24,96 phdHA cmp
Mg17Sr2(Th2Ni17,SR26.175)H10.533;10.342A=bH(√19;4)=cFH(2√19;10/3) N=76,304 phdHA
Mg38Sr9(H76.18,ACB38.1982.1797)H10.500;28.251A, see SR30.24 cmp
Mg23Sr6(Th6Mn23,SR26.176)14.914A=bC(6)=cFU(12;17/2) N=232,928
Mg2Sr(MgZn2,SR9.31)H6.439;10.494A=idmMg2Ca N=24,96 cmp
MgSr(CsCl,SR9.46,doubted see phd)3.908A=bF(1)=cB̃(√8;3)
CaSrM(W,Mg,Cu) phdE
Mg17Ba2(Th2Zn17,SR27.64)H10.664;15.593A phdHA cmp
Mg23Ba6(Th6Mn23,SR30.117)15.263A=idmMg23Sr9
Mg2Ba(MgZn2,SR9.31)H6.649;10.676A=idmMg2Ca
CaBaM.h(W) phdHA
CaBa(NaTl,seeHA)
SrBaM.h(W) phdHA

A1A3M

NaScM KScM RbScM CsScM
NaYM KYM RbYM CsYM
NaLaM KLaM RbLaM CsLaM

A2A3M

Mg24Sc5(Mn.r,71Eck)9.65A=bC(5)=cC(10) phdM
Mg3Sc2(CsCl,SR30.152)3.597A=bFU(√2.25;2.1)=cC(3)
CaScM SrScM BaScM
Mg24Y5(Mn.r,SR27.195)11.257A=idmMg24Sc5
Mg5Y2(Q ,SR24.176)5.9;11.0;9.8A phdE
Mg2Y(MgZn2,SR29.123)H6.037;9.752A=bFH(√5.25;4.5/3)=cH(√21;7.4)
MgY(CsCl,SR24.176)3.80A=bFU(√2.25;2.1)=cC(3)
CaYM(nic,tm)phd M SrYM(nic,tm)phd M BaYm
Mg17La2(Th2Ni17,SR28.47)H10.36;10.24A=bH(√19;4.3)=cHK(2) N=80,304
Mg3La(Fe3Si,SR23.215)7.509A=bFU(3;4.2/2)=cFUK(2) N=36,128 phdHA cmp
Mg2La.h(MgCu2,SR23.214)8.787A=bU(√8;3.5)=cB(√32;5.6) N=56,192
MgLa(CsCl,SR9.46)3.963A=idmMgY FUC2
CaLaM(nic,tm)phd E, SrLaM BaLaM

A3A3M

ScYM.h(W)phd S ScYM.r(Mg) ScLaM(nic)phd M YLaM.h(W)phd E
YLa(Sm,see S)H3.699;26.70A=bH(√2.3;11)=cUH(√7;22) phd S

$A^1A^3_{\underline{M}}$ phases. Little is known on these mixtures.

$A^2A^3_{\underline{M}}$ phases. $Mg_{24}Sc_5$(Mn.r) is homeotypic to Cr_3Si and U.h_1 (see drawing 64Sch p.155). As for $MoRe_3$(Mn.r) from the binding given below a valence electron concentration $\underline{N}_{\underline{b}}^{/A}$=2.16 is to be inferred, it is satisfactory that the electron count $Mg_{24}^{2,8}Sc_5^{3,8}$ just yields $\underline{N}_{\underline{b}}^{/A}$=2.17 and a similar binding may be assumed as in $MoRe_3$. As from the binding in Mo_2Re_3.h(U.h_1) the valence electron concentration $\underline{N}_{\underline{b}}^{/A}$=2.5 may be deduced, it could be expected that "MgSc" might show this type. However, the stability of Mg_3Sc_2(CsCl) suggests that the phase is contented with the value $N_{P''}^{/P'}$=5.6 while U.h_1 has 6.

The electron count $Mg^{2,8}Y_{M}^{3,8}$ is confirmed by the interpretation of the phases observed in $MgY_{\underline{M}}$ and $MgLa_{\underline{M}}$. Both mixtures have a phase whith $\underline{N}_{P''}^{/P'}$=8 and in $MgLa_{\underline{M}}$ even two phases yield an XX2 binding.

$A^3A^3_{\underline{M}}$ phases. Homologous miscibility prevails in this mixture class. The phase YLa(Sm type,drawing 64Sch p.74) is a close packed structure with 9 layers per $\underline{a}_3$ axis. The binding $\underline{a}=\underline{b}_H(\sqrt{2.3};11)=\underline{c}_{UH}(\sqrt{7};22/2)$ has less than 27 $\underline{b}$ places per cell and if it is assumed that the exceeding electrons somehow strain the binding in the $\underline{a}_3$ direction the binding is only $\underline{a}=\underline{b}_H(\sqrt{2.3};10.5)=\underline{c}_{UH}(\sqrt{7};21/2)$. In this case it is easy to verify that the $\underline{b}$ correlation generates electrical dipoles E at the atoms changing their E_3 component just after 3 layers parallel to the basal phase and causing thus the shears as compared with the Mg type.

$A^{1..2}A^4_{\underline{M}}$ phases. No compounds are formed and two melts are frequent.

$A^3A^4_{\underline{M}}$ phases. These mixtures are intermediary between the preceding and the following classes.

$A^4A^4_{\underline{M}}$ phases. Homologous miscibility is the only form of this class.

$A^{1..3}A^5_{\underline{M}}$ phases. No intermediary compounds are found and two melts are frequent.

$A^{4..5}A^5_{\underline{M}}$ phases. Complete miscibility is stable when the atomic radii are similar enough, and 3,4 coalescence is chosen when the radii are sufficiently different. Because of paucity of intermediate phases the interpretation has only a tentative value as yet. A rare structure has $Ti_{84}V_{16}$(H3), the so called omega phase, a I-homeotype of W (I=inhomogenous deformation). It might be that here, like as in Ti.h, three correlations are of influence.

A1A4M

NaTiM(nic,tm)phd M	KTiM(nic,tm)phd M	RbTiM	CsTiM
NaZrM(nic,tm)phd M	KZrM(nic,tm)phd M	RbZrM	CsZrM
NaHfM(nic,tm)phd M	KHfM(nic,tm)phd M	RbHfM	CsHfM

A2A4M

MgTiM(nic)phdHA	CaTiM(nic)phd E	SrTiM	BaTiM
MgZrM(nic)phd S	CaZrM	SrZrM	BaZrM
MgHfM(nic)seeHA	CaHfM	SrHfM	BaHfM

A3A4M

ScTiM.h(W)phd E	YTiM(nic)phd E	LaTiM(nic,tm)phd M	
ScZrM.h(W)phd S	ScZrM.r(Mg)	YZrM(nic)phd E	LaZrM(nic,tm)see E
ScHfM.h(W)phd M	ScHfM.r(Mg)	YHfM(nic)phd E	LaHfM

A4A4M

TiZrM.h(W)phd M	TiZrM.r(Mg)		
TiHfM.h(W)phd M	TiHfM.r(Mg)	ZrHfM.h(W)phd E	ZrHfM.r(Mg)

A1A5M

NaVM	KVM	RbVM	CsVM
NaNbM(nic)see S	KNbM(nic)see S	RbNbM	CsNbM
NaTaM	KTaM(nic)phd M	RbTaM	CsTaM

A2A5M

MgVM(nic,tm)phd M	CaVM see S	SrVM	BaVM
MgNbM(nic,tm)phd M	CaNbM(nic)see E	SrNbM	BaNbM
MgTaM	CaTaM	SrTaM	BaTaM

A3A5M

ScVM(nic)phd M	YVM(nic,tm)phd E	LaVM(nic,tm)phd M
ScNbM(nic)phd M	YNbM(nic,tm)phd E	LaNbM(nic,tm)phd M
ScTaM(nic,tm)phd M	YTaM(nic,tm)phd M	LaTaM(nic,tm)phd M

A4A5M

TiVM.h(W)
Ti84V16(H3,Omega,SR22.99)H4.60;2.82A=bH(√3;1)=cUH(3;2) phdHA
ZrV2(MgZn2,SR9.49)H5.288;8.664A=bH(√7;4.3)=cUH(√21;8.6/2) N=24,128 phd HA
HfV2(MgCu2,SR26.162)7.400A=bC(4)=cU(√32;7) N=48,256

TiNbM.h(W)phd E	ZrNbM.h(W)phd E	HfNbM.h(W)phd M
TiTaM.h(W)phdHA	ZrTaM.h(W)phd E	HfTaM.h(W)phd S

A5A5M

VNbM(W) phd HA
V2Ta.h(MgZn2,SR30.170)H5.058;8.250A=idmZrV2 phd M
V2Ta.r(MgCu2,SR31.68) 7.16A=idmHfV2
NbTaM(W) phd E

A1A6M

NaCrM	KCrM	RbCrM	CsCrM
NaMoM	KMoM(nic)see S	RbMoM	CsMoM
NaWM	KWM	RbWM	CsWM

$A^{1..3}A^{6}_{M}$ phases. Just as in $A^{n}A^{5}_{M}$ intermediate phases do not occur earlier than with A^{4}.

$A^{4..6}A^{6}_{M}$ phases. Prevailing are the 3,4 coalescence structures, but by impurities structures of later phases are stabilized like $ZrMo_3$.i(Cr_3Si) or Zr_3W_5.i(W_5Si_3) or $NbCr_2$.i(Ti_2Ni). With respect to the great stability of the binding in W many mixtures display the continous quasi homologous miscibility. It should be of interest to know more exactly the structure of $Zr_{95}Mo_5$.m(T4).

$A^{1..2}A^{7}_{M}$ phases. No intermediate phases have been reported.

$A^{3}A^{7}_{M}$ phases. The most frequent structure is that of $A^{3}A^{7}_{2}$($MgZn_2$) but YMn_2($MgCu_2$) is heterotypic. The electron count might be assessed for $ScTc_8$(Mn.r) from the valence electron concentration $N^{/A}_{\underline{b}}=2.16$ assumed for $MoRe_3$ as $Sc^{3,8}Tc^{2,5}_{8}$. This might permit for $ScMn_2$ a HUH√3 binding. The preference for the $MgZn_2$ type might be promoted by the √7 commensurability.

The phase Y_6Mn_{23}(Th_6Mn_{23},drawing 64Sch p.156) is homeotypic to Cr_3Si in so far it displays tetrahedral stars (see64Sch p.156) and homeotypic to Mn.h_3(W) in so far it may be derived by RLI-homeotypism from W (R=replacement, L=lacuna) a HTU√2 binding might be possible. YMn_{12}($ThMn_{12}$) belongs to the 3,4 coalescent structures and a CU√2 binding is probable.

$A^{4}A^{7}_{M}$ phases. Unfortunately several structures are not yet completely analysed. The remaining structures belong to the Cr_3Si family (see 64Sch) or to the $MgCu_2$ family. The electron count is near $Ti^{4,8}Mn^{1,14}_{M}$.

The Cr_3Si structure itself (see $A^{6}A^{7}_{M}$) does not yet become stable as for the FB2 binding there are too few $\underline{b}$ electrons. The place number ratio $\underline{N}^{/P'}_{P''}$ ($\underline{N}'_2$) extrapolates well against 8 for $\underline{N}'_2 \rightarrow 1$.

$A^{5}A^{7}_{M}$ phases. The quasi homologism of VMn.r(CsCl) to Cr might suggest a BC2F2 binding, but an isodesmism with TiTc(CsCl) gives a better fitting electron distance. The stabilisation of Mn.r by V to higher temperatures conforms excellently to the binding given for $MoRe_3$: as V increases the $\underline{b}$ electron concentration and the $\underline{b}$ electron contribution of Mn deacreases with increasing temperature (83Sch), the temperature may be higher without destabilizing the B29 type when the V content is increased. $NbMn_2$($MgZn_2$) may have the count $Nb^{5,8}Mn^{1,14}_{2}$ and a HUH√3 binding. The remaining phases obey Raub's rule (57Rau,58Haw) which asserts that in certain $A^{n}A^{n'}_{M}$ alloys there is a sequence of structure types W(B1), Cr_3Si(C6.2), U.h_1(T30), Mn.r(B29), W_6Fe_7(R6.7), Mg(H2) for increasing

A2A6M

MgCrM(compounds?HA)	CaCrM	SrCrM	BaCrM
MgMoM(nic)see S	CaMoM	SrMoM	BaMoM
MgWM(nic)seeHA	CaWM(nic)see HA	SrWM	BaWM

A3A6M

ScCrM(nic)phd M	YCrM(nic)phd E	LaCrM(nic)phd E
ScMoM(nic)see S	YMoM(nic)phd E	LaMoM(nic)see S
ScWM(nic)see S	YWM(nic)see S	LaWM

A4A6M

TiCrM.h(W) phd M
Ti10Cr.m(H3,Omega,SR19.113)H4.61;2.83A=idmTi84V16
Ti2Cr3(MgCu2,SR15.47)6.943A
TiCr2.h(MgZn2,SR17.124)H4.932;7.961A=idmZrV2
TiCr2.r(MgNi2,Bull Alloy Phase Diagr.2.1981.174)
Zr10Cr.m(Ti10Cr.m,see E)
ZrCr2.h(MgZn2,SR29.111)H5.108;8.232A=idmZrV2
ZrCr2.r(MgCu2,SR29.111)7.20A=idmHfV2
HfCr2.h(MgZn2,SR29.111)H5.066;8.232A=idmZrV2 phd M cmp
HfCr2.r(MgCu2,SR29.111)7.261A=idmHfV2
TiMo.h(W) phd HA
Ti10Mo.m(Ti10Cr.m,SR22.99)
ZrMo2(MgCu2,SR18.124)7.596A=idmHfV2 phd M
ZrMo3.i(Cr3 Si,SR9.111)4.952A=seeMo3Si(Cr3Si)
Zr95Mo5.m(T4 ,SR21.157)440;6.38A
HfMo2.h(MgNi2,SR26.163)H5.341;17.347A phd M
HfMo2.r(MgCu2,SR26.163)7.560A=idmHfV2
TiWM.h(W) phd M
Zr3W5.i(W5Si3,71Eck)9.50;4.85A
ZrW2(MgCu2,SR18.124)7.615A=idmHfV2
HfW2(MgCu2,SR24.156)7.593A=idmHfV2 phd E

A5A6M

VCrM(W) phd M
NbCr2.h(MgZn2,SR26.112)H4.93;8.12A=idmZrV2 phd E
NbCr2.r(MgCu2,SR26.112)6.988A=idmHfV2
NbCr2.i?(Ti2Ni,SR30.125)11.46A
TaCr2.h(MgZn2,SR18.123)H4.932;8.082A=idmZrV2
TaCr2.r(MgCu2,SR17.111)6.979A=idmHfV2
TaCr2.i?(Ti2Ni,SR30.126)11.45A

VMoM(W)phd E	NbMoM(W)phd E	TaMoM(W)phd HA
VWM(W)phd M	MbWM(W)phd M	TaWM(W)phd M

A6A6M

CrMoM(W)phd HA	CrWM.h(W)phd HA	MoWM(W)phd HA

A1A7M

NaMnM	KMnM	RbMnM	CsMnM
NaTcM	KTcM	RbTcM	CsTcM
NaReM	KReM	RbReM	CsReM

A2A7M

MgMnM(nic)phd HA	CaMnM(nic,tm)phd S	SrMnM(nic,tm)phd S	BaMnM(nic,tm)phd S
MgTcM	CaTcM	SrTcM	BaTcM
MgReM	CaReM	SrReM	BaReM

A3A7M

ScMn2(MgZn2,SR26.237)H5.033;8.278A=bH(√7;4.3)=cUH(√21;8.6/2) N=28,136 phdS
Sc6Mn23?(see S)
YMn2(MgCu2,SR24.35)7.680A=bC(4)=cB(√32;5.5) N=56,270 phd S
Y6Mn23(Th6Mn23,SR30.154)12.44A=bHT(6;7/2)=cU(√72;10) N=256,1388
YMn4(U12.48,SR27.280)8.808;12.521A
YMn5(orth,SR24.110)7.12;4.34;3.05A
YMn12(ThMn12,U1.12,SR27.280)8.541;4.785A=bC(√20;2.5)=cU(√40;4.3)N=54;328
LaMnM(nic,two melts) phd HA
ScTc2(MgZn2,SR27.366)H5.223;8.571A=idmScMn2
ScTc8(Mn.r,SR26.255)9.509A=bC(5)=cU(√50;9)
YTc2(MgZn2,SR29.134)H5.373;8.847A=idmScMn2
LaTcM
ScRe2(MgZn2,SR28.49)H5.271;8.592A=idmScMn2 phd M
Sc5Re24(Mn.r,SR28.49)9.65A=idmScTc8
YRe2(MgZn2,SR23.216)H5.397;8.824A=idmScMn2 phd E
LaReM(nic,two melts) phd M

A4A7M

TiMn(HfRe,T   ,SR27.278)8.19;12.81A phd E
TiMn2(MgZn2,SR22.150)H4.86;7.97A=bH(√7;4.3)=cUH(√21;8.6/2) N=32,136 cmp
TiMn3(O   ,SR26.193)
TiMn4(R53,SR26.143)H11.003;19.446A
ZrMn2(MgZn2,SR24.181)H5.039;8.251A=idmTiMn2 phd E
Hf3Mn2(Ti2Ni,SR24.133)11.812A
HfMn2(MgZn2,SR26.162,192)H4.956;8.122A=idmTiMn2 cmp
TiTc(CsCl,SR27.360)3.110A=bU(√2;1.7)=cFU(√8;4/2) N=6,21
Ti14Tc86(Mn.r,SR27.360)9.579A=bC(5)=cU(√50;9)
ZrTc2(MgZn2,SR27.360)H5.219;8.655A=idmTiMn2
ZrTc6(Mn.r,SR27.360)9.637A=idmTi14Tc86
HfTc(CsCl,SR27.361)3.270A=idmTiTc
HfTc2(MgZn2,SR27.360)H5.200;8.616A=idmTiMn2
HfTc6(Mn.r,SR27.360)9.603A=idmTiTc6
TiRe(CsCl,SR21.145)3.104A=idmTiTc phd E
Ti5Re24(Mn.r,SR19.268)9.609=idmTiTc6
Zr2Re(U.h1,SR23.226)10.12;5.42A=bHT(5;3/2)=cU(√50;4.5) phd E
ZrRe2(MgZn2,SR24.243)H5.270;8.635A=idmTiMn2
Zr5Re24(Mn.r,SR26.221)9.712A=idmTiTc6
Hf2Re(U.h1,71Eck) phd S
HfRe(T   ,71Eck)8.906;13.890A
HfRe2(MgZn2,SR27.233)H5.248;8.592A=idmTiMn2
Hf5Re24(Mn.r,SR27.233)9.682A=idmTiTc6

A5A7M

VMnM.h(W) phd S
VMn.r(CsCl,SR27.279)2.904A=bU(√2;1.7)=cF(2)
VMn3(U.h1,SR23.231)8.906;4.612A=idmMo2Re3.h HTU√2
NbMn2(MgZn2,SR24.179)H4.891;7.969A=bH(√7;4.3)=cUH(√21;8.6/2) N=20, phd E
TaMn2(MgZn2,SR18.124)H4.864;7.947A=idmNbMn2
VTc(CsCl,SR27.361)3.025A=idmVMn.r phdM
V3Tc5.h
VTc2.h
NbTc5(Mn.r,SR27.361)9.547A=idmMoRe3 CU√2
TaTc(CsCl,SR27.361)3.172A=idmVMn.r UFU2
TaTc5(Mn.r,SR27.361)9.565A=idmNbTc5 CU√2

mole fraction $\underline{N}'_{An'}$. The structures of Cr_3Si, $U.h_1$ and Mn.r are closely homeotypic. They are composed of quasi hexagonal layers (in Cr_3Si parallel (001)) which contain atom contact distances and are stacked essentially with the support number 2. They have been named "primary layers" (58Fra), as in between of them there are "secondary layers" which do not contain contact distances but permit simple Schläfli symbols $\tilde{S}$, Cr_3Si $\tilde{S}=4^4$, $U.h_1$ $\tilde{S}=4343^2$, W_6Fe_7 $\tilde{S}=3^6$ which give an easy insight into the structure. From the secondary layers it may be seen for instance that $Cr_3Si \rightarrow U.h_1$ is a shrinking homeotypism, so that the Cr_3Si family must be considered as not closest packed. This view is confirmed by a low $\underline{N}_{p''}^{/P'}$ value for instance 4 in the FB2 binding of $Mo_3Re(Cr_3Si)$, see $A^6A^7_{\underline{M}}$. The Cr_3Si type is not yet stable in $A^5A^7_M$ as the $\underline{b}$ electron concentration is too low, but it will appear in $A^6A^7_{\underline{M}}$. The Cr_3Si type may be considered as homeotypic to NaCl by a RC-homeotypism (R=replacement, C=chain shear); the C-homeotypism is a means of compensation between narrow and less narrow atom distances and this appears to be an indication of weak core interaction as caused by the low occupation of the $\underline{c}$ correlation.

$\underline{A^6A^7_M \text{ phases.}}$ 3,4 coalescence structures do not occur as the difference of atomic radii is no more great enough. Raub's rule (see $A^5A^7_M$) is well followed. The bindings for $MoRe_M$ are Mo(B1,CF1), Mo_3Re(C6.2,FB2), Mo_2Re_3(T30,$HTU\sqrt{2}$), $MoRe_3$(B29,$CU\sqrt{2}$) and probably Re(Mg,UU2). In $MoRe_3$(Mn.r) the electrical dipole rule applies (83Sch).

$\underline{A^7A^7_M \text{ phases.}}$ The absence of the Cr_3Si type in $MnTc_M$ is clear as Mn.r the most $\underline{b}$ rich phase has $\underline{N}_{p''}^{/P'}=6.9$ while the Cr_3Si type should come near to $N_{p''}^{/P'}=4$. The stability of $Mn_2Tc_3(U.h_1)$ is an exception of Raub's rule requiring $\underline{N}_b^{/A}(Mn.r) < \underline{N}_b^{/A}(U.h_1)$, but this is not serious, as the dependence of $\underline{N}_b^{/A}$ from the mole fraction is not very well determined here and also dependent on temperature.

Concluding remarks

The two-correlations model for alloys gives in fact many new stability arguments so that it makes possible a thorough systematics of alloy phases. Such a systematics is needed for the selection of appropriate materials for technical purposes. A good example are the well-known sigma phases (phases with $U.h_1$ structure) which must be avoided in steels because of their embrittlement danger. The knowledge of the $\underline{b}$ electron concentration rule for the sigma phases immediately suggests alloy components which favour or disfavour sigma phase formation.

Another interesting example are the Cr_3Si isotypes which embrace the phases with highest transformation temperatures into the supra-conducting state (see

VRe(CsCl?) phd E
VRe3.h(U.h1,SR26.221)9.36;4.86A=idmVMn3 HTU√2
NbRe.h(U.h1,SR20.75)9.72;5.07A=idmVMn3 phd E
NbRe 3(Mn.r,SR23.198)9.780A=idmNbTc5 CU√2
Ta2Re3.h(U.h1,SR24.219)9.69;5.04A=idmVMn3 phdE
TaRe~3(Mn.r,SR24.220)9.76A=idmNbTc5

A6A7M

CrMn2?(htpMn.r,see HA) phd HA
CrMn3.h(U.h1,SR20.163)8.86;4.59A=idmMo2Re3.h HTU√2
CrMn3.r(U.h1ordered,SR24.30)8.860;4.590A=idmCrMn3.h
MoMn2.h(U.h1,SR18.213)9.10;4.74A=idmMo2Re3.h
WMnM(nic) see HA
CrTc2(U.h1,SR27.361)9.25;4.82A=idmMo2Re3.h
MoTc1.1(Cr3Si,SR27.361)4.94A= phd S
MoTc2(U.h1,SR27.361)9.509;4.945A
WTc3(U.h1,SR27.361)9.479;5.166A
Cr2Re3(U.h1,SR21.95)9.29;4.83A=idmMo2Re3.h HTU√2 phd E
Mo3Re(Cr3Si,JLCM12.1967.510)5.01A=bF(2)=cB(4) N=36,62
Mo2Re3.h(U.h1,SR23.184)9.54;4.95A=bHT(5;3/2)=cU(√50;4.5) N=72,222 phd E
MoRe3(Mn.r,SR23.184)9.55A=bC(5)=cU(√50;9) N=87,420
W3Re(Cr3Si,SR30.165)5.018A=idmMo3Re FB2 N=36,62
WRe(U.h1,SR20.75)9.627;5.015A=idmMo2Re3.h HTU√2 phd E
WRe3(Mn.r,SR20.75)9.588A=idmMoRe3 CU√2

A7A7M

Mn2Tc3(U.h1,SR27.361)9.15;4.80A=idmMo2Re3.h
Mn3Re2(Mn.r,SR33.152)9.10A=at variance with phd E
Mn7Re8(U.h1,SR26.192)9.14;4.75A=idmMo2Re3.h
TcReM(Mg) see S

67Rob). The new electron count presented in this analysis might give an explanation for the puzzeling phenomeon that the Cr_3Si isotypes display strongly varying transformation temperatures. The electron count used in the present analysis may suggest alloying components to increase the transformation temperature.

Finely the present view might contribute to the better understanding of the more rare and complex homeotypes of Cr_3Si which have been ingeniously investigated in the past 69Sho.

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