Crystallography and ordering

Nathalie Dupin

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Calcul Thermodynamique

SATA / Port-Royal / 2015

Crystal structure data

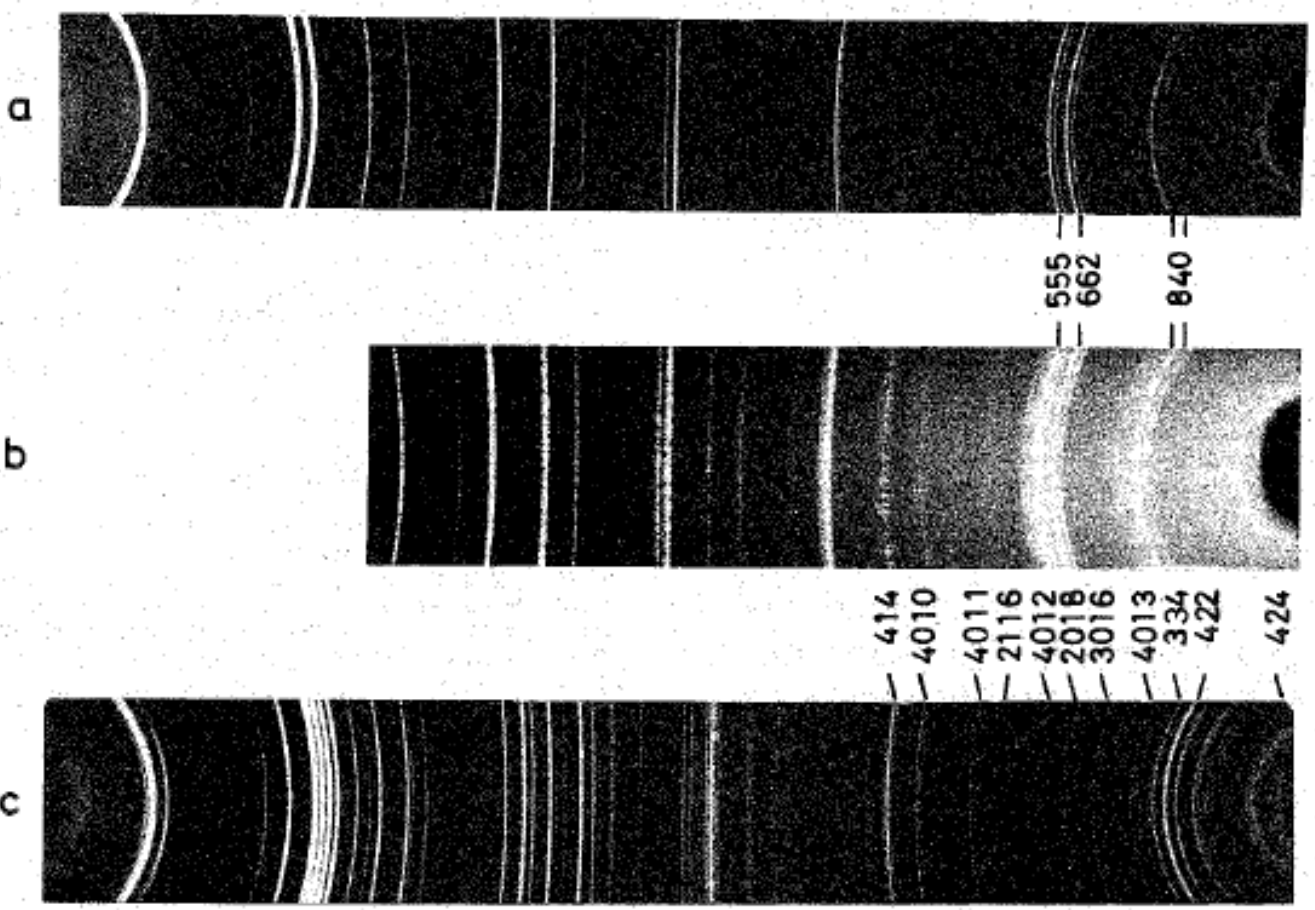


Fig. 7a. $Mg_{33,3}Cu_{66,6}$ recuit 20 jours à 500°C ($K_\alpha Cu$)
Fig. 7b. $Mg_{37,6}Cu_{62,4}$ non recuit ($K_\alpha Cu$)
Fig. 7c. $Mg_{33,4}Ni_{66,6}$ recuit 22 jours à 480°C ($K_\alpha Cu$) avec indication des raies utilisées pour le calcul du paramètre *a*.

Crystal structure data

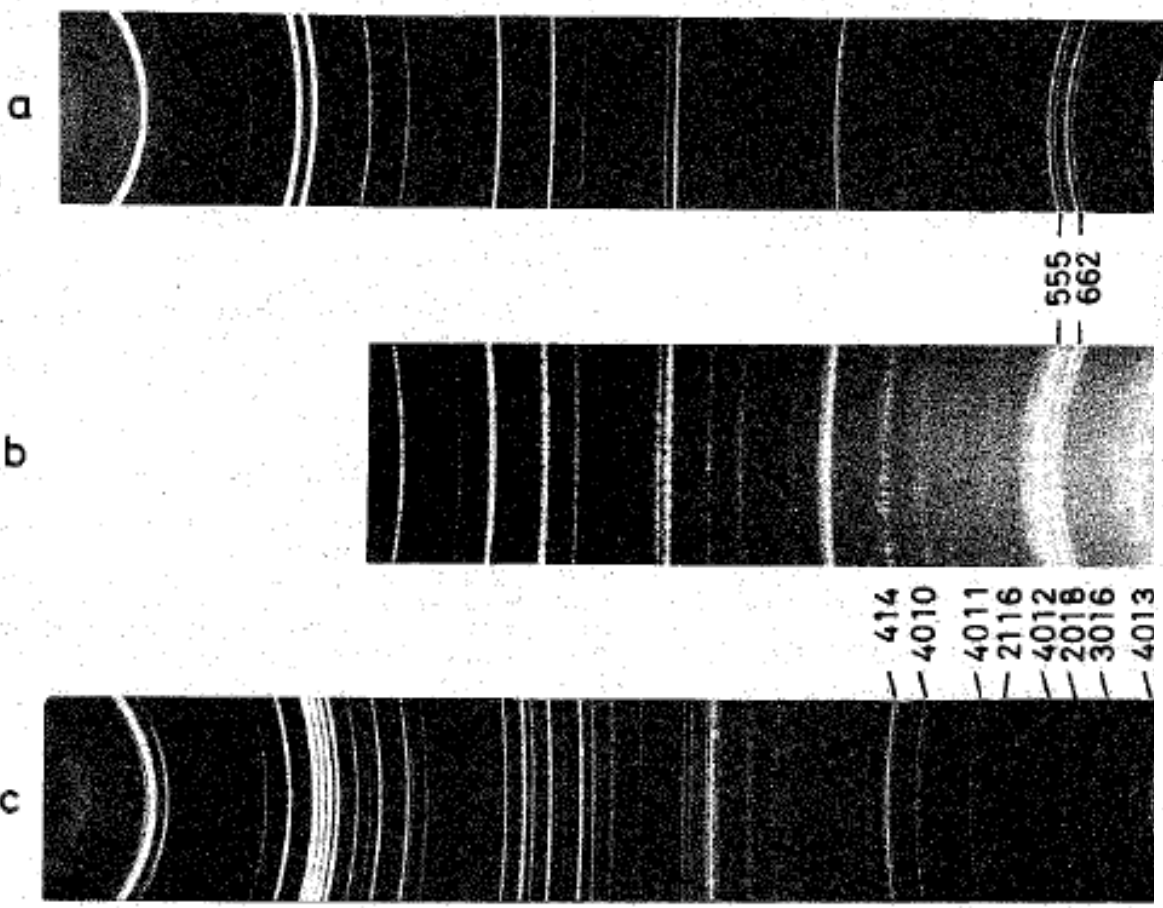


Fig. 7a. $Mg_{33,3}Cu_{66,6}$ recuit 20 jours à 500°C ($K_\alpha Cu$)
Fig. 7b. $Mg_{37,6}Cu_{62,4}$ non recuit ($K_\alpha Cu$)
Fig. 7c. $Mg_{33,4}Ni_{66,6}$ recuit 22 jours à 480°C ($K_\alpha Cu$) avec indication des raies utilisées pour le calcul du paran

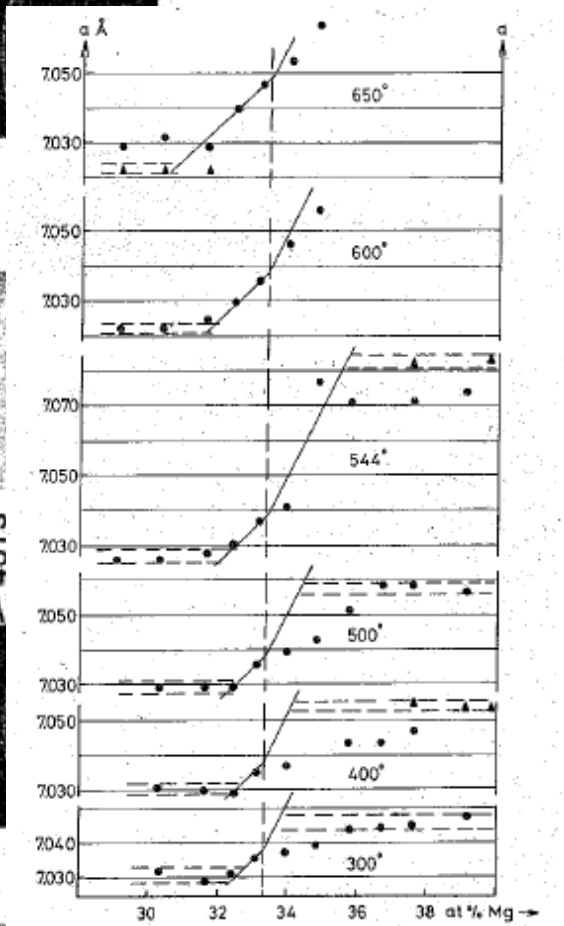


Fig. 4. Paramètre a de la maille cubique de $MgCu_2$ en fonction de la composition (at.% Mg) et de la température (1 Å = 10^{-10} m)

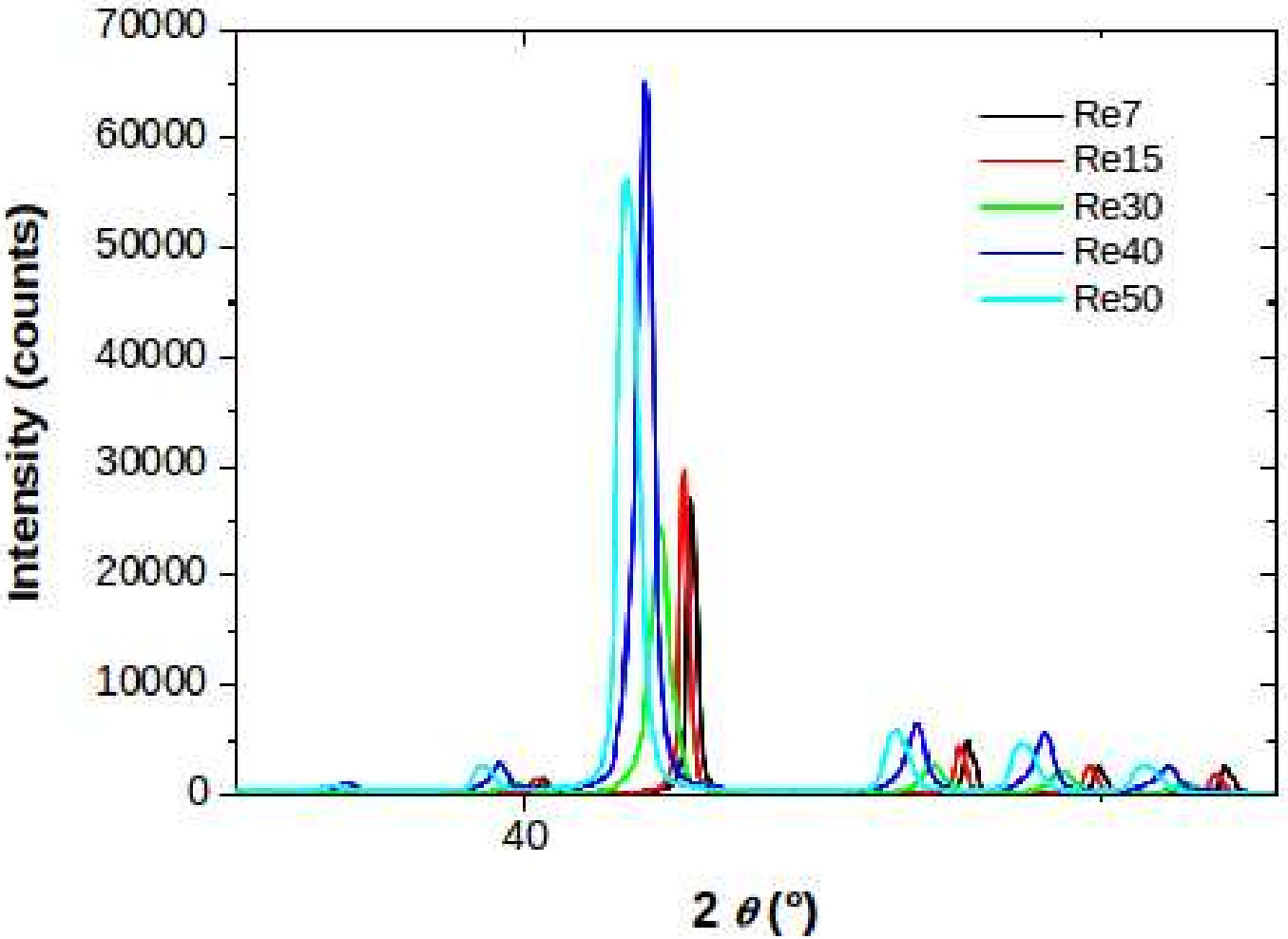
Crystal structure data

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_α (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



Crystal structure data

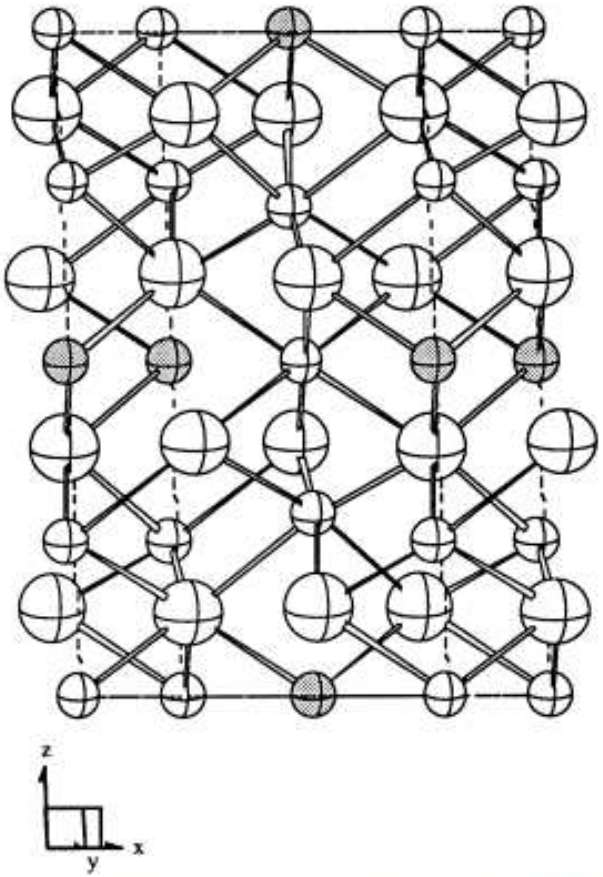


Fig. 3. Perspective view of the $Rh_{1+x}Te_2$ structures ($x>0.5$). The gray sphere corresponds to the octahedral sites filled by rhodium (Rh(3)) beyond the $Rh_{1.5}Te_2$ composition (see Fig. 2 for details of the other rhodium position). Larger open circles are Te atoms.

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)
$Rh_{1.87}Te_2$					
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

- Nature of the phase
  - $\rightsquigarrow$ prototype, StrukturBericht
- Number of sites
- Site multiplicity
  - $\rightsquigarrow$ 2/1 to be preferred to 0.67/0.33
- Site occupancy
- Volume

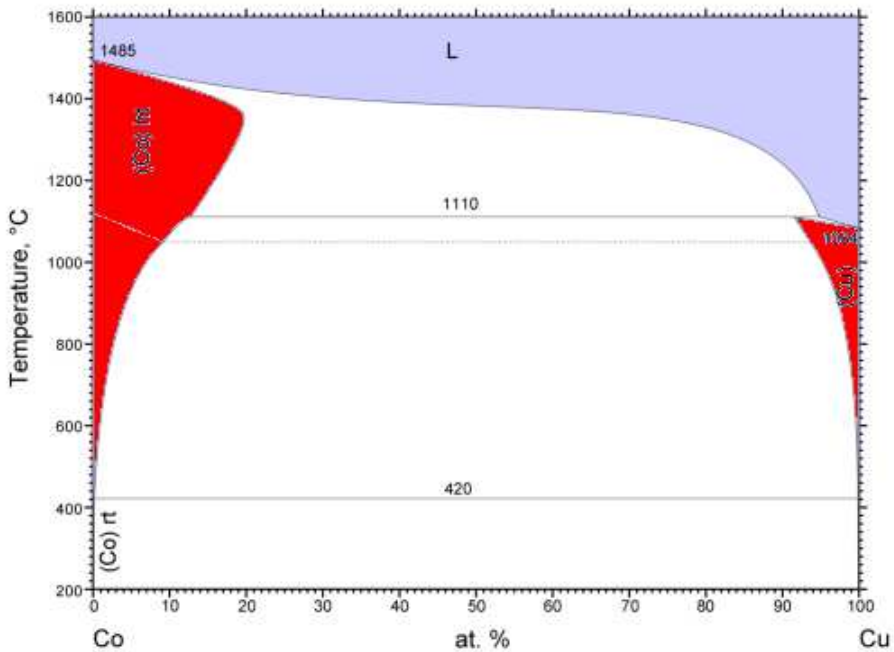
Same crystallographic structure
$\Rightarrow$ Same phase in the database

- Obvious when similar composition, similar elements, known continous solubility
- Not obvious when different compositions in simple systems, very different crystallographic parameters, no reciprocal solubility
- Not recommended when no common elements, no reciprocal solubility, very different interactions, ex: CsCl/NiAl

Same crystallographic structure
$\Rightarrow$ Same phase in the database

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

(Cu) and (Co) ht prototype Cu
$\Rightarrow$ same model.



Bibiographic data
Binary Alloy Phase Diagrams, II Ed., Ed. T.B. Massalski,1990,2,,1181-1183,Nishizawa T.

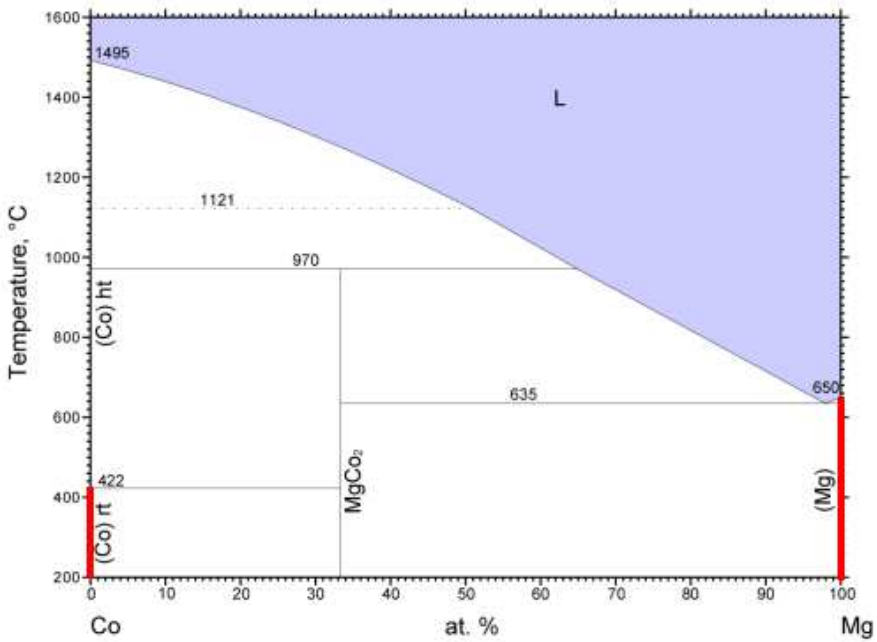
Same crystallographic structure

$\Rightarrow$ Same phase in the database

Phase	Structure type	Peason symbol	Space group No.	Material search
(Mg)	Mg	hP2	194	Search
(Co) ht	Cu	cF4	225	No Data
(Co) rt	Mg	hP2	194	No Data
$MgCo_2$	$MgZn_2$	hP12	194	Search

(Mg) and (Co) rt prototype Mg

$\Rightarrow$ same model.

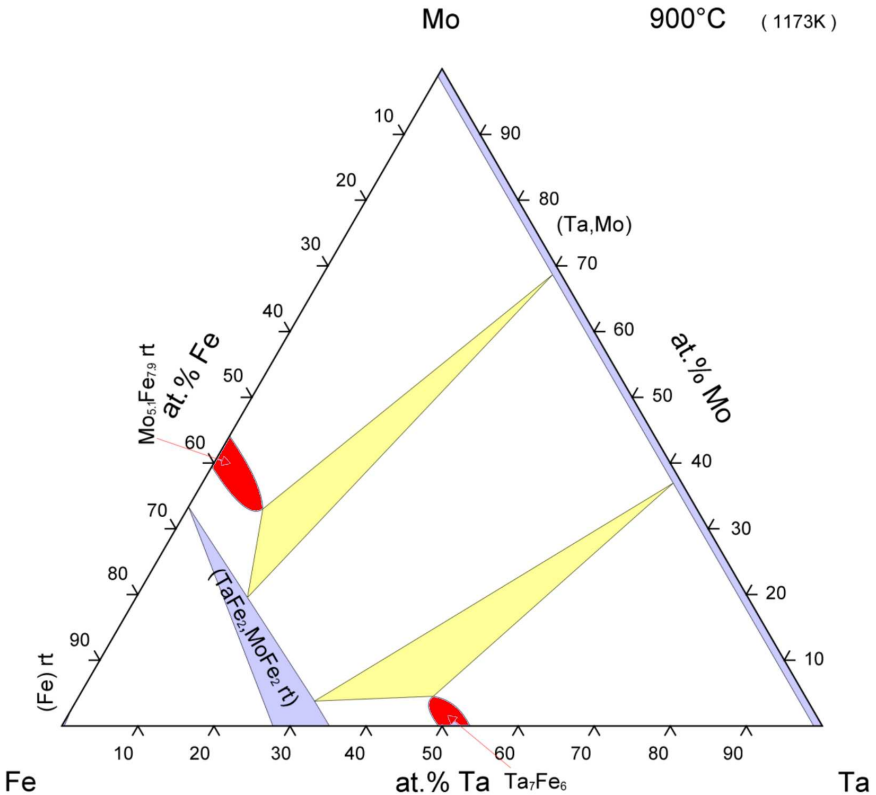


Bibliographic data

Binary Alloy Phase Diagrams, II Ed., Ed. T.B. Massalski,1990,2,,1205-1206,Nayeb Hashemi A.A.

Same crystallographic structure
$\Rightarrow$ Same phase in the database

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

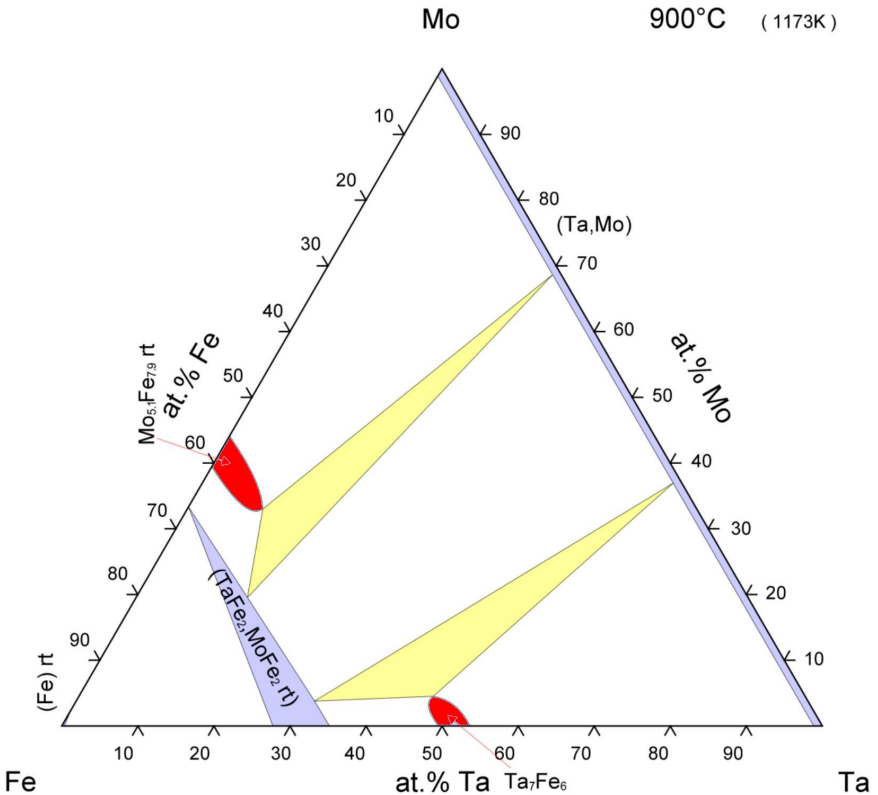


APD phase label / Published phase label	Formula	Prototype	Pearson symbol / Space group
Phases shown in this diagram:			
(Fe) rt α	Fe	W	cI2 Im-3m
Mo5.1Fe7.9 rt Fe7Mo6,μ	Mo5.08Fe7.92	W6Fe7	hR39 R-3m
Ta7Fe6 FeTa,μ	Ta6.5Fe6.5	W6Fe7	hR39 R-3m
(Ta,Mo) (Mo,Ta)	Ta0.5Mo0.5	W	cI2 Im-3m
(TaFe2,MoFe2 rt) Fe2(Mo,Ta)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

© ASM International 2006. Diagram No. 2000191.

Same crystallographic structure
$\Rightarrow$ Same phase in the database

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



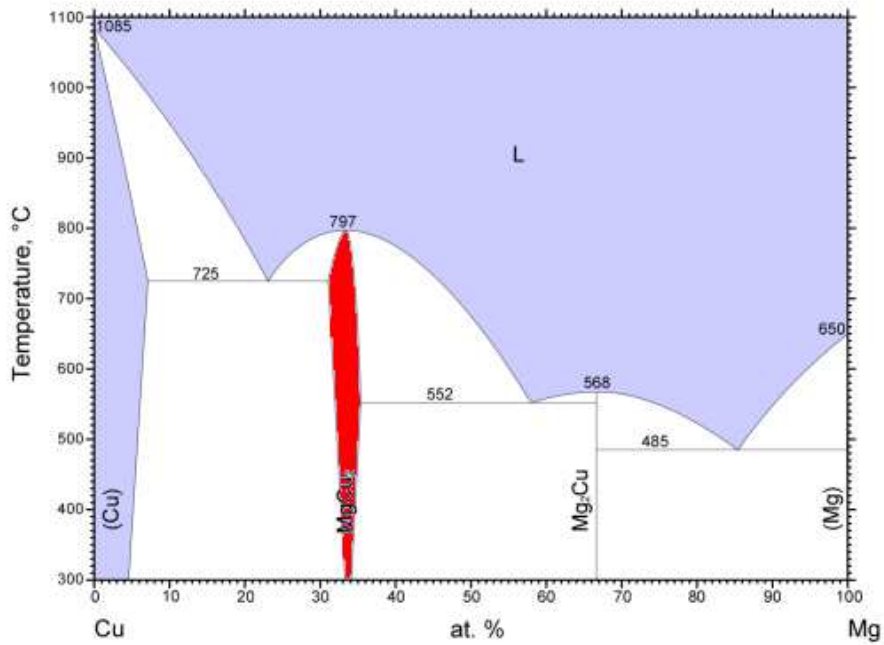
APD phase label / Published phase label	Formula	Prototype	Pearson symbol / Space group
Phases shown in this diagram:			
(Fe) rt α	Fe	W	cI2 Im-3m
Mo5.1Fe7.9 rt Fe7Mo6,μ	Mo5.08Fe7.92	W6Fe7	hR39 R-3m
Ta7Fe6 FeTa,μ	Ta6.5Fe6.5	W6Fe7	hR39 R-3m
(Ta,Mo) (Mo,Ta)	Ta		
(TaFe2,MoFe2 rt) Fe2(Mo,Ta)	Mo		

Fe_2Ta and Fe_2Mo prototype W_6Fe_7 $\Rightarrow$ same model.

© ASM International 2006. Diagram No. 2000191.

Crystallographic structure
$\Rightarrow$ thermodynamic model

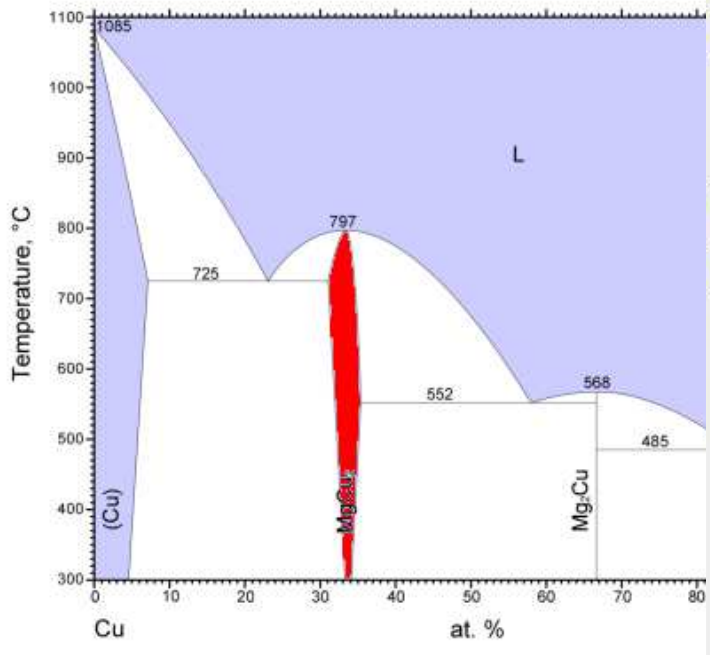
Phase	Structure type	Peason symbol	Space group No.	Material search
(Mg)	Mg	hP2	194	Search
$MgCu_2$	$MgCu_2$	cF24	227	Search
(Cu)	Cu	cF4	225	No Data
Mg_2Cu	Mg_2Cu	oF48	70	Search



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

Crystallographic structure
$\Rightarrow$ thermodynamic

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



$MgCu_2$	Structure type	Pearson symbol	Space group	No
	$MgCu_2$	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)

Crystallographic data

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

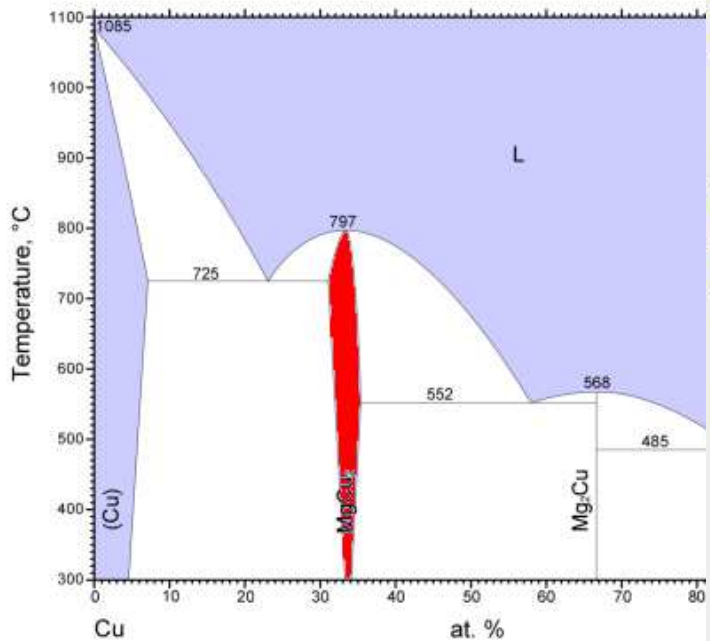
No	Site notation	Atom	Multiplicity	Wyckoff	Site symmetry	x	y	z	Occupancy
1	Cu	Cu	16	c	.-3m	0	0	0	1.0
2	Mg	Mg	8	b	-43m	3/8	3/8	3/8	1.0

Bibliographic data

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

Crystallographic structure
$\Rightarrow$ thermodynamic

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



$MgCu_2$	Structure type	Pearson symbol	Space group	No
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*Standardiz

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

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

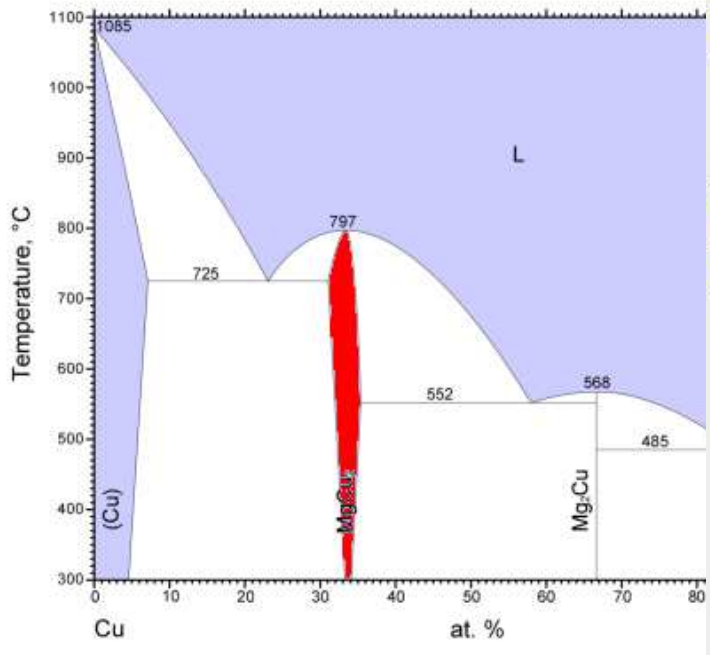
$\Rightarrow$ **$(Cu)_2(Mg)$**

Bibliographic data

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

Crystallographic structure
$\Rightarrow$ thermodynamic

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



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*Standardiz

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

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Crystallographic data

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Cell volume 0.3480 nm^3

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

Z 8

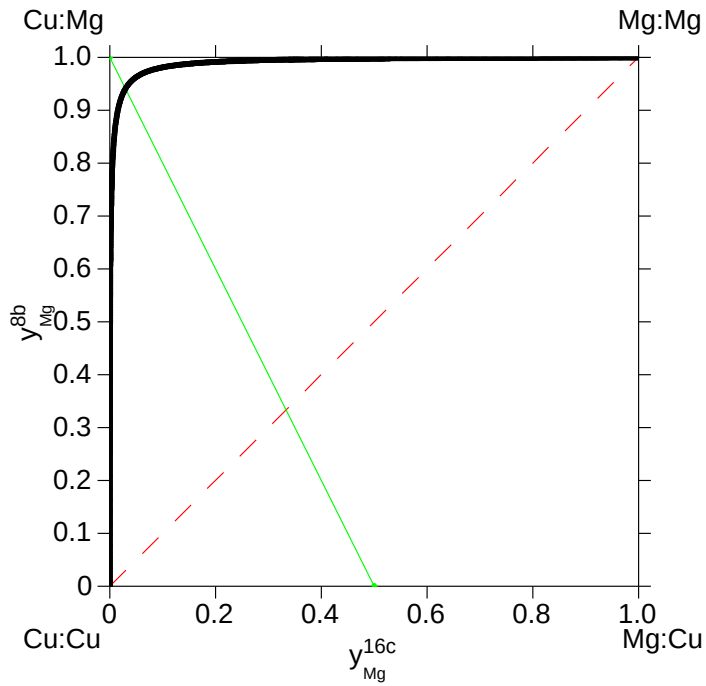
Atom coordinates

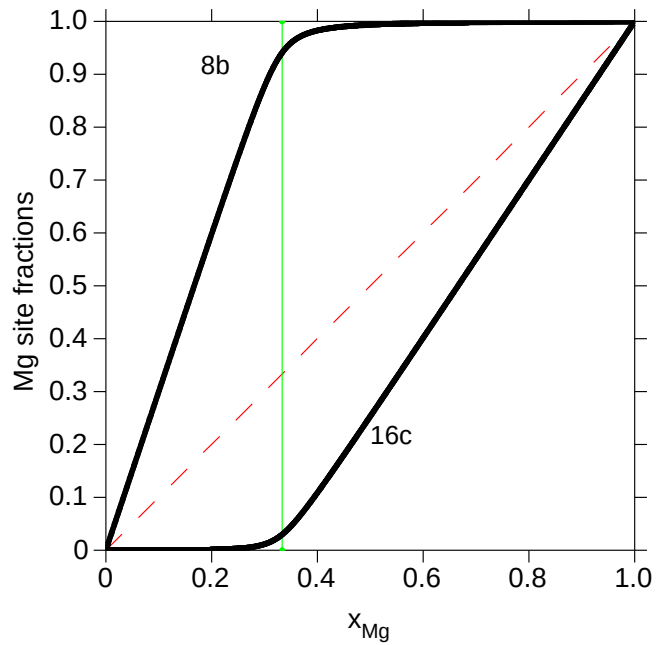
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1	Cu	Cu	16	c	.-3m	0	0	0	1.0
2	Mg	Mg	8	b	-43m	3/8	3/8	3/8	1.0

+ homogeneity range $\Rightarrow$ $(Cu,Mg)_2(Cu,Mg)$

Crystallographic structure
$\Rightarrow$ thermodynamic model

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





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

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

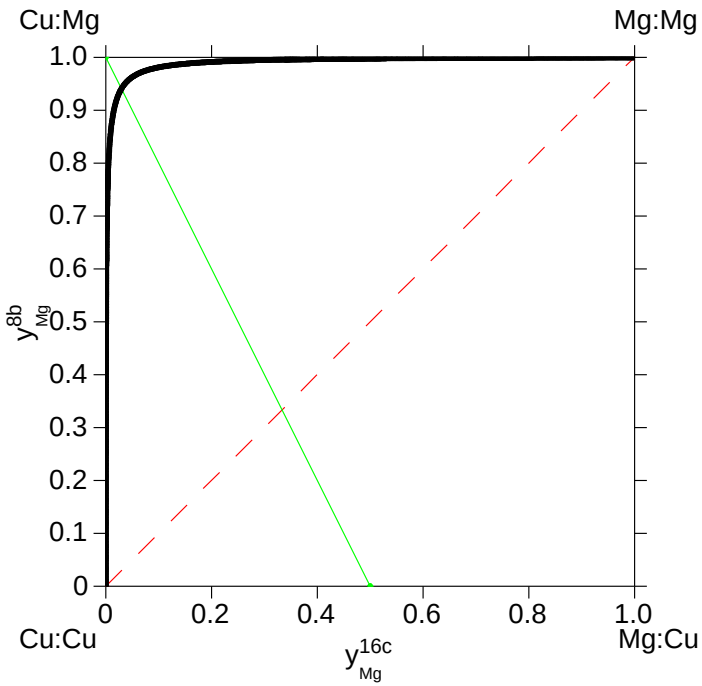
Crystallographic structure
$\Rightarrow$ thermodynamic model

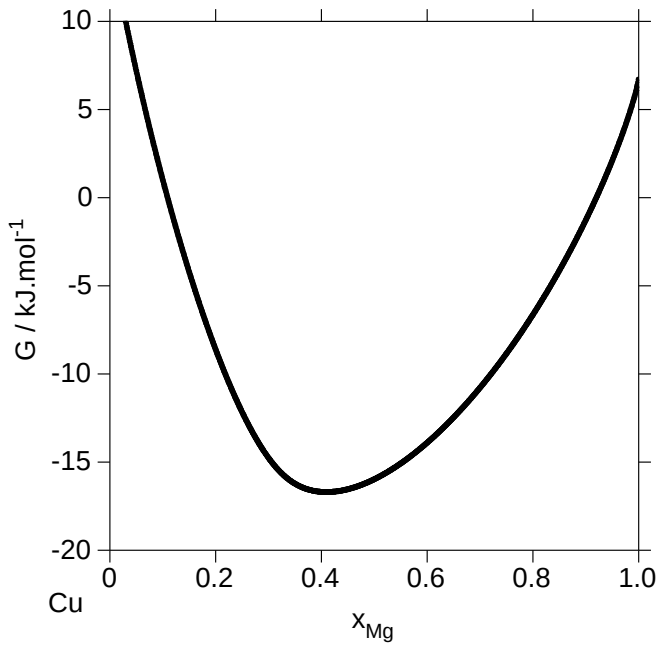
$$(Cu,Mg)_2(Cu,Mg)$$

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

Crystallographic structure
$\Rightarrow$ thermodynamic model

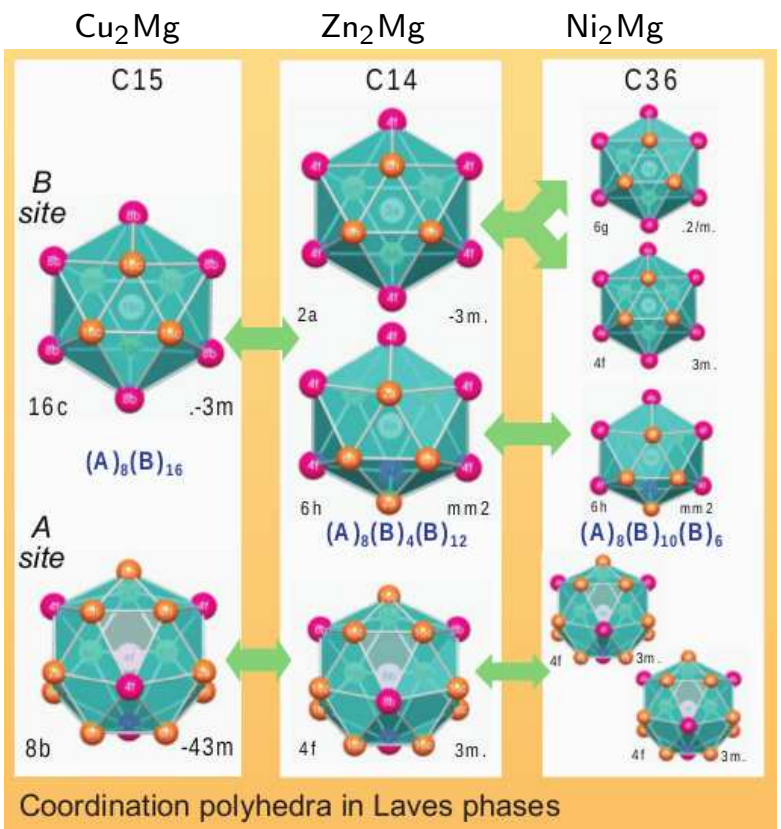
$(Cu,Mg)_2(Cu,Mg)$





Crystallographic structure
$\Rightarrow$ thermodynamic model





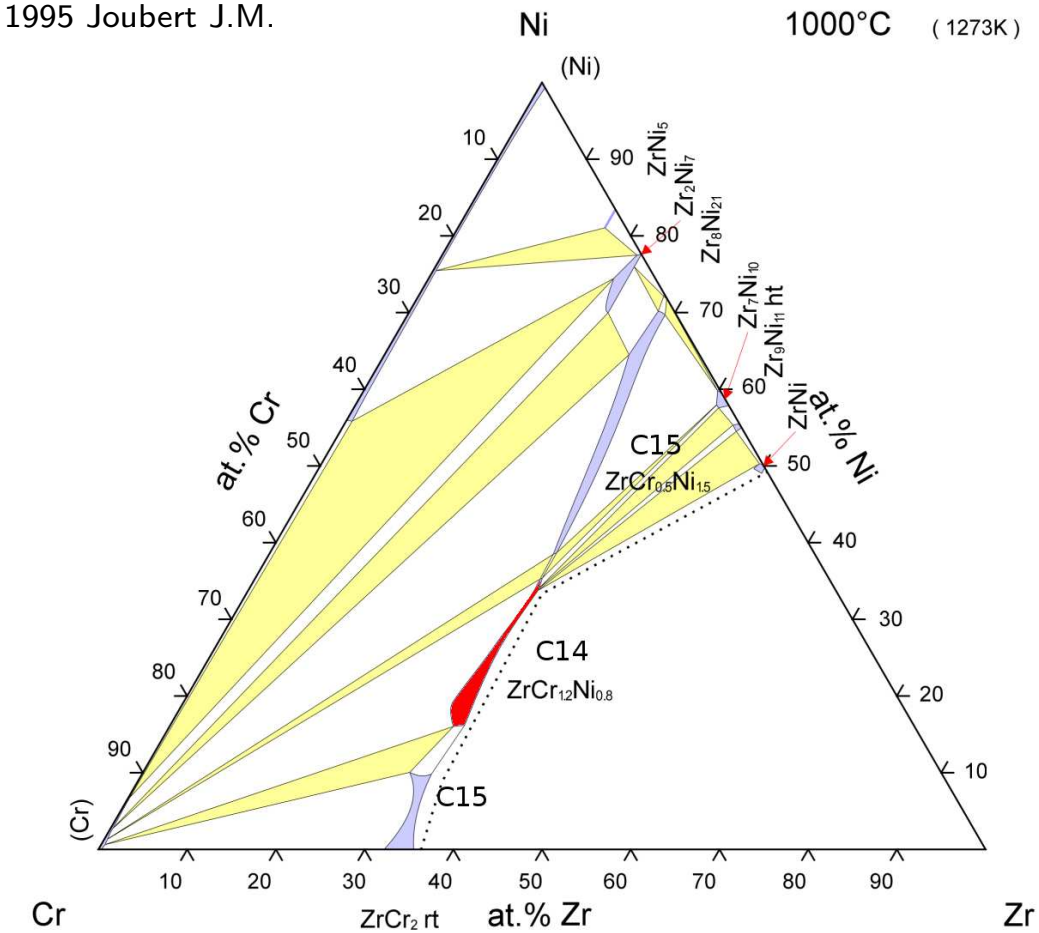
U. Kattner et al., Calphad XLII

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 substitution in order to describe their stoichiometry.

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

Crystallographic structure
$\Rightarrow$ thermodynamic model

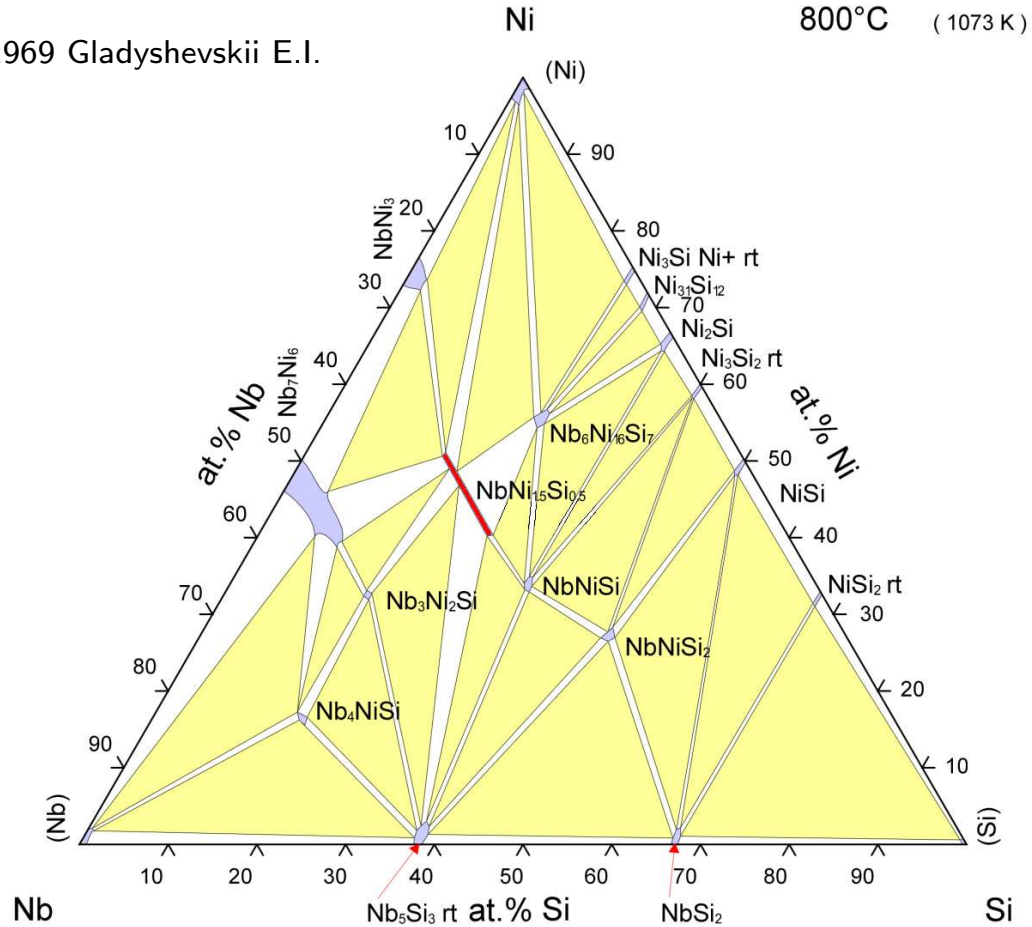


The C14 often appears as an extension of a binary phase in temperature and composition along an almost constant composition line,

© ASM International 2009. Diagram No. 200795

Crystallographic structure
$\Rightarrow$ thermodynamic model

1969 Gladyshevskii E.I.



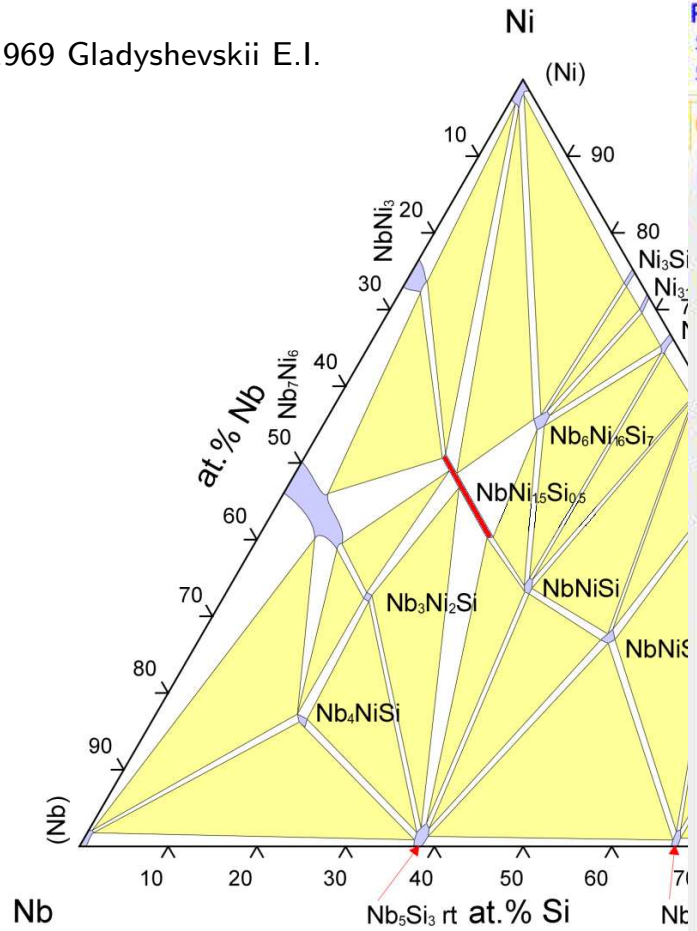
as a ternary phase,

© ASM International 2006. Diagram No. 952160

Crystallographic structure

$\Rightarrow$ thermodynami

1969 Gladyshevskii E.I.



$NbNi_{1.5}Si_{0.5}$	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 F

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

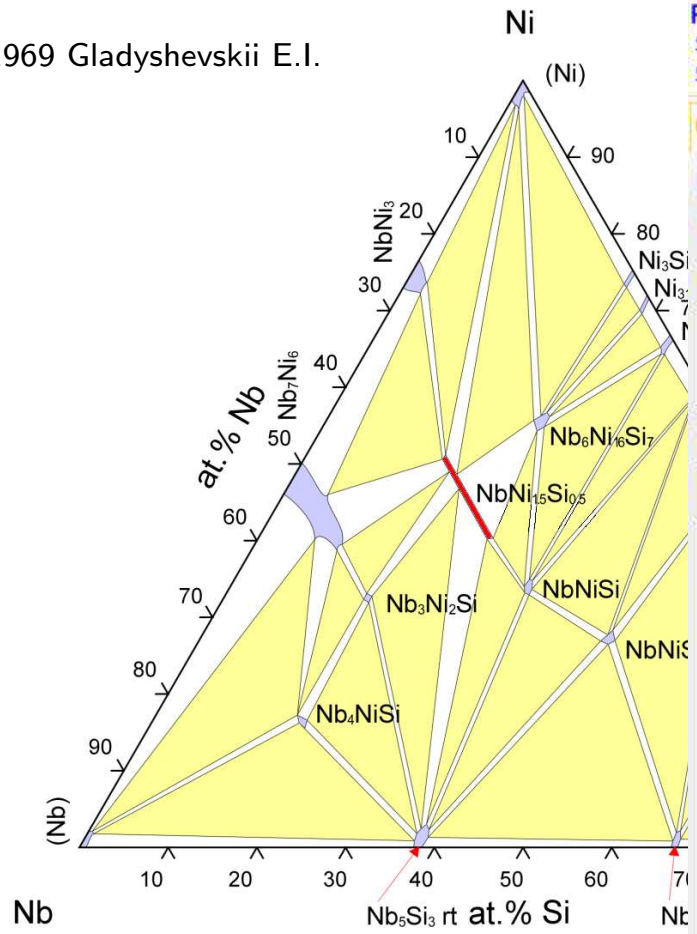
No	Site notation	Atom	Multiplicity	Wyckoff	Site symmetry	x	y	z	Occupancy
1	M1	0.750Ni + 0.250Si	6	h	mm2	0.1697	0.3394	1/4	1.0
2	Nb1	Nb	4	f	3m.	1/3	2/3	0.5629	1.0
3	M2	0.750Ni + 0.250Si	2	a	-3m.	0	0	0	1.0

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

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Crystallographic structur
⇒ thermodynami

1969 Gladyshevskii E.I.



$NbNi_{1.5}Si_{0.5}$	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	h	mm2	0.1697	0.3394	1/4	1.0
2	M1	0.800Nb + 0.200Si	4	f	3m.	1/3	2/3	0.5629	1.0
3	Ni2	Ni	2	a	-3m.	0	0	0	1.0

1	M1								1.0
2	Nb1								1.0
3	M2	0.250Si	2	a	-3m.	0	0	0	1.0

⇒ $(Ni)_6(Nb,Si)_4(Ni)_2$

⇒ $(Ni,Si)_6(Nb)_4(Ni,Si)_2$

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Crystallographic structur
⇒ thermodynami

$NbNi_{1.5}Si_{0.5}$	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

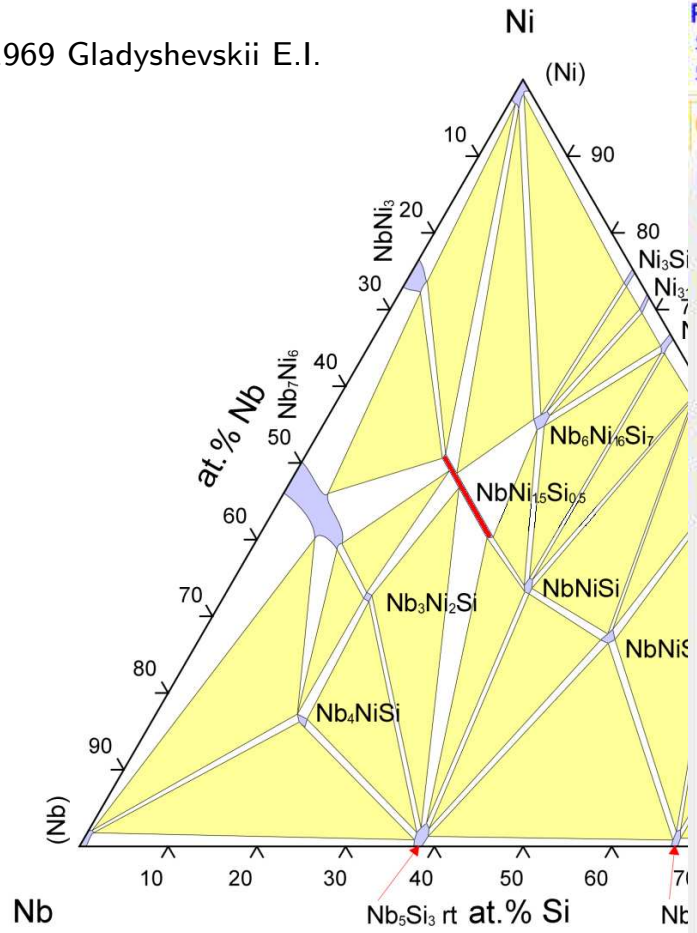
Starting materials No data.

Crystal Structure | X-ray Diffraction | Properties

▶ **Crystal Structure (Published)**

▼ **Niggli-reduced cell**

1969 Gladyshevskii E.I.



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

Atom coordinates

No	Site notation	Atom	Multiplicity	Wyckoff	Site symmetry	x	y	z	Occupancy
1	Ni1	Ni	6	h	mm2	0.1697	0.3394	1/4	1.0
2	M1	0.800Nb + 0.200Si	4	f	3m.	1/3	2/3	0.5629	1.0
3	Ni2	Ni	2	a	-3m.	0	0	0	1.0

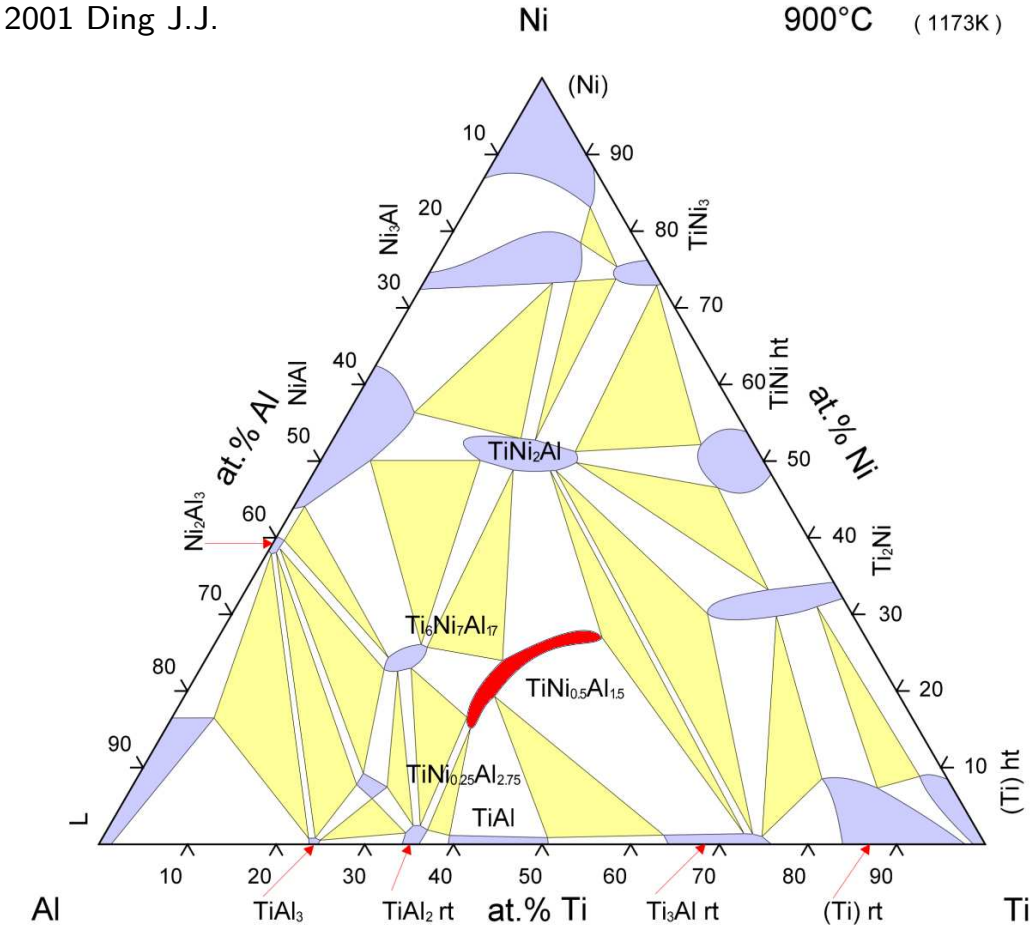
1	M1								1.0
2	Nb1								1.0
3	M2	0.250Si	2	a	-3m.	0	0	0	1.0

⇒ $(Ni)_6(Nb,Si)_4(Ni)_2$

⇒ $(Ni,Si)_6(Nb)_4(Ni,Si)_2$

© ASM International 2006. D

Crystallographic structure
$\Rightarrow$ thermodynamic model



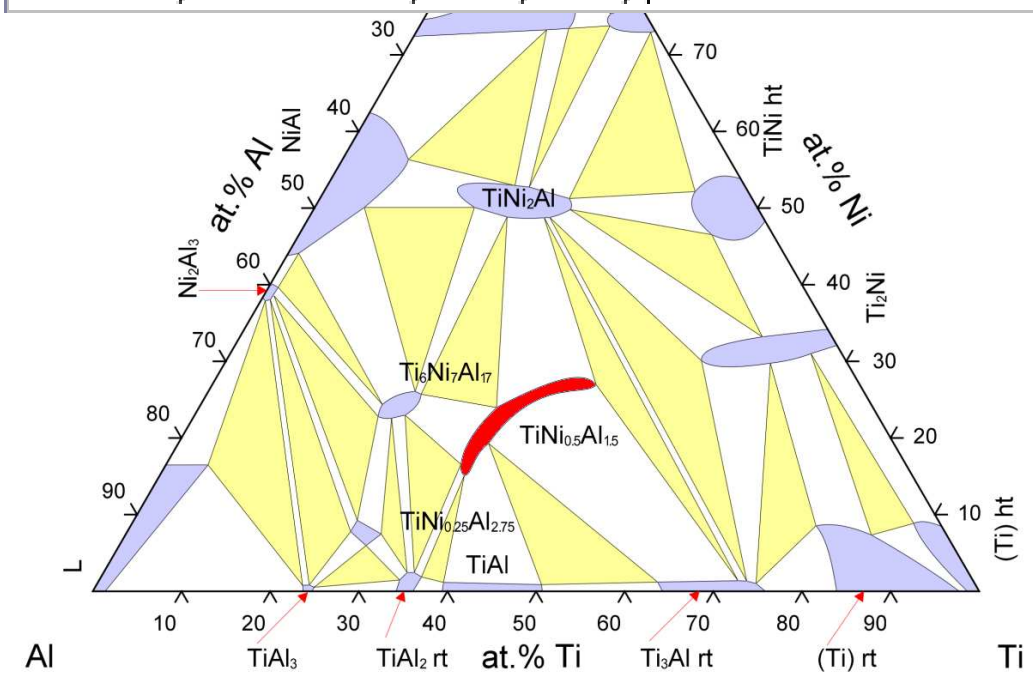
with different homogeneity range topology.

© ASM International 2009. Diagram No. 200336

Crystallographic structure
$\Rightarrow$ thermodynamic model

$TiNi_{0.5}Al_{1.5}$ T_3,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



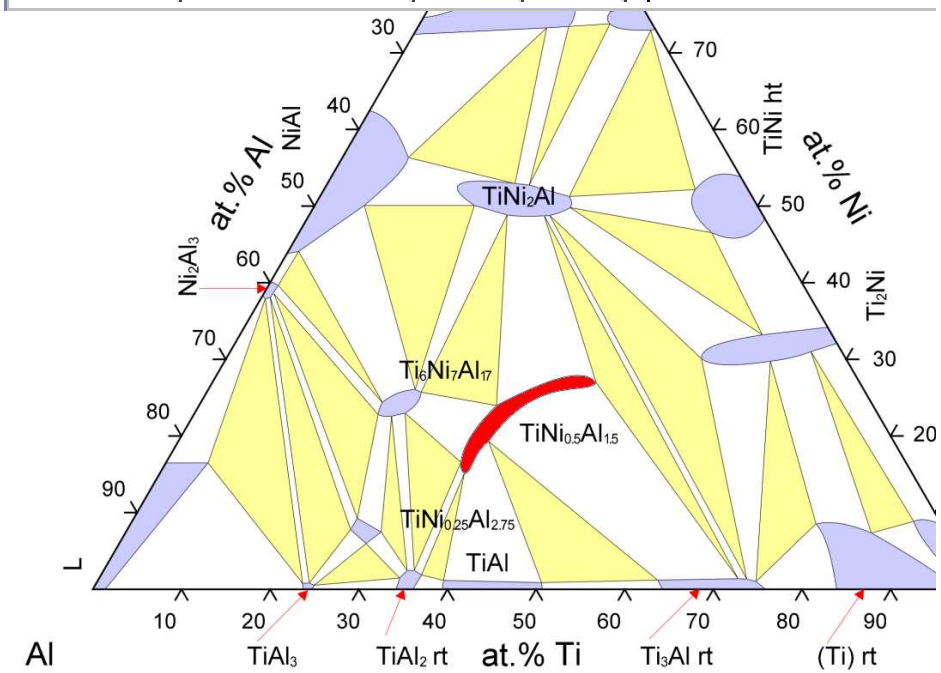
with different homogeneity range topology.

© ASM International 2009. Diagram No. 200336

Crystallographic structure
$\Rightarrow$ thermodynamic model

$TiNi_{0.5}Al_{1.5}$ τ_3,TiNiAl	$Ti_{2.13}Ni_{1.30}Al_{2.57}$	Mg_2Cu_3Si	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



T_3 - "$Al_3 Ni Ti_2$"
($Mg Zn_2$-type)

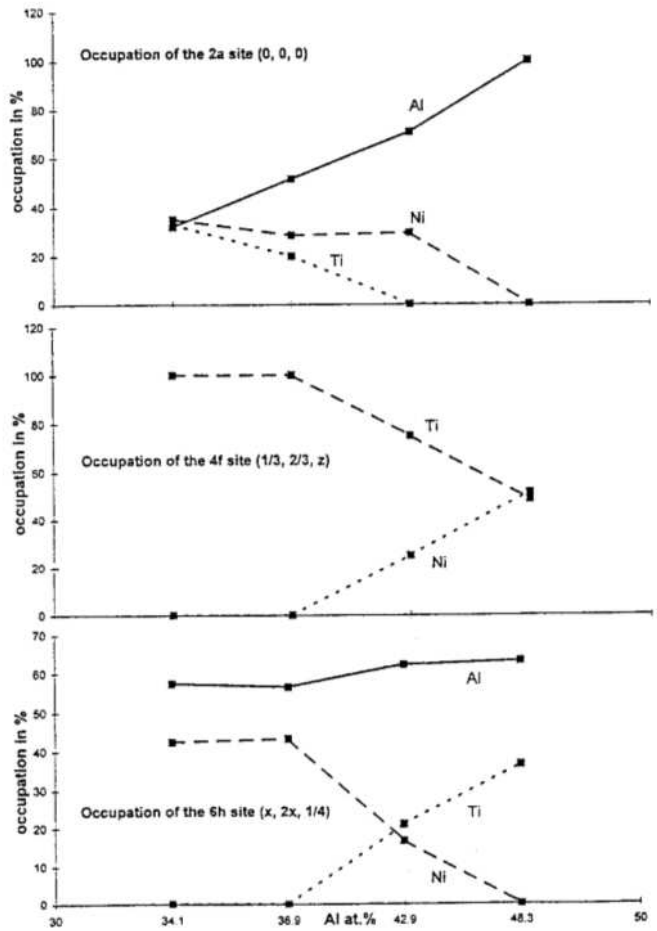


Fig. 8. Occupation of the atomic sites for the τ_3-phase as a function of the Al-content.

© ASM International 2009. Diagram No. 200336

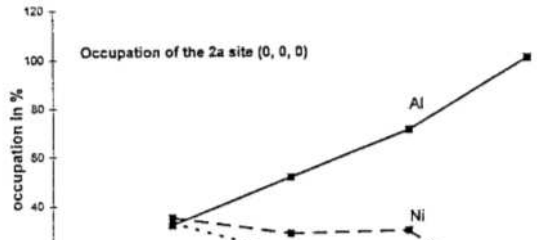
Crystallographic structure

$\Rightarrow$ thermodynamic model

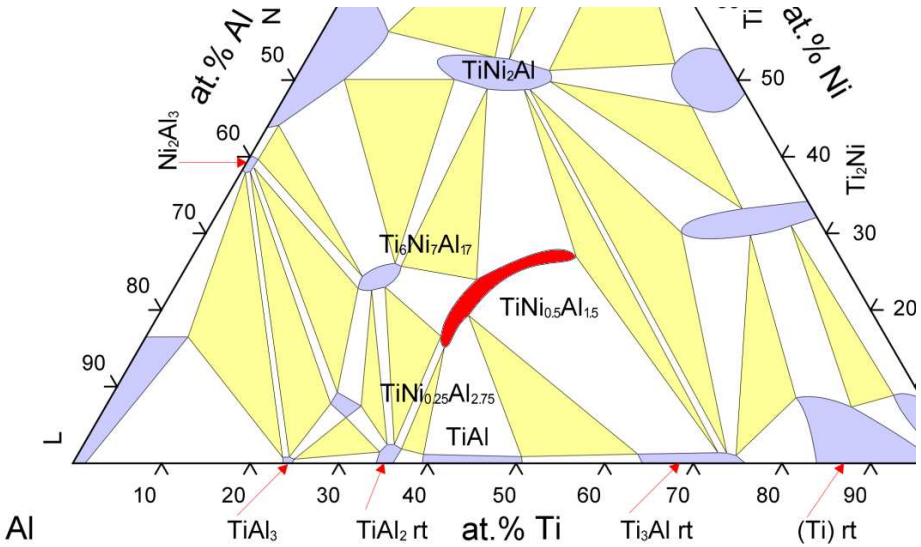
T_3 - "$Al_3 Ni Ti_2$" ($Mg Zn_2$-type)

$TiNi_{0.5}Al_{1.5}$ τ_3,TiNiAl	$Ti_{2.13}Ni_{1.30}Al_{2.57}$	Mg_2Cu_3Si	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



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



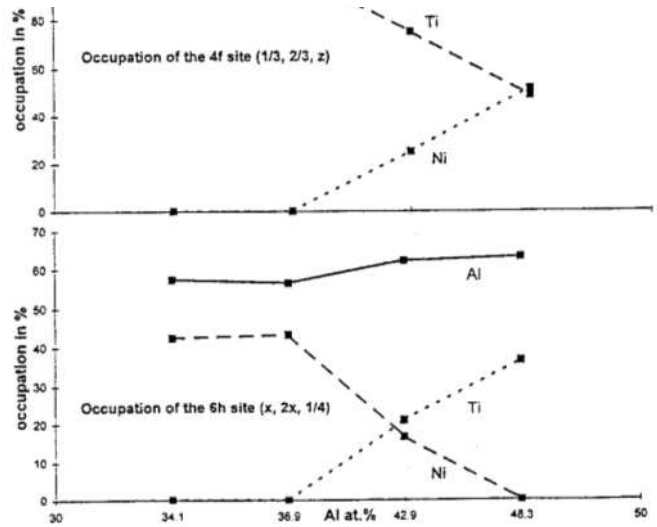
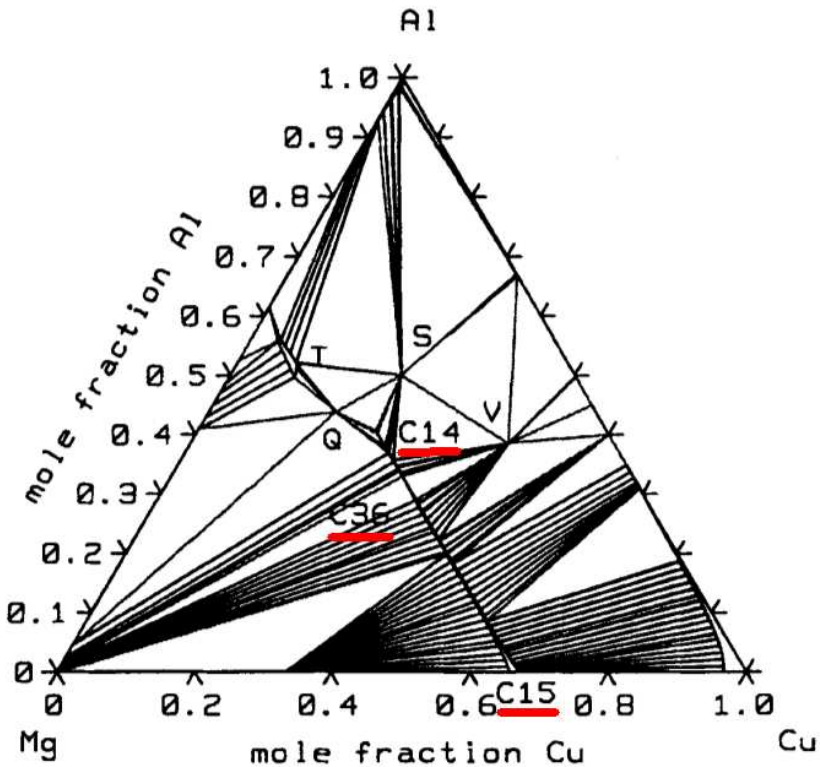


Fig. 8. Occupation of the atomic sites for the τ_3-phase as a function of the Al-content.

© ASM International 2009. Diagram No. 200336

Crystallographic structure
$\Rightarrow$ thermodynamic model

1998 Buhler T.



Crystallographic structure
$\Rightarrow$ thermodynamic model

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.

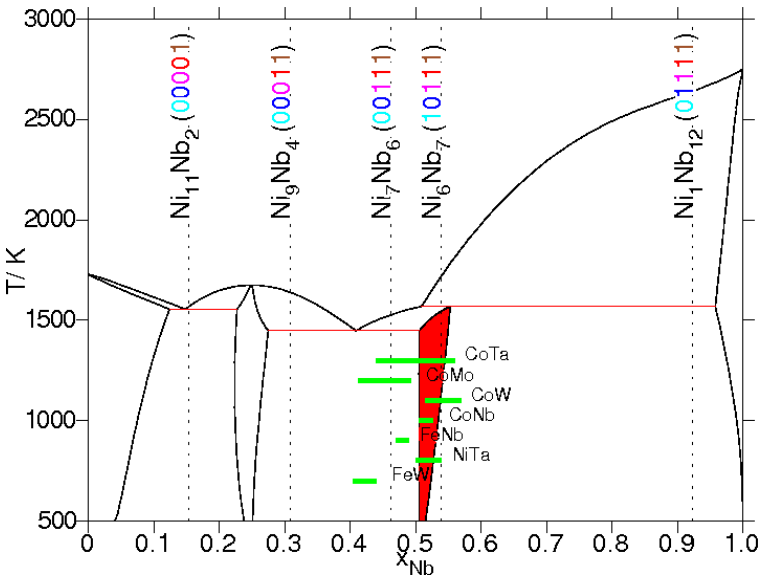
Crystallographic structure
$\Rightarrow$ thermodynamic model

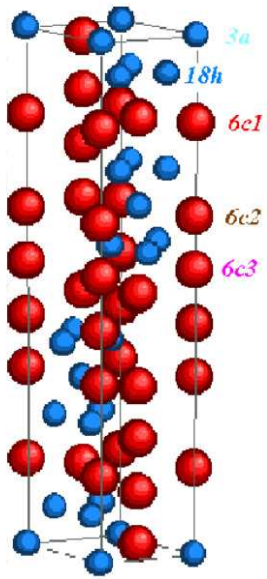
For decades simplified models were used because of computers limitations and the impossibility to assess all the compounds.

These simplications were made grouping together similar crystallographic sites. It is still interesting to use them for phases that can be considered as stoichiometric.

However they oversimplify phases presenting large multicomponent area. Nowadays that DFT can help, models closer to the crystallography should be used.

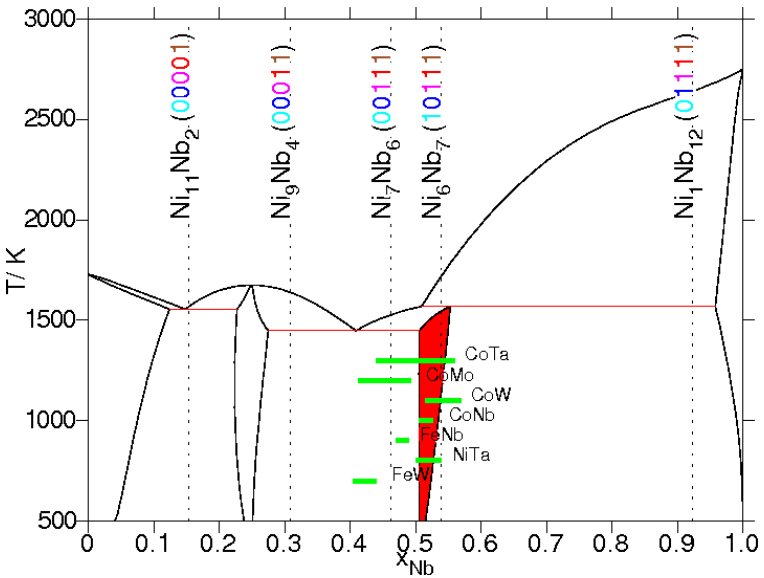
Crystallographic structure + DFT
$\Rightarrow$ thermodynamic model

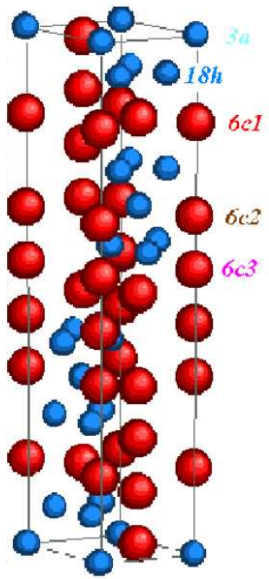




Prototype μ	Fe_7W_6				
Space group Pearson symbol	$R\bar{3}m$ $hR13$				
Wyckhoff	$3a$	$6c1$	$6c2$	$6c3$	$18h$
Coordination number	12	15	16	14	12
Site occupation	Fe	W	W	W	Fe

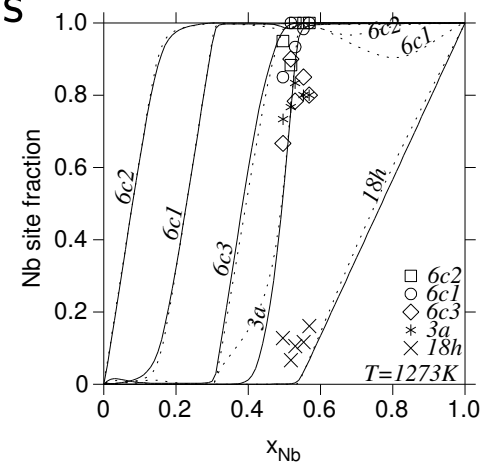
Crystallographic structure + DFT
$\Rightarrow$ thermodynamic model

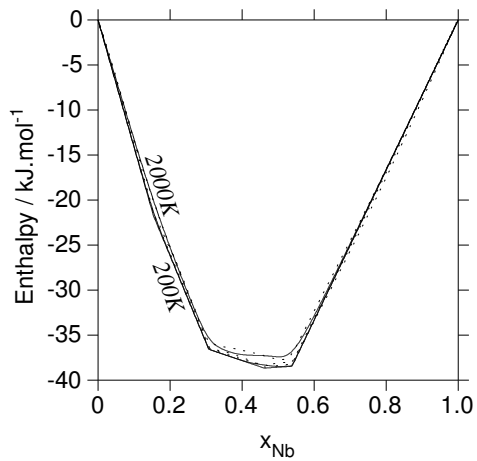


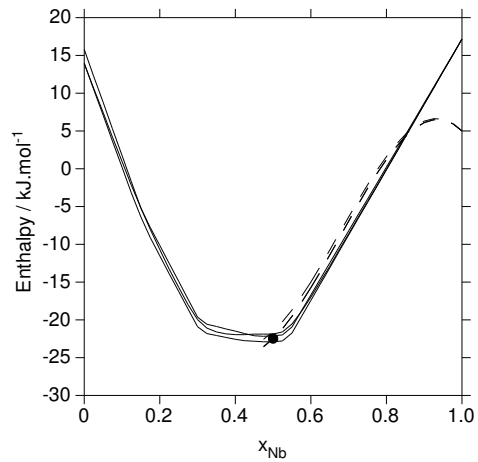


Prototype μ	Fe_7W_6				
Space group Pearson symbol	$R\bar{3}m$ $hR13$				
Wyckhoff	$3a$	$6c1$	$6c2$	$6c3$	$18h$
Coordination number	12	15	16	14	12
Site occupation	Fe	W	W	W	Fe

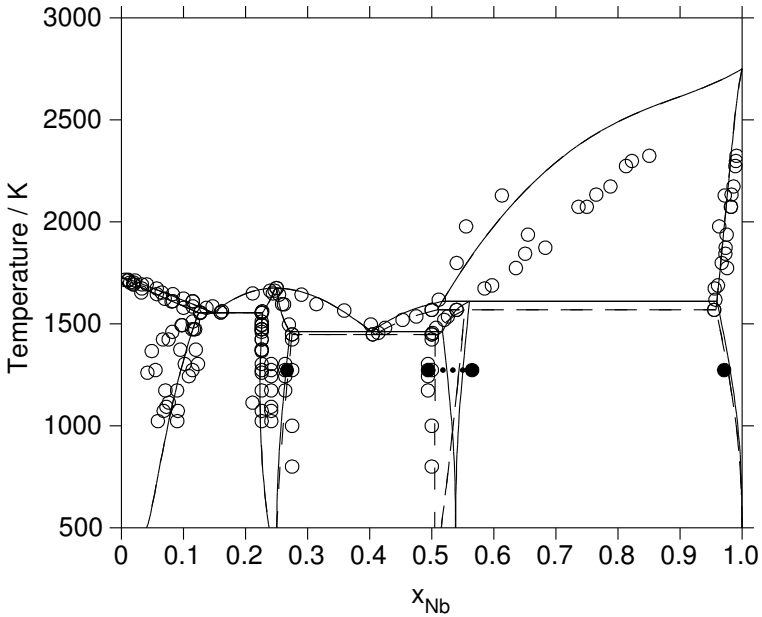
32 compounds
from VASP
+ CEF

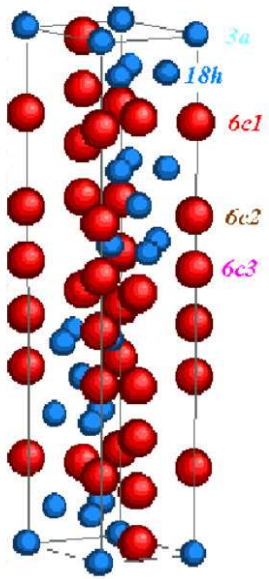






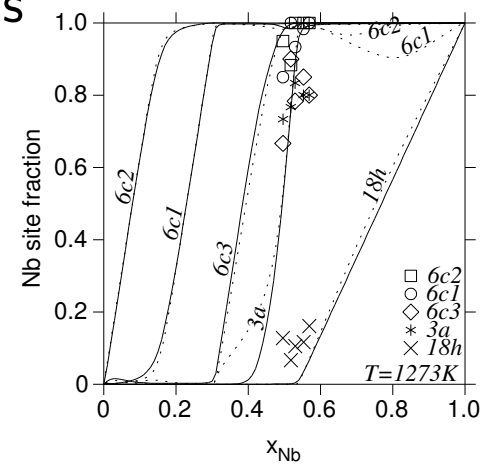
Crystallographic structure + DFT
$\Rightarrow$ thermodynamic model

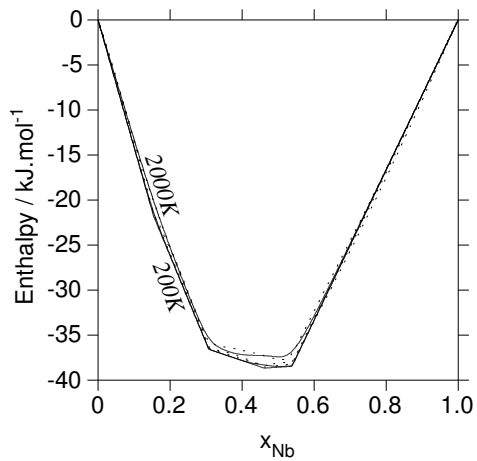


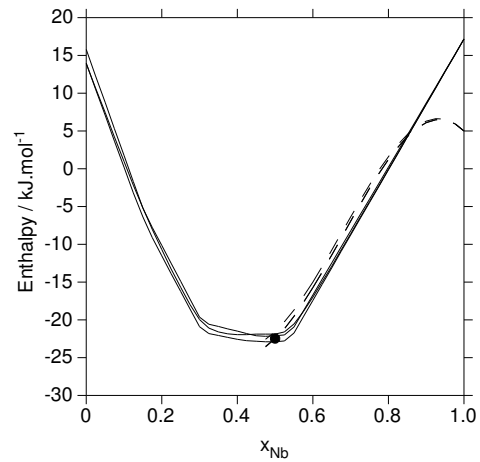


Prototype μ	Fe_7W_6				
Space group Pearson symbol	$R\bar{3}m$ $hR13$				
Wyckhoff	3a	6c1	6c2	6c3	18h
Coordination number	12	15	16	14	12
Site occupation	Fe	W	W	W	Fe

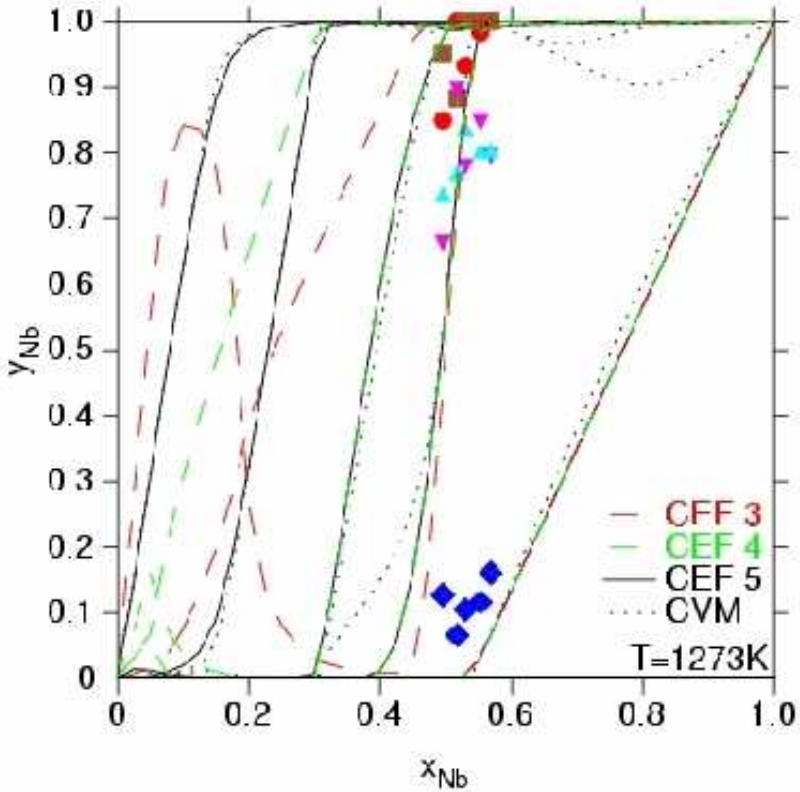
32 compounds
from VASP
+ CEF

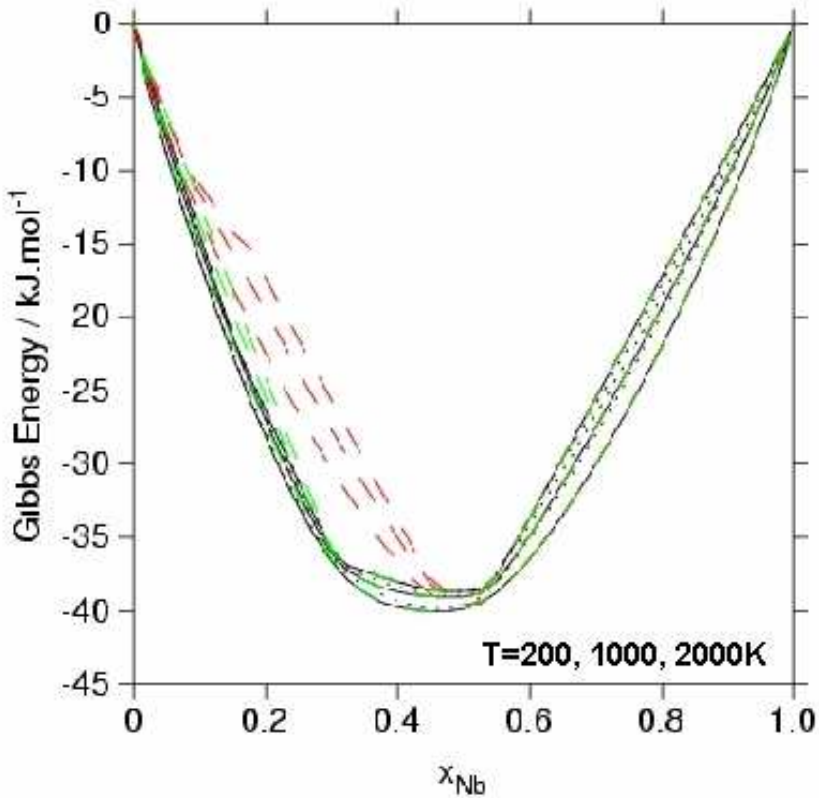






Crystallographic structure + DFT
$\Rightarrow$ thermodynamic model





CEF 5 VASP 32 compounds
$(Nb,Ni)_3(Nb,Ni)_6(Nb,Ni)_6(Nb,Ni)_6(Nb,Ni)_{18}$

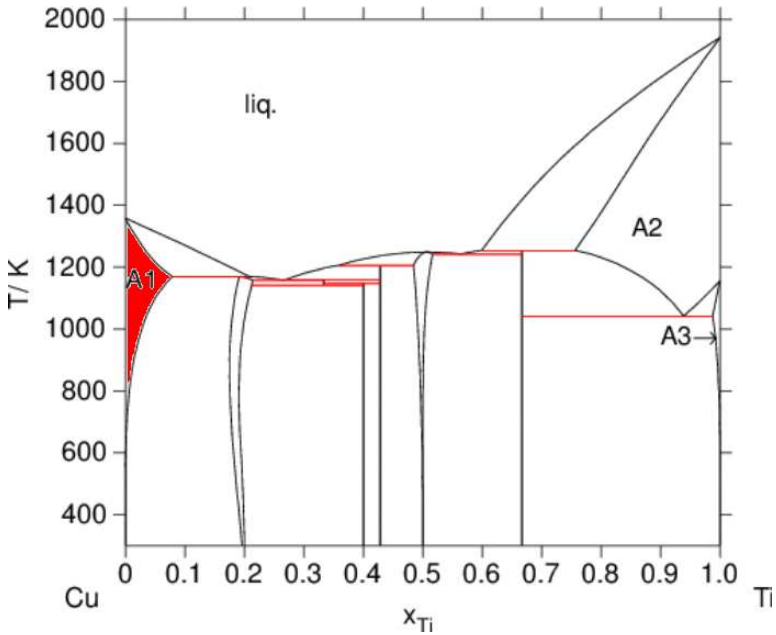
CEF 4 VASP 16 compounds (6c1+6c2)
$(Nb,Ni)_3(Nb,Ni)_{12}(Nb,Ni)_6(Nb,Ni)_{18}$

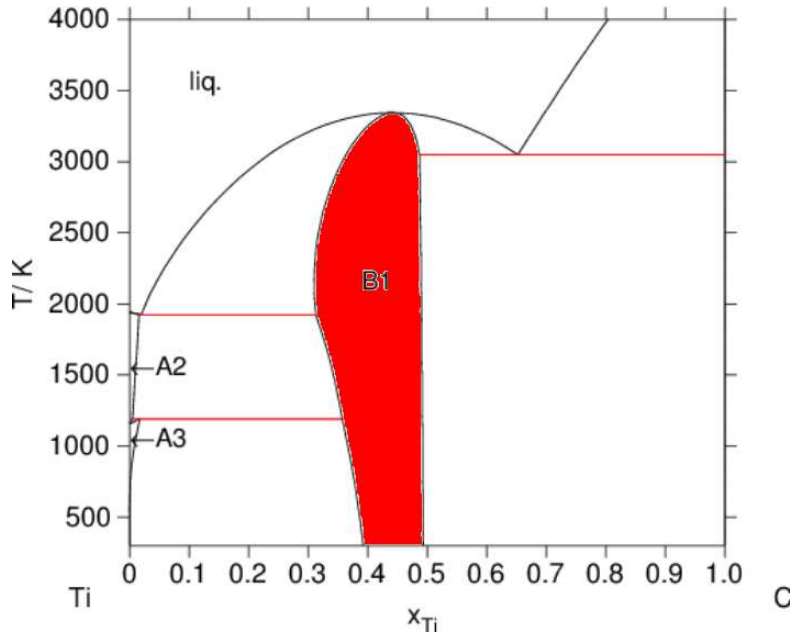
CEF 3 VASP 8 compounds
$(Nb,Ni)_3(Nb,Ni)_{18}(Nb,Ni)_{18}$
away from CVM for low Nb content,
possible problem in multicomponent extension

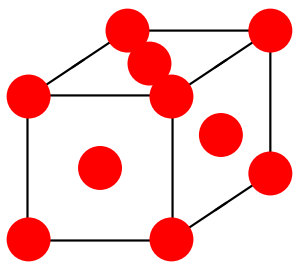
Same phase in the database
$\Rightarrow$ Different crystallography

- Interstitials
- Metallic ordering
- Interstitials and metallic ordering

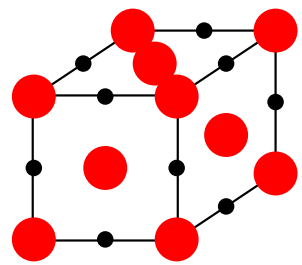
Interstitials







A1 (Cu,Ti)(□)

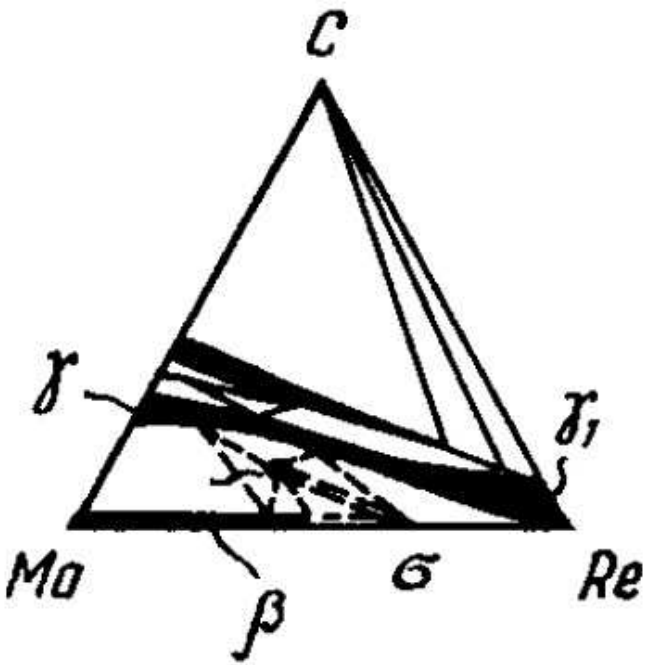


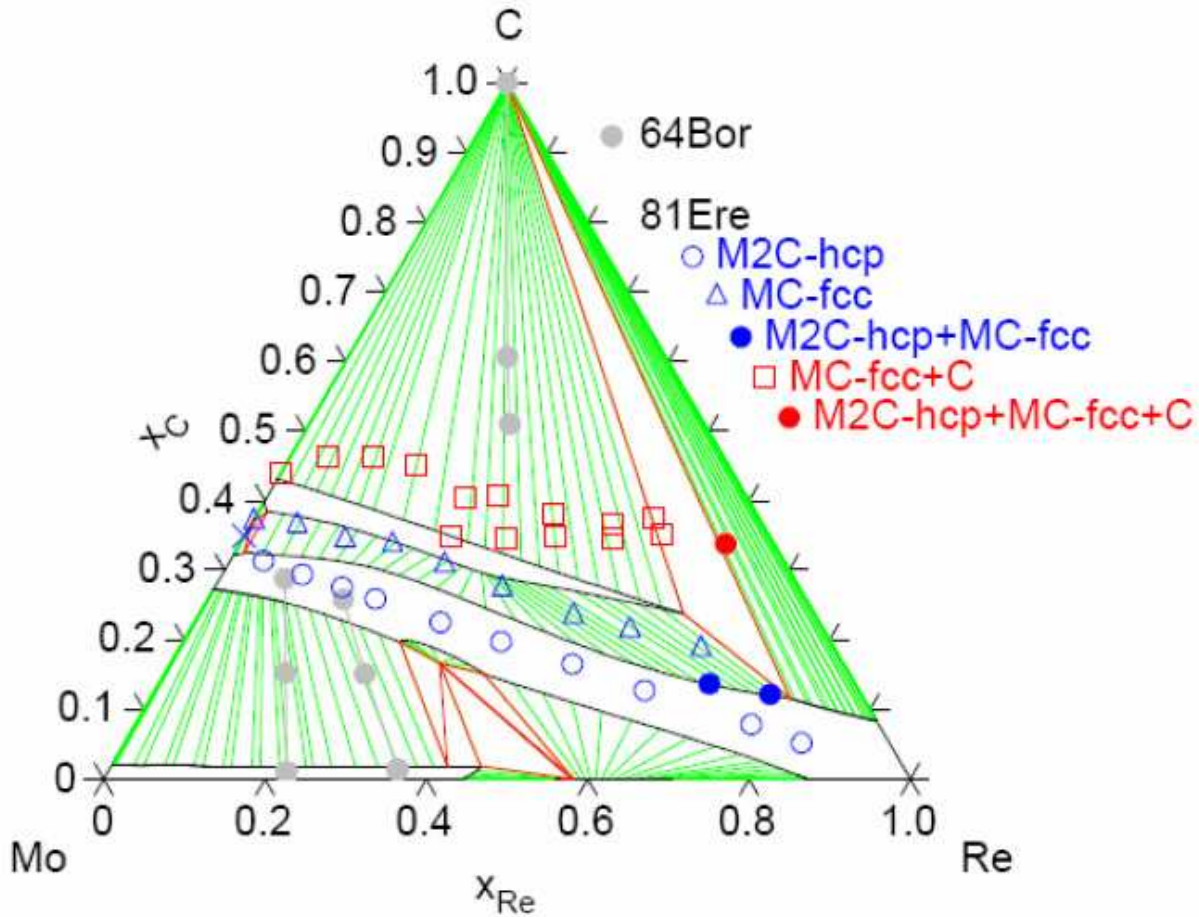
B1 (Ti)(C,□)

$\Rightarrow$ C-Cu-Ti: (Cu,Ti)(C,□) both A1 and B1

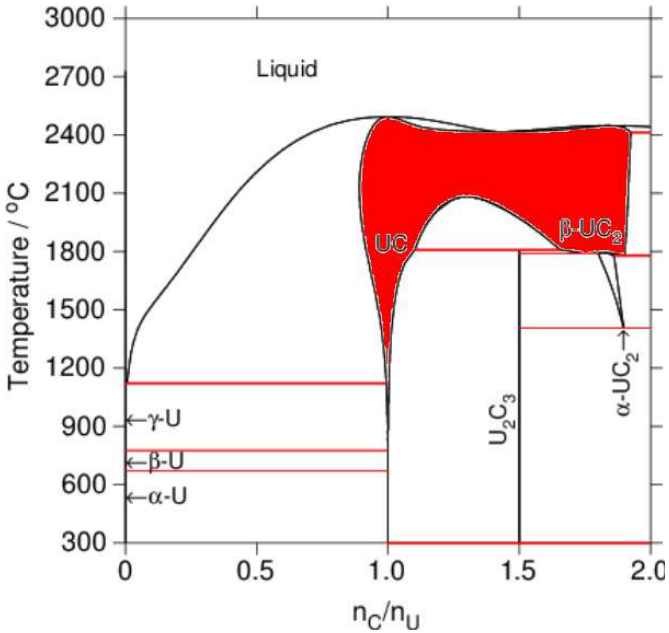
Interstitials

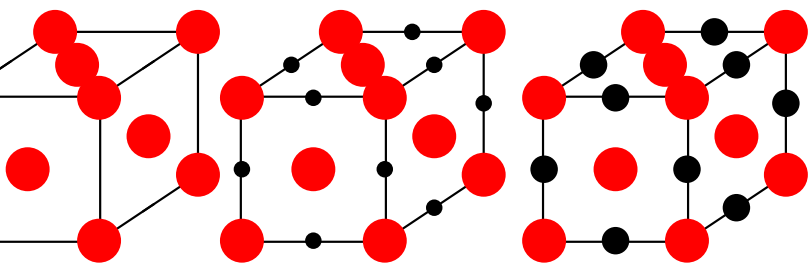
The continuity between metallic solutions and carbides is observed in very few systems.

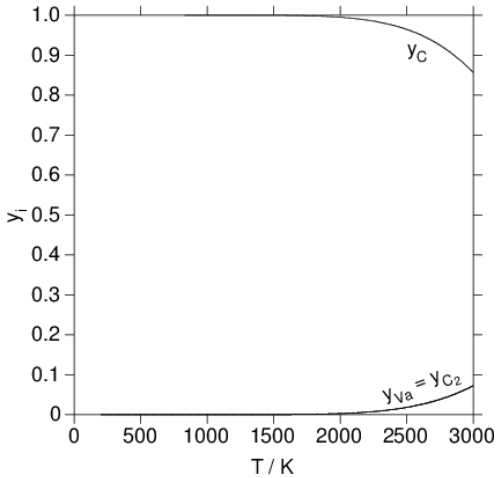




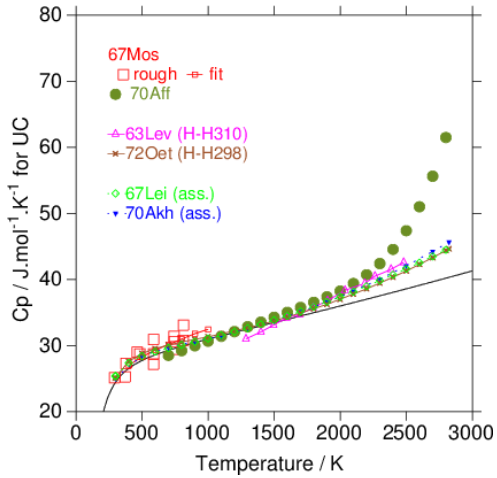
Interstitials



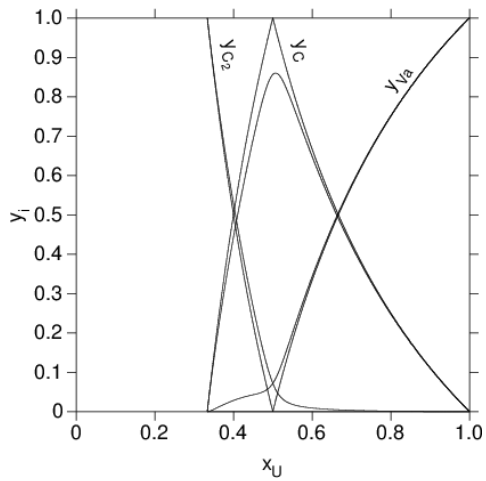




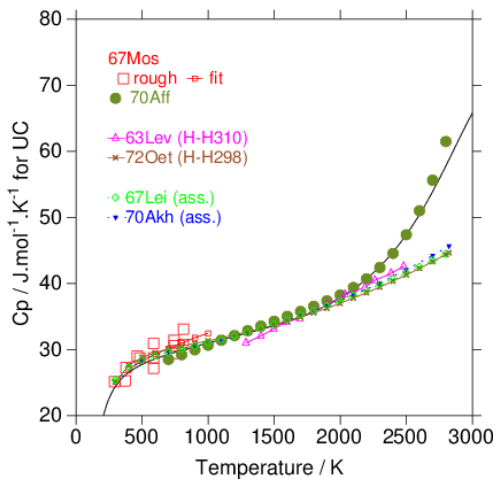
vs temperature for x_C=0.5



(U)(C)



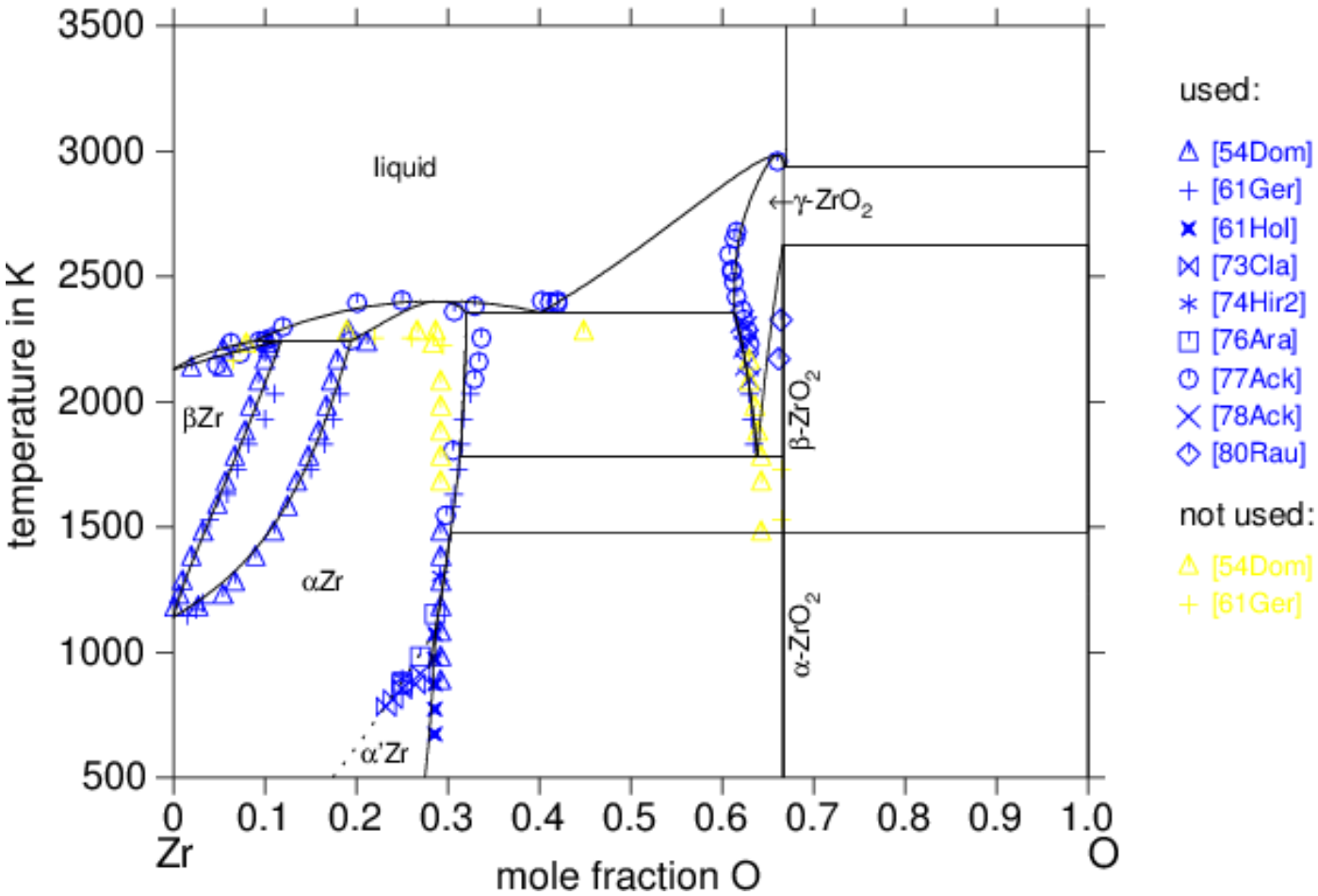
vs composition at 1500 and 3000K



(U)(C,C_2,□) at x_C=0.5

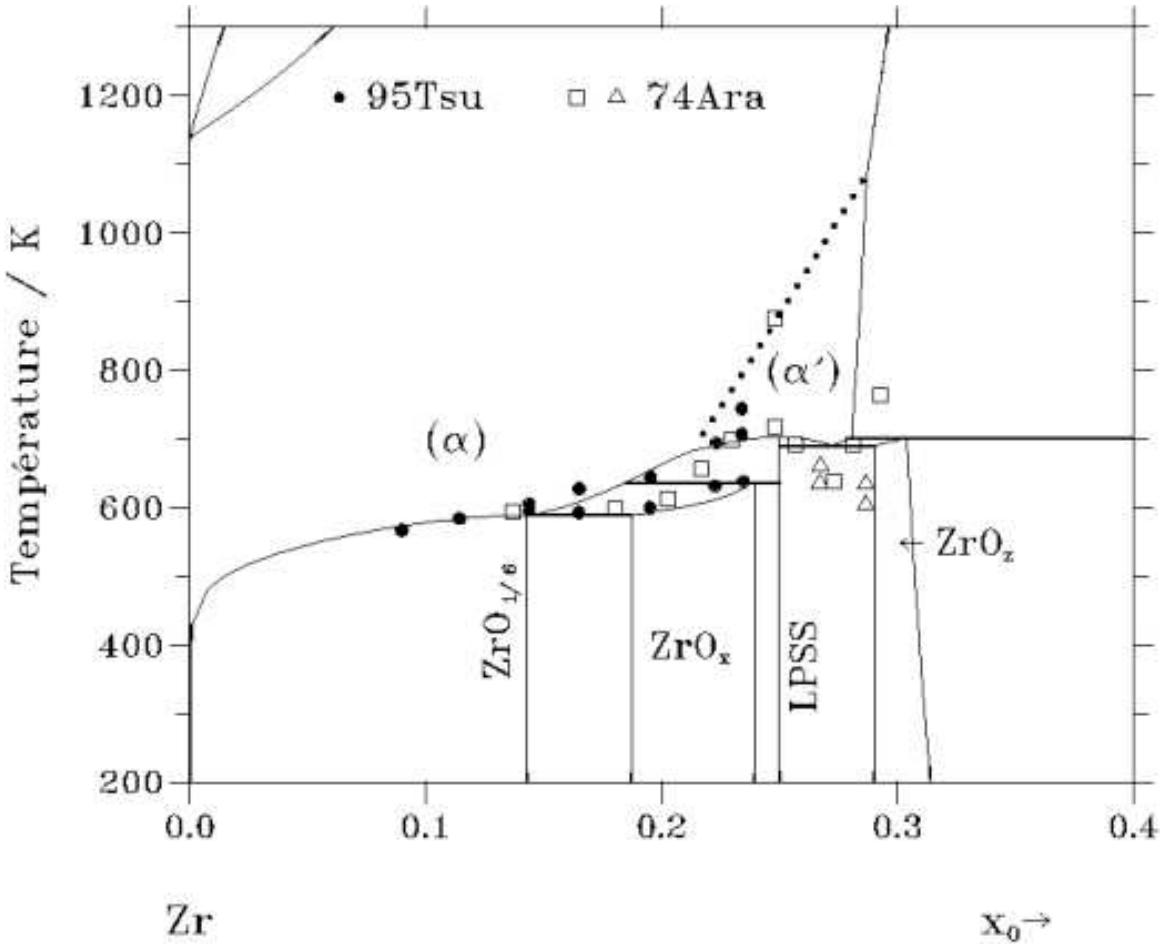
Interstitials

2001 Liang et al.: α and α'$\Rightarrow$ Zr_3 (O,□) (O,□) (O,□)



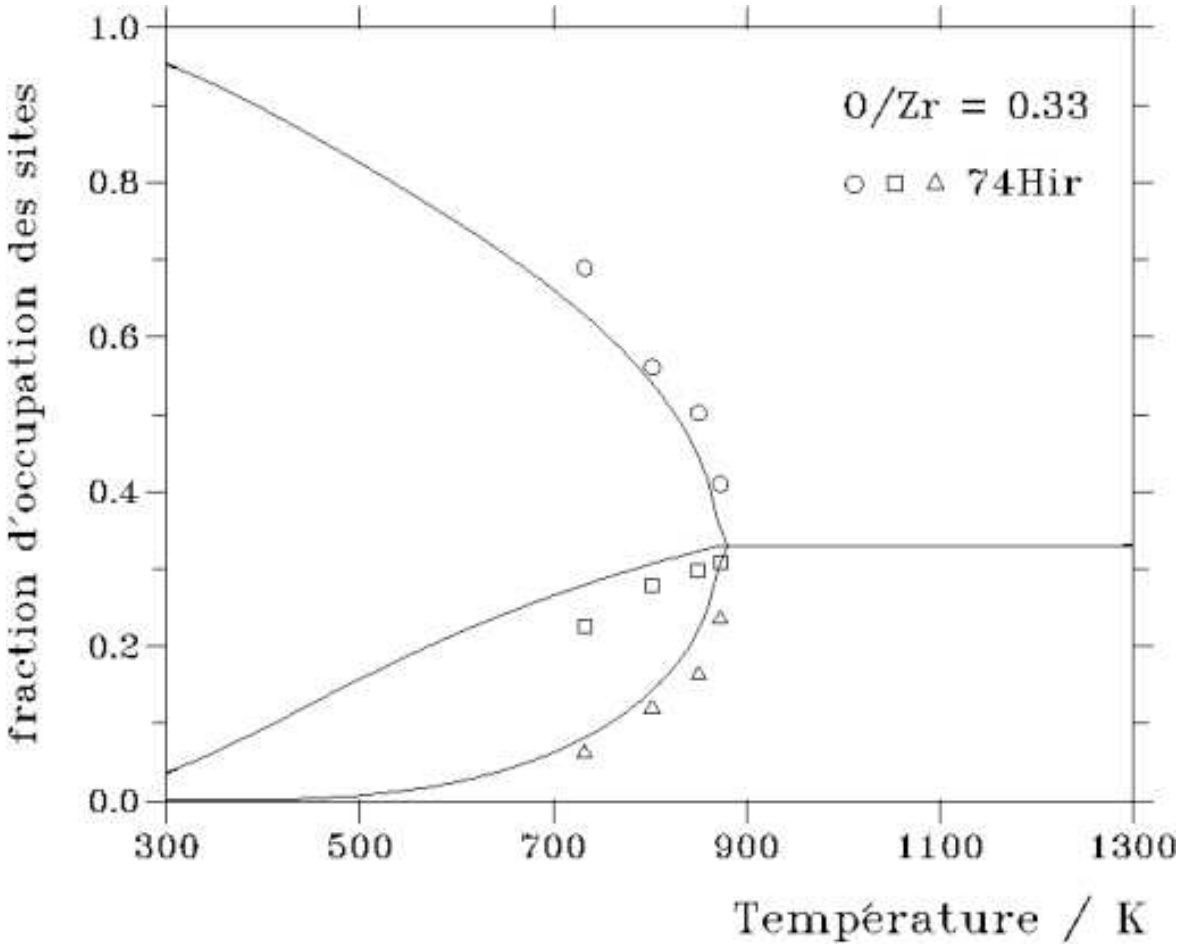
Interstitials

2001 Liang et al.: α and α'$\Rightarrow$ Zr_3 (O,□) (O,□) (O,□)

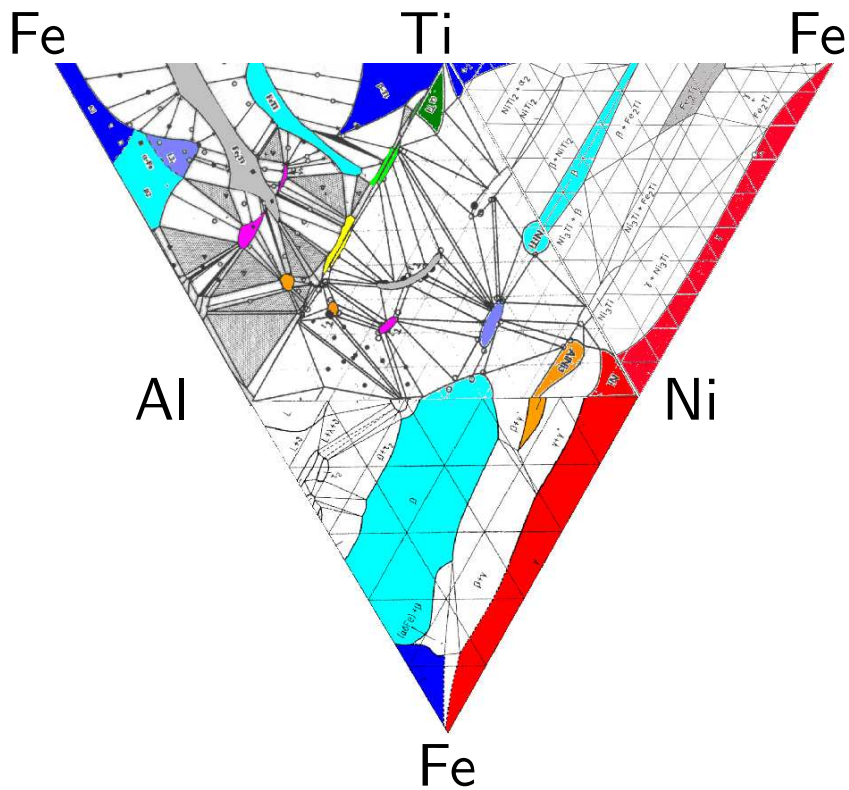


Interstitials

2001 Liang et al.: α and α'$\Rightarrow$ Zr_3 (O,□) (O,□) (O,□)

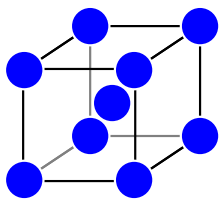


Metallic ordering

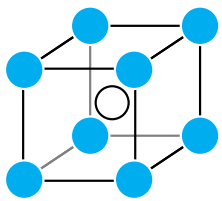


Metallic ordering

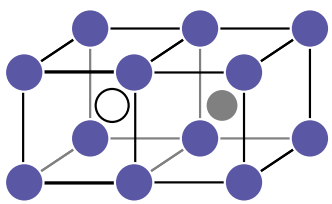
A2

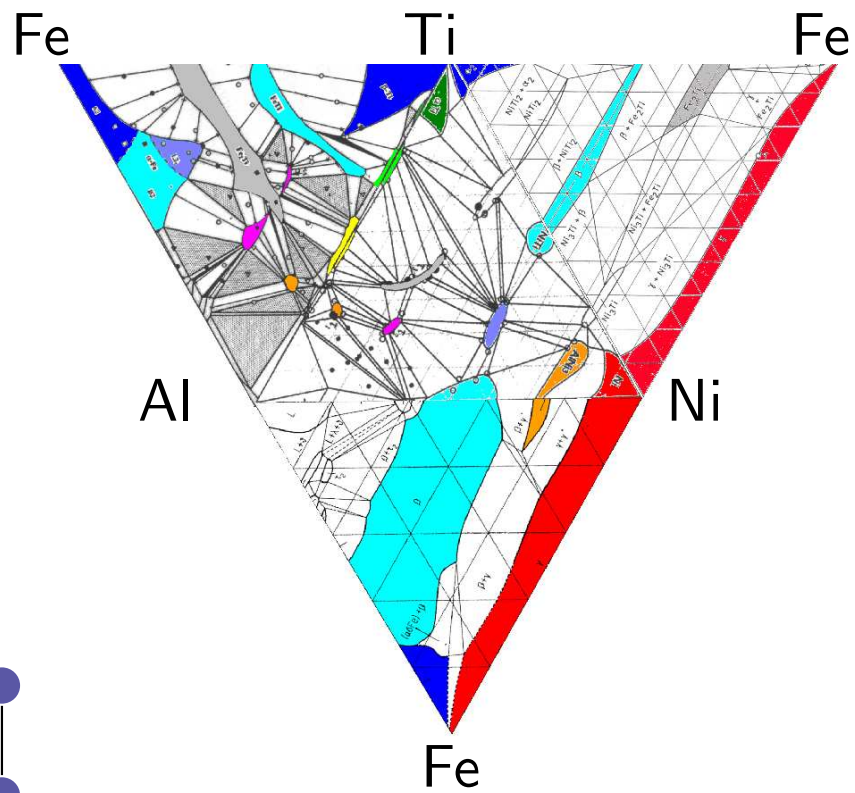


B2



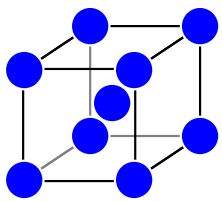
$L2_1$



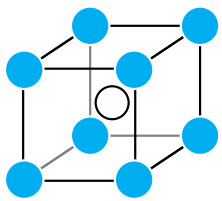


Metallic ordering

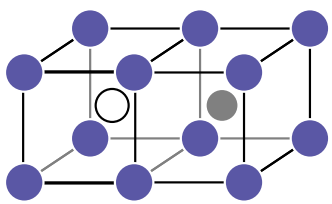
A2

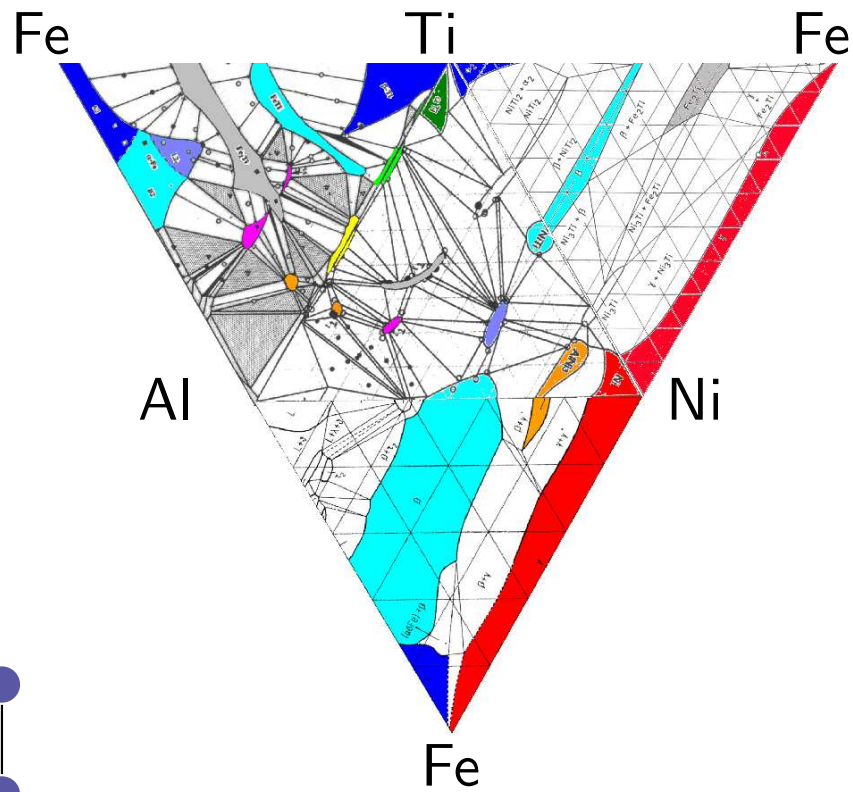


B2

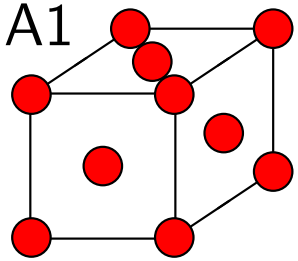


$L2_1$

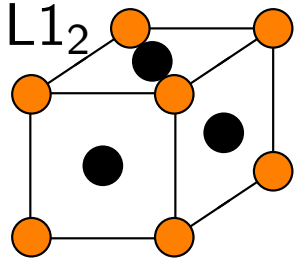




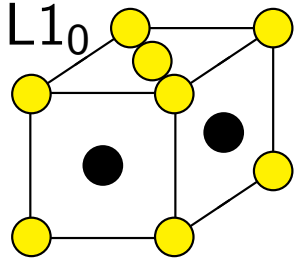
A1



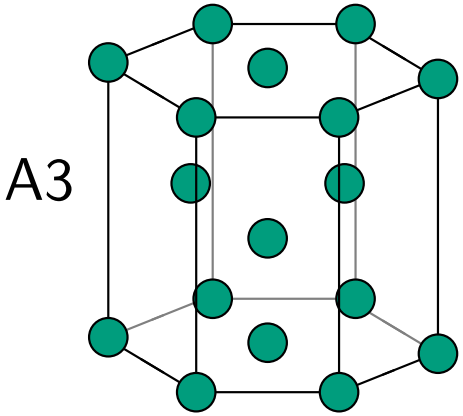
$L1_2$

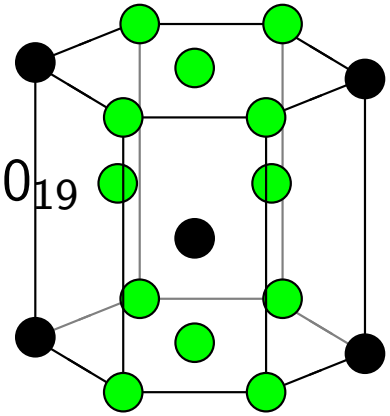


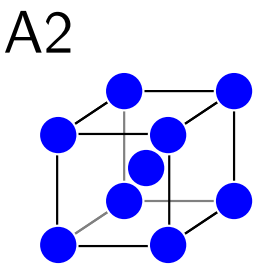
$L1_0$

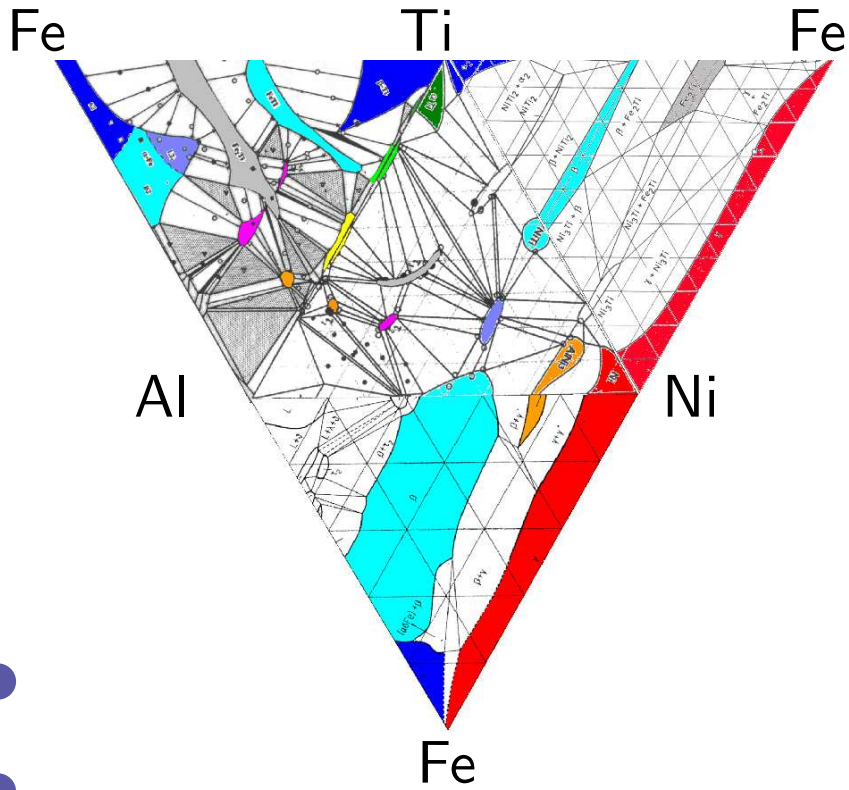


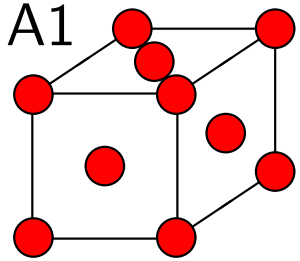
Metallic ordering

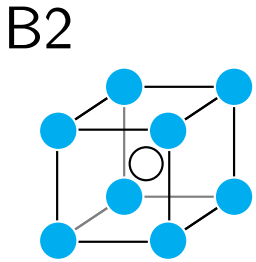


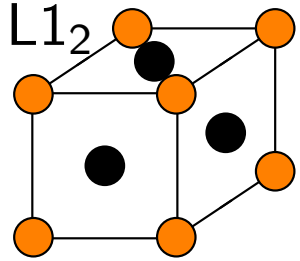


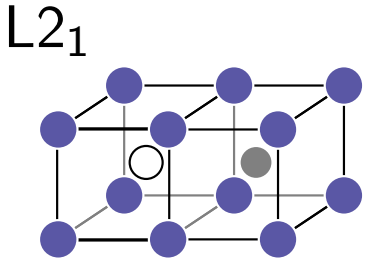


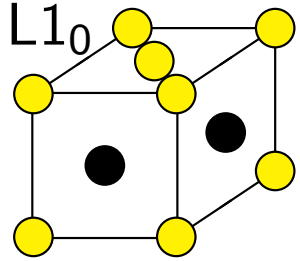












Metallic ordering

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

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(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.

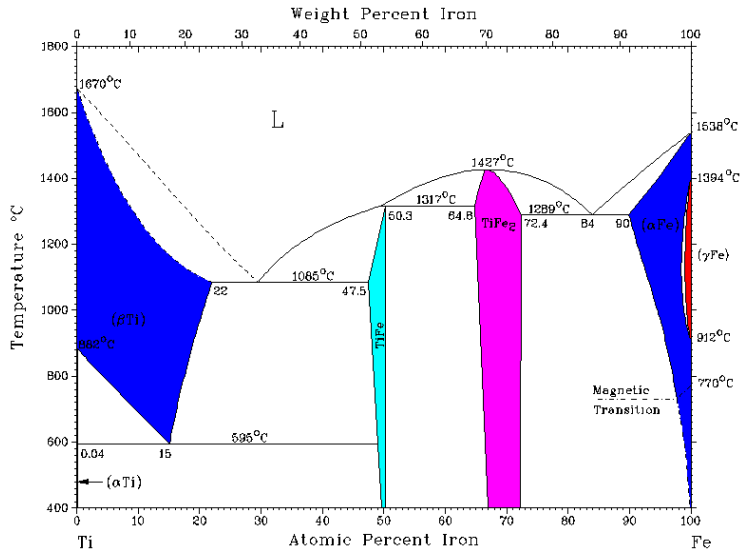
$$G(y_i^s) = G^{dis}(x_i) + \Delta G^{ord}(y_i^s)$$

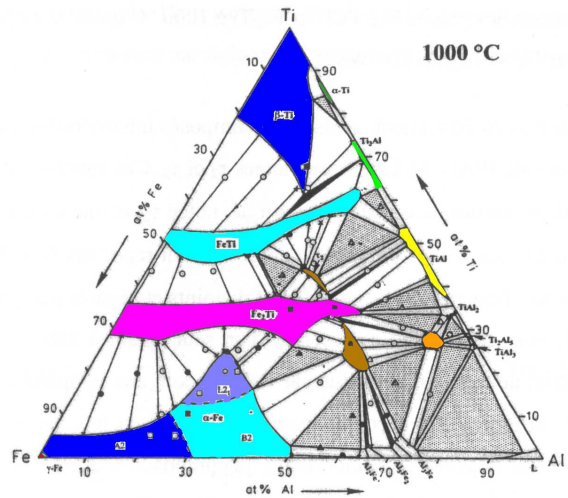
The ordering part itself is the difference of two terms, expressed in the CEF, allowing it to cancel when the phase is disordered.

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

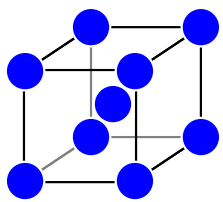
The relations allowing the phase to disorder are to be imposed between the parameters defining $G^{ord}(y_i^s)$. They can easily be related to the crystallographic symmetry of the lattice.

A2/B2 modelling

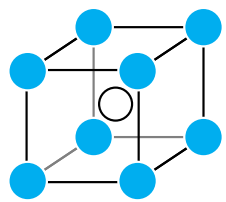




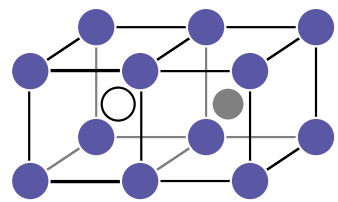
A2



B2

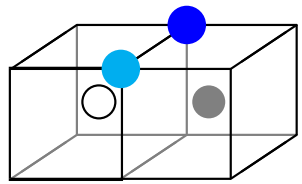


$L2_1$

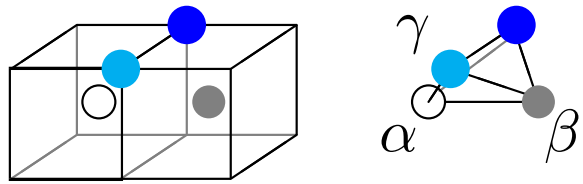


To be able to describe the 2nd order transition between the A2, B2 and $L2_1$ phases in the ternary system Al-Fe-Ti, the A2 and B2 phases have to be described with 4SL in Fe-Ti.

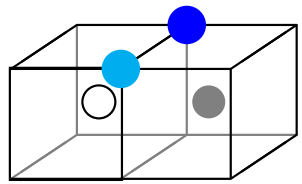
bcc ordering

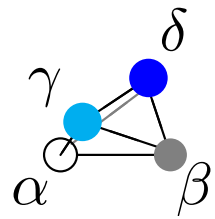


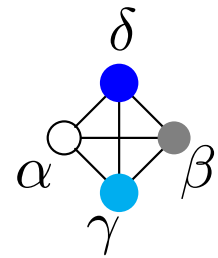
bcc ordering



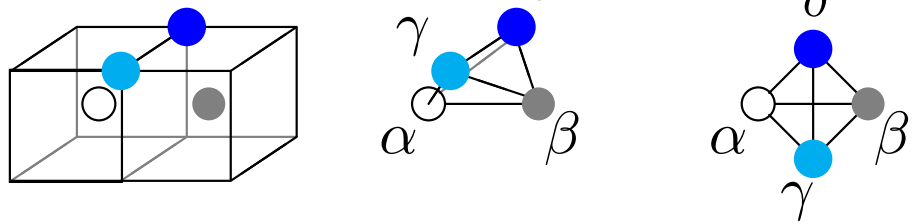
bcc ordering



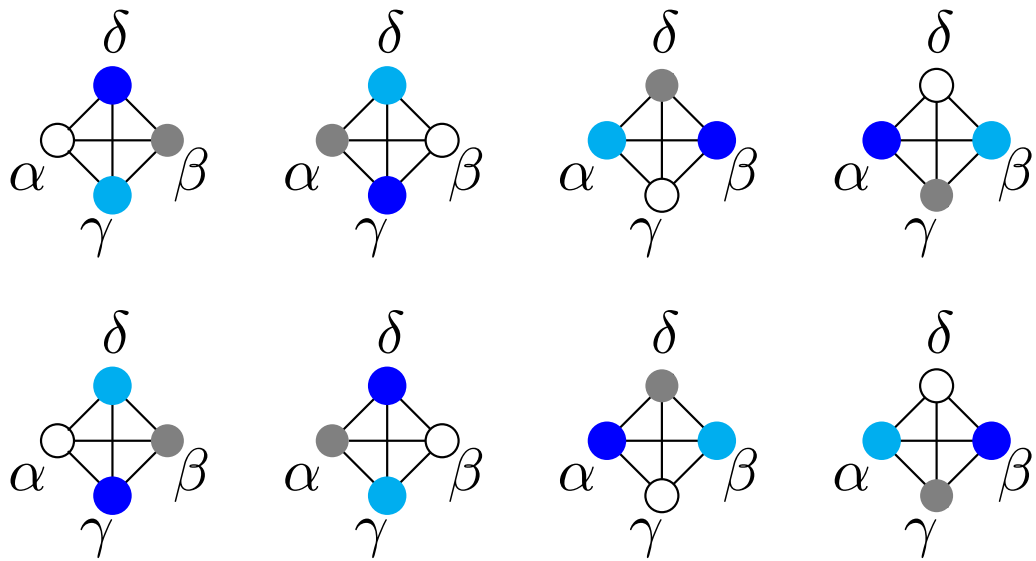




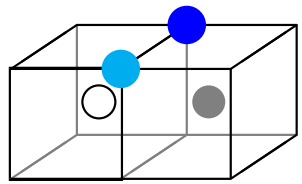
bcc ordering

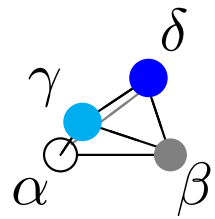


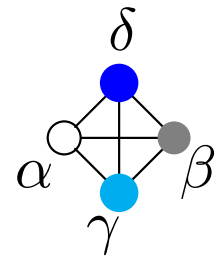
From crystallographic symmetry,
the following configurations are equivalent.



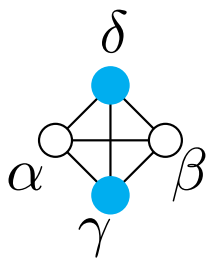
bcc ordering

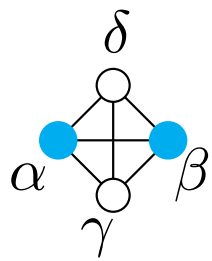






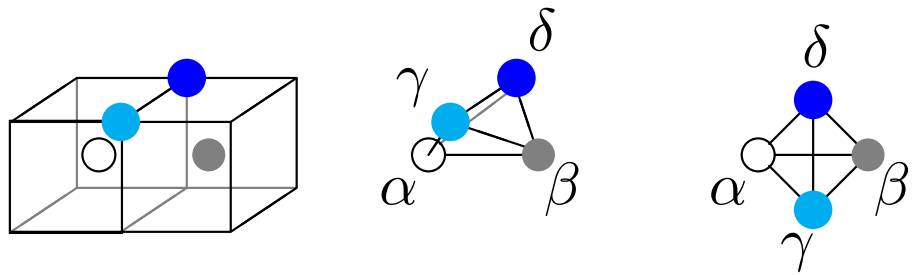
From crystallographic symmetry,
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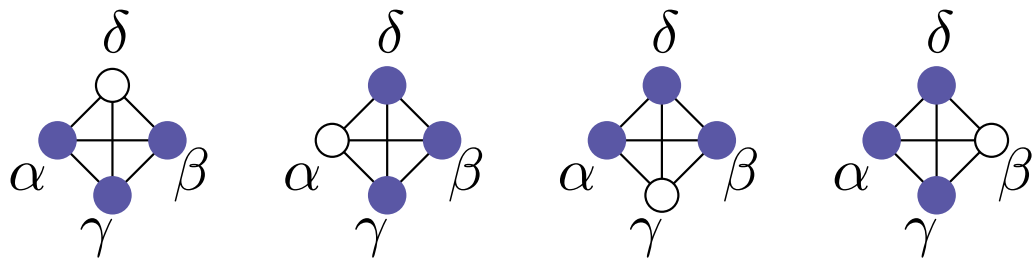


B2 configurations

bcc ordering

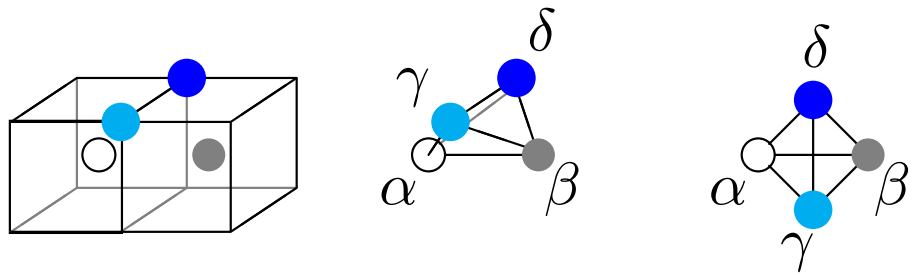


From crystallographic symmetry,
the following configurations are equivalent.

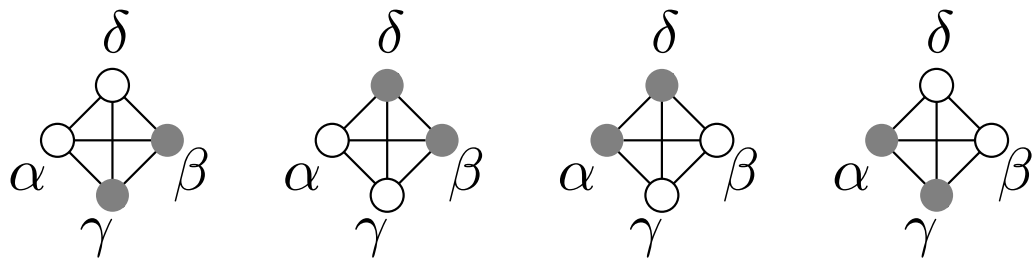


$D0_3$ configurations

bcc ordering



From crystallographic symmetry,
the following configurations are equivalent.



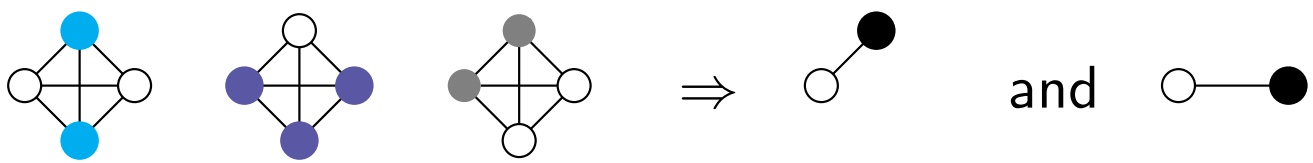
B32 configurations

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 the interaction parameters.

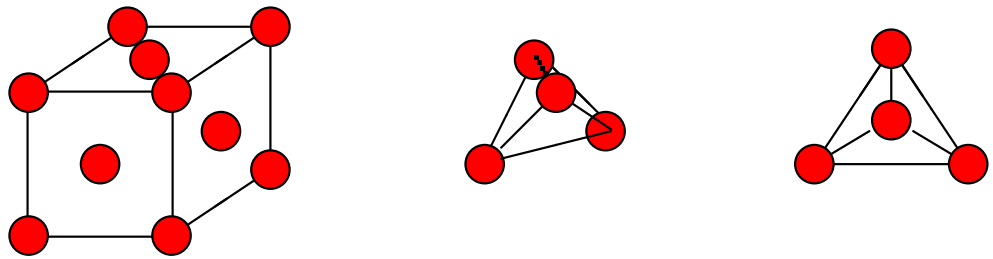
In Thermo-Calc software, there is an option - B - where the equivalence of the Gibbs energy of the equivalent configurations of the irregular tetrahedron constituting the bcc lattice is built in.

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



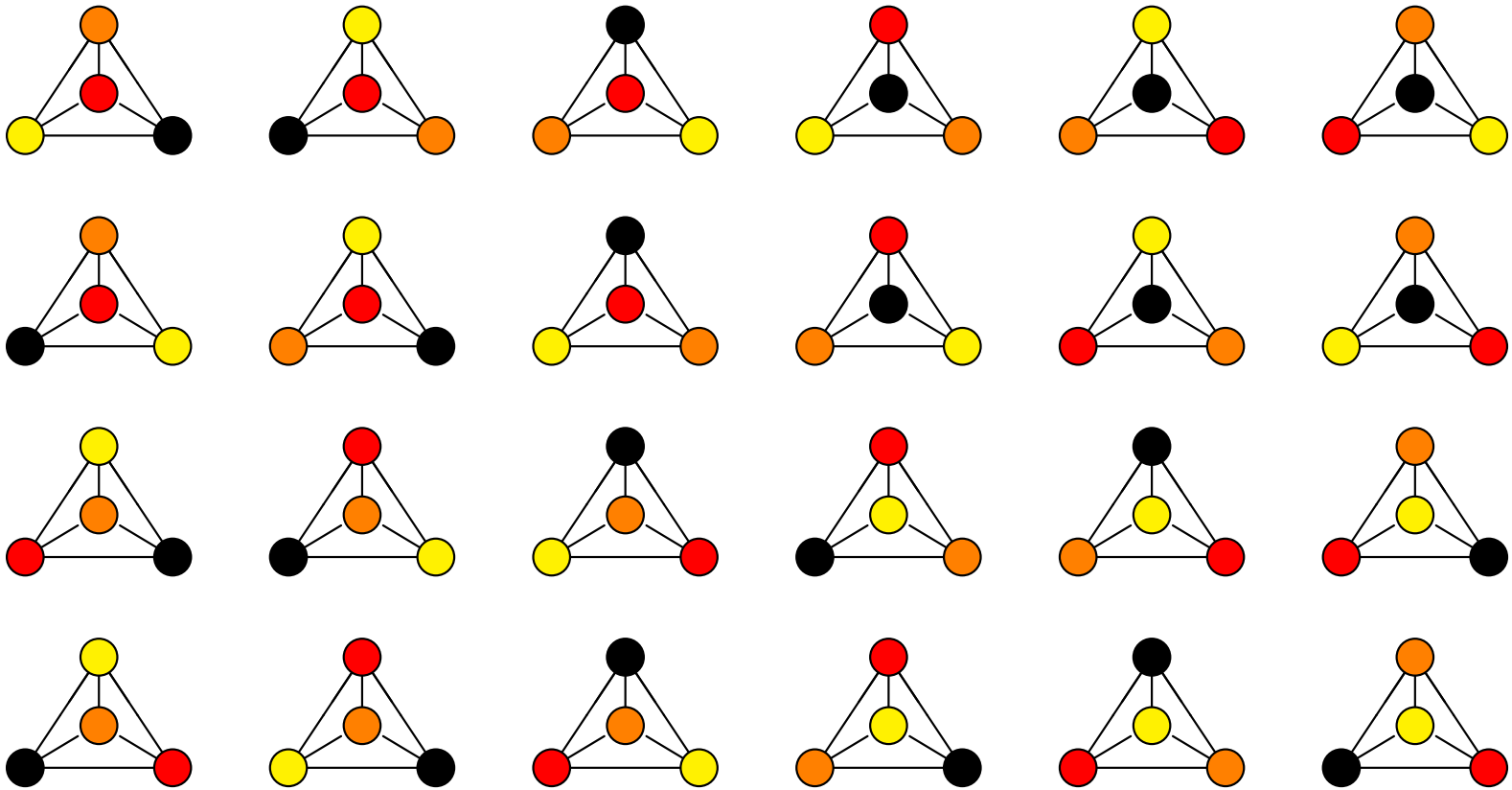
fcc ordering

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



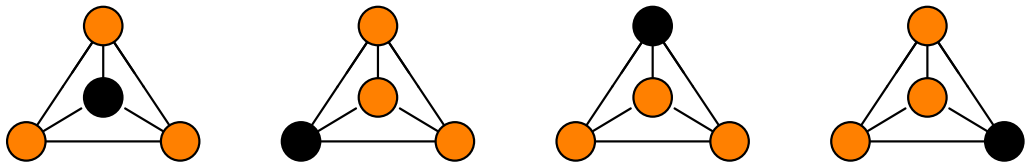
fcc ordering

From crystallographic symmetry,
the following configurations are equivalent.



fcc ordering

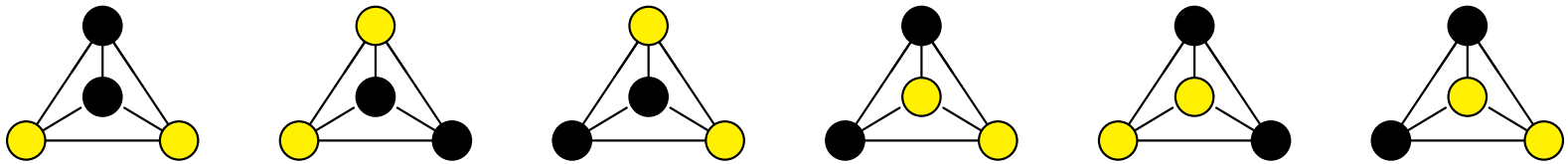
From crystallographic symmetry,
the following configurations are equivalent.



$L1_2$ configurations

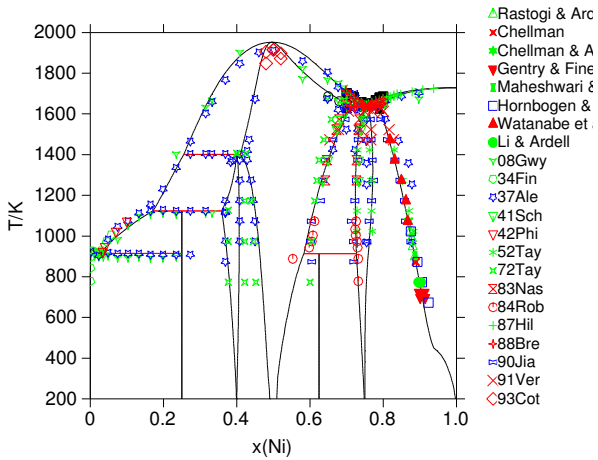
fcc ordering

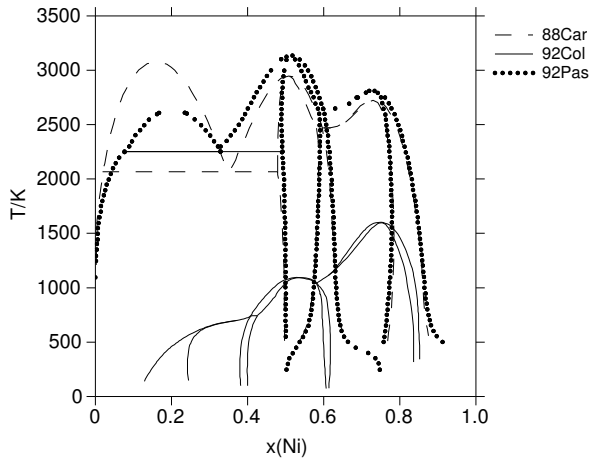
From crystallographic symmetry,
the following configurations are equivalent.

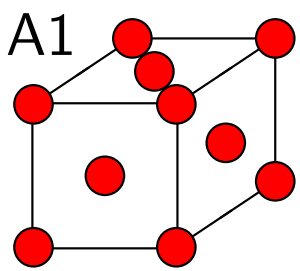


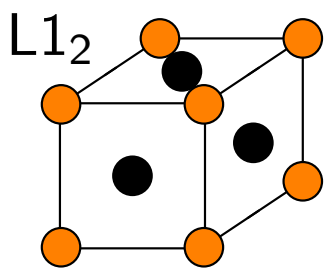
$L1_0$ configurations

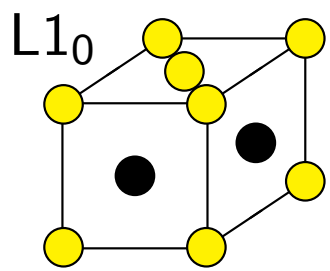
A1/L12 modelling

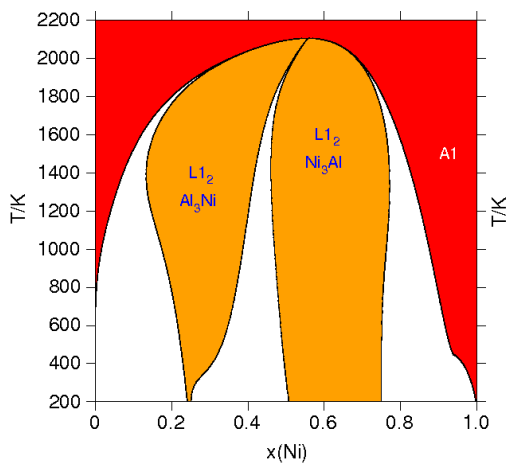


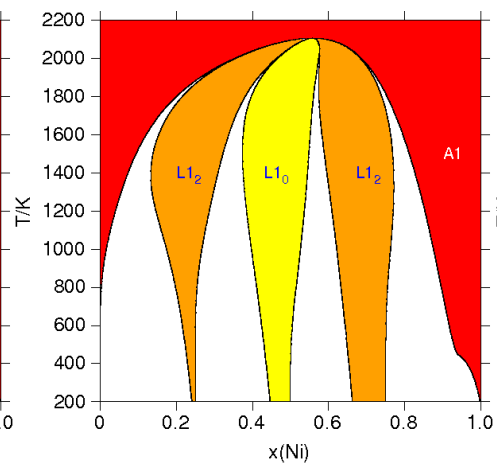


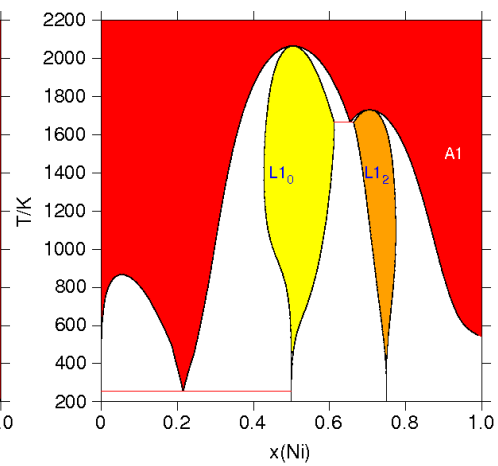




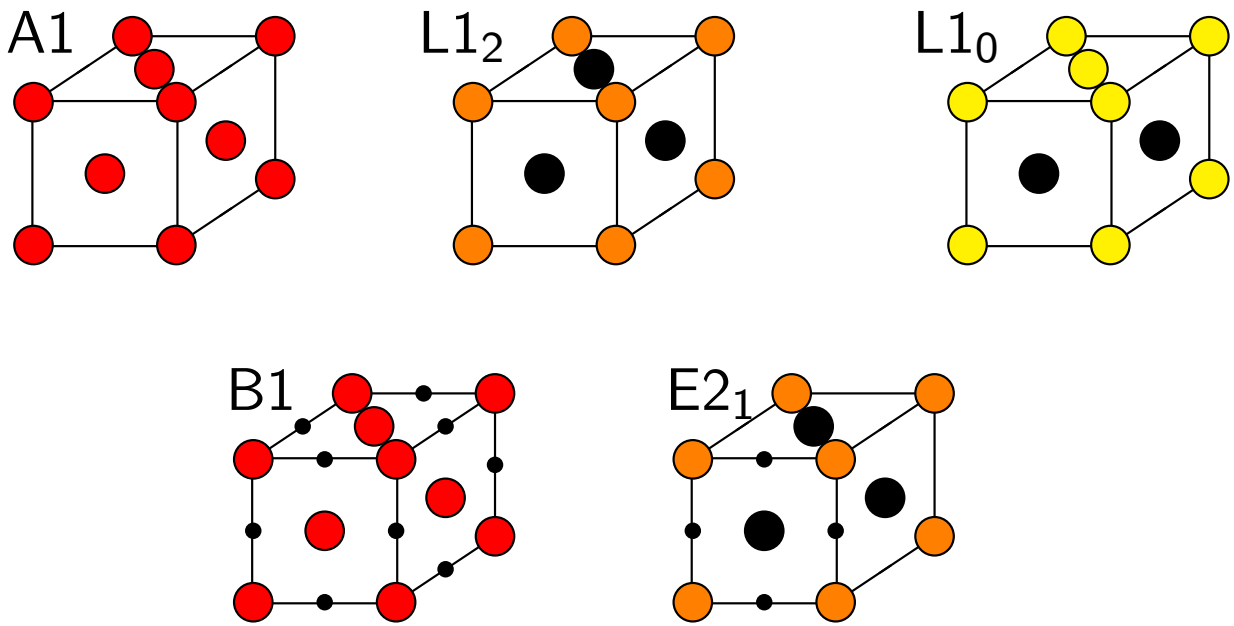








Interstitial and metallic ordering



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 phases crystallography knowledge is a 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.

Bibliography

National Institute for Materials Science (NIMS) AtomWork <http://crystdb.nims.go.jp/> Yibin Xu, Masayoshi Yamazaki, and Pierre Villars: Inorganic Materials Database for Exploring the Nature of Material: Jpn. J. Appl. Phys. 50 (2011) 11RH02.

ASM Alloy Phase Diagrams Center, P. Villars, editor-in-chief; H. Okamoto and K. Cenzual, section editors; http://www1.asminternational.org/AsmEnterprise/APD, ASM International, Materials Park, OH, 2006.

Computational Thermodynamics, The Calphad Method, Bo Sundman, Hans Lukas, Suzana Fries, CAMBRIDGE UNIVERSITY PRESS, United Kingdom, 2007, IBSN 9780521868112

Thermodynamic models for crystalline phases. Composition dependent models for volume, bulk modulus and thermal expansion, Hallstedt, B., Dupin, N., Hillert, M., Hoglund, L., Lukas, H. L., Schuster, J. C., et al. (2007). Thermodynamic models for crystalline phases. Composition dependent models for volume, bulk modulus and thermal expansion. CALPHAD, 31(1), 28-37.

N. Dupin, S. G. Fries, B. Sundman, A. Pasturel, M. H. F. Sluiter, Using Nb-Ni μ-phase first principles results in the Bragg-Williams approximation, Philosophical magazine, 86, 1631 - 1641, (2006)

A. Kussofsky, N. Dupin and B. Sundman, On the Compound Energy Formalism Applied to fcc Ordering, CALPHAD 25 (2001), pp. 549565.

http://nathdupin.free.fr/public/Lectures/TCSAB-10years.pdf

http://nathdupin.free.fr/public/Lectures/Tofa2004_bcc.pdf