Crystallography and ordering

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Calcul Thermodynamique

SATA / Giens Peninsula / 2017

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Outline

- Crystallography
  - Experimental data
  - Nature of the phase
  - Sublattice model
  - + DFT
- A same model for different structures
  - interstitials
  - metallic ordering
  - Interstitials and metallic ordering
- Conclusion

Crystal structure data

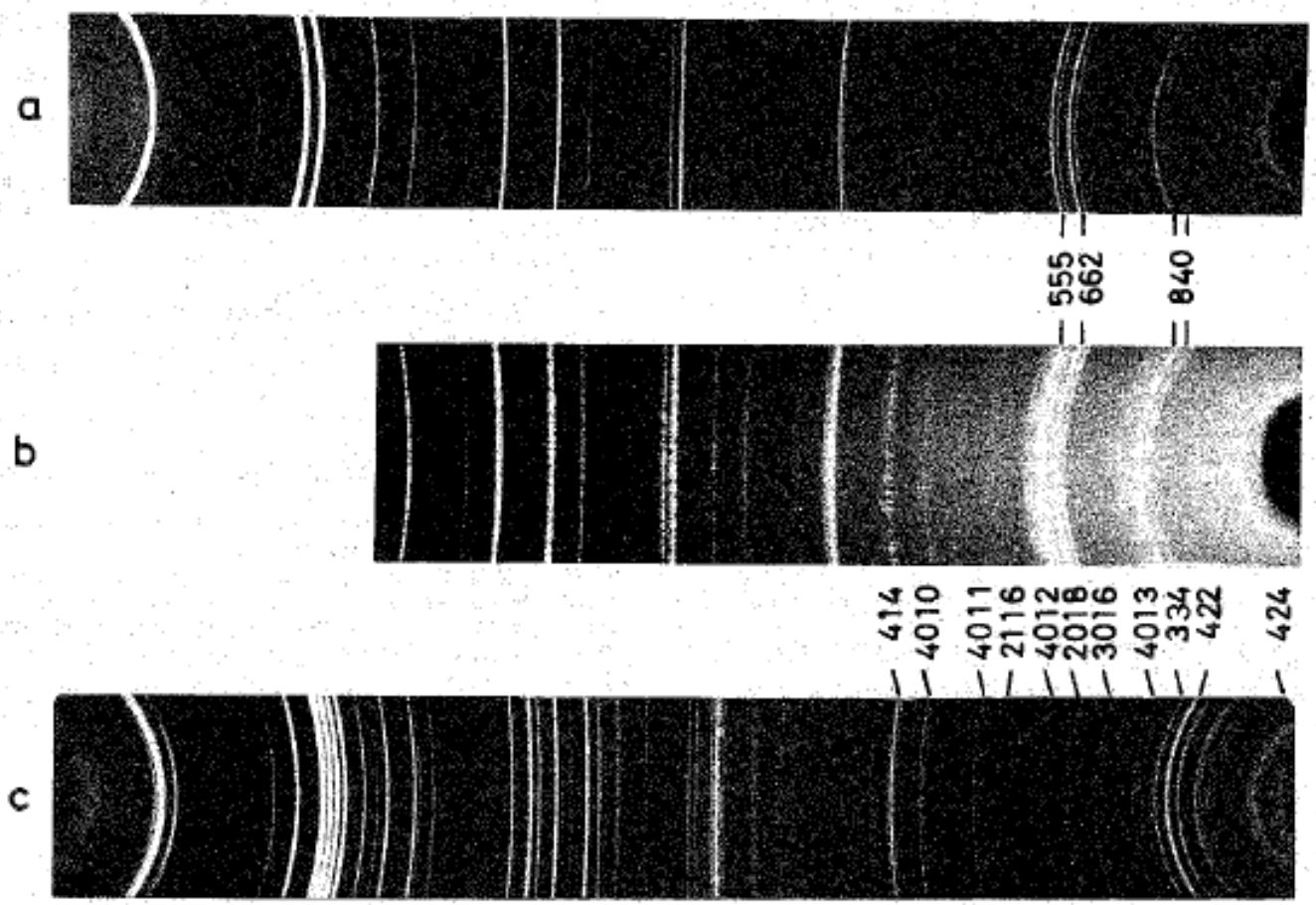


Fig. 7a. $Mg_{33,3}Cu_{66,6}$ recuit 20 jours à 500°C ($K_\alpha Cu$)
Fig. 7b. $Mg_{37,6}Cu_{62,4}$ non recuit ($K_\alpha Cu$)
Fig. 7c. $Mg_{33,4}Ni_{66,6}$ recuit 22 jours à 480°C ($K_\alpha Cu$) avec indication des raies utilisées pour le calcul du paramètre *a*.

Crystal structure data

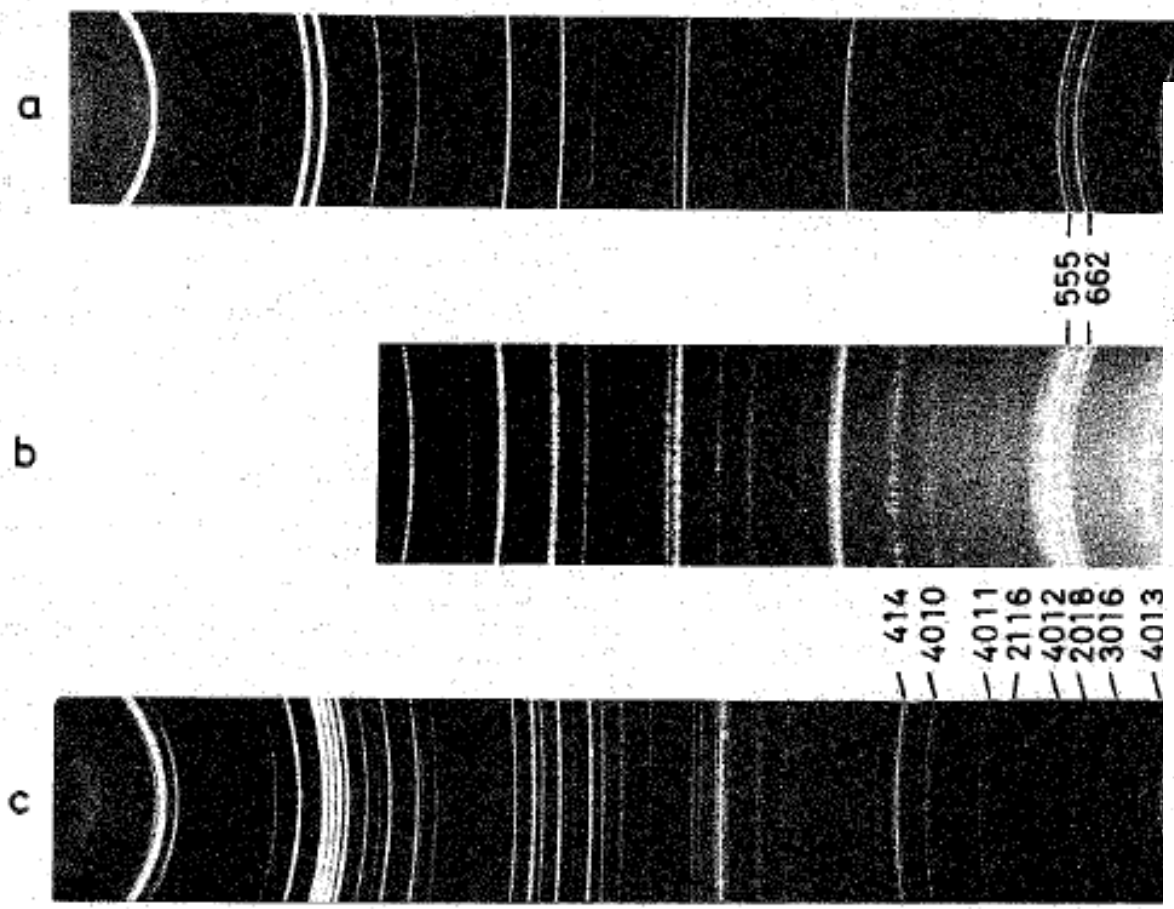


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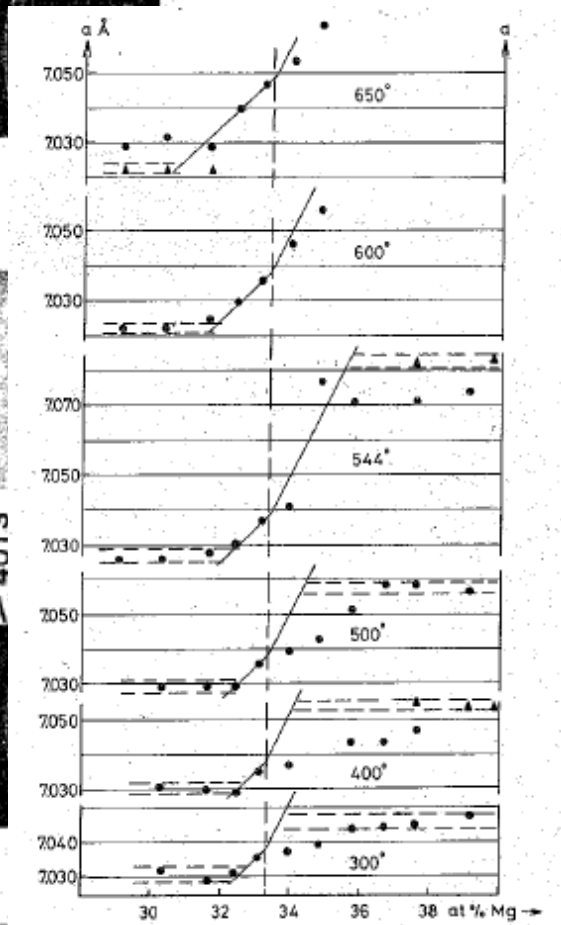


Fig. 4. Paramètre a de la maille cubique de $MgCu_2$ en fonction de la composition (at.% Mg) et de la température (1 Å = 10^{-10} m)

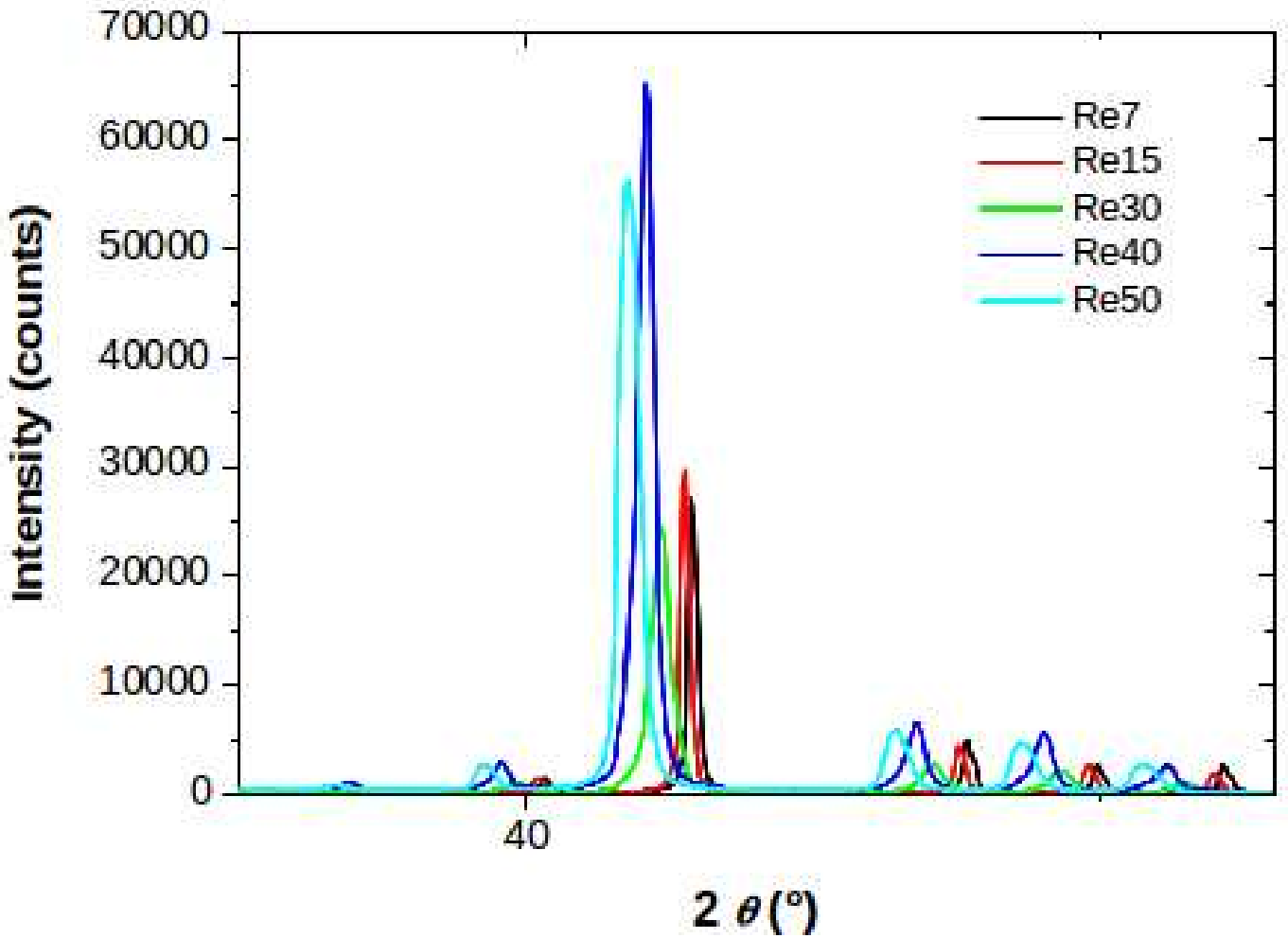
Crystal structure data

TABLE III.—Alloy A (5 per cent. Mg).
(Face-centred cubic.)

Radiation.	$h\,k\,l$.	Intensity.	d/n observed.	d/n calculated.
* K_β	111	V.W.	4·186	4·043
* K_α	111	V.W.	4·029	4·043
K_β	111	M.	2·089	2·089
K_α	111	St.	2·098	2·098
L_α (tungsten) .	100 (2)	W.	1·820	1·817
K_α	100 (2)	St.	1·821	1·817
K_α	110 (2)	St.	1·283	1·284
$L\alpha$ (tungsten) .	131	W.	1·093	1·096
K_α	131	St.	1·094	1·095

NOTE.—Lines of β phase are marked with an asterisk (*).

Crystal structure data



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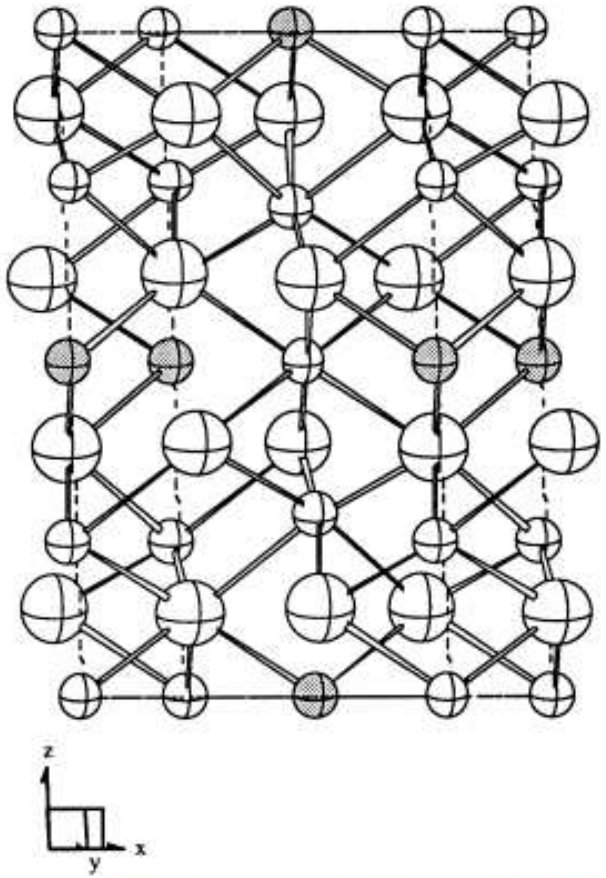


Fig. 3. Perspective view of the $Rh_{1+x}Te_2$ structures ($x>0.5$). The gray sphere corresponds to the octahedral sites filled by rhodium (Rh(3)) beyond the $Rh_{1.5}Te_2$ composition (see Fig. 2 for details of the other rhodium position). Larger open circles are Te atoms.

Table 4
Atomic coordinates and atomic displacement parameters of the $Rh_{1+x}Te_2$ compounds ($0.15<x<0.84$) as refined in the I2/m space group

Atom	x	y	z	Occupancy rate * site multiplicity	B
$Rh_{1.15}Te_2$					
Te(1)	0.339(2)	0	0.373(1)	4	1.12(6)
Te(2)	0.337(3)	0	0.878(1)	4	1.12(6)
Rh(1)	0.006(5)	0	0.251(1)	4	1.02(1)
Rh(2)	0	0	0	0.55(3)	1.02(1)
Rh(3)	0.5	0.5	0	empty	
$Rh_{1.28}Te_2$					
Te(1)	0.338(1)	0	0.368(6)	4	1.6(7)
Te(2)	0.333(1)	0	0.879(7)	4	1.6(7)
Rh(1)	−0.009(3)	0	0.256(1)	4	1.6(1)
Rh(2)	0	0	0	1.11(4)	1.6(1)
Rh(3)	0.5	0.5	0	empty	
$Rh_{1.40}Te_2$					
Te(1)	0.343(7)	0	0.3669(4)	4	1.7(6)
Te(2)	0.335(1)	0	0.8797(4)	4	1.7(6)
Rh(1)	−0.015(1)	0	0.261(5)	4	1.9(1)
Rh(2)	0	0	0	1.59(2)	1.9(1)
Rh(3)	0.5	0.5	0	empty	
$Rh_{1.52}Te_2$					
Te(1)	0.338(1)	0	0.3773(6)	4	2.45(1)
Te(2)	0.343(1)	0	0.8698(6)	4	2.45(1)
Rh(1)	−0.019(1)	0	0.2303(6)	4	1.2(1)
Rh(2)	0	0	0	2	1.2(1)
Rh(3)	0.5	0.5	0	0.12(3)	1.2(1)
$Rh_{1.57}Te_2$					
Te(1)	0.3308(7)	0	0.3808(3)	4	0.88(6)
Te(2)	0.3420(6)	0	0.8824(4)	4	0.88(6)
Rh(1)	0.0166(9)	0	0.2411(5)	4	0.93(8)
Rh(2)	0	0	0	2	0.93(8)
Rh(3)	0.5	0.5	0	0.61(2)	0.93(8)
$Rh_{1.84}Te_2$					
Te(1)	0.336(2)	0	0.377(2)	4	0.36(5)
Te(2)	0.343(2)	0	0.869(1)	4	0.36(5)
Rh(1)	0.0011(4)	0	0.259(2)	4	1.57(9)
Rh(2)	0	0	0	2	1.57(9)
Rh(3)	0.5	0.5	0	1.49(6)	1.57(9)

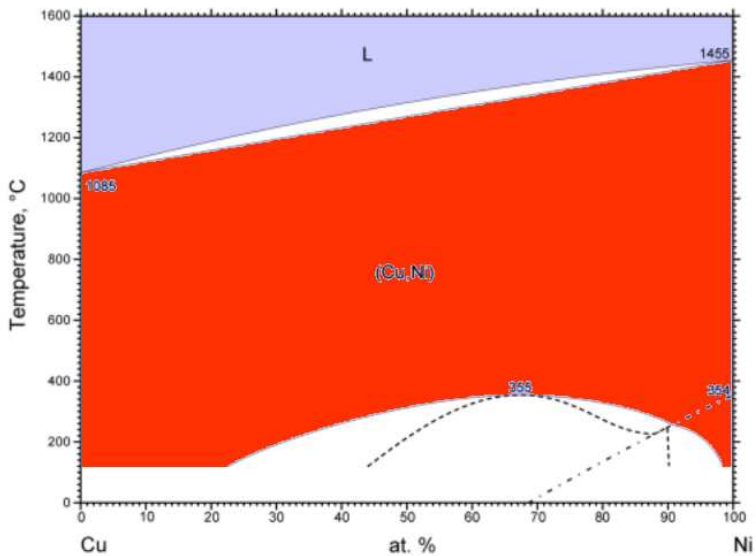
Crystallographic information

Of interest for the thermodynamic modelling

- ⇝ Nature of the phase: prototype, StrukturBericht
  - ⇒ continuous model, phase name
- ⇝ Number of sites, multiplicity
  - ⇒ sublattice model
- ⇝ Site occupancy
  - ⇒ species to consider in the modelling
  - ⇒ can be fitted
- ⇝ Volume
  - ⇒ can be fitted

Continuous modelling

Phase	Structure type	Peason symbol	Space group No.	Material search
(Cu,Ni)	Cu	cF4	225	Search



Bibliographic data
Binary Alloy Phase Diagrams, II Ed., Ed. T.B. Massalski,1990,2,,1442-1446,Chakrabarti D.J., Chen S.W., Chang Y.A.

Continuous modelling is obvious when there is a continuous solution.

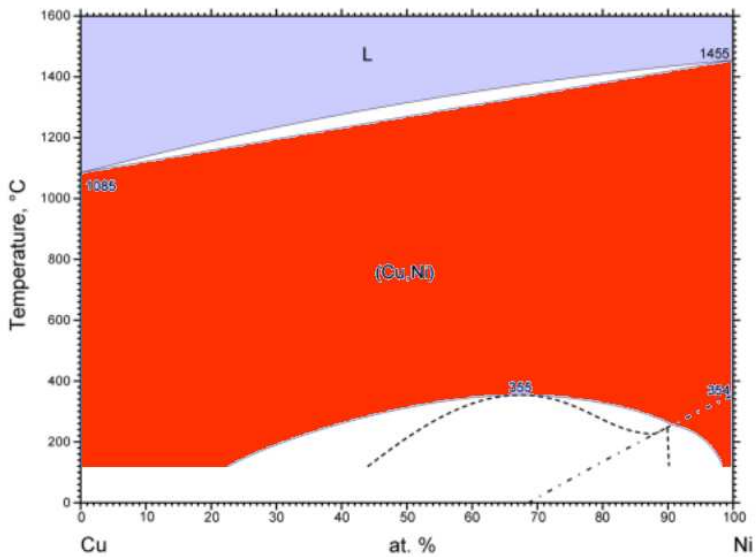
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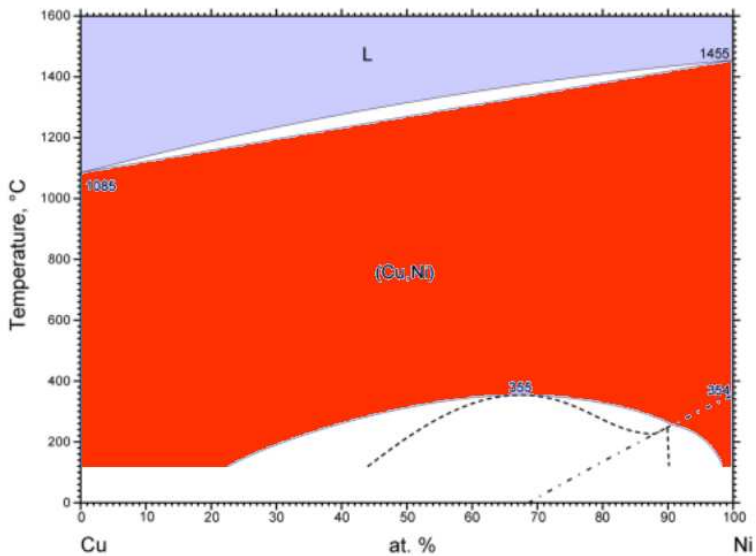
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$$G^{fcc} = x_{Cu} G^{fcc}_{Cu} + x_{Ni} G^{fcc}_{Ni} + RT\left(x_{Cu} \ln x_{Cu} + x_{Ni} \ln x_{Ni}\right) + x_{Cu} x_{Ni} L^{fcc}_{Cu,Ni}$$

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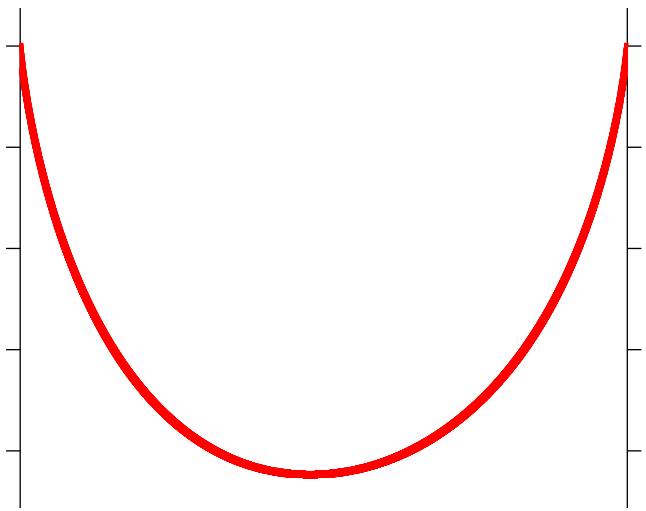
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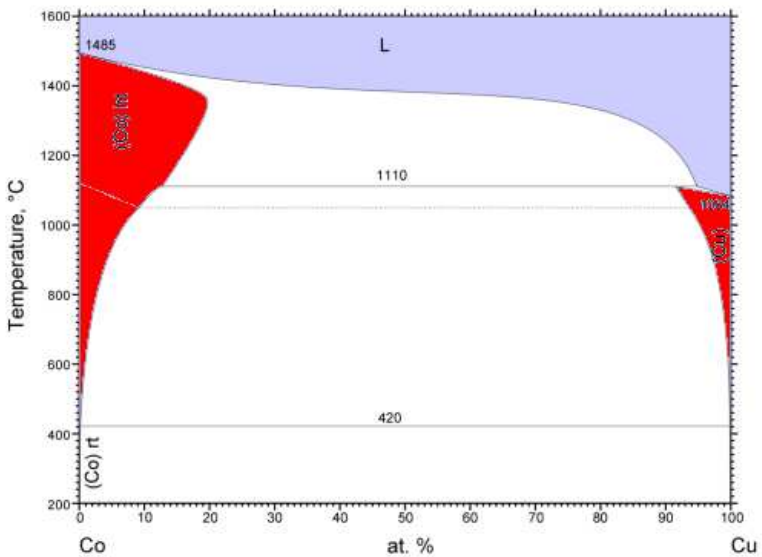
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Phase	Structure type	Peason symbol	Space group No.	Material search
(Cu)	Cu	cF4	225	Search
(Co) ht	Cu	cF4	225	No Data
(Co) rt	Mg	hP2	194	No Data



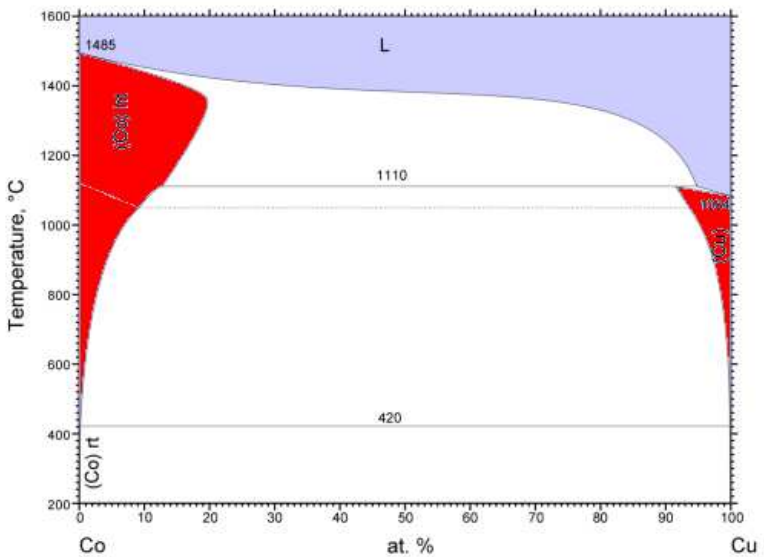
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Continuous modelling may be less obvious when there is a miscibility gap.

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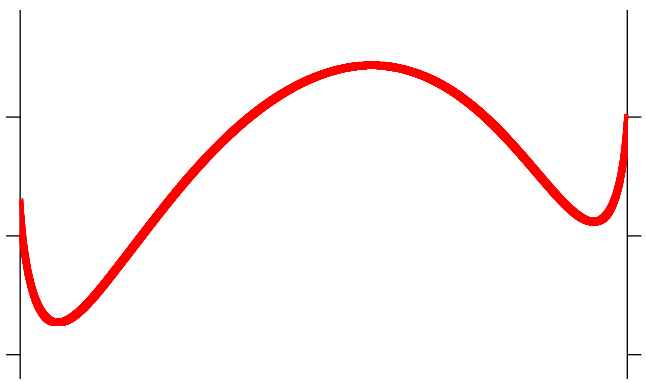
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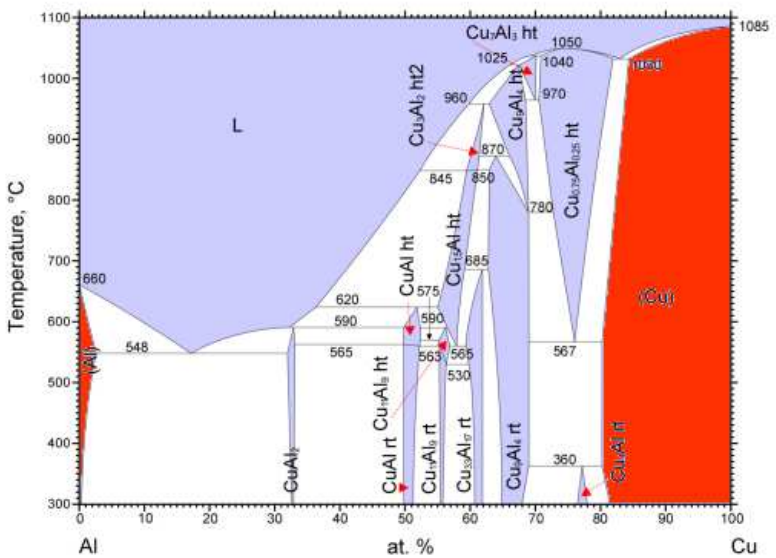
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$CuAl_2$	$CuAl_2$	tI12	140	Search
$Cu_{1.5}Al$ ht	$Co_{1.75}Ge$	hP6	194	No Data
(Cu)	Cu	cF4	225	No Data
Cu_9Al_4 rt	Cu_9Al_4	cP52	215	Search
Cu_4Al rt	Au_4Al	cP20	198	No Data
CuAl rt	CuAl	mS20	12	No Data
$Cu_{33}Al_{17}$ rt	$Cu_{31.27}(Cu_{0.57}Al_{0.43})_3Al_{16}$	hR156	160	No Data
$Cu_{0.75}Al_{0.25}$ ht	W	cI2	229	No Data
(Al)	Cu	cF4	225	No Data
Cu_9Al_4 ht	Cu_5Zn_8	cI52	217	No Data



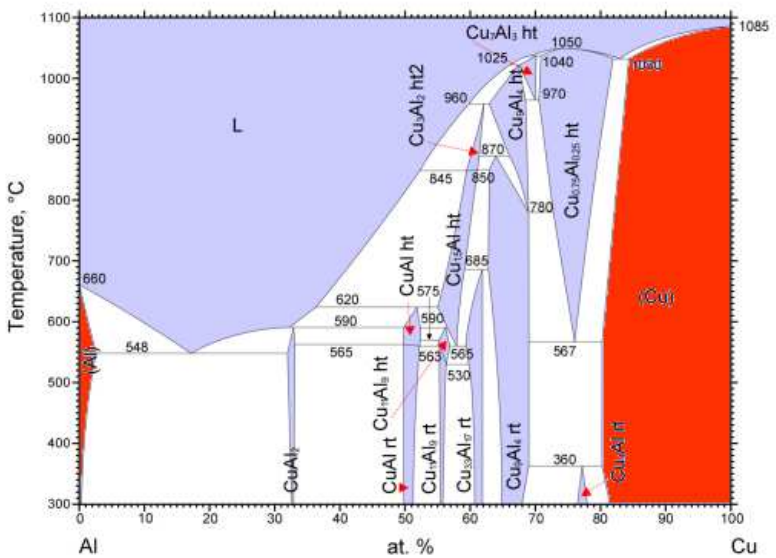
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The reciprocal solubility can also be limited due to intermediate phases.

(Al) and (Cu):
prototype Cu
$\Rightarrow$ substitutional
model: (Al,Cu)

Continuous modelling

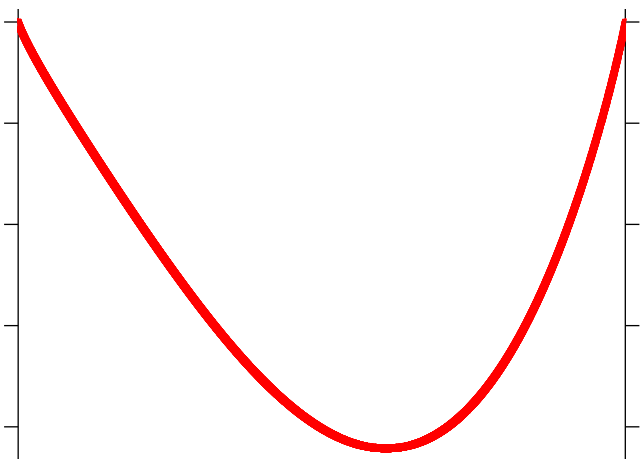
Phase	Structure type	Peason symbol	Space group No.	Material search
$CuAl_2$	$CuAl_2$	tI12	140	Search
$Cu_{1.5}Al$ ht	$Co_{1.75}Ge$	hP6	194	No Data
(Cu)	Cu	cF4	225	No Data
Cu_9Al_4 rt	Cu_9Al_4	cP52	215	Search
Cu_4Al rt	Au_4Al	cP20	198	No Data
CuAl rt	CuAl	mS20	12	No Data
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(Al)	Cu	cF4	225	No Data
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$\Rightarrow$ substitutional
model: (Al,Cu)



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  ex: CsCl/NiAl

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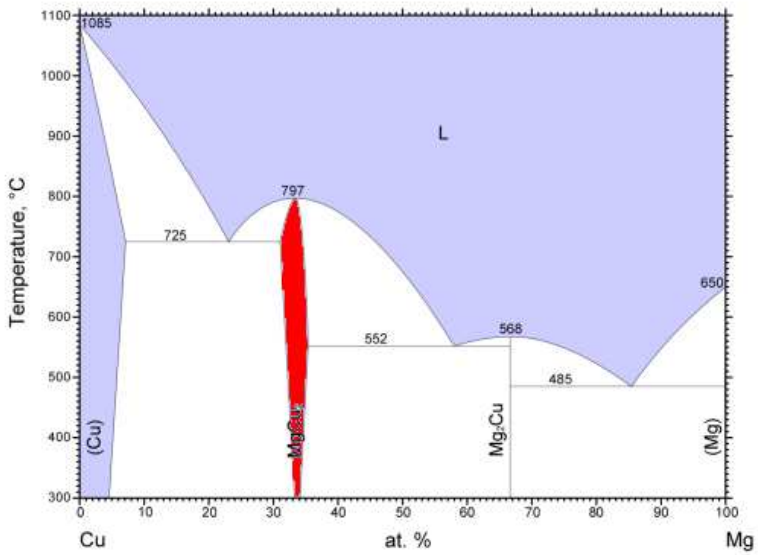
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- It is not recommended when no common elements, no possible solubility, very different interactions. ex: CsCl/NiAl

Using a phase name related to the crystallographic structure may avoid names losing their meaning when considering different systems. BCC_A2 is α or δ for Fe, β for Ti, γ for U.

Laves phases

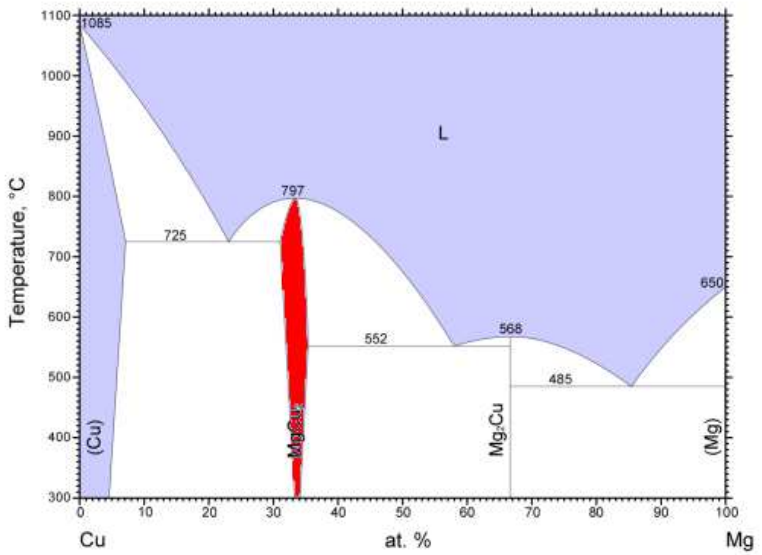
Phase	Structure type	Peason symbol	Space group No.	Material search
(Mg)	Mg	hP2	194	Search
$MgCu_2$	$MgCu_2$	cF24	227	Search
(Cu)	Cu	cF4	225	No Data
Mg_2Cu	Mg_2Cu	oF48	70	Search



Bibiographic data
Binary Alloy Phase Diagrams, II Ed., Ed. T.B. Massalski,1990,2,,1433-1435,Nayeb Hashemi A.A.

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	$MgCu_2$	cF24	Fd-3m	22

*Standardiz

Acta Crystallogr. C,1984,40,,1-5,Ohba T., Kitano Y., Komura Y.

Preparation

Synthesis No data.

Starting materials No data.

Crystal Structure | X-ray Diffraction | Properties

Crystal Structure (Published)

Niggli-reduced cell

Crystallographic data

Cell parameters a = 0.49738 nm, b = 0.49738 nm, c = 0.49738 nm, α = 60 °, β = 60 °, γ = 60 °

Cell volume 0.08701 nm^3

Crystal Structure (Standardized)

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Cell parameters a = 0.7034 nm, b = 0.7034 nm, c = 0.7034 nm, α = 90 °, β = 90 °, γ = 90 °

Cell volume 0.3480 nm^3

Cell density (calculated) 5.78 Mg m^{-3}

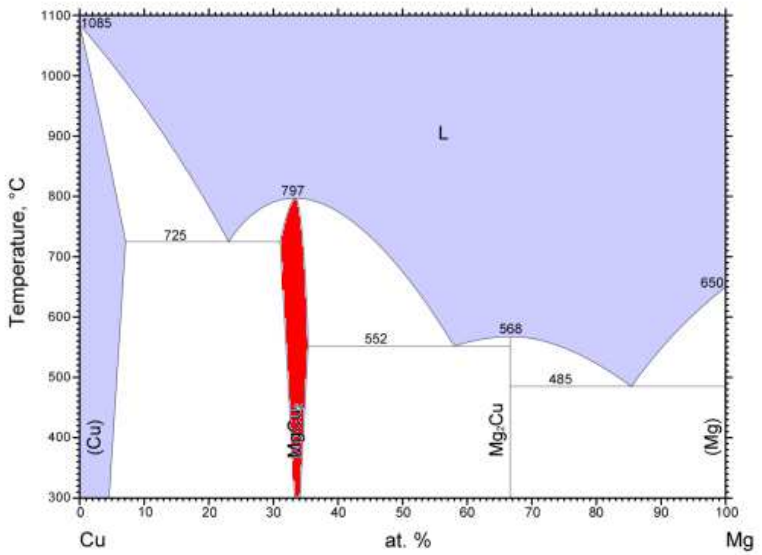
Z 8

Atom coordinates

No	Site notation	Atom	Multiplicity	Wyckoff	Site symmetry	x	y	z	Occupancy
1	Cu	Cu	16	c	.-3m	0	0	0	1.0
2	Mg	Mg	8	b	-43m	3/8	3/8	3/8	1.0

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Mg_2Cu	Mg_2Cu	oF48	70	Search



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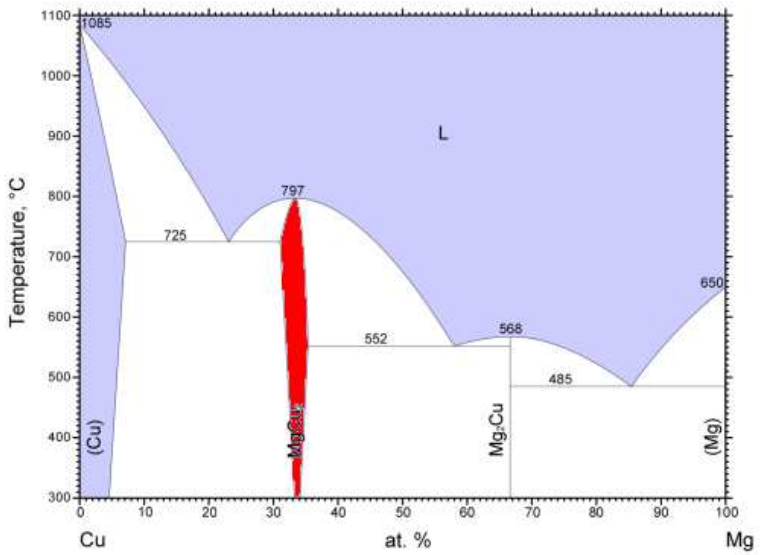
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$\Rightarrow (Cu)_2(Mg)$

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2	Mg	Mg	8	b	-43m	3/8	3/8	3/8	1.0

+ homogeneity range ⇒ $(Cu,Mg)_2(Cu,Mg)$

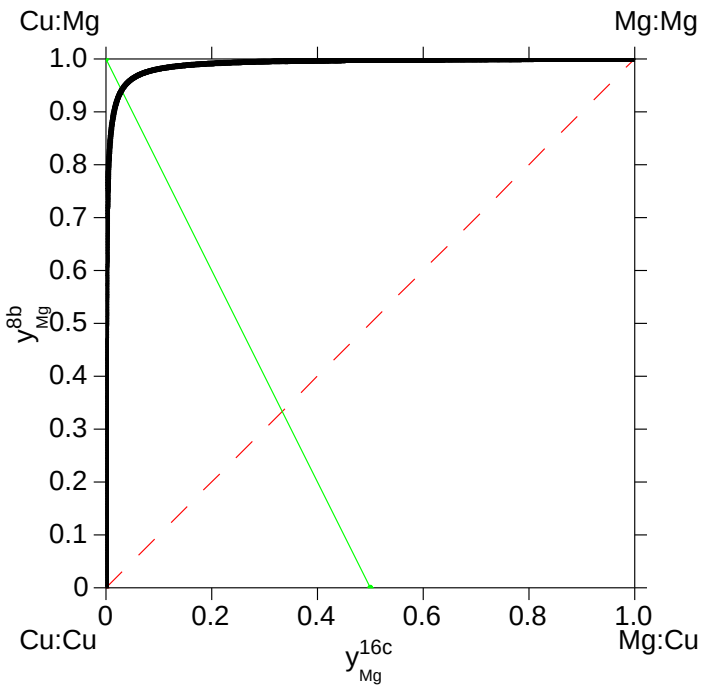
Laves phases

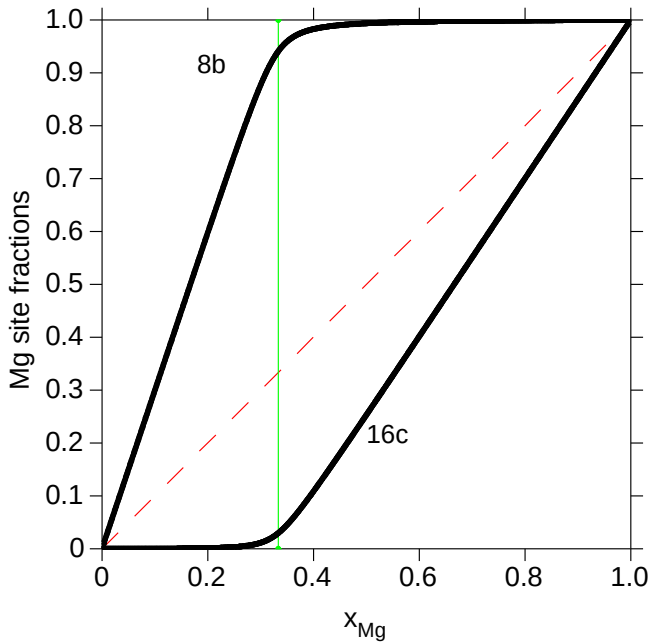
$$(\mathrm{Cu,Mg})_2(\mathrm{Cu,Mg})$$

$$\begin{aligned} G^{C15} = \; & y_{\mathrm{Cu}}^{16c}\, y_{\mathrm{Cu}}^{8b}\, G_{\mathrm{Cu:Cu}}^{C15} + y_{\mathrm{Cu}}^{16c}\, y_{\mathrm{Mg}}^{8b}\, G_{\mathrm{Cu:Mg}}^{C15} \\ & + y_{\mathrm{Mg}}^{16c}\, y_{\mathrm{Cu}}^{8b}\, G_{\mathrm{Mg:Cu}}^{C15} + y_{\mathrm{Mg}}^{16c}\, y_{\mathrm{Mg}}^{8b}\, G_{\mathrm{Mg:Mg}}^{C15} \\ & + RT \left(2 \sum_i y_i^{16c} \ln y_i^{16c} + \sum_i y_i^{8b} \ln y_i^{8b} \right) \\ & + y_{\mathrm{Cu}}^{16c}\, y_{\mathrm{Mg}}^{16c} \sum_j y_j^{8b}\, L_{\mathrm{Cu,Mg:}j}^{C15} \\ & + y_{\mathrm{Cu}}^{8b}\, y_{\mathrm{Mg}}^{8b} \sum_i y_i^{16c}\, L_{i\mathrm{:Cu,Mg}}^{C15} \end{aligned}$$

Laves phases

$$(Cu,Mg)_2(Cu,Mg)$$



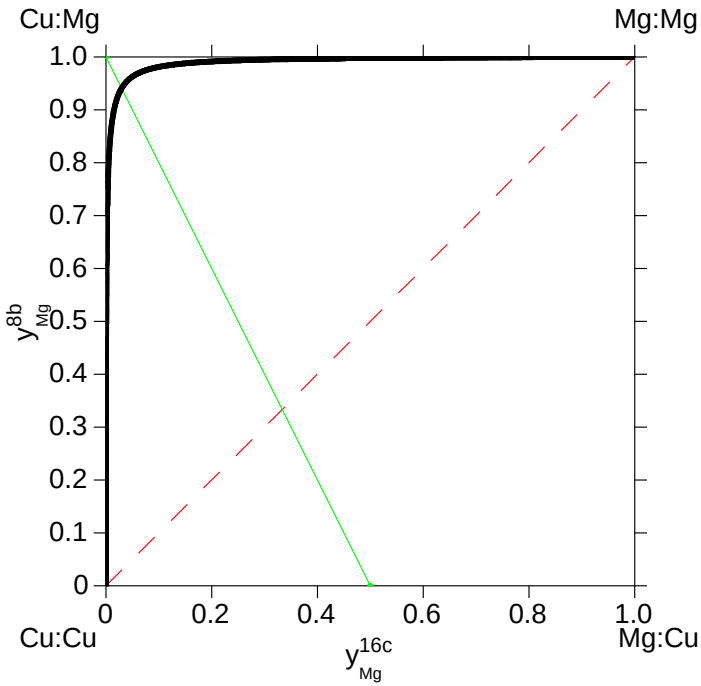


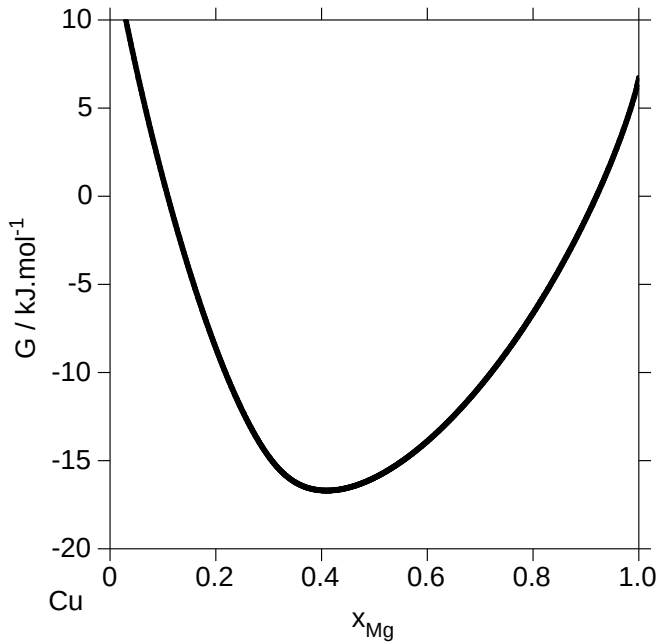
$$x_i = \frac{2}{3} y_i^{16c} + \frac{1}{3} y_i^{8b}$$

$$y_i^{8b} = 3x_i - 2y_i^{16c}$$

Laves phases

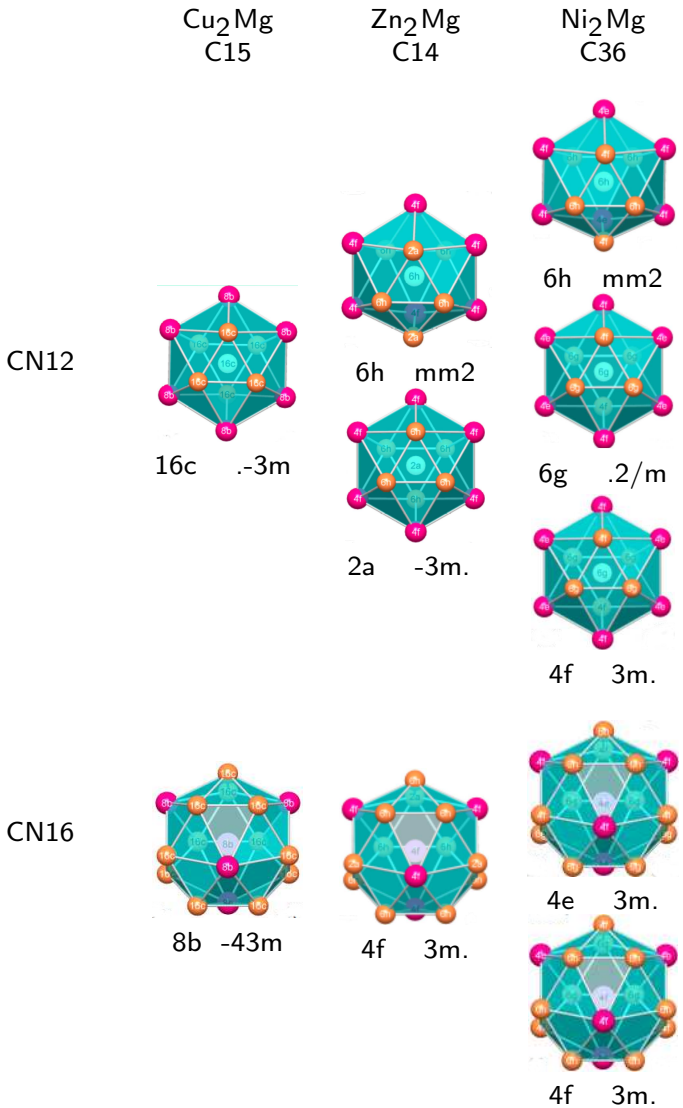
$(Cu,Mg)_2(Cu,Mg)$







Laves phases



U. Kattner et al., Calphad XLII

Cu_2Mg is the prototype for the C15 Laves phases.

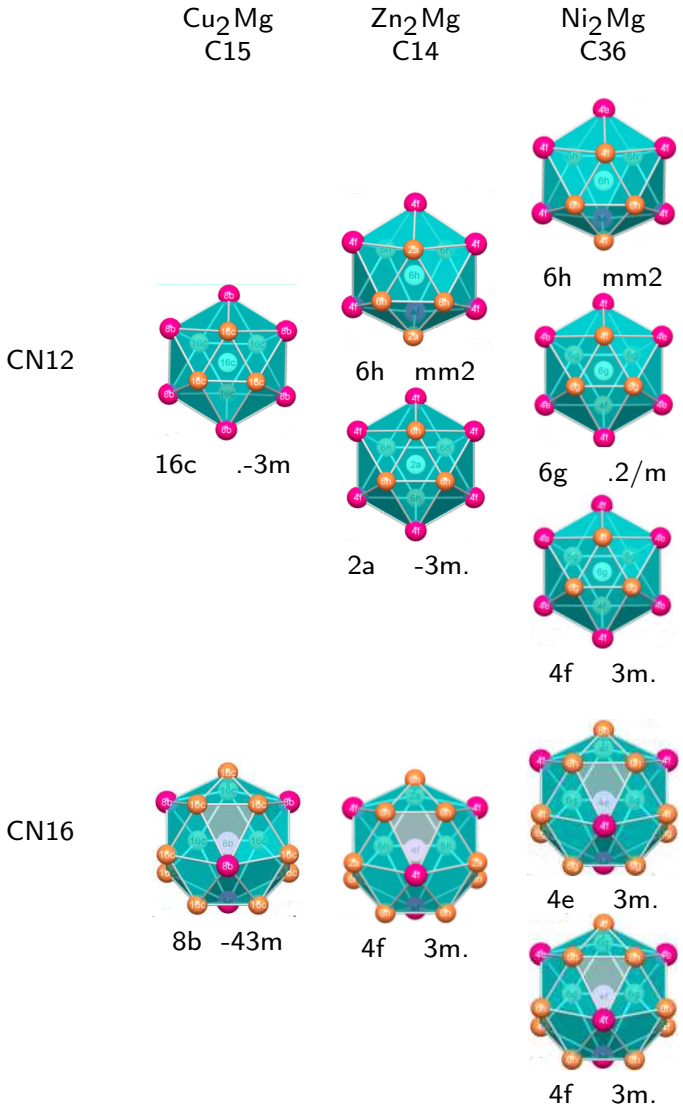
The Laves phases are a familly of intermetallic phases appearing in many binary and ternary systems.

They have all often been modelled with a 2SL model with reciprocal substitution in order to describe their range of homogeneity.

The C14 is often identified in multicomponent alloys of industrial interest.



Laves phases



U. Kattner et al., Calphad XLII

Cu_2Mg is the prototype for the C15 Laves phases.

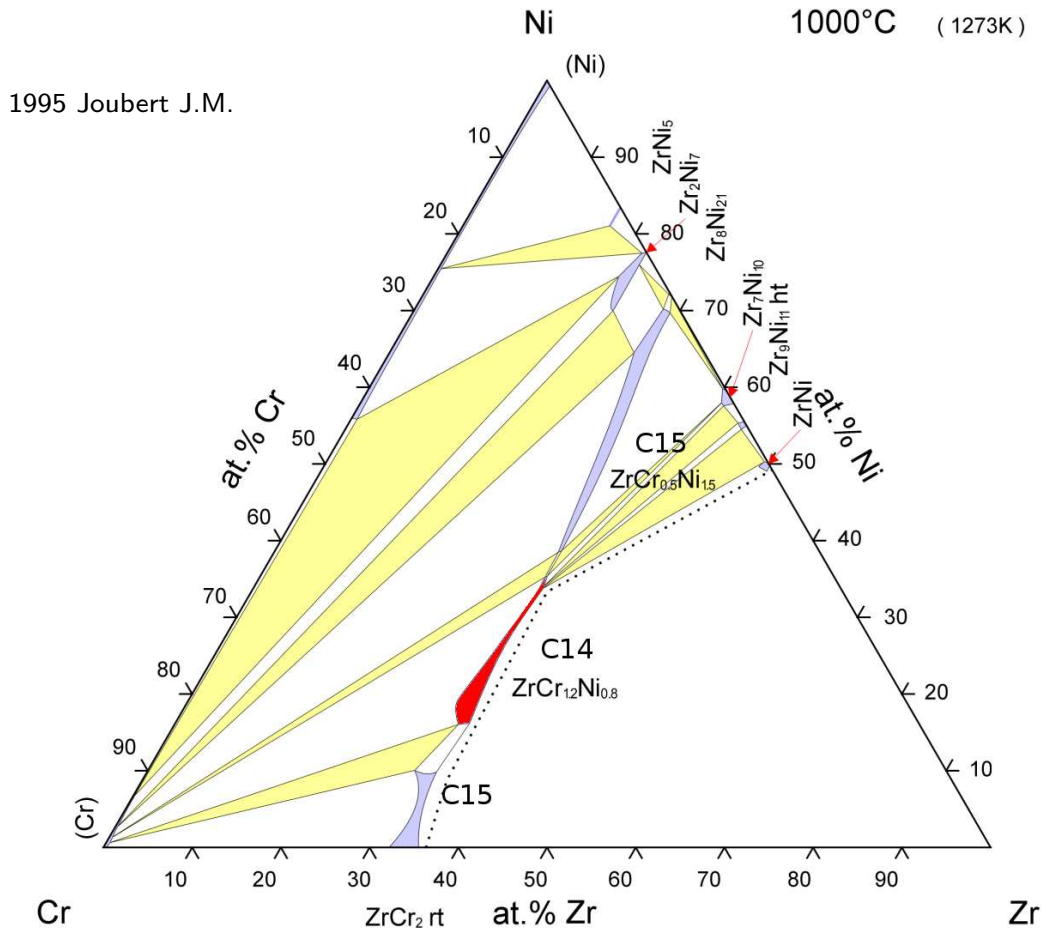
The Laves phases are a familly of intermetallic phases appearing in many binary and ternary systems.

They have all often been modelled with a 2SL model with reciprocal substitution in order to describe their range of homogeneity.

The C14 is often identified in multicomponent alloys of industrial interest.

C14: $(A,B)_2(A,B)$ or $(A,B)_3(A,B)(A,B)_2$?

Laves phases

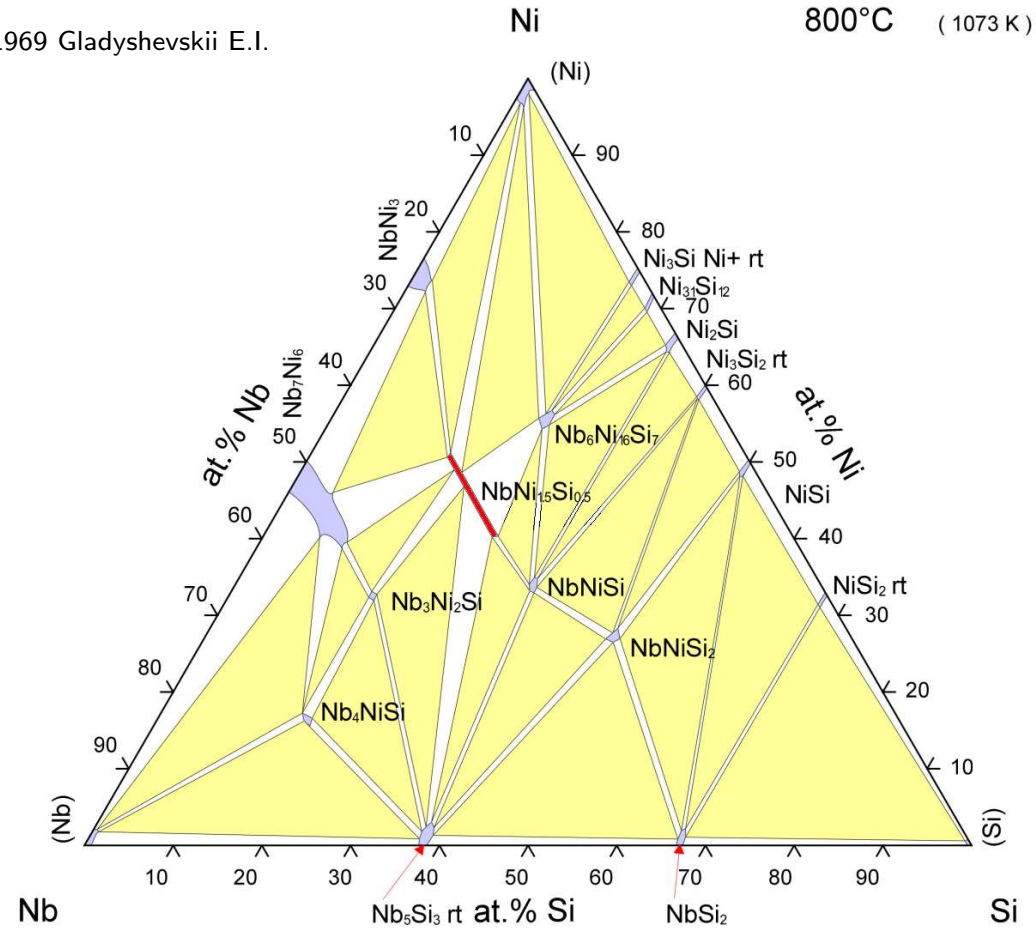


The C14 often appears as an extension of a binary phase in temperature and composition along an almost constant composition line, ...

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Laves phases

1969 Gladyshevskii E.I.

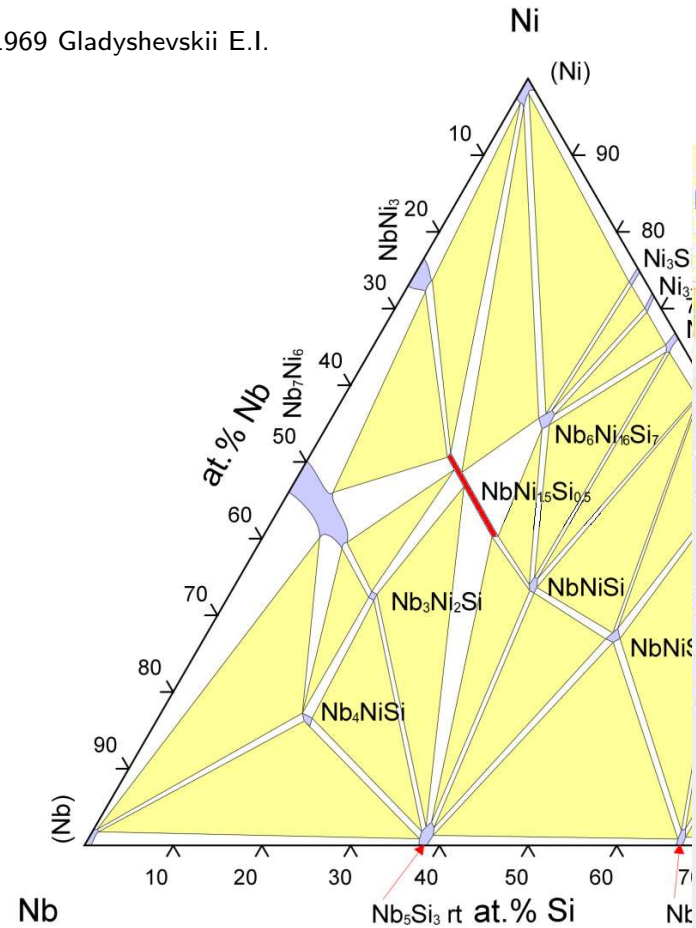


... as a ternary phase,

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Laves phases

1969 Gladyshevskii E.I.



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800°C (1073 K)

$NbNi_{1.5}Si_{0.5}$	Structure type	Pearson symbol	Space group	No.
	$MgZn_2$	hP12	$P6_3/mmc$	194

*Standardized

Inorg. Mater.,1969,5,,1882-1884,Gladyshevskii E.I., Koshel' O.S., Skolozdra

Preparation

Synthesis No data.

Starting materials No data.

Crystal Structure | X-ray Diffraction | Properties

Crystal Structure (Published)

Niggli-reduced cell

Crystallographic data

Cell parameters a = 0.4804 nm, b = 0.4804 nm, c = 0.7825 nm, α = 90 °, β = 90 °, γ = 120 °

Cell volume 0.15639 nm^3

Crystal Structure (Standardized)

Crystallographic data

Cell parameters a = 0.4804 nm, b = 0.4804 nm, c = 0.7825 nm, α = 90 °, β = 90 °, γ = 120 °

Cell volume 0.1564 nm^3

Cell density (calculated) 8.28 Mg m^{-3}

Z 4

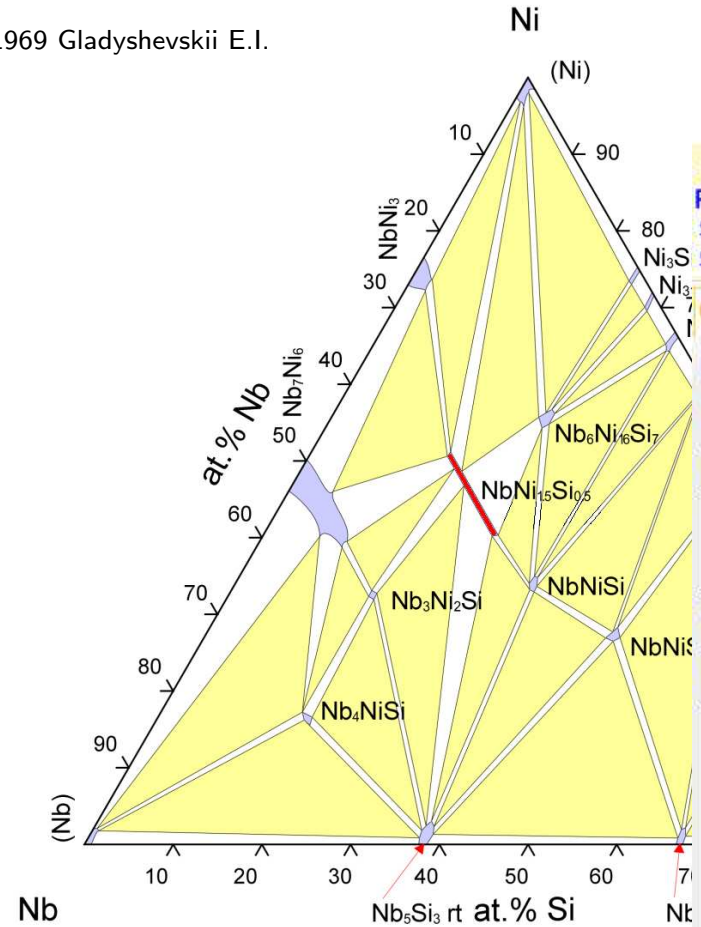
Atom coordinates

No	Site notation	Atom	Multiplicity	Wyckoff	Site symmetry	x	y	z	Occupancy
1	M1	0.750Ni + 0.250Si	6						
2	Nb1	Nb	4						
3	M2	0.750Ni + 0.250Si	2						

$\Rightarrow (Ni,Si)_6(Nb)_4(Ni,Si)_2$

Laves phases

1969 Gladyshevskii E.I.



© ASM Internatio

$NbNi_{1.5}Si_{0.5}$	Structure type	Pearson symbol	Space group	No.
	$MgZn_2$	hP12	$P6_3/mmc$	194

*Standardized

J. Less-Common Met.,1985,106,,293-300,Trojko R., Blazina Z.

Preparation

Synthesis: arc-melted, several times remelted

Starting materials: No data.

Crystal Structure | X-ray Diffraction | Properties

Crystal Structure (Published)

Niggli-reduced cell

Crystallographic data

Cell parameters	a = 0.4796 nm, b = 0.4796 nm, c = 0.7907 nm, α = 90 °, β = 90 °, γ = 120 °
Cell volume	0.15751 nm^3

Crystal Structure (Standardized)

Crystallographic data

Cell parameters	a = 0.4796 nm, b = 0.4796 nm, c = 0.7907 nm, α = 90 °, β = 90 °, γ = 120 °
Cell volume	0.1575 nm^3
Cell density (calculated)	8.32 Mg m^{-3}
Z	4

Atom coordinates

No	Site notation	Atom	Multiplicity	Wyckoff	Site symmetry	x	y	z	Occupancy
1	Ni1	Ni	6						
2	M1	0.800Nb + 0.200Si	4						
3	Ni2	Ni	2						

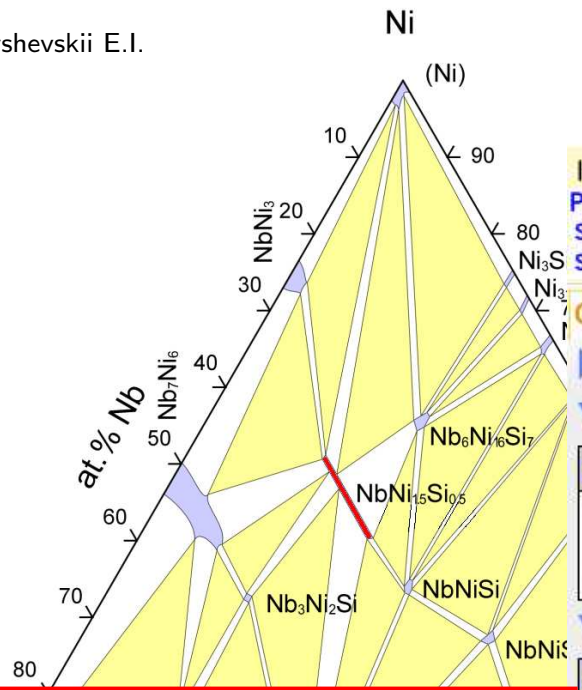
$\Rightarrow (Ni)_6(Nb,Si)_4(Ni)_2$

No	Site notation	Atom	Multiplicity	Wyckoff	Site symmetry	x	y	z	Occupancy
1	M1	0.750Ni + 0.250Si	6						
2	Nb1	Nb	4						
3	M2	0.750Ni + 0.250Si	2						

$\Rightarrow (Ni,Si)_6(Nb)_4(Ni,Si)_2$

Laves phases

1969 Gladyshevskii E.I.



Experimental site occupancies are not directely from diffraction patterns. Assumptions are made. Critical assessment is also needed for these data.

$NbNi_{1.5}Si_{0.5}$	Structure type	Pearson symbol	Space group	No.
	$MgZn_2$	hP12	$P6_3/mmc$	194

*Standardized

J. Less-Common Met.,1985,106,,293-300,Trojko R., Blazina Z.

Preparation

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Cell density (calculated)	8.32 Mg m^{-3}
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Atom coordinates

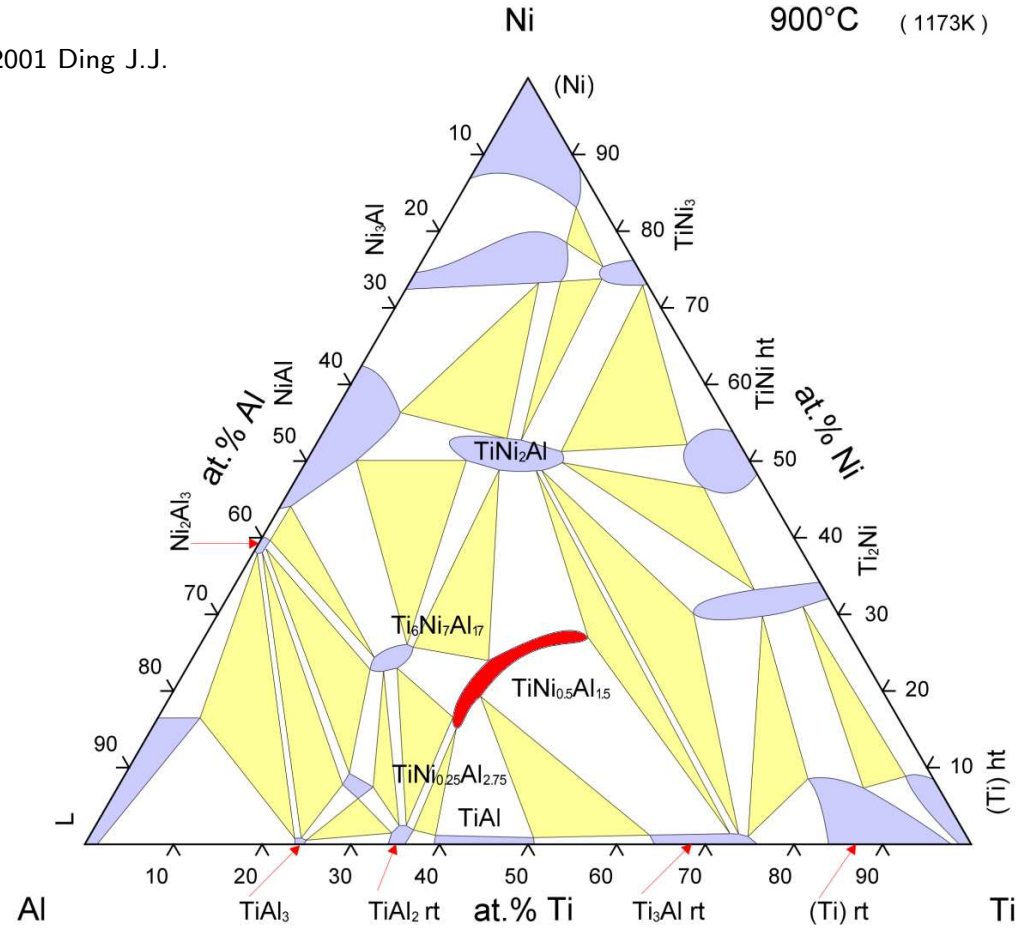
No	Site notation	Atom	Multiplicity	Wyckoff	Site symmetry	x	y	z	Occupancy
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⇒ $(Ni)_6(Nb,Si)_4(Ni)_2$

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1	M1	0.750Ni + 0.250Si	6						
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3	M2	0.750Ni + 0.250Si	2						

⇒ $(Ni,Si)_6(Nb)_4(Ni,Si)_2$

Laves phases



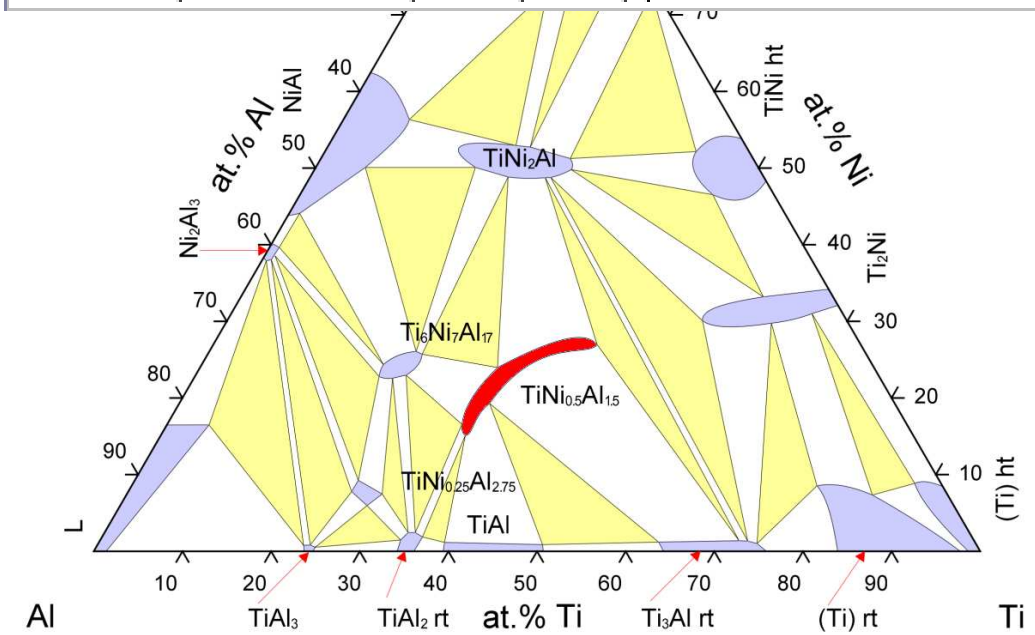
... but also with different homogeneity range topology.

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Laves phases

$TiNi_{0.5}Al_{1.5}$ T3,TiNiAl	$Ti_{2.13}Ni_{1.30}Al_{2.57}$	Mg_2Cu_3Si	hP12 $P6_3/mmc$	4.67 0.1763	a=0.50095 b=0.50095 c=0.81117	α=90 β=90 γ=120	[12]

[**12**] Huneau B., Rogl P., Zeng K., Schmid Fetzer R., Bohn M., and Bauer J., The ternary system Al-Ni-Ti Part I: Isothermal section at 900 °C; Experimental investigation and thermodynamic calculation, Intermetallics, Vol. 7, 1999, p 1337-1345



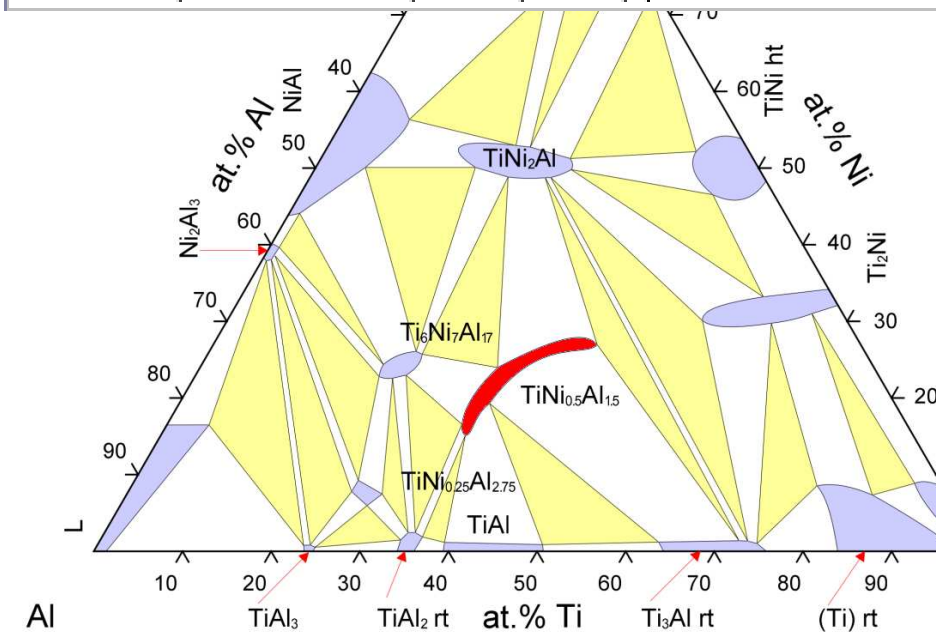
... but also with different homogeneity range topology.

© ASM International 2009. Diagram No. 200336

Laves phases

TiNi0.5Al1.5 T3,TiNiAl	Ti2.13Ni1.30Al2.57	Mg2Cu3Si	hP12 P63/mm

[12] Huneau B., Rogl P., Zeng K., Schmid Fetzer R., Bohn M
Al-Ni-Ti Part I: Isothermal section at 900 °C; Experimental i
calculation, Intermetallics, Vol. 7, 1999, p 1337-1345



© ASM International 2009. Diagram

T_3 - "Al_3NiTi_2"
($MgZn_2$-type)

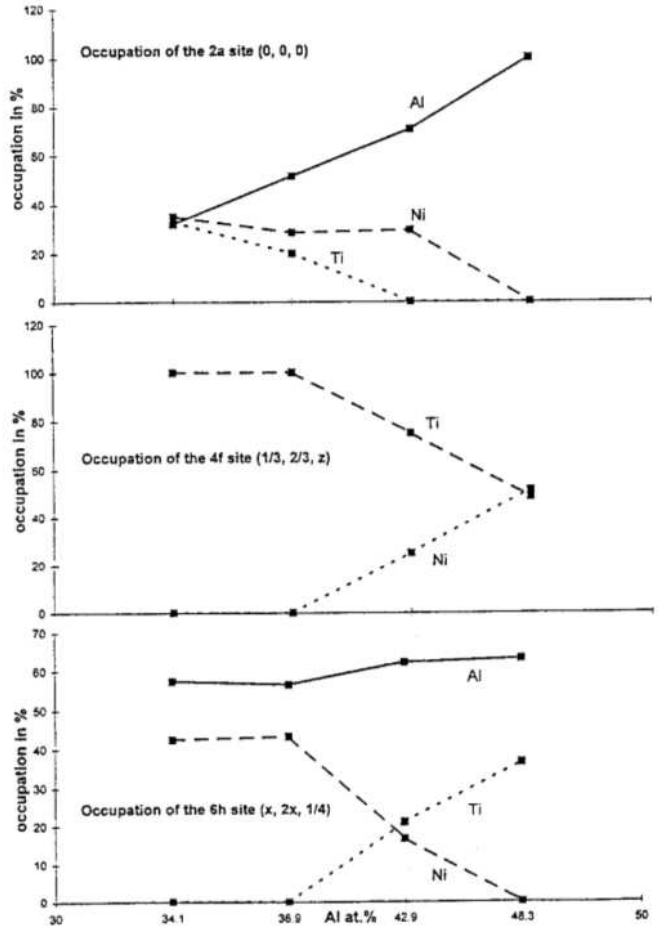


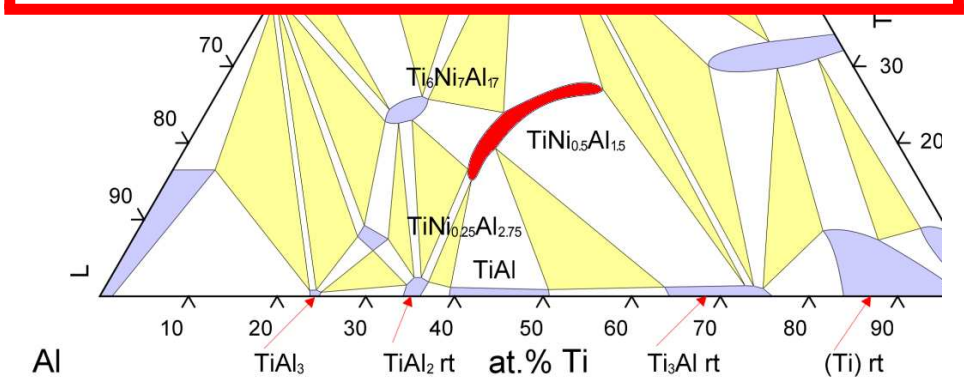
Fig. 8. Occupation of the atomic sites for the τ_3-phase as a function of the Al-content.

Laves phases

TiNi$_{0.5}$Al$_{1.5}$ τ3,TiNiAl	Ti$_{2.13}$Ni$_{1.30}$Al$_{2.57}$	Mg$_2$Cu$_3$Si	hP12 P63/mr

[12] Huneau B., Rogl P., Zeng K., Schmid Fetzer R., Bohn M
Al-Ni-Ti Part I: Isothermal section at 900 °C; Experimental i
calculation, Intermetallics, Vol. 7, 1999, p 1337-1345

Compilations may reinterpret original data. Original data are safer for crystallography also.



© ASM International 2009. Diagram

τ_3 - "Al$_3$NiTi$_2$"
(Mg Zn$_2$-type)

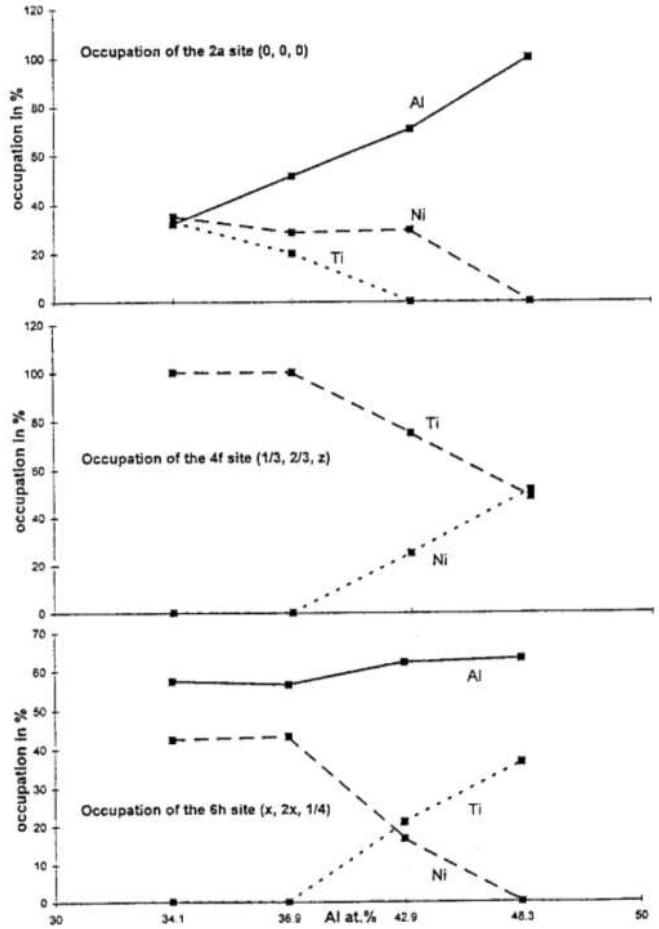
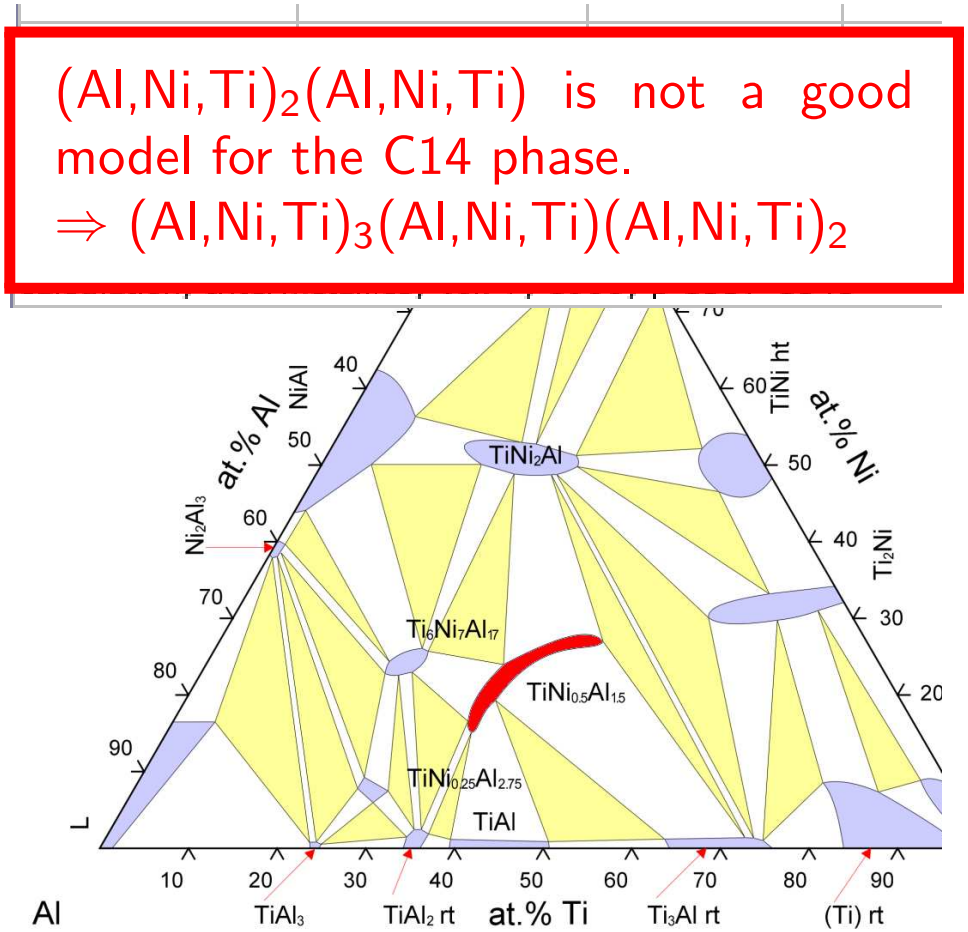


Fig. 8. Occupation of the atomic sites for the τ_3-phase as a function of the Al-content.

Laves phases

$(Al,Ni,Ti)_2(Al,Ni,Ti)$ is not a good model for the C14 phase.
$\Rightarrow (Al,Ni,Ti)_3(Al,Ni,Ti)(Al,Ni,Ti)_2$



© ASM International 2009. Diagram

T_3 - "Al_3NiTi_2"
($MgZn_2$-type)

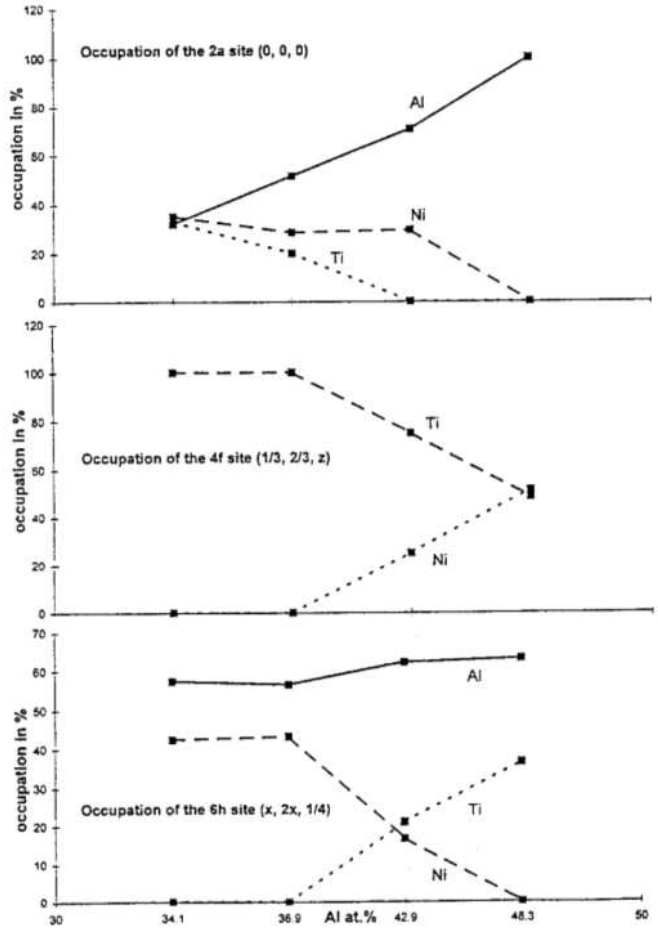


Fig. 8. Occupation of the atomic sites for the τ_3-phase as a function of the Al-content.

Laves phases

Based on its limited non-stoichiometry in some systems and on partial or bad site occupancies experimental results, the C14 has often been modelled with two sublattices only, like the C15.

However, in order to describe properly the C14, $MgZn_2$-type, phase, 3 sublattices are needed to allow different occupations for the 3 crystallographic sites.

Laves phases

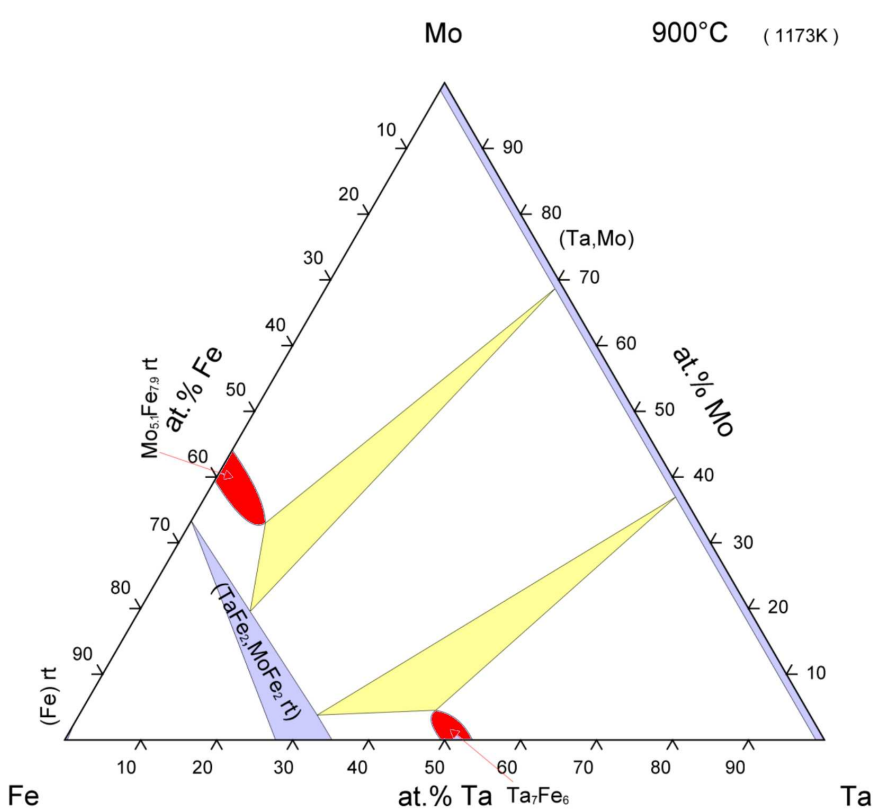
For decades simplified models have been used because of computers limitations and the impossibility to assess all the compounds.

These simplications were made grouping together similar crystallographic sites. It is still interesting to use them in some cases.

However they may oversimplify phases presenting large multicomponent area. Nowadays that DFT can help, models close to the crystallography are recommended.

μ Phase

Fe-Mo-Ta Phase Diagram (1992 Raghavan V.)

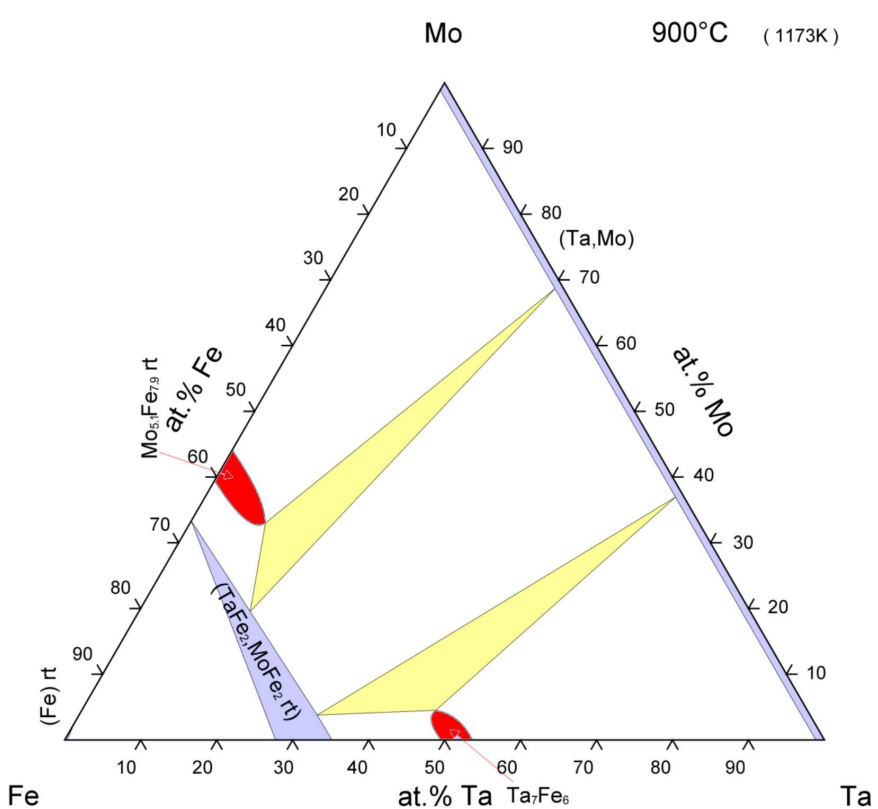


APD phase label / Published phase label	Formula	Prototype	Pearson symbol / Space group
Phases shown in this diagram:			
(Fe) rt α	Fe	W	cI2 Im-3m
Mo5.1Fe7.9 rt Fe7Mo6,μ	Mo5.08Fe7.92	W6Fe7	hR39 R-3m
Ta7Fe6 FeTa,μ	Ta6.5Fe6.5	W6Fe7	hR39 R-3m
(Ta,Mo) (Mo,Ta)	Ta0.5Mo0.5	W	cI2 Im-3m
(TaFe2,MoFe2 rt) Fe2(Mo,Ta)	MoFe2	MgZn2	hP12 P63/mmc

© ASM International 2006. Diagram No. 2000191.

μ Phase

Fe-Mo-Ta Phase Diagram (1992 Raghavan V.)

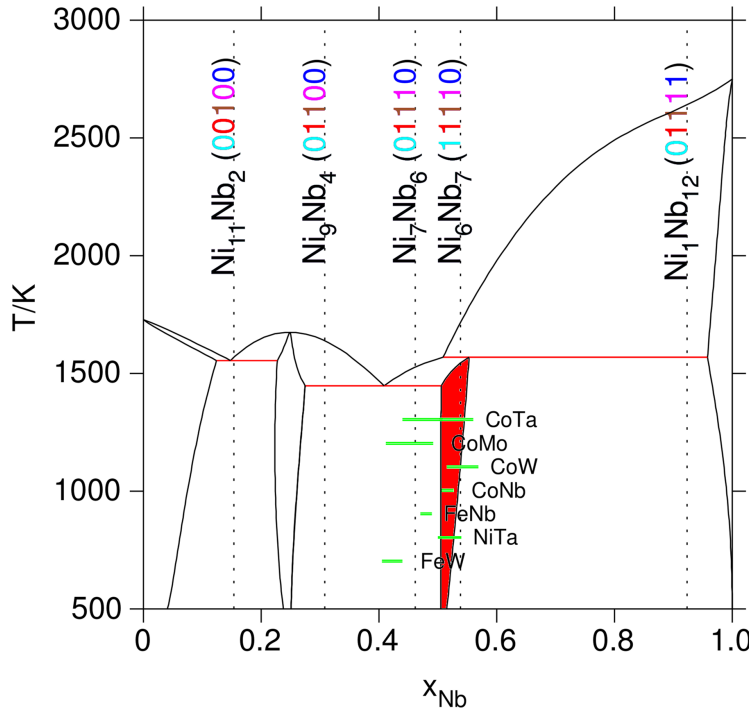


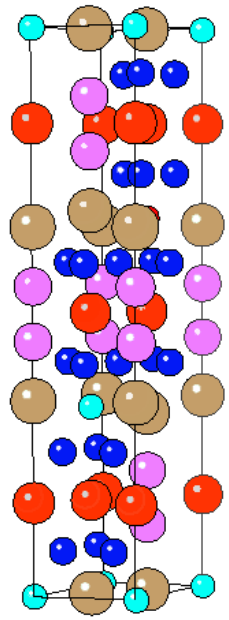
APD phase label / Published phase label	Formula	Prototype	Pearson symbol / Space group
Phases shown in this diagram:			
(Fe) rt α	Fe	W	cI2 Im-3m
Mo5.1Fe7.9 rt Fe7Mo6,μ	Mo5.08Fe7.92	W6Fe7	hR39 R-3m
Ta7Fe6 FeTa,μ	Ta6.5Fe6.5	W6Fe7	hR39 R-3m
(Ta,Mo) (Mo,Ta)	Ta0.5Mo0.5	W	cI2 Im-3m
(TaFe2,MoFe2 rt) Fe2(Mo,Ta)	MoFe2	MgZn2	hP12 P63/mmc

© ASM International 2006. Diagram No. 2000191.

$Mo_{5.1}Fe_{7.9}$ and Ta_7Fe_6
prototype W_6Fe_7
$\Rightarrow$ same model.

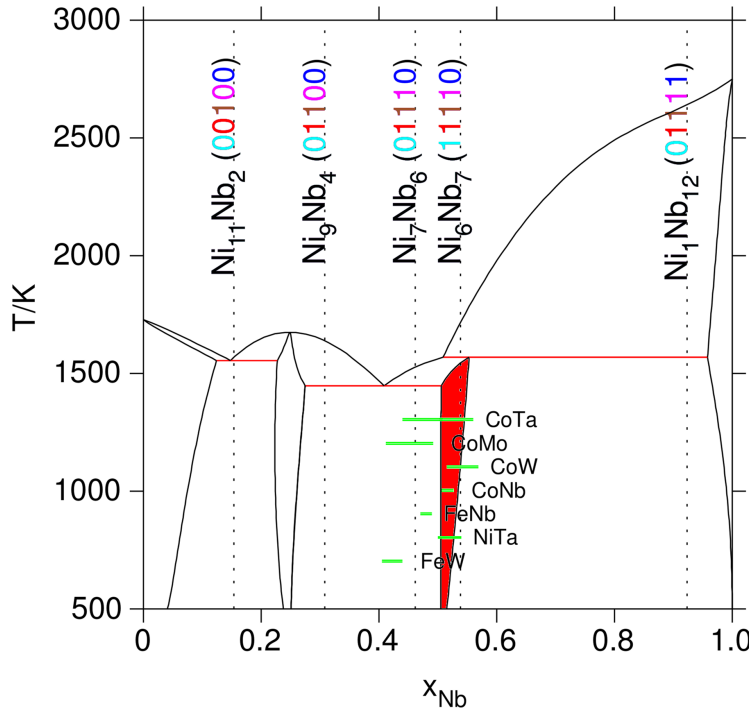
μ Phase

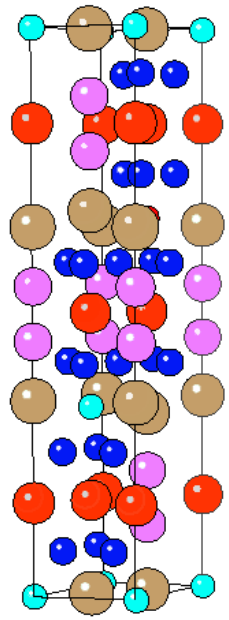




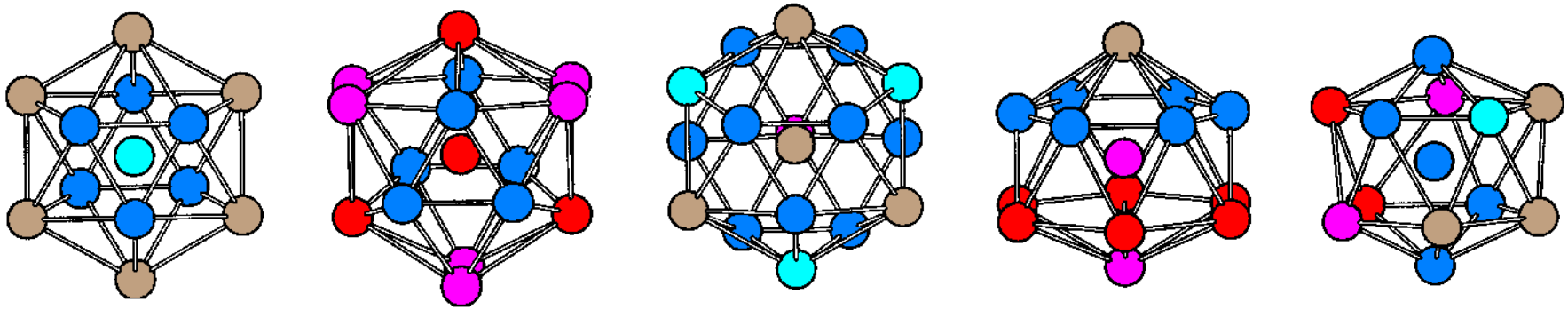
Prototype μ	Fe_7W_6				
Space group Pearson symbol	$R\bar{3}m$ $hR13$				
Wyckhoff	$3a$	$6c1$	$6c2$	$6c3$	$18h$
Coordination number	12	15	16	14	12
Site occupation	Fe	W	W	W	Fe

μ Phase





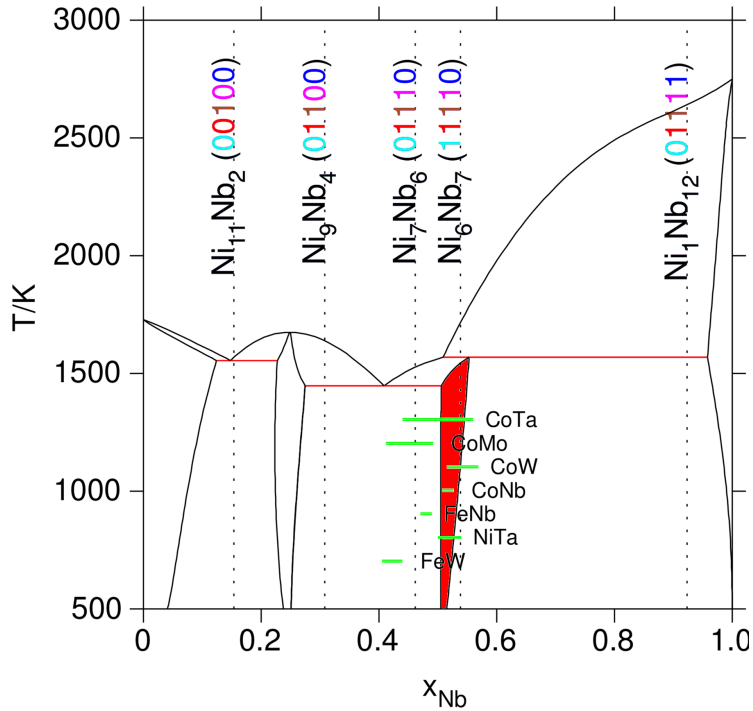
Prototype μ	Fe_7W_6				
Space group Pearson symbol	$R\bar{3}m$ $hR13$				
Wyckhoff	$3a$	$6c1$	$6c2$	$6c3$	$18h$
Coordination number	12	15	16	14	12
Site occupation	Fe	W	W	W	Fe

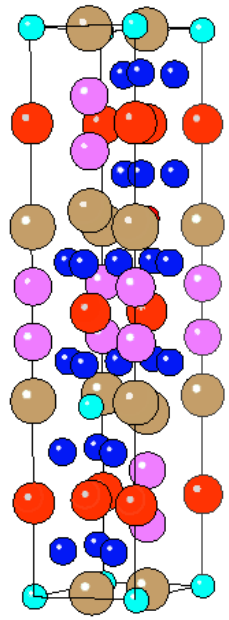


3a 6c1 6c2 6c3 18h

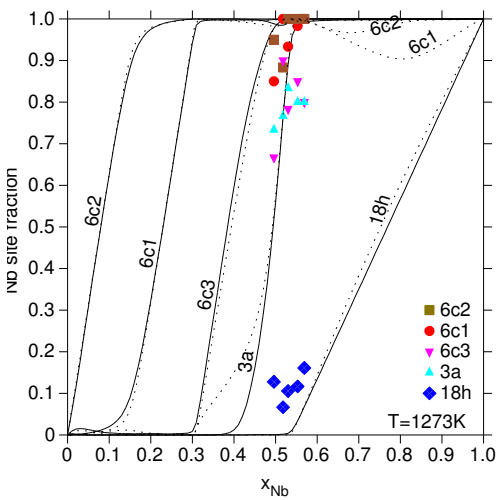
V. Wagner, M. Conrad, B. Harbrecht, Acta Cryst. (1995) C15, 1241-1243

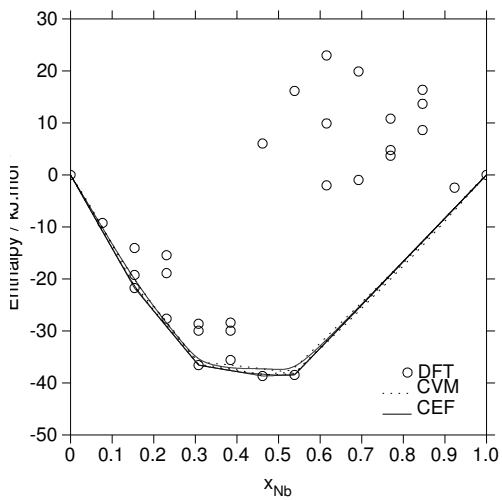
μ Phase

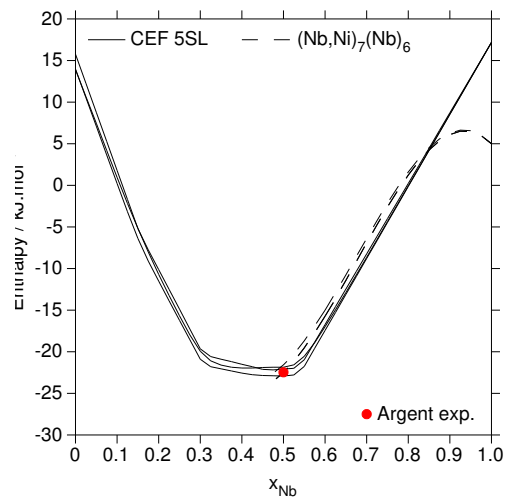




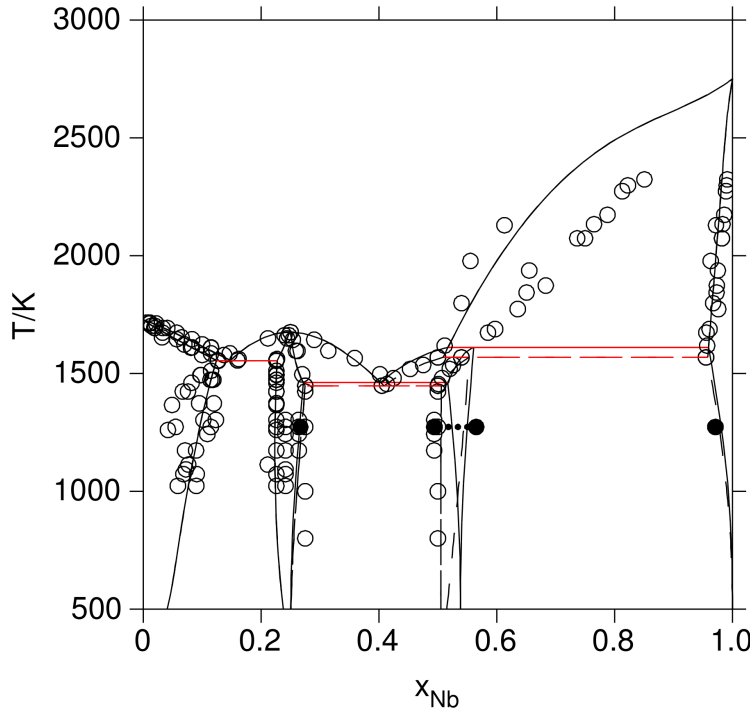
Prototype μ	Fe_7W_6				
Space group Pearson symbol	$R\bar{3}m$ $hR13$				
Wyckhoff	$3a$	$6c1$	$6c2$	$6c3$	$18h$
Coordination number	12	15	16	14	12
Site occupation	Fe	W	W	W	Fe

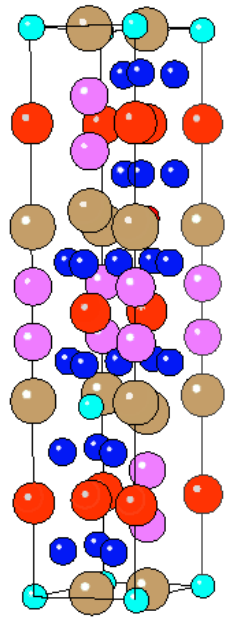




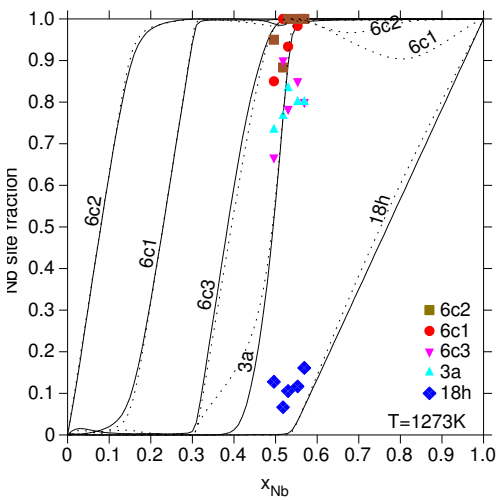


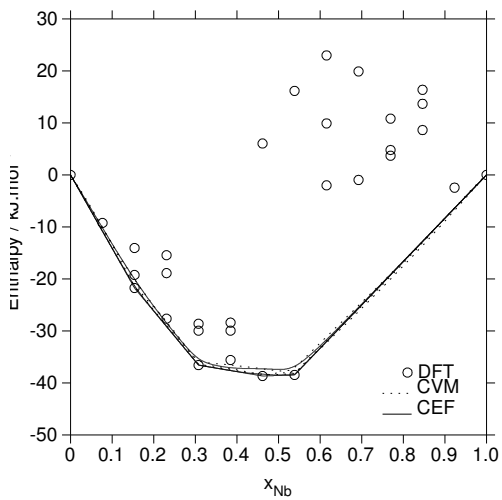
μ Phase

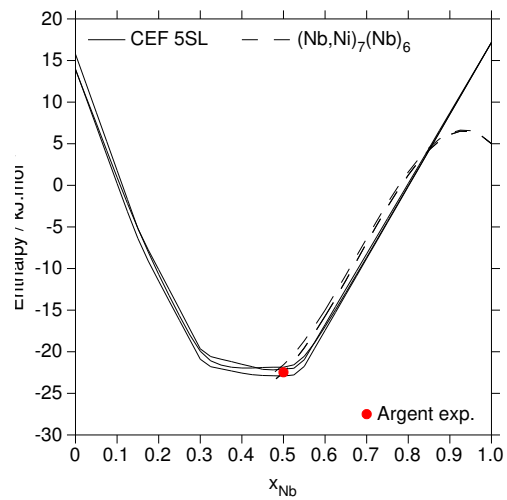




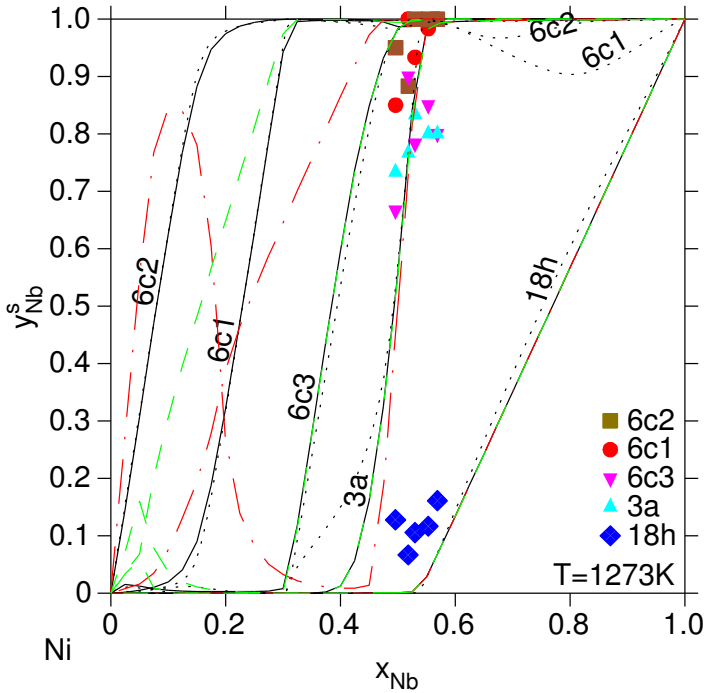
Prototype μ	Fe_7W_6				
Space group Pearson symbol	$R\bar{3}m$ $hR13$				
Wyckhoff	$3a$	$6c1$	$6c2$	$6c3$	$18h$
Coordination number	12	15	16	14	12
Site occupation	Fe	W	W	W	Fe

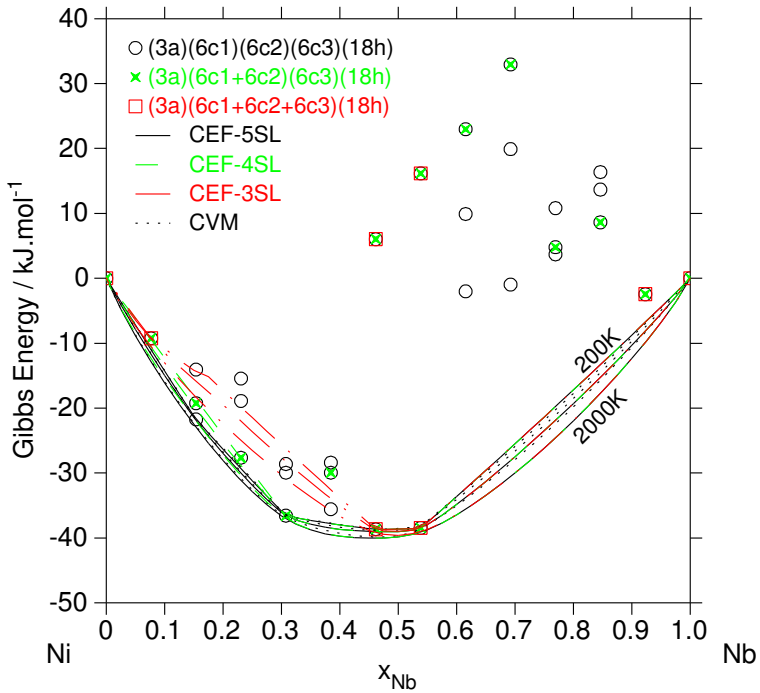






μ Phase





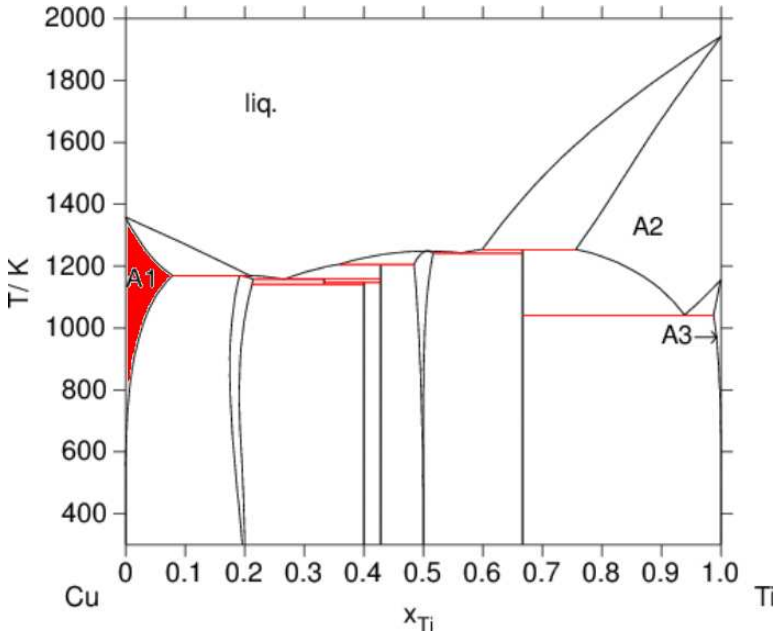
The CEF 5SL using the 32 compounds from VASP and the CEF 4SL using the 16 compounds from VASP are very close to CVM.

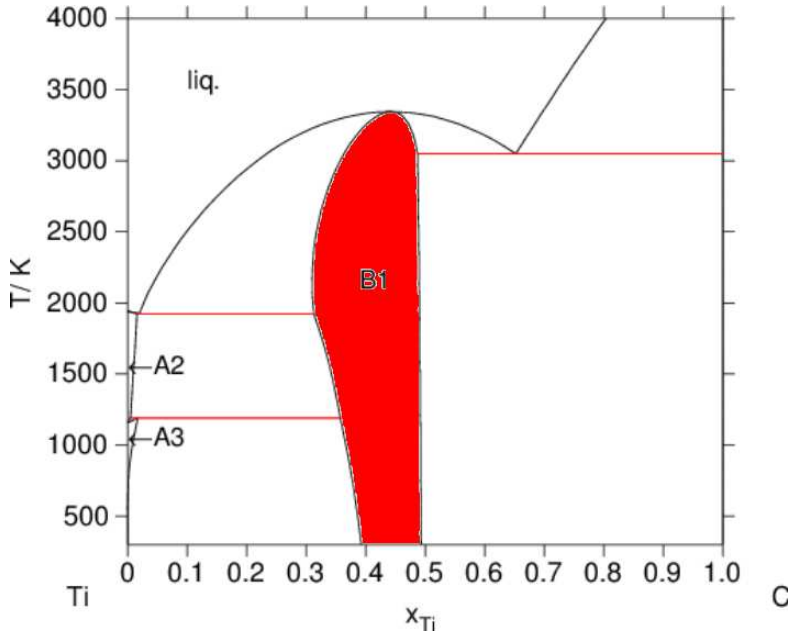
The CEF 3SL using 8 compounds from VASP 8 is far from CVM for low Nb content. It will not work properly for all systems.

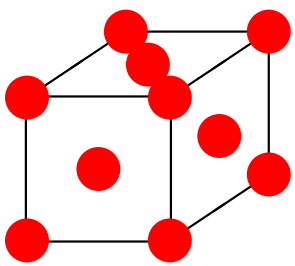
A same model for different structures

- Interstitials
- Metallic ordering
- Interstitials and metallic ordering

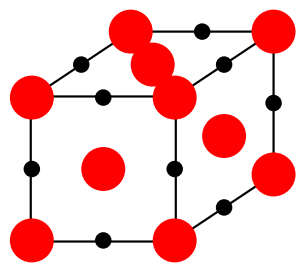
(M,M')(C,□)







A1 (Cu,Ti)(□)

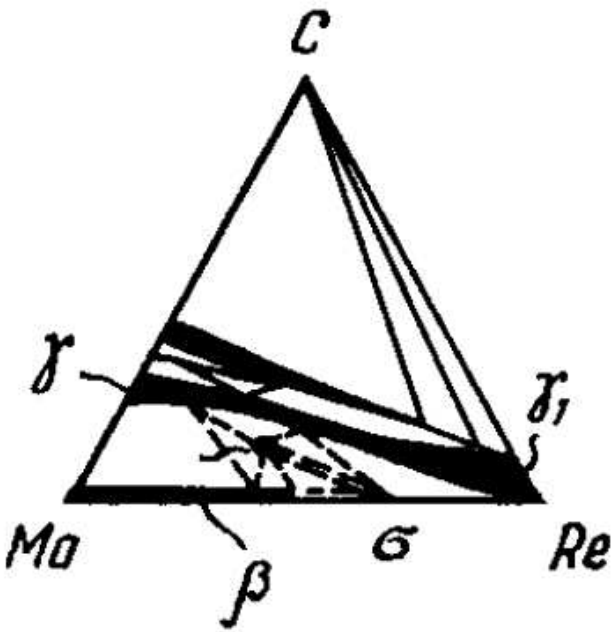


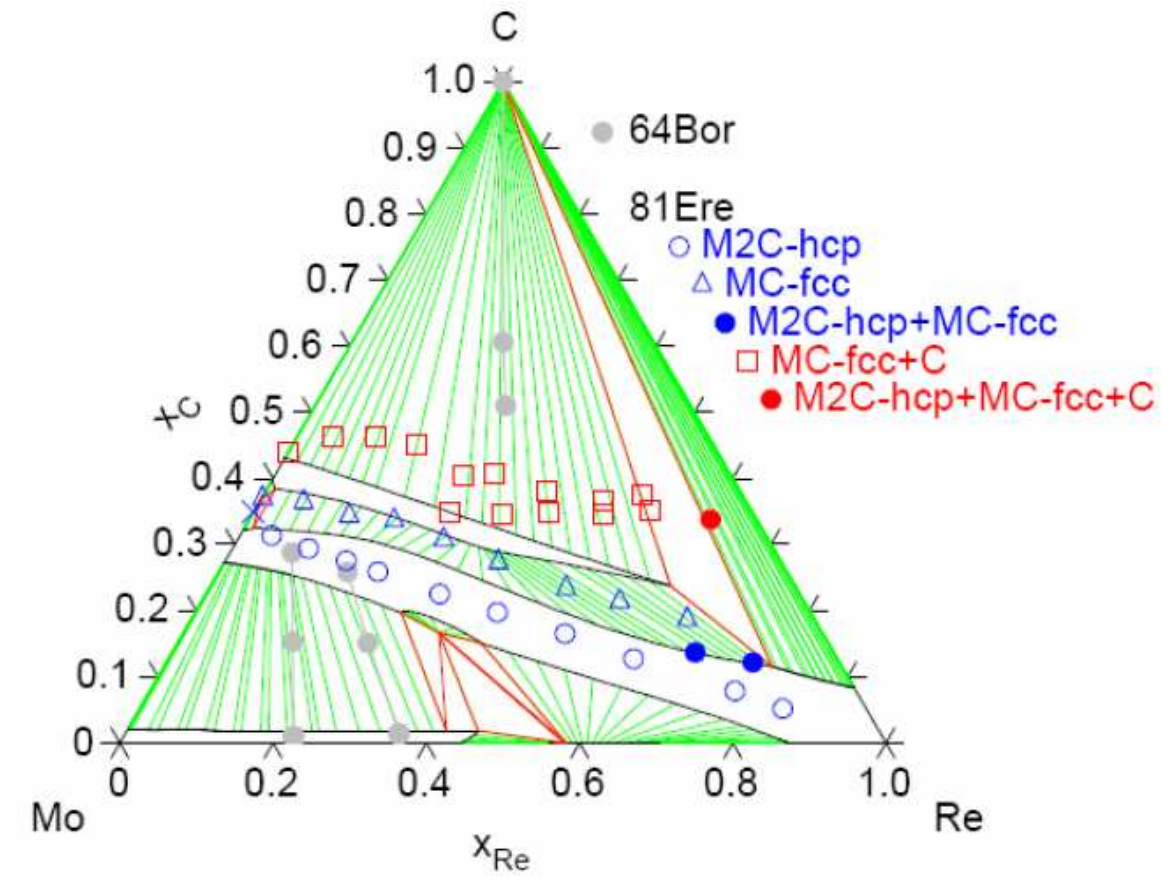
B1 (Ti)(C,□)

⇒ C-Cu-Ti: (Cu,Ti)(C,□) both A1 and B1

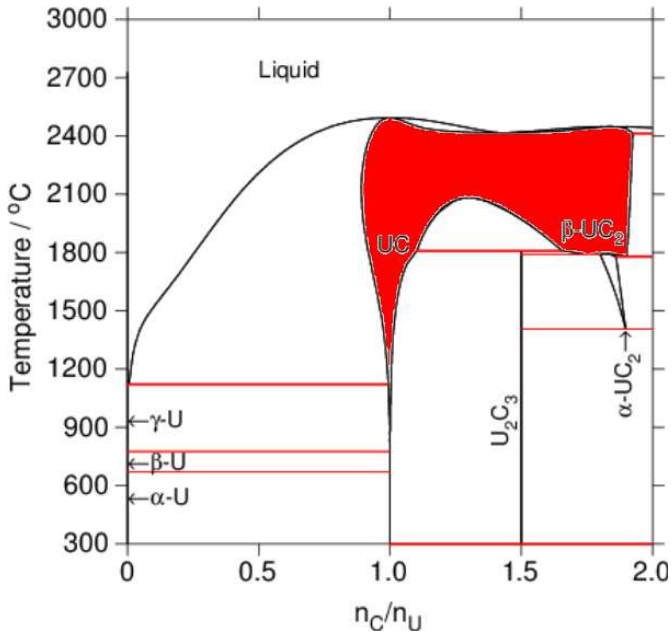
$(M,M')_a(C,\square)_b$

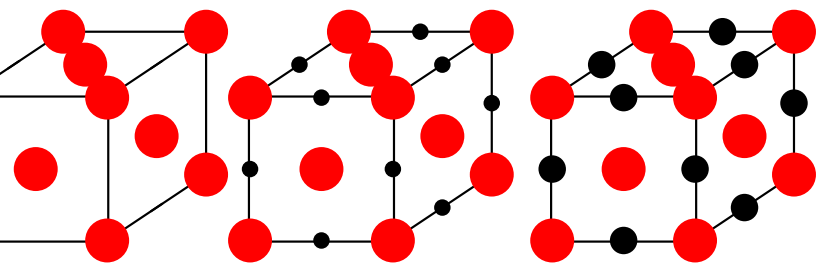
The continous modelling between metallic solutions and carbides is based on crystallographic consideration. This continuity is experimentally observed in very few systems.

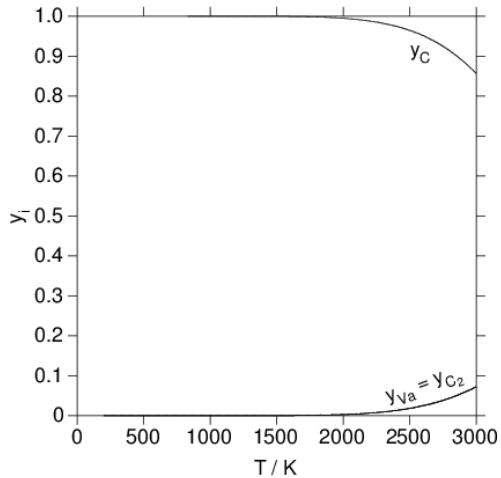




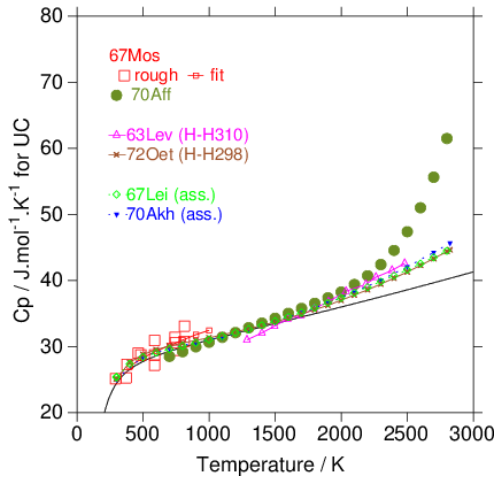
U(C,C_2,□)



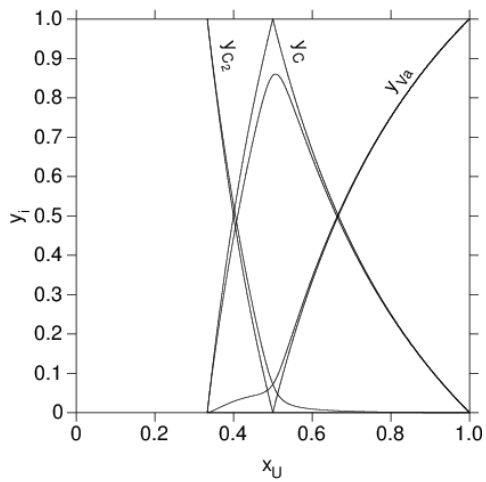




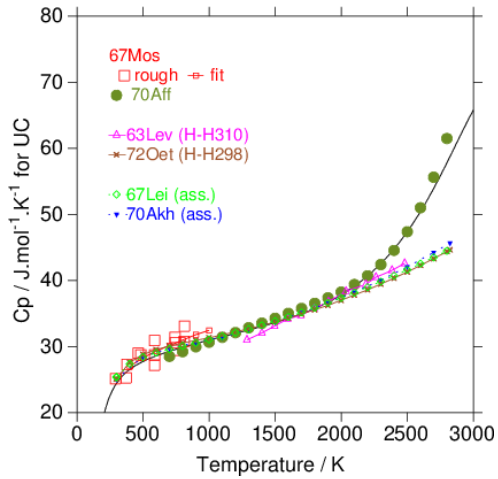
vs temperature for x_C=0.5



(U)(C)



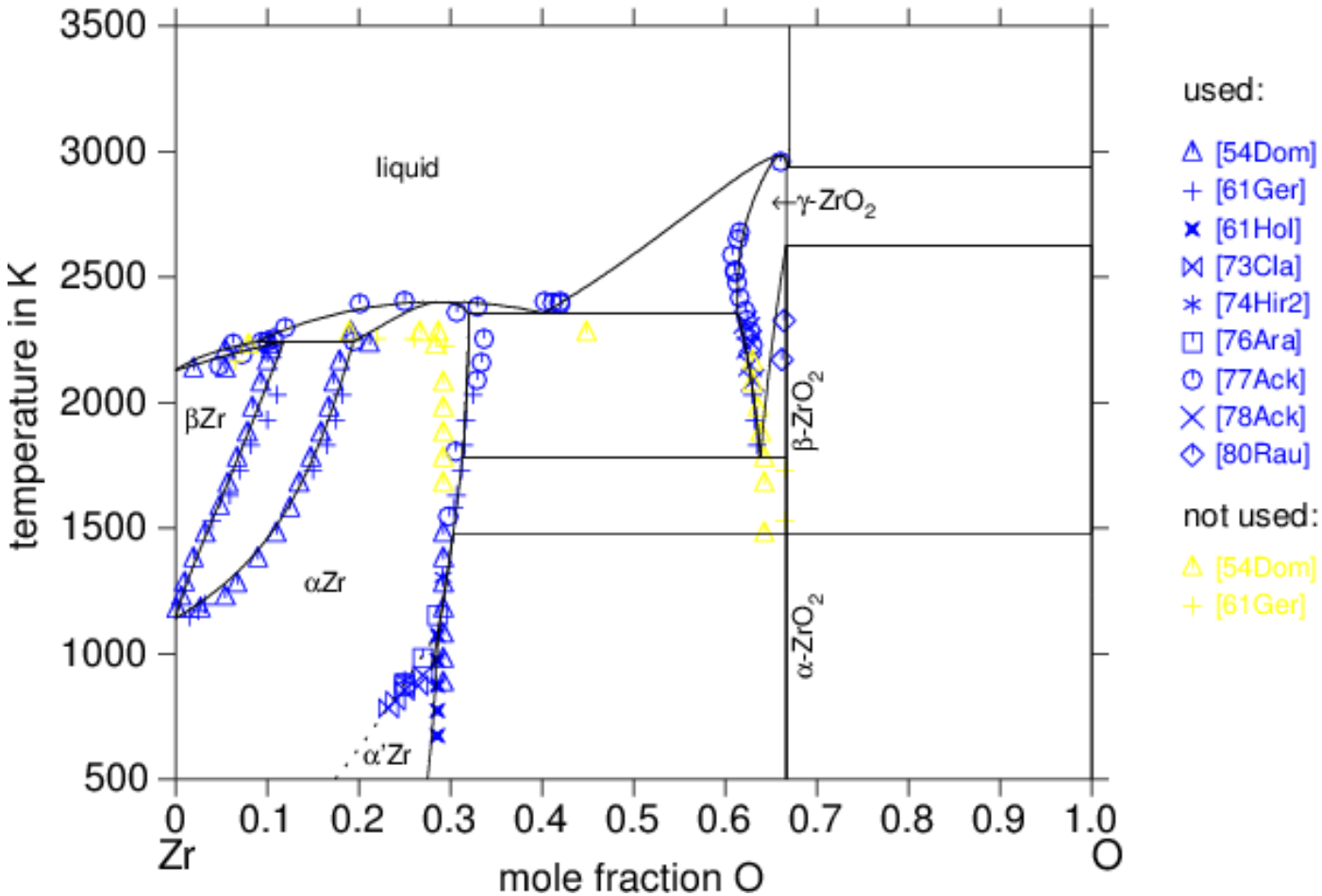
vs composition at 1500 and 3000K



(U)(C,C_2,□) at x_C=0.5

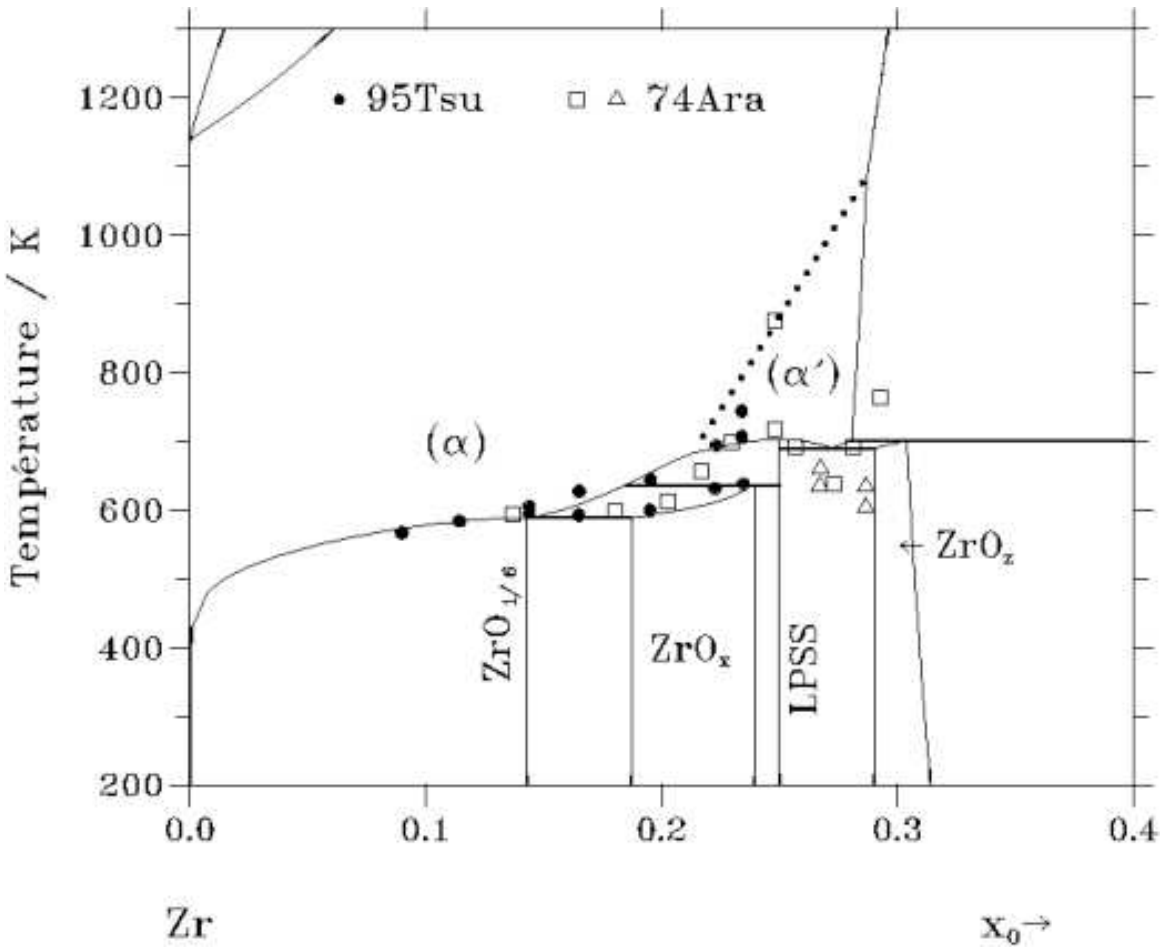
$Zr_3(O,\square)(O,\square)(O,\square)$

2001 Liang et al.: α and α'



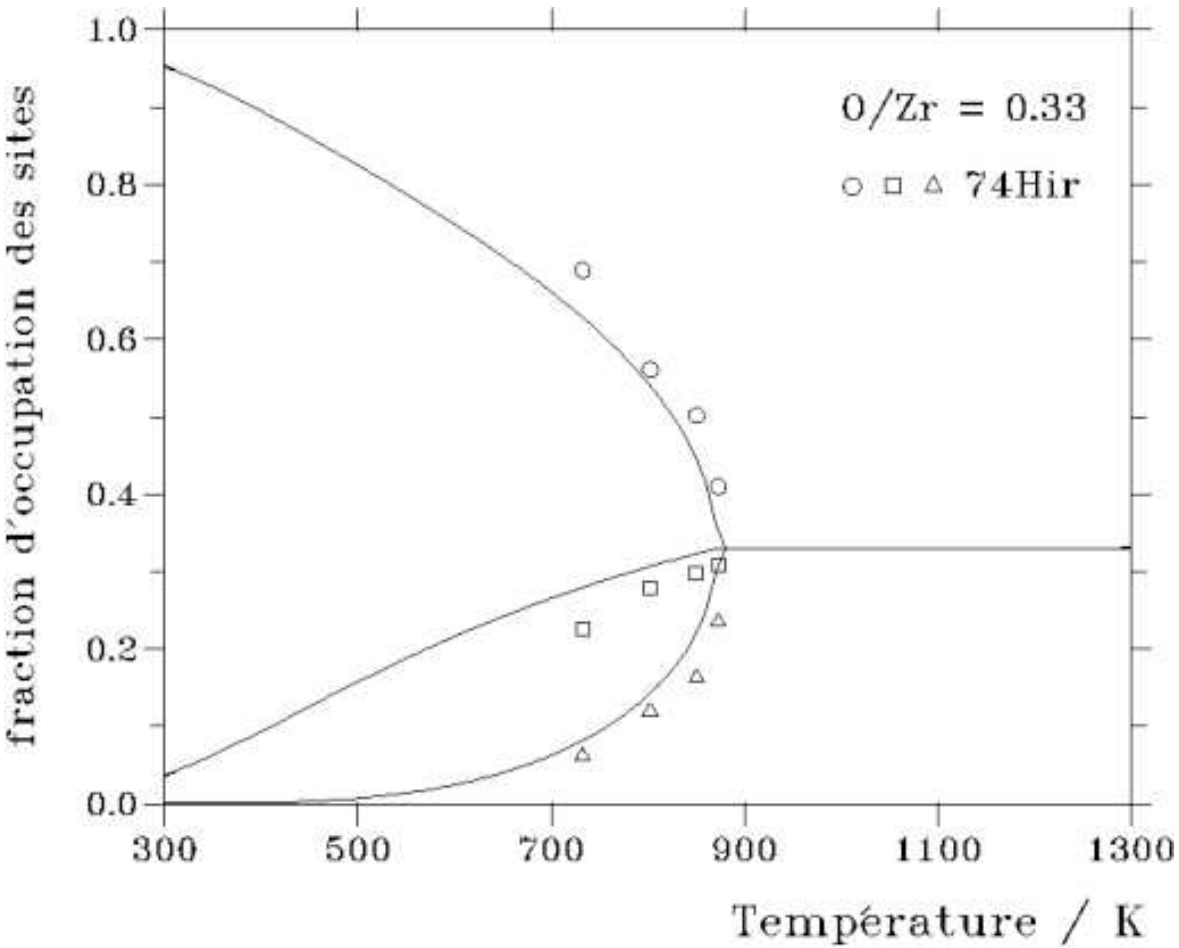
$Zr_3(O,\square)(O,\square)(O,\square)$

2001 Liang et al.: α and α'

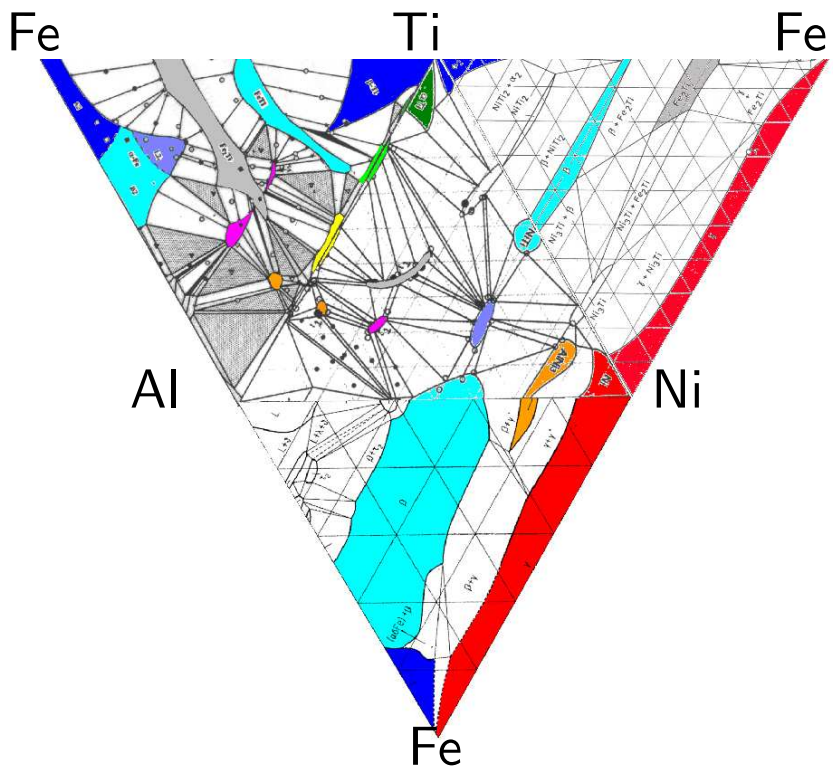


$Zr_3(O,\square)(O,\square)(O,\square)$

2001 Liang et al.: α and α'

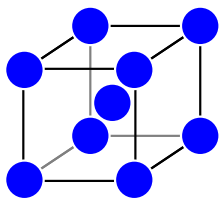


Metallic ordering

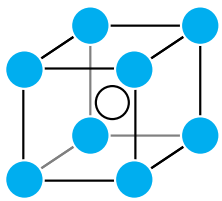


Metallic ordering

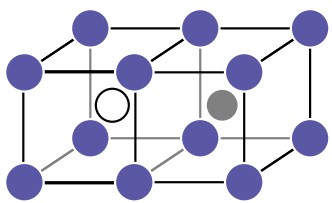
A2

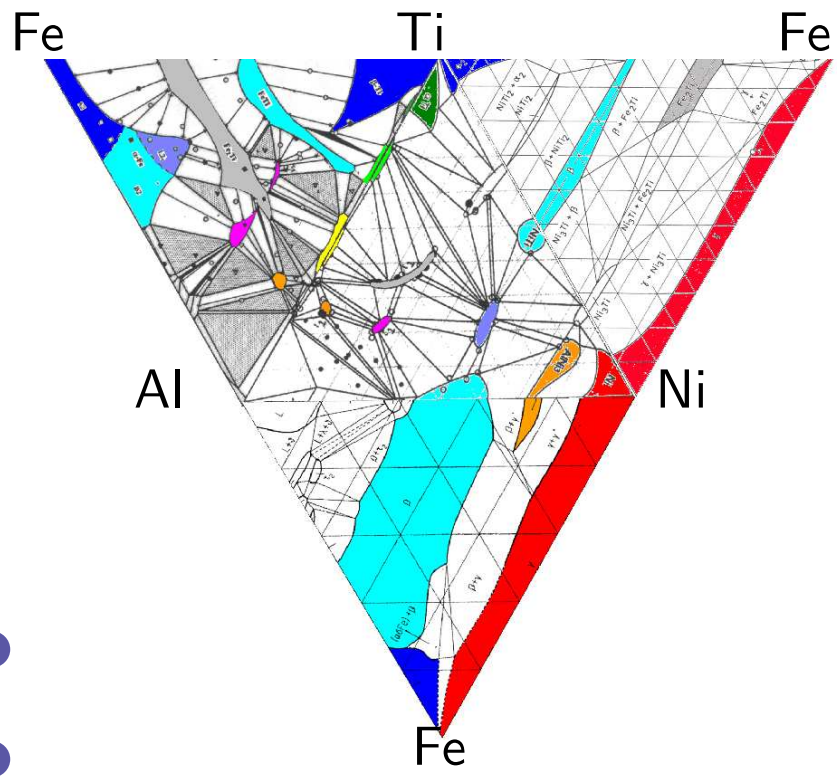


B2



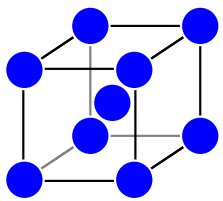
$L2_1$



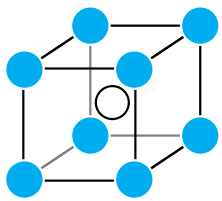


Metallic ordering

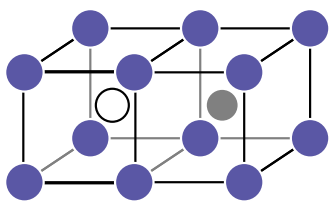
A2

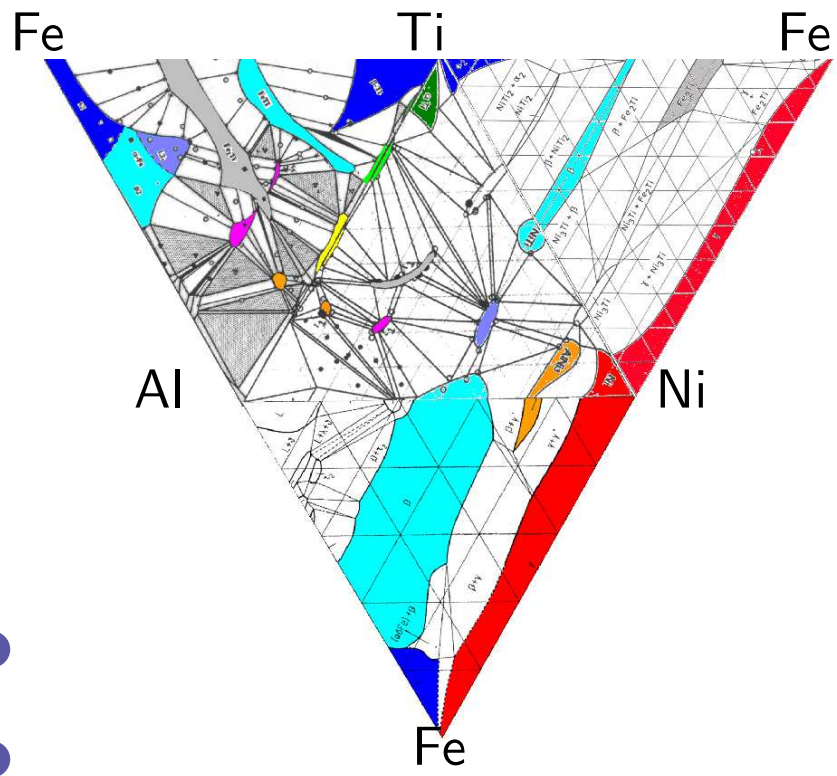


B2

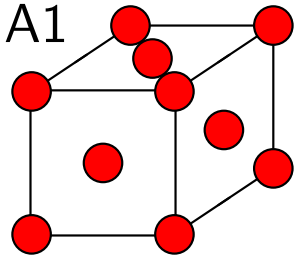


$L2_1$

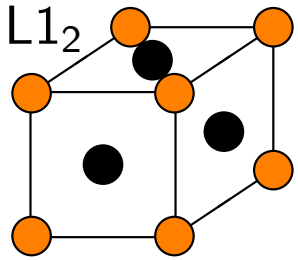




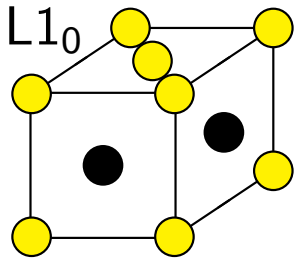
A1



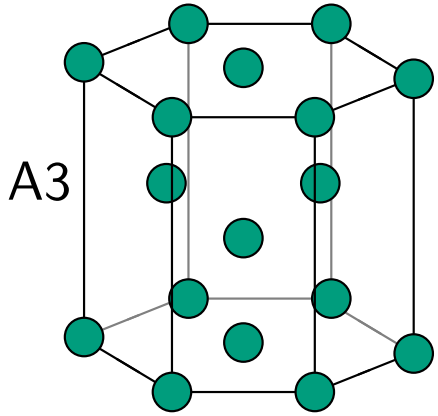
$L1_2$

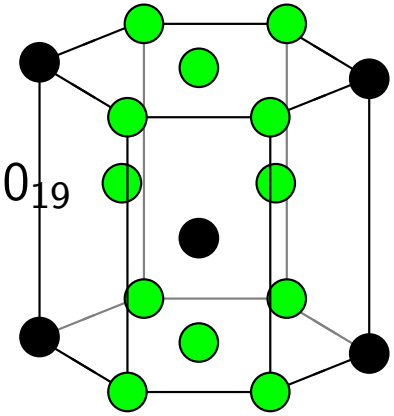


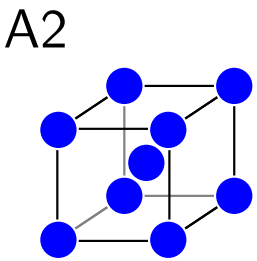
$L1_0$

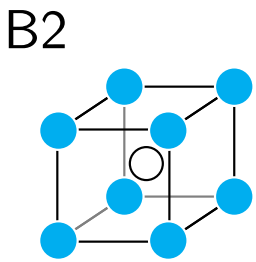


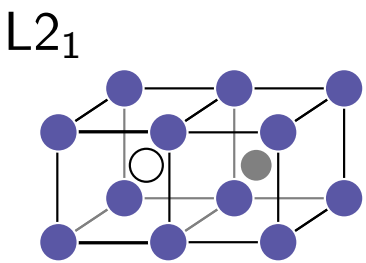
Metallic ordering

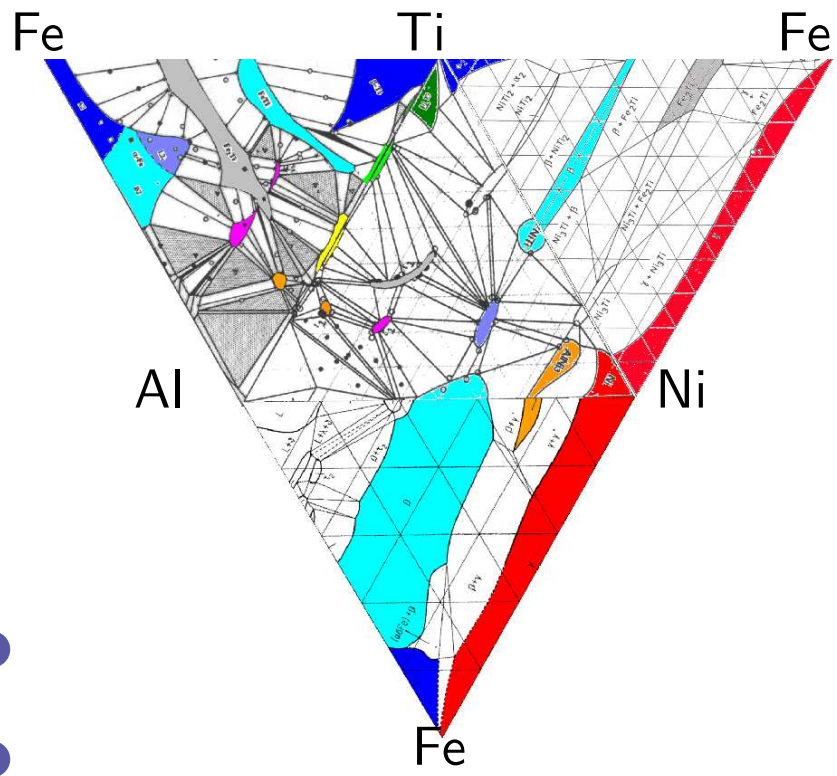


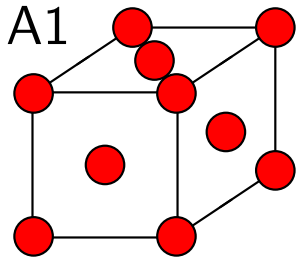


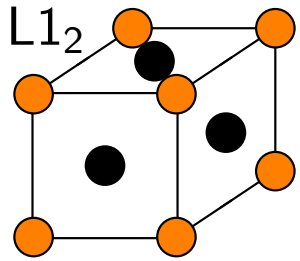


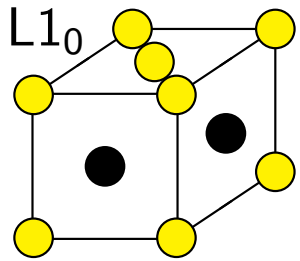












Metallic ordering

The Gibbs energy of the different phases of a same familly can be described with a single expression, $G(y_i^s)$, using the CEF, function of the site occupation of the different sublattices, y_i^s.

Metallic ordering

The Gibbs energy of the different phases of a same familly can be described with a single expression, $G(y_i^s)$, using the CEF, function of the site occupation of the different sublattices, y_i^s.

(A,B)(A,B)(A,B)(A,B) fcc based

$\rightsquigarrow$ $y_i^{(1)} = y_i^{(2)} = y_i^{(3)} = y_i^{(4)}$ $A1$

$\rightsquigarrow$ $y_i^{(1)} = y_i^{(2)} = y_i^{(3)} \neq y_i^{(4)}$ $L1_2$

$\rightsquigarrow$ $y_i^{(1)} = y_i^{(2)} \neq y_i^{(3)} = y_i^{(4)}$ $L1_0$

Metallic ordering

The Gibbs energy of the different phases of a same familly can be described with a single expression, $G(y_i^s)$, using the CEF, function of the site occupation of the different sublattices, y_i^s.

(A,B)(A,B)(A,B)(A,B) bcc based

$\rightsquigarrow$ $y_i^{(1)} = y_i^{(2)} = y_i^{(3)} = y_i^{(4)}$ $A2$

$\rightsquigarrow$ $y_i^{(1)} = y_i^{(2)} \neq y_i^{(3)} = y_i^{(4)}$ $B2$

$\rightsquigarrow$ $y_i^{(1)} = y_i^{(2)} \neq y_i^{(3)} \neq y_i^{(4)}$ $D0_3$ or $L2_1$

$\rightsquigarrow$ $y_i^{(1)} = y_i^{(3)} \neq y_i^{(2)} = y_i^{(4)}$ $B32$

Metallic ordering

The Gibbs energy of the different phases of a same familly can be described with a single expression, $G(y_i^s)$, using the CEF, function of the site occupation of the different sublattices, y_i^s.

(A,B)(A,B)(A,B)(A,B) hcp based

$\rightsquigarrow$ $y_i^{(1)} = y_i^{(2)} = y_i^{(3)} = y_i^{(4)}$ $A3$

$\rightsquigarrow$ $y_i^{(1)} = y_i^{(2)} = y_i^{(3)} \neq y_i^{(4)}$ $D0_{19}$

$\rightsquigarrow$ $y_i^{(1)} = y_i^{(2)} \neq y_i^{(3)} = y_i^{(4)}$ B_{19}

Metallic ordering

The Gibbs energy of the different phases of a same familly can be described with a single expression, $G(y_i^s)$, using the CEF, function of the site occupation of the different sublattices, y_i^s.

$$G(y_i^s) = \sum_{ijkl} y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)} G_{i:j:k:l}$$

$$+RT \sum_s a^s \sum_i y_i^s \ln y_i^s + G^{xs}$$

Relations between the parameters of $G(y_i^s)$ are to be imposed so that the disorder can become stable. This is obtained taking into account the symmetries of the lattices.

Metallic ordering

The Gibbs energy of the different phases of a same familly can be described with a single expression, $G(y_i^s)$, using the CEF, function of the site occupation of the different sublattices, y_i^s.

It is in general splitted into two contributions.

$$G(y_i^s) = G^{dis}(x_i) + \Delta G^{ord}(y_i^s)$$

This is not a requirement. It allows easier management of big databases, avoiding to introduce the CEF for systems without significant ordering.

$$G^{dis}(x_i) = \sum_i x_i G_i^{dis} + RT \sum_i x_i \ln x_i + \sum_{i,j} x_i x_j L_{i,j}^{dis} + \sum_{i,j,k} x_i x_j x_k L_{i,j,k}^{dis}$$

Metallic ordering

The Gibbs energy of the different phases of a same familly can be described with a single expression, $G(y_i^s)$, using the CEF, function of the site occupation of the different sublattices, y_i^s.

It is in general splitted into two contributions.

$$G(y_i^s) = G^{dis}(x_i) + \Delta G^{ord}(y_i^s)$$

The ordering part itself is the difference of two terms, expressed in the CEF, allowing it to cancel when the phase is disordered.

$$\Delta G^{ord}(y_i^s) = G^{ord}(y_i^s) - G^{ord}(y_i^s = x_i)$$

The relations allowing the phase to disorder are to be imposed between the parameters defining $G^{ord}(y_i^s)$. They can easily be related to the crystallographic symmetry of the lattice.

Metallic ordering

The Gibbs energy of the different phases of a same familly can be described with a single expression, $G(y_i^s)$, using the CEF, function of the site occupation of the different sublattices, y_i^s.

It is in general splitted into two contributions.

$$G(y_i^s) = G^{dis}(x_i) + \Delta G^{ord}(y_i^s)$$

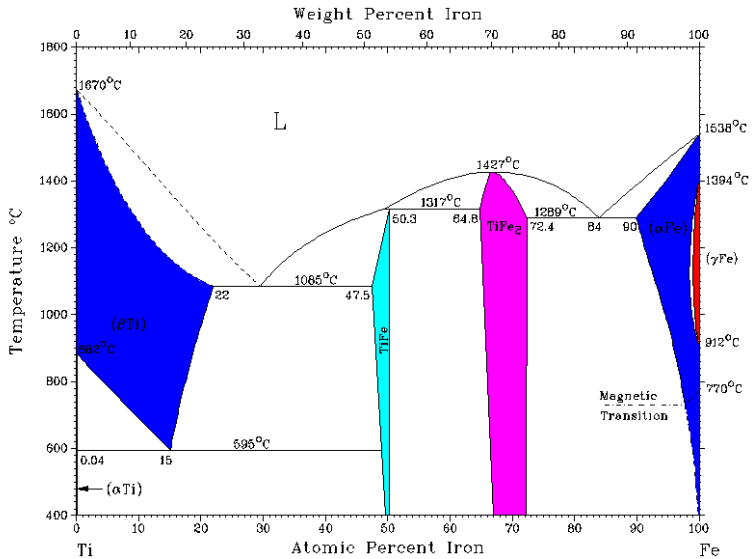
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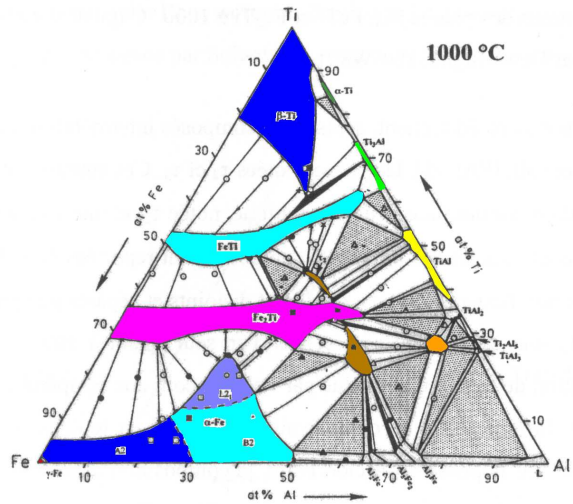
$$\Delta G^{ord}(y_i^s) = G^{ord}(y_i^s) - G^{ord}(y_i^s = x_i)$$

In order to use this formalism in Thermo-Calc the following command has to be given in `G_E_S`

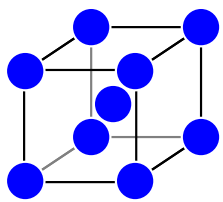
`AMEND_PHASE_DESCRIPTION` *ord* `DIS_PART` *dis*

A2/B2 modelling

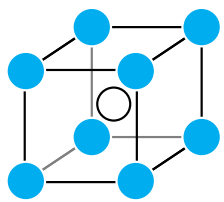




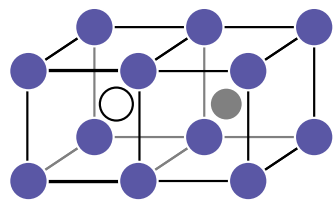
A2



B2

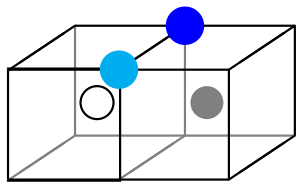


$L2_1$

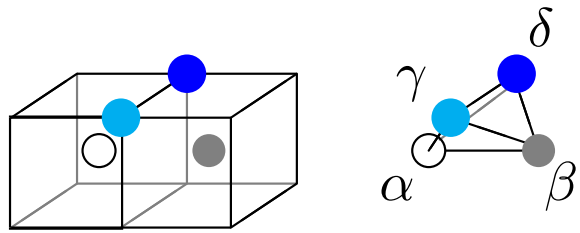


To be able to describe the 2nd order transition between the A2, B2 and $L2_1$ phases in the ternary system Al-Fe-Ti, the A2 and B2 phases have to be described with 4SL in Fe-Ti.

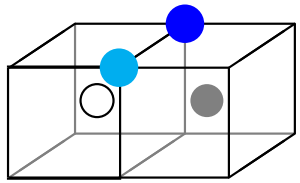
bcc ordering

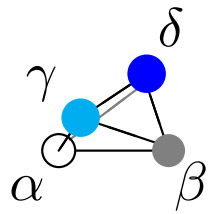


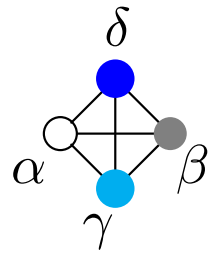
bcc ordering



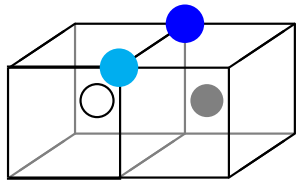
bcc ordering

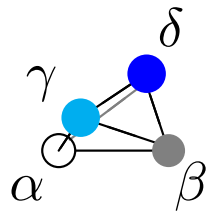


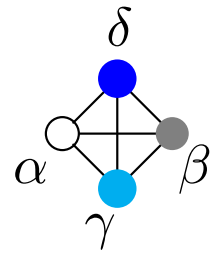




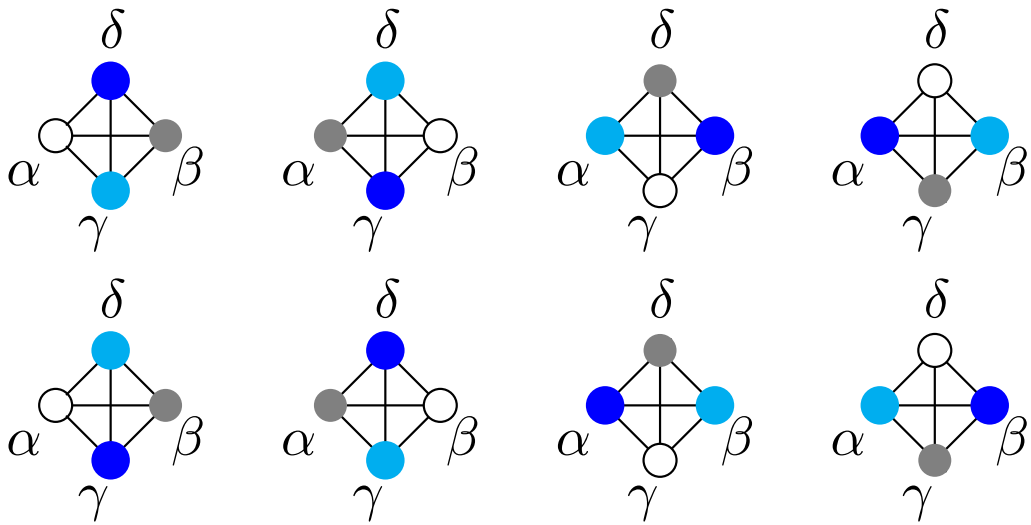
bcc ordering



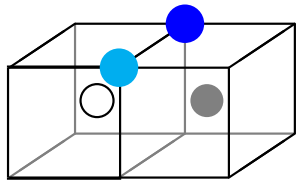


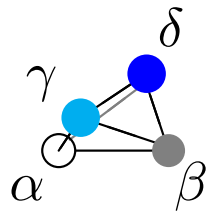


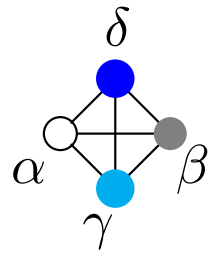
From crystallographic symmetry,
the following configurations are equivalent.



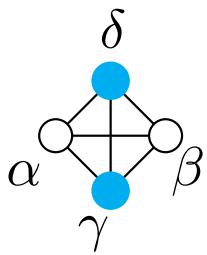
bcc ordering

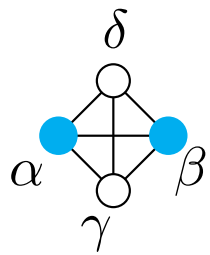






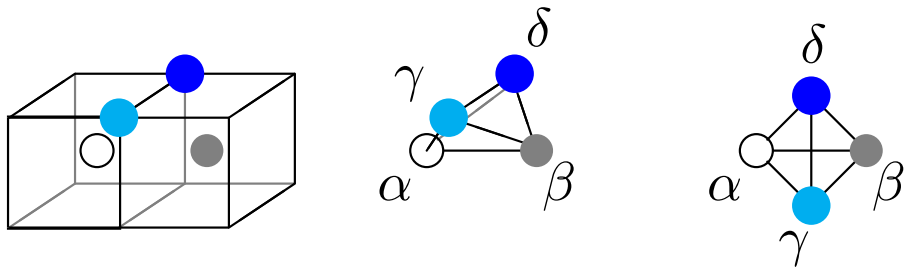
From crystallographic symmetry,
the following configurations are equivalent.



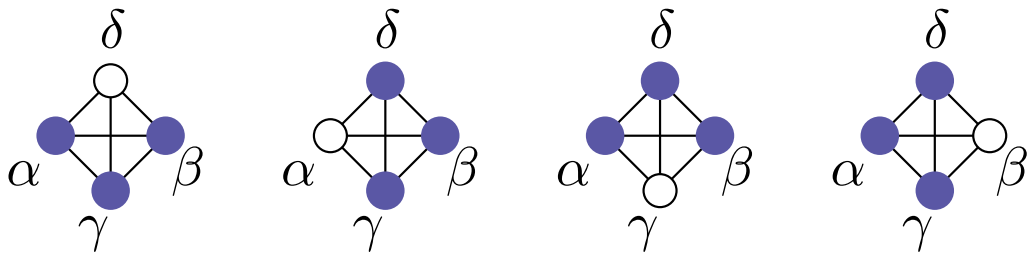


B2 configurations

bcc ordering

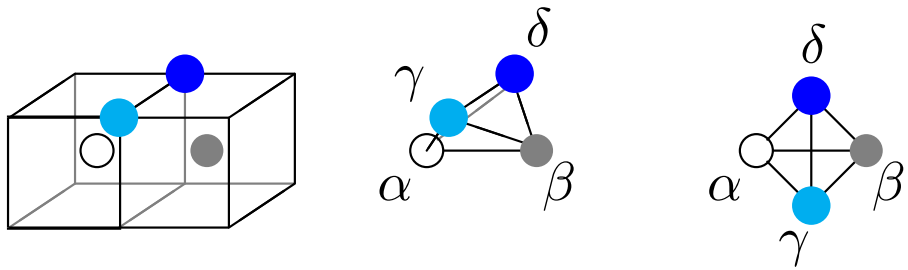


From crystallographic symmetry,
the following configurations are equivalent.

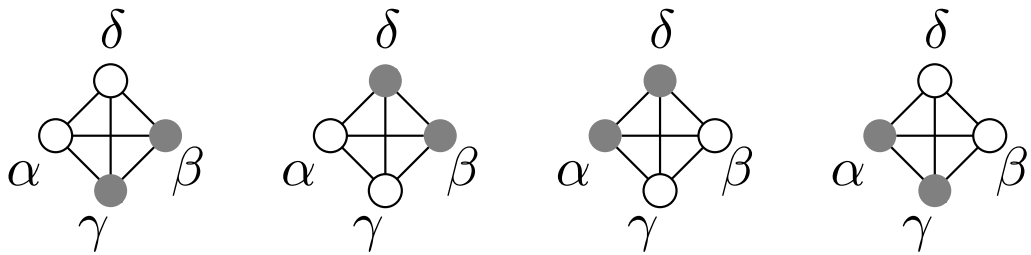


$D0_3$ configurations

bcc ordering



From crystallographic symmetry,
the following configurations are equivalent.



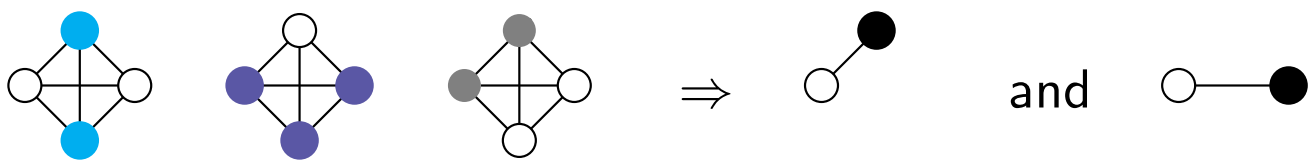
B32 configurations

bcc ordering

The fact to assign the same Gibbs energy to equivalent configurations allows the disordered phase to be stable. This stands for Gibbs energy of the stoichiometric compounds as well as for interaction parameters.

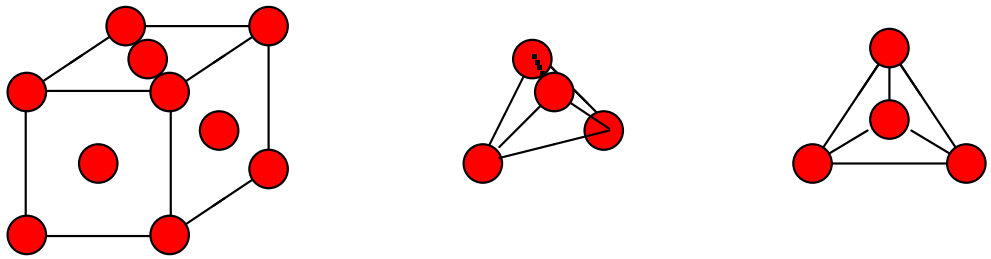
In Thermo-Calc software, there is an option - B - where the equality of the Gibbs energy of the equivalent configurations of the irregular tetrahedron constituting the bcc lattice is built in.

The use of DFT estimates for the compounds that are not stable is recommended. However, up to the quaternary compounds, a cluster expansion on the 1st and 2nd neighbours bonds can be used as first approximation for extrapolation.



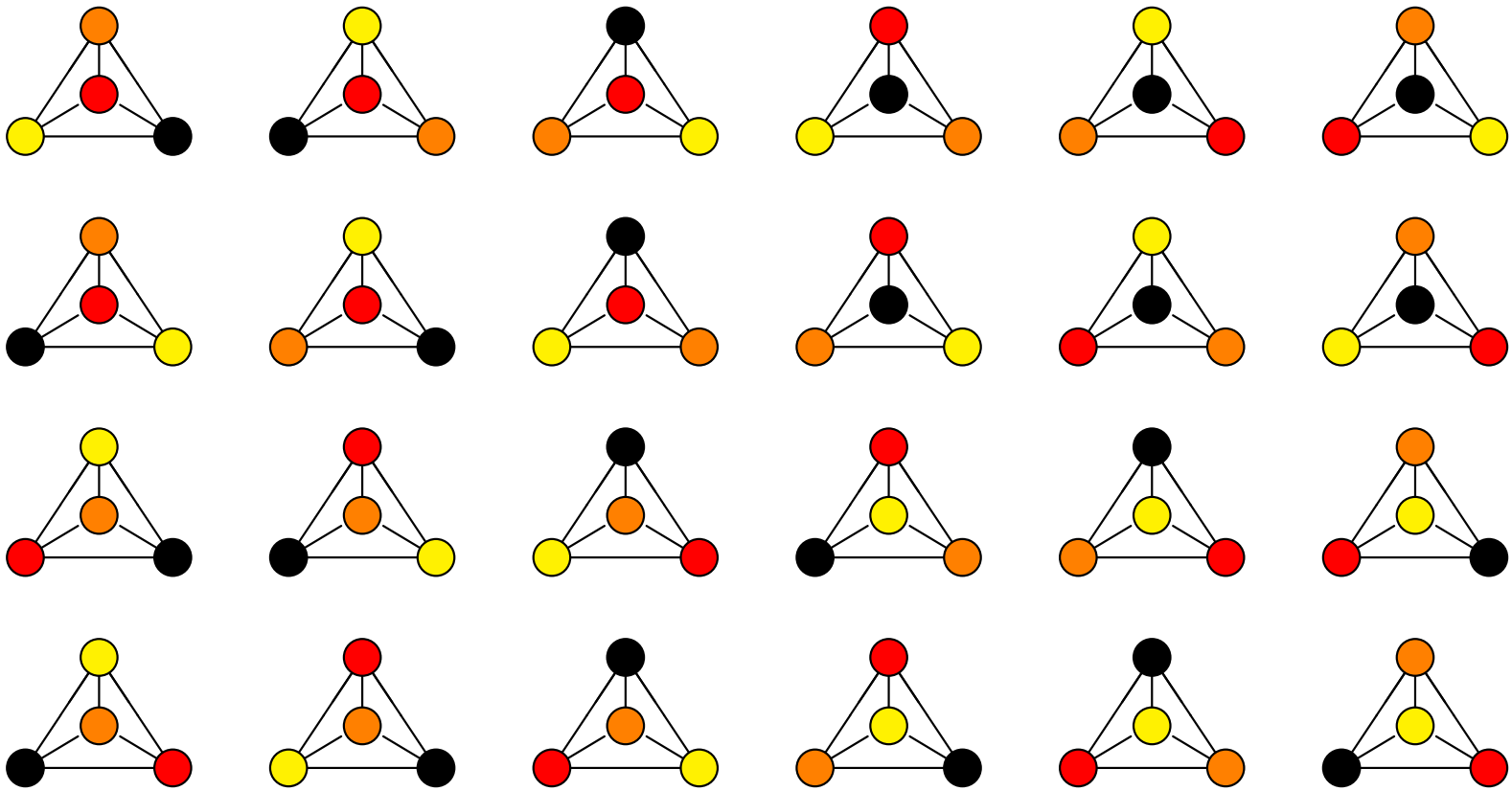
fcc ordering

The fcc ordering is more simple as the lattice is built on regular tetrahedra.



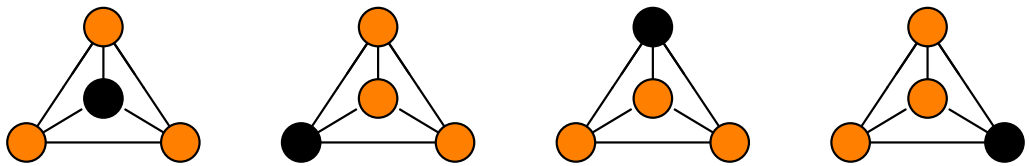
fcc ordering

From crystallographic symmetry,
the following configurations are equivalent.



fcc ordering

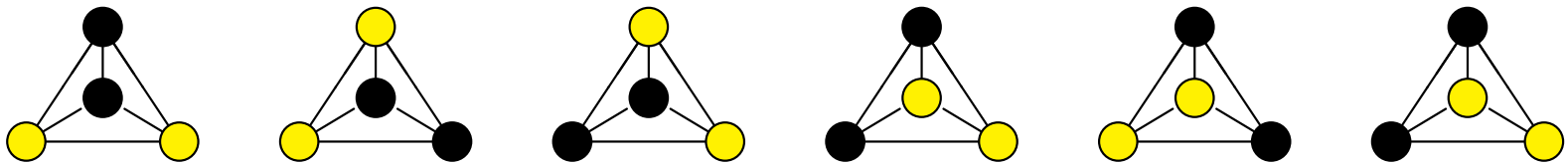
From crystallographic symmetry,
the following configurations are equivalent.



$L1_2$ configurations

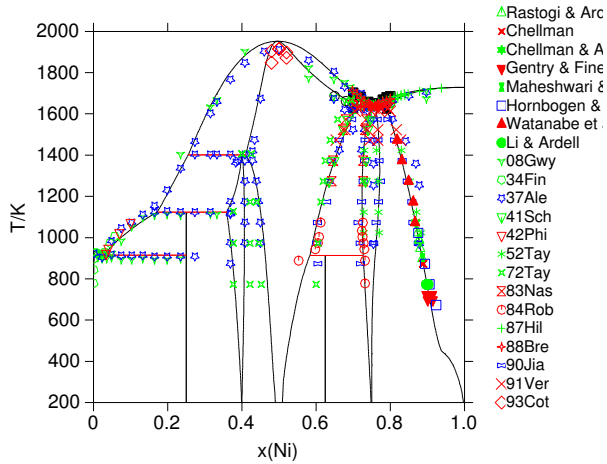
fcc ordering

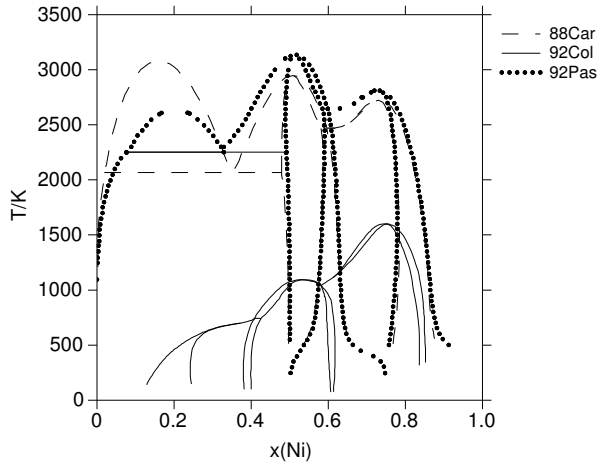
From crystallographic symmetry,
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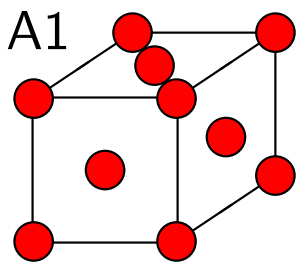


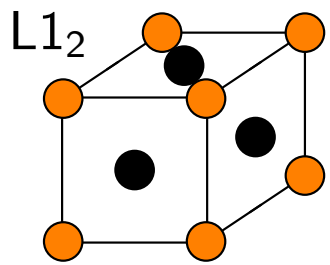
$L1_0$ configurations

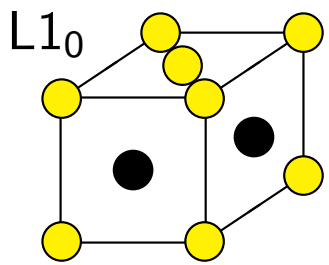
A1/L12 modelling

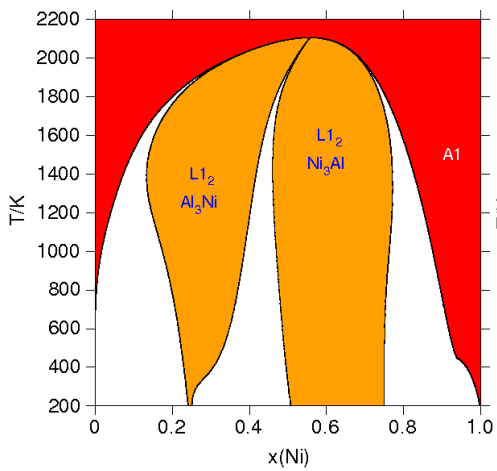


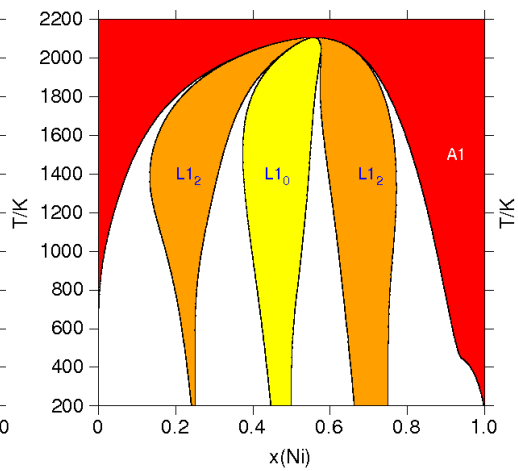


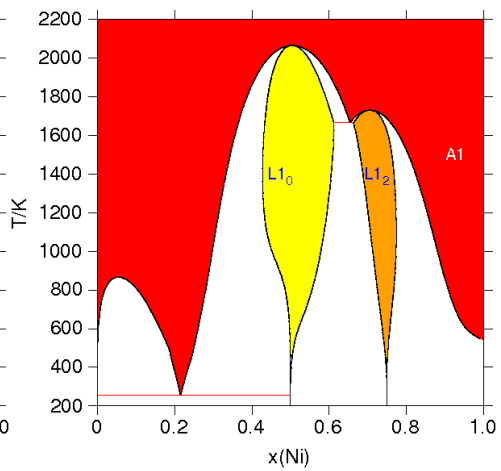




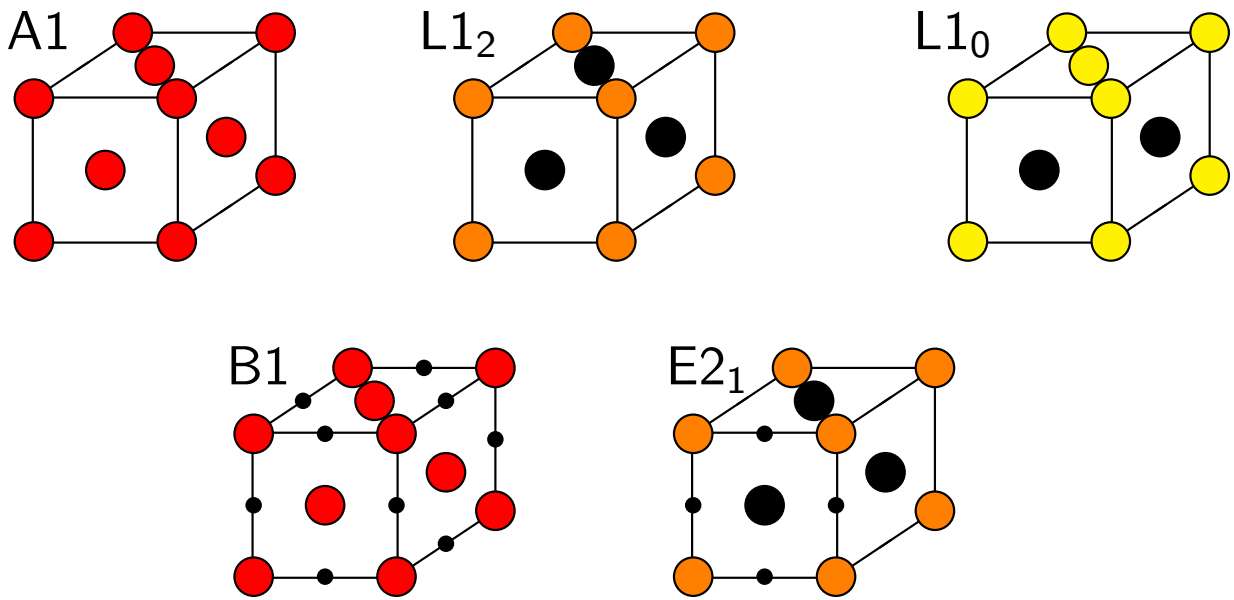








Interstitial and metallic ordering



The E2$_1$ κ phase, stable in Al-Fe-C for instance, should be described with the same model as all these crystallographic structures, considering ordering between metallic elements and between C and vacancies.

Conclusion

The knowledge of the crystallography of the phases is key for a good thermodynamic modelling.

To estimate properly the configurational entropy of phases showing large homogeneity range, it is important to use a model close to the crystallography.

Such models are in general more complex but the parameters assessment can be tremendously simplified by the use of DFT estimates for metastable configurations.

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