Inputs from crystallography

Nathalie Dupin

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Calcul Thermodynamique

SATA / Toulouse / 2022

Outline

Same structure means same model

One model describes ≠ structures

Conclusion

How crystallography can help thermodynamic modelling

Same crystallographic structure ⇒ Same Gibbs energy equation

- Substitutional solutions
- Several sites (CEF)

One Gibbs energy equation describes ≠ crystallographic structures

- Interstitial
- Metallic ordering

Outline

Same structure means same model

Substitutional solutions

Sublattice Model

One model describes ≠ structures

Conclusion

Same crystallographic structure means same model

General rule to treat multicomponent cases

Same crystallographic structure ⇒ same model

It is obvious when
- similar composition,
- similar elements,
- continous solubility.

It is not obvious when
- $\neq$ compositions in $\neq$ systems,
- $\neq$ crystallographic parameters,
- no or partial reciprocal solubility.

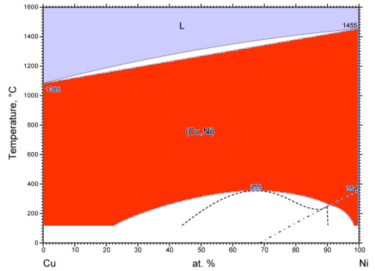
Using phase names related to the crystallographic structure allows to keep their meaning when considering different systems. BCC_A2 is α-Fe, δ-Fe, β-Ti, γ-U.

Exception

Very different interactions
No common elements
No possible solubility
e.g. CsCl/NiAl

Substitutional solutions

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



Bibliographic data

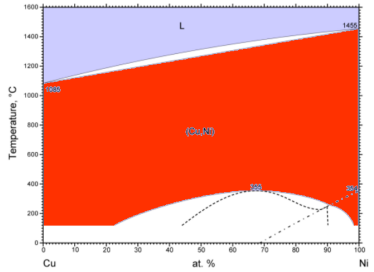
Binary Alloy Phase Diagrams, II Ed., Ed. T.B. Massalski,1990,2,,1442-1446,Chakrabarti D.J., Chen S.W., Chang Y.A.

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Continuous solution ⇒ (Cu,Ni)

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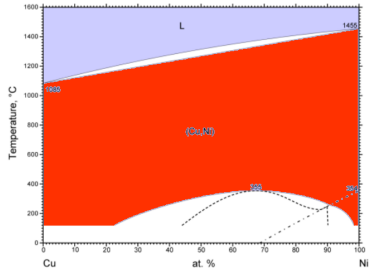
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Continuous solution ⇒ (Cu,Ni)

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

Substitutional solutions

Phase	Structure type	Peason symbol	Space group No.	Material search
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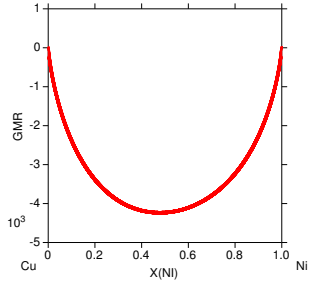
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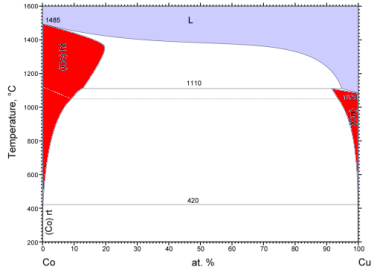
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Substitutional solutions

Phase	Structure type	Pearson 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



Bibliographic data

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

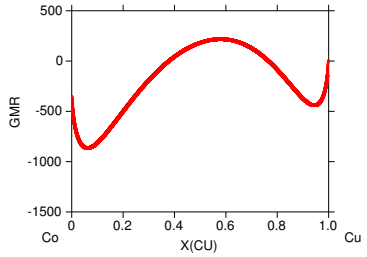
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Continuous modelling may be less obvious when there is a miscibility gap.

(Cu) and (Co) ht: prototype Cu

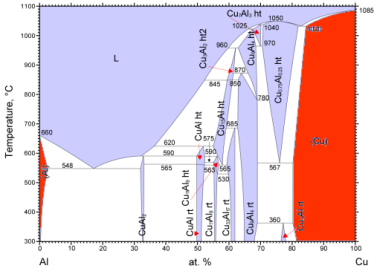
$\Rightarrow$ substitutional model: (Cu,Co)

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



Substitutional solutions

Phase	Structure type	Pearson symbol	Space group No.	Material search
$CuAl_2$	$CuAl_2$	tI12	140	Search
$Cu_{1-x}Al_{1+x}$ ht	$Cu_{1-x}Ge$	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
$Cu_{0.35}Al_{0.65}$ ht	W	cI2	229	No Data
(Al)	Cu	cF4	225	No Data
Cu_9Al_4 ht	Cu_5Zn_8	cI52	217	No Data



Bibliographic data

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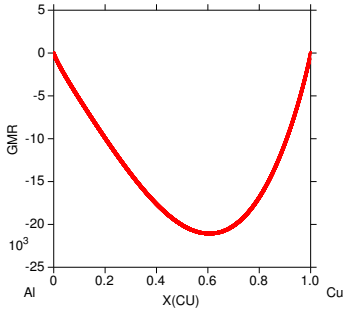
https://crystdb.nims.go.jp/> (Accessed: 2022/06/04)

Intermediate phases can hide continuity.

(Al) and (Cu) : prototype Cu

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

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



Outline

Same structure means same model

Substitutional solutions

Sublattice Model

One model describes ≠ structures

Conclusion

Sublattice Model

Before running an optimisation, a model has to be chosen for each phase and in particular for those showing a significant composition range.

After these choices, the equation of the phase Gibbs energy with respect to the occupation of the different sublattices can be expressed and the available parameters to be assessed.

The **crystallography** helps in these choices.

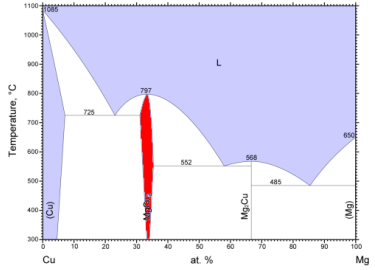
For phases with several sites, as for substitutional solutions : phases with the **same prototype** should be described with the **same model**.

Such a model defines the **number of sublattices**, their **site number** and the **species** allowed in each of them.

Very often, the choice of a model just follows the one made in the past or in the database you want to extend. It is a very good reason but it is better to understand it and the possible limitations when applying it in another context.

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



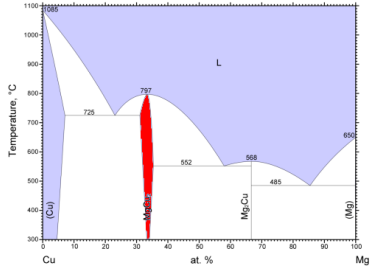
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$MgCu_2$	$MgCu_2$	cF24	227	Search
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$MgCu_2$	Structure type	Pearson symbol	Space group	No.
	$MgCu_2$	cF24	Fd-3m	227

*Standardized

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 | Calculated Electronic Structure

▶ **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

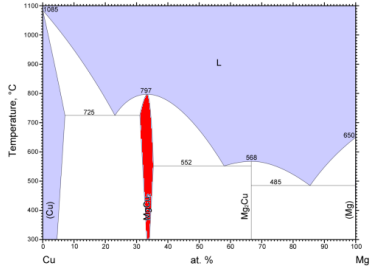
Atom coordinates

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

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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



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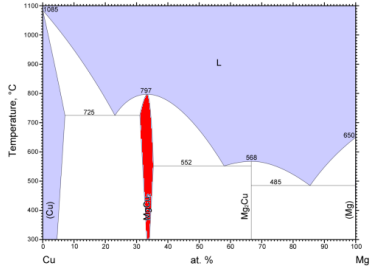
No	Site notation	Atom	Multiplicity	Wyckoff
1	Cu	Cu	16	c
2	Mg	Mg	8	b

$\Rightarrow (Cu)_2(Mg)$

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Laves phases

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(Mg)	Mg	hP2	194	Search
$MgCu_2$	$MgCu_2$	cF24	227	Search
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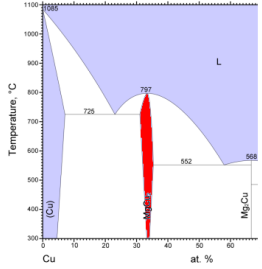
⇒ $(Cu)_2(Mg)$

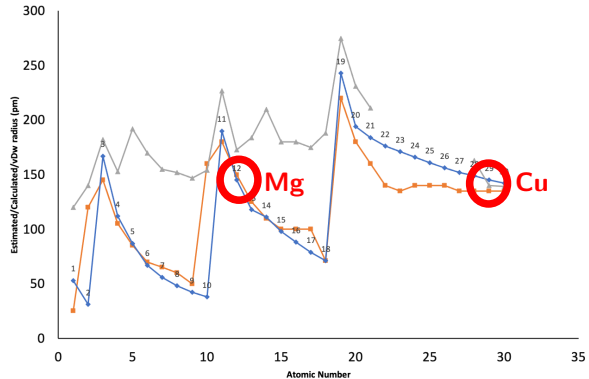
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+ homogeneity range ⇒ $(Cu,Mg)_2(Cu,Mg)$

Laves phases

Phase	Structure type	Peason symbol	Space gr
(Mg)	Mg	hP2	1
$MgCu_2$	$MgCu_2$	cF24	22
(Cu)	Cu	cF4	22
Mg_2Cu	Mg_2Cu	oF48	7





Atomic radii by Smk 6ix - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=97216371

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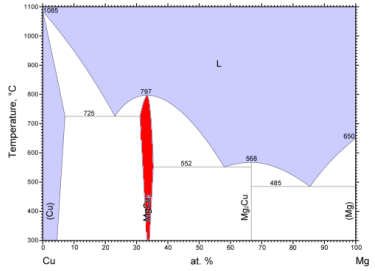
$\Rightarrow (Cu)_2(Mg)$

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

Laves phases

Different defects (substitution, vacancies, interstitials, ...) can be considered.

(Cu)	Cu	cF4	225	No data
Mg_2Cu	Mg_2Cu	oF48	70	Search



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p	No.
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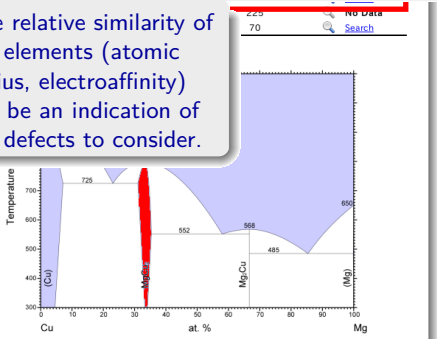
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+ homogeneity range ⇒ $(Cu,Mg)_2(Cu,Mg)$

Laves phases

Different defects (substitution, vacancies, interstitials, ...) can be considered.

The relative similarity of the elements (atomic radius, electroaffinity) can be an indication of the defects to consider.



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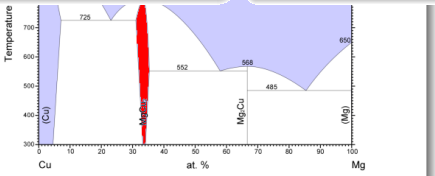
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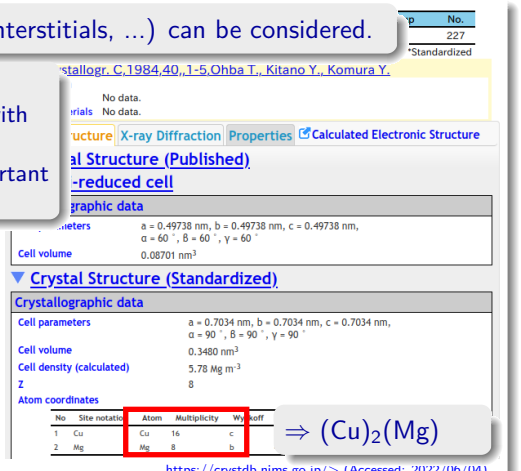
The position of the homogenity range with respect to the ideal composition is important to consider.



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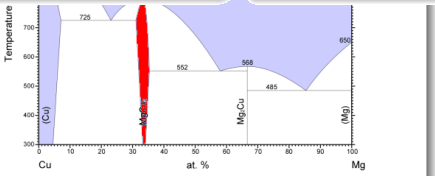
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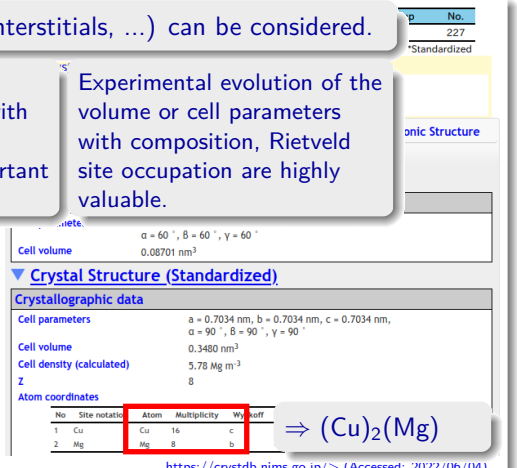
Experimental evolution of the volume or cell parameters with composition, Rietveld site occupation are highly valuable.



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Laves phases

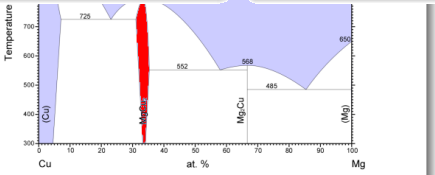
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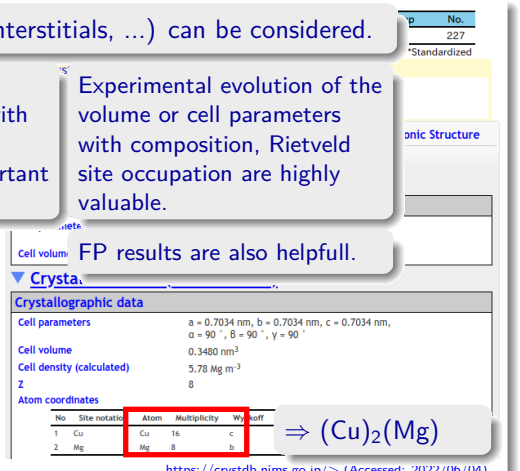
FP results are also helpfull.



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

Laves phases

$$\overset{16c}{(Cu,Mg)_2}\overset{8b}{(Cu,Mg)}$$

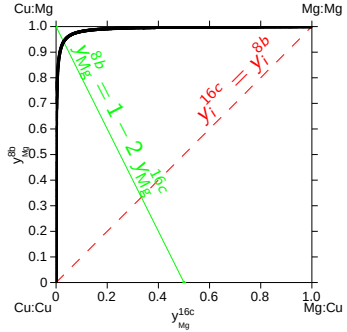
$$\begin{aligned} G^{C15} = {} & y_{Cu}^{16c}\, y_{Cu}^{8b}\, G_{Cu:Cu}^{C15} + y_{Cu}^{16c}\, y_{Mg}^{8b}\, G_{Cu:Mg}^{C15} \\ & + y_{Mg}^{16c}\, y_{Cu}^{8b}\, G_{Mg:Cu}^{C15} + y_{Mg}^{16c}\, y_{Mg}^{8b}\, G_{Mg:Mg}^{C15} \\ & + RT\left(2\sum_i y_i^{16c} \ln y_i^{16c} + \sum_i y_i^{8b} \ln y_i^{8b}\right)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

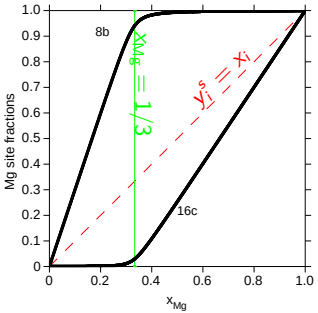
Laves phases

16c 8b
$(Cu,Mg)_2(Cu,Mg)$

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

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



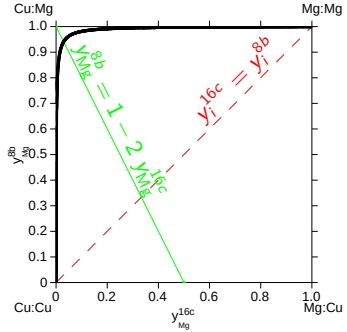


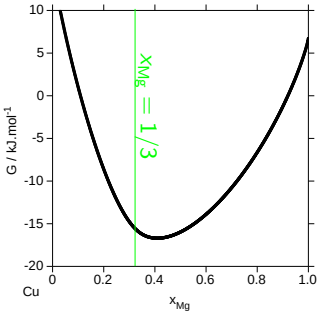
Laves phases

$$\underset{(\mathrm{Cu,Mg})_2}{16c}\underset{(\mathrm{Cu,Mg})}{8b}$$

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

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





Laves phases



F. Laves 1906-1978

U. Kattner et al., Calphad XLII

Cu_2Mg

prototype for the C15 Laves phases.

Laves phases

familly of intermetallic phases appearing in many binary and ternary systems.

C14

constituted by 3 different sites, often identified in industrial multicomponent alloys.

Laves phases



F. Laves 1906-1978

U. Kattner et al., Calphad XLII

Cu_2Mg

prototype for the C15 Laves phases.

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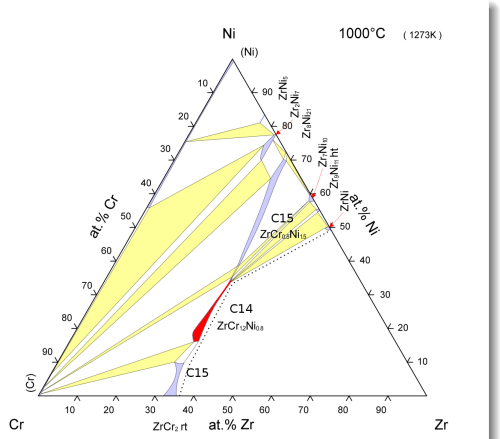
Calphad model for all Laves phases

Most often 2SL and substitution in both sub-lattices to describe their homogeneity range.

C14 thermodynamic model

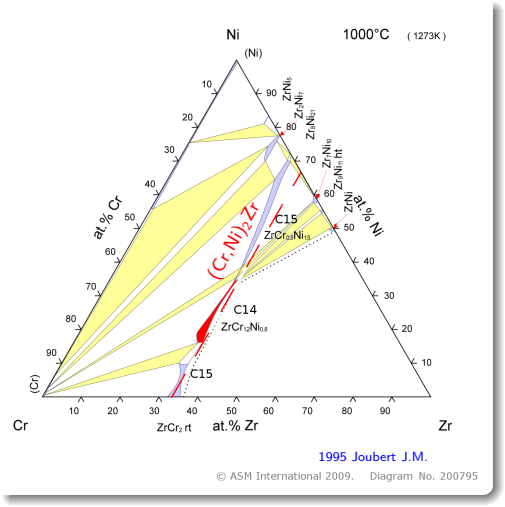
$(A,B)_2(A,B)$ or $(A,B)_3(A,B)_1(A,B)_2$?

Laves phases



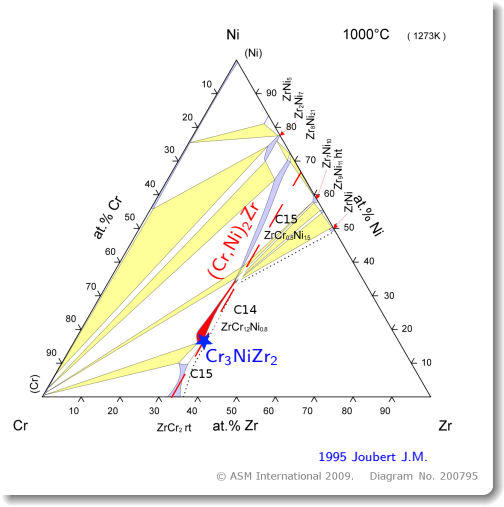
The C14 often appears as an extension of a binary phase along an almost constant composition line.

Laves phases



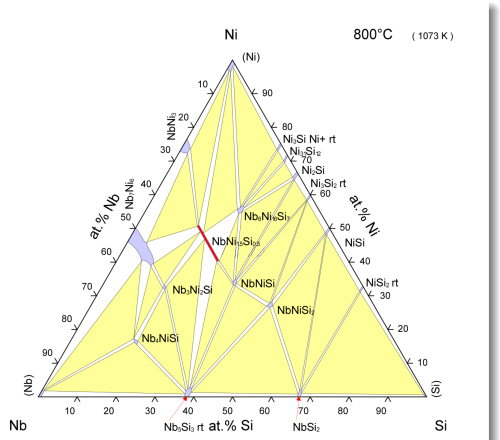
The C14 often appears as an extension of a binary phase along an almost constant composition line.

Laves phases



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

Laves phases

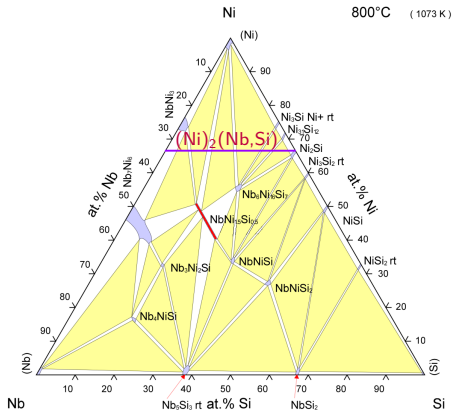


1969 Gladyshevskii E.I.

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The C14 also appears in ternary systems without being stable in the constituting binary systems.

Laves phases



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

*Standardized

J. Less-Common Met.,1986,119,,297-305,Blazina Z., Trojko R.

Preparation

Synthesis arc-melted, several times remelted

Starting materials No data.

Crystal Structure | X-ray Diffraction | Properties | Calculated Electronic Structur

▶ **Crystal Structure (Published)**

▼ **Niggli-reduced cell**

Crystallographic data

Cell parameters	a = 0.4811 nm, b = 0.4811 nm, c = 0.8023 nm, α = 90 °, β = 90 °, γ = 120 °
Cell volume	0.16082 nm^3

▼ **Crystal Structure (Standardized)**

Crystallographic data

Cell parameters	a = 0.4811 nm, b = 0.4811 nm, c = 0.8023 nm, α = 90 °, β = 90 °, γ = 120 °
Cell volume	0.1608 nm^3
Cell density (calculated)	8.42 $Mg\ m^{-3}$
Z	4

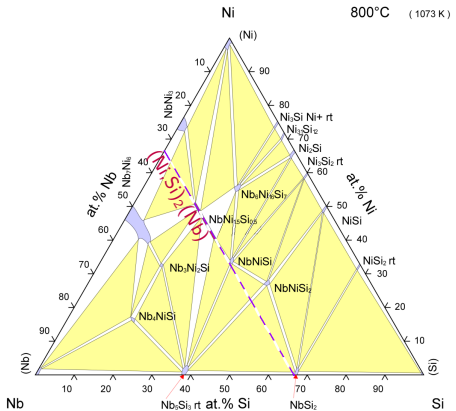
Atom coordinates

No	Site notation	Atom	Multiplicity	Wyckoff	Site symmetry	x	y	z	Occupancy
1	M1	0.900Nb + 0.100Si	4	f					
2	Ni1	Ni	6	h					
3	Ni2	Ni	2	a					

⇒ $(Ni)_6(Ni)_2(Nb,Si)_4$

https://crystdb.nims.go.jp/> (Accessed: 2022/06/04)

Laves phases



1969 Gladyshevskii E.I.

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$NbNi_{1.5}Si_{0.5}$	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 R.V.

Preparation

Synthesis No data.

Starting materials No data.

Crystal Structure | X-ray Diffraction | Properties | Calculated Electronic Structure

▶ 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					
2	M2	0.750Ni + 0.250Si	2	a					
3	Nb1	Nb	4	f					

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

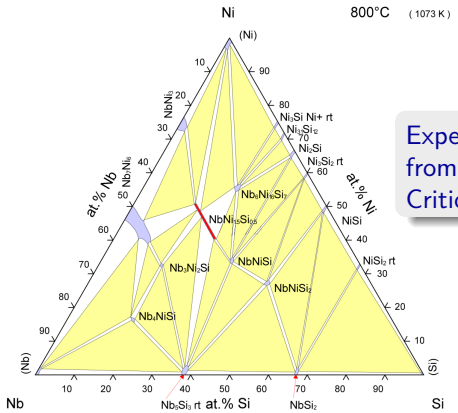
https://crystdb.nims.go.jp/> (Accessed: 2022/06/04)

1	M1	0.900Nb + 0.100Si	4	f	
2	Ni1	Ni	6	h	
3	Ni2	Ni	2	a	

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

https://crystdb.nims.go.jp/> (Accessed: 2022/06/04)

Laves phases



1969 Gladyshevskii E.I.

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$NbNi_{1.5}Si_{0.5}$	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 R.V.

Preparation

Synthesis No data.

Starting materials No data.

Crystal Structure | X-ray Diffraction | Properties | Calculated Electronic Structure

▶ Crystal Structure (Published)

▼ Niggli-reduced cell

Crystallographic data

Cell parameters a = 0.4804 nm, b = 0.4804 nm, c = 0.7825 nm,

Cell density (calculated) 8.20 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					
2	M2	0.750Ni + 0.250Si	2	a					
3	Nb1	Nb	4	f					

https://crystdb.nims.go.jp/> (Accessed: 2022/06/04)

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

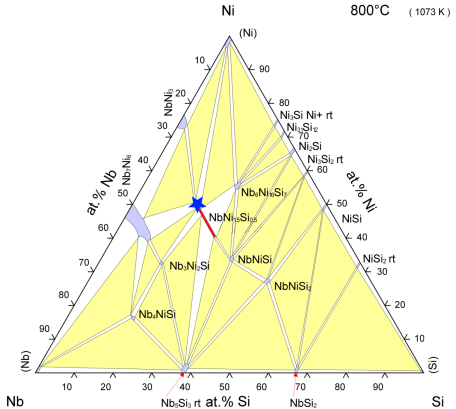
$\Rightarrow (Ni,Si)_6(Ni,Si)_2(Nb)_4$

No	Site notation	Atom	Multiplicity	Wyckoff	Site symmetry	x	y	z	Occupancy
1	M1	0.900Nb + 0.100Si	4	f					
2	Ni1	Ni	6	h					
3	Ni2	Ni	2	a					

https://crystdb.nims.go.jp/> (Accessed: 2022/06/04)

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

Laves phases



1969 Gladyshevskii E.I.

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

*Standardized

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

Preparation

Synthesis No data.

Starting materials No data.

Crystal Structure | X-ray Diffraction | Properties | Calculated Electronic Structure

▶ 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 nm³

▼ 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 °
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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					
2	M2	0.750Ni + 0.250Si	2	a					
3	Nb1	Nb	4	f					

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

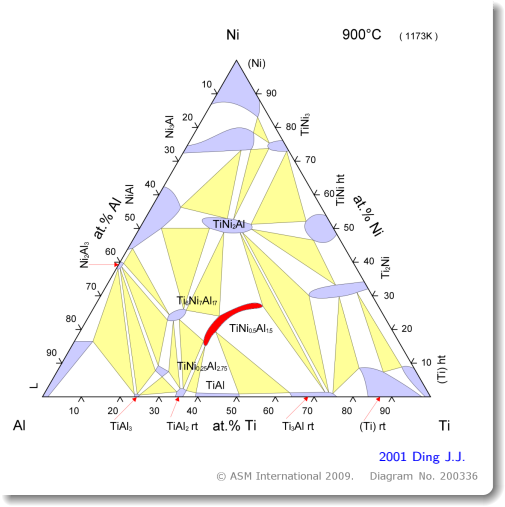
https://crystdb.nims.go.jp/> (Accessed: 2022/06/04)

1	M1	0.900Nb + 0.100Si	4	f					
2	Ni1	Ni	6	h					
3	Ni2	Ni	2	a					

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

https://crystdb.nims.go.jp/> (Accessed: 2022/06/04)

Laves phases



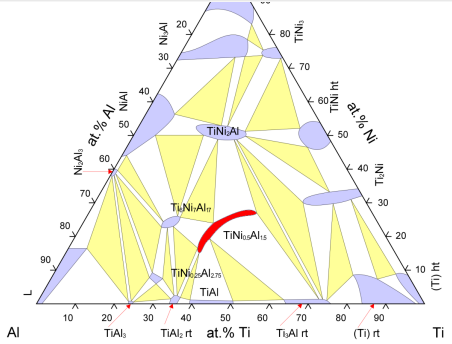
The C14 can also appear with more complex homogeneity range topology like here with a banana shape.
$(Al,Ni)_2(Ti) \rightarrow (Al,Ti)_2(Ni)$.

Laves phases

$TiNiI_{0.5}Al_{1.5}$ τ_3,TiNiAl	$Ti_{2.13}Ni_{1.30}Al_{2.57}$	Mg_2Cu_3Si	hP12 P63/mmc	4.67 0.1763	a=0.50095 α=90 b=0.50095 β=90 c=0.81117 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

ASM Alloy Phase Diagram Database accessed 2014/06/11



2001 Ding J.J.

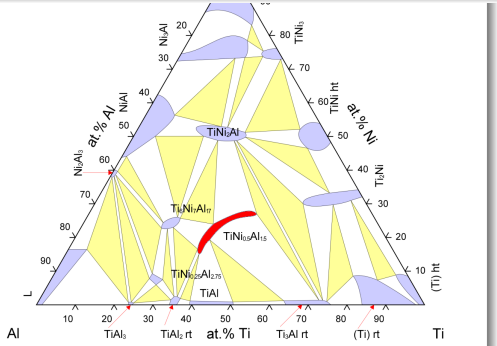
© ASM International 2009. Diagram No. 200336

Laves phases

$TiNl_{0.5}Al_{1.5}$ τ_3,TiNiAl	$Tl_{2.13}Nl_{1.30}Al_{2.57}$	Mg_2Cu_3Sl	hP12 P63/mmc	4.67 0.1763	a=0.50095 α=90 b=0.50095 β=90 c=0.81117 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

ASM Alloy Phase Diagram Database accessed 2014/06/11



2001 Ding J.J.

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τ_3 - "Al_3NiTi_2" ($MgZn_2$-type)

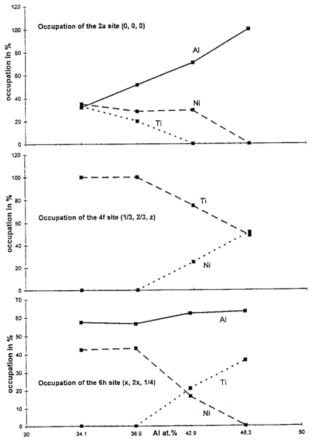


Fig. 8. Occupation of the atomic sites for the τ_3-phase as a function of the Al-content.

1999 Huneau B.

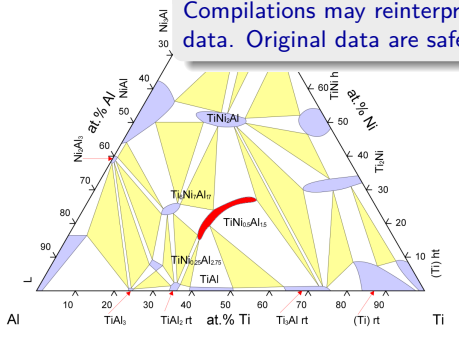
Laves phases

$TiNi_{0.5}Al_{1.5}$ τ_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 α=90 b=0.50095 β=90 c=0.81117 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

ASM Alloy Phase Diagram Database accessed 2014/06/11

Compilations may reinterpret original data. Original data are safer.



2001 Ding J.J.

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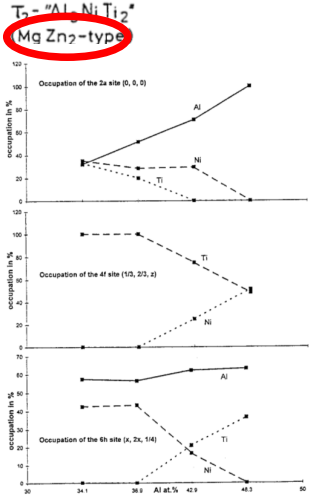


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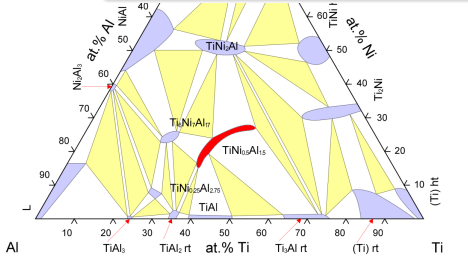
Laves phases

TiNi$_{0.5}$Al$_{1.5}$ τ$_3$,TiNiAl	Ti$_{2.13}$Ni$_{1.30}$Al$_{2.57}$	Mg$_2$Cu$_3$Si	hP12 P6$_3$/mmc	4.67 0.1763	a=0.50095 α=90 b=0.50095 β=90 c=0.81117 γ=120	[12]

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ASM Alloy Phase Diagram Database accessed 2014/06/11

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



2001 Ding J.J.

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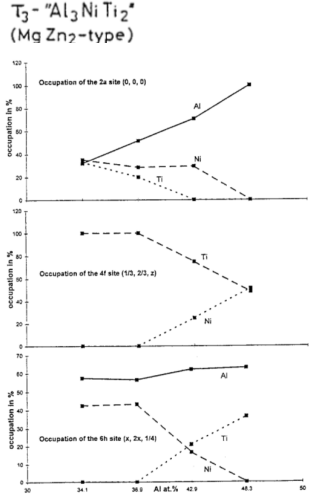


Fig. 8. Occupation of the atomic sites for the τ$_3$-phase as a function of the Al-content.

1999 Huneau B.

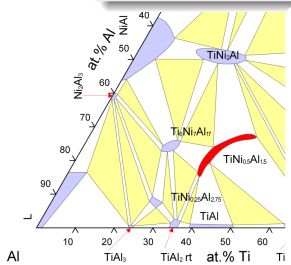
Laves phases

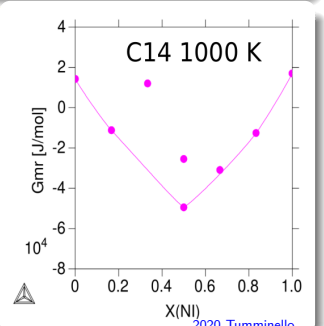
TiNi0.5Al1.5 τ3,TiNiAl	Ti2.13Ni1.30Al2.57	Mg2Cu3Si	hP12 P63/mmc	4.67 0.1763	a=0.50095 α=90 b=0.50095 β=90 c=0.81117 γ=120	[12]

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ASM Alloy Phase Diagram Database accessed 2014/06/11

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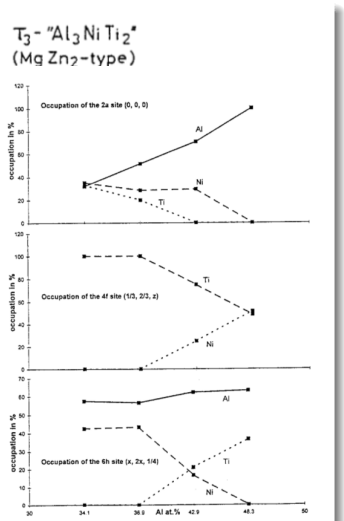
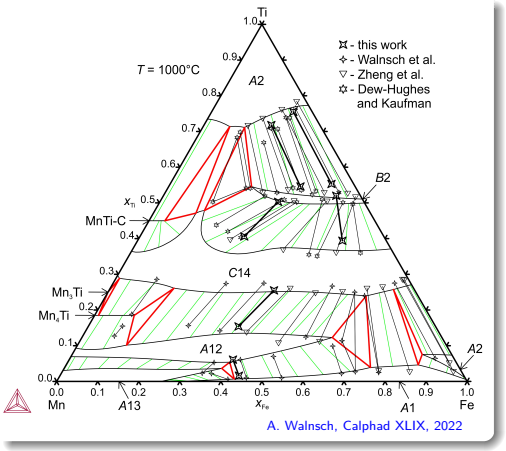


Fig. 8. Occupation of the atomic sites for the τ_3-phase as a function of the Al-content.

1999 Huneau B.

Laves phases



A. Walnsch, Calphad XLIX, 2022

Laves phases

For decades simplified models have been used because of computers limitations and the difficulty to assess all the end-members.

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

But they may oversimplify phases presenting large stability area.

Nowadays that DFT can help, models closer to the crystallography are expected to give better extrapolations.

Outline

Same structure means same model

One model describes ≠ structures

Interstitials

Metallic ordering

Interstitial and metallic ordering

Conclusion

One model describes ≠ structures

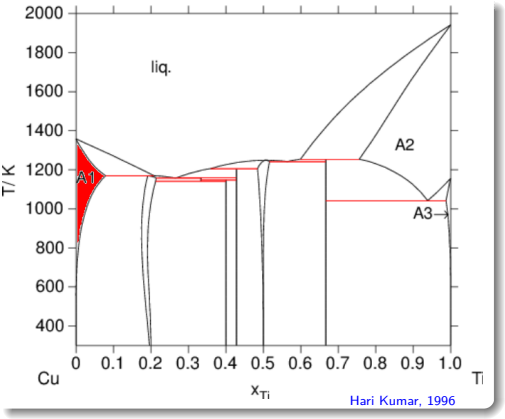
Interstitials

Metallic ordering

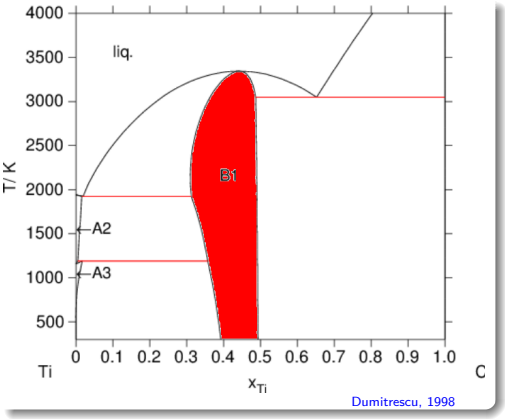
Interstitials and metallic ordering

Interstitials

(M,M')(C,□)



Hari Kumar, 1996



Dumitrescu, 1998

Outline

Same structure means same model

One model describes ≠ structures

Interstitials

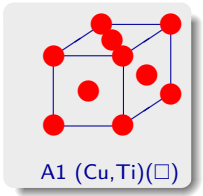
Metallic ordering

Interstitial and metallic ordering

Conclusion

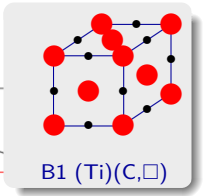
Interstitials

(M,M')(C,□)



A1 (Cu,Ti)(□)

Hari Kumar, 1996



B1 (Ti)(C,□)

Dumitrescu, 1998

Outline

Same structure means same model

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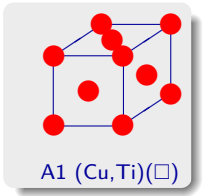
Interstitial and metallic ordering

Conclusion

Interstitials

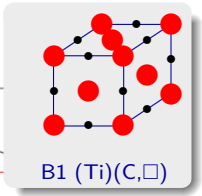
(M,M')(C,□)

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



A1 (Cu,Ti)(□)

Hari Kumar, 1996



B1 (Ti)(C,□)

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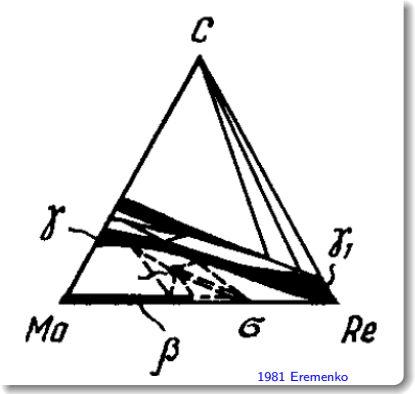
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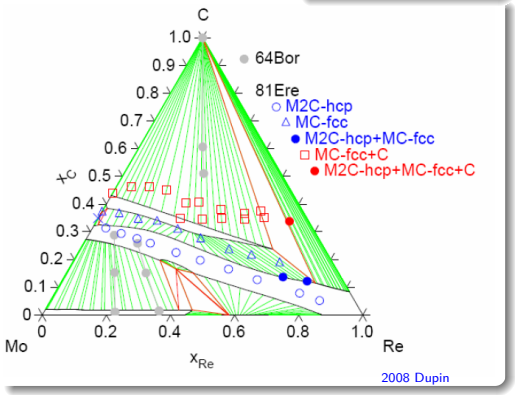
(M,M')(C,□)

Continous modelling between metallic solutions and carbides is based on crystallographic consideration.

Such a continuity is observed in a few systems.



1981 Eremenko

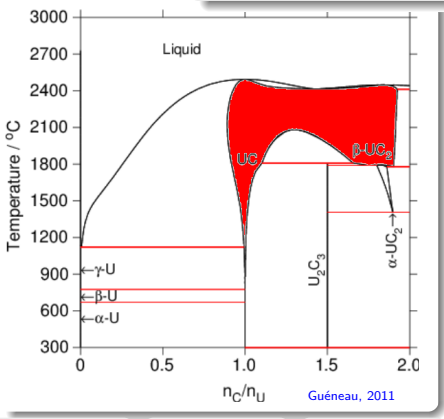


2008 Dupin

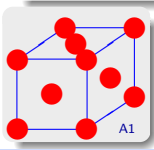
Interstitials

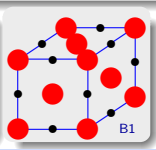
U(C,C_2,□)

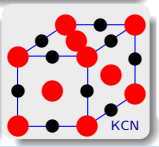
Models based on crystallography allow to describe properly phase diagram as well as thermodynamics.

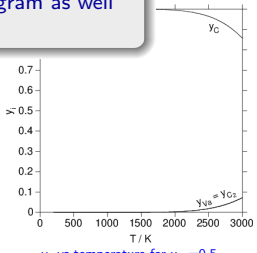


Guéneau, 2011

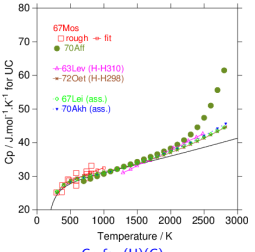




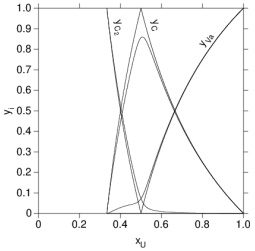




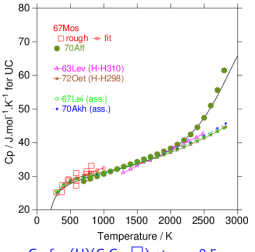
y_i vs temperature for x_C=0.5



Cp for (U)(C)



y_i vs composition at 1500 and 3000K



Cp for (U)(C,C_2,□) at x_C=0.5

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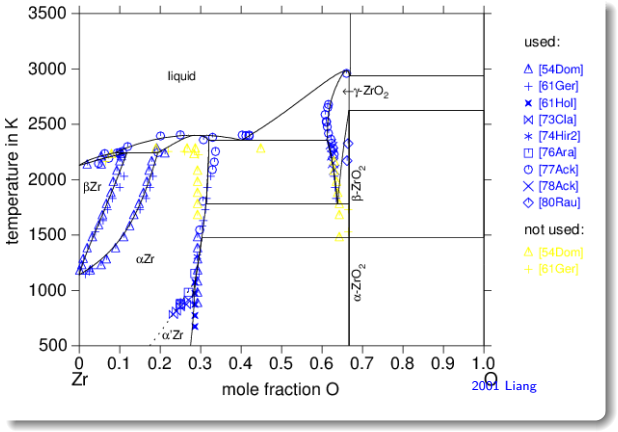
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Interstitial and metallic ordering

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Interstitials

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



2001 Liang

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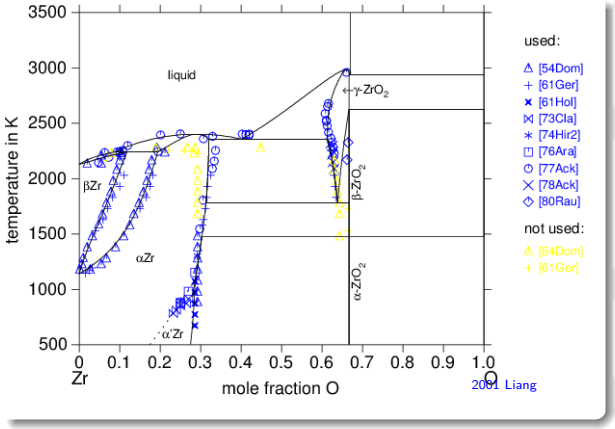
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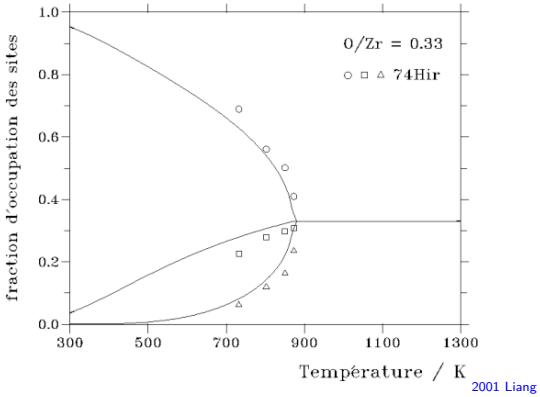
In many databases, the interstitials in the hcp phase are models with the model $M(C,\square)_{0.5}$ in order to model easily the carbides M_2C (NiAs, $B8_1$).

When the metallic hcp solid solution is important for the material under consideration, it is better to consider all the intertitial sites in order to get a better ideal configurational entropy.

Several interstitial sites can be used to describe the configurations where the interstitials are largely filled.

Interstitials

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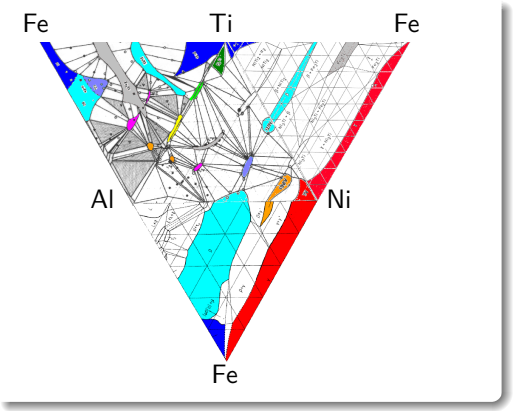
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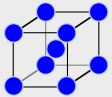
Metallic ordering



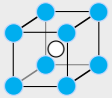
Metallic ordering

bcc family

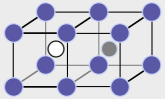
A2

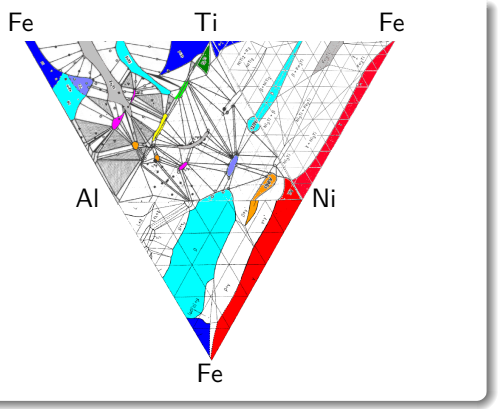


B2



$L2_1$





Outline

Same structure means same model

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Interstitials

Metallic ordering

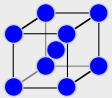
Interstitial and metallic ordering

Conclusion

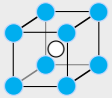
Metallic ordering

bcc family

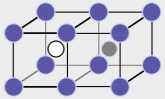
A2

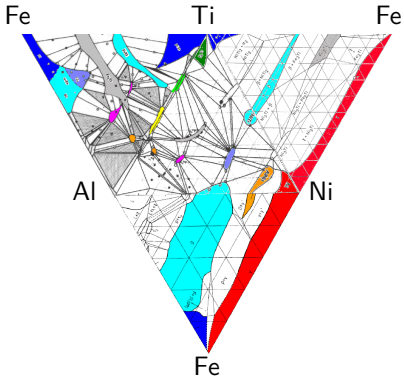


B2



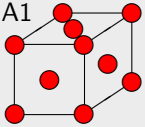
$L2_1$



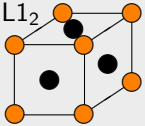


fcc family

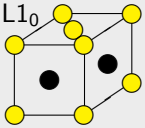
A1



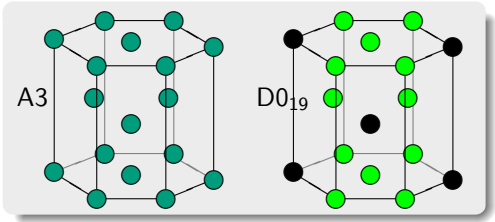
$L1_2$



$L1_0$

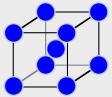


Metallic ordering

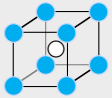


bcc family

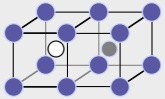
A2

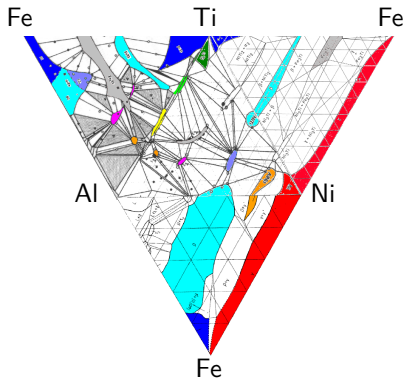


B2



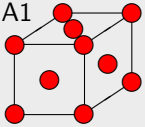
L2$_1$



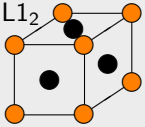


fcc family

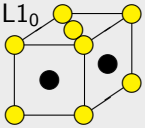
A1



L1$_2$



L1$_0$



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

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

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

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

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

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

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

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

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

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

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The Gibbs energy of the different phases of a same familly can be described with a single expression, $G(y_i^s)$, 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 occur. This is obtained taking into account the symmetry of the lattice.

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Often splitted into two contributions.

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

This is not a requirement. It was meant to avoid to introduce the CEF for systems without significant ordering.

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

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Ordering part

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

cancels when the phase is disordered.

$$G^{ord}(y_i^s) = \sum_{ijkl} y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)} G_{i:j:k:l}^{ord} + RT \sum_s a^s \sum_i y_i^s \ln y_i^s + G^{ord,xs}$$

Relations allowing the phase to disorder are to be imposed to the parameters of $G^{ord}(y_i^s)$.
For that, when using 4SL, the `B` and `F` options can help.

```
ENTER-PHASE ord F 4 0.25 0.25 0.25 0.25
```

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$$G^{ord}(y_i^s) = \sum_{ijkl} y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)} G_{i:j:k:l}^{ord} + RT \sum_s a^s \sum_i y_i^s \ln y_i^s + G^{ord,xs}$$

To use this formalism, in `GES` :

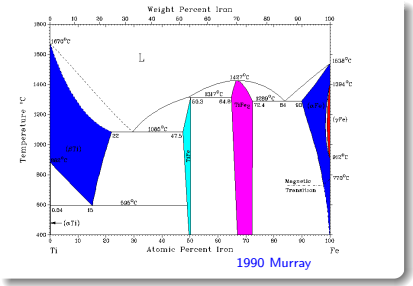
`AMEND-PHASE-DESCRIPTION` *ord* `DIS-PART` *dis*

Relations allowing the phase to disorder are to be imposed to the parameters of $G^{ord}(y_i^s)$.

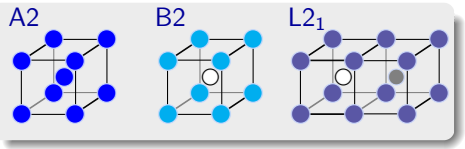
For that, when using 4SL, the `B` and `F` options can help.

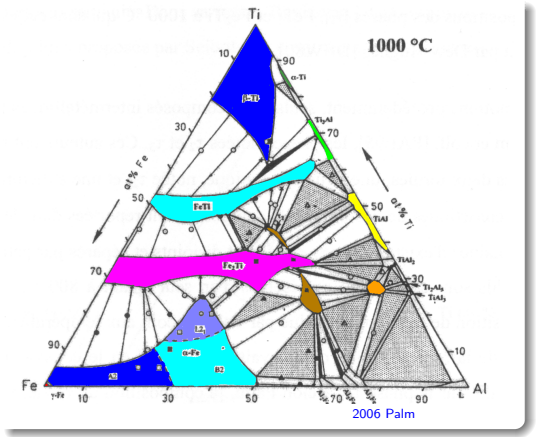
`ENTER-PHASE` *ord* `F 4 0.25 0.25 0.25 0.25`

A2/B2 modelling



1990 Murray





2006 Palm

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.

Outline

Same structure means same model

One model describes ≠ structures

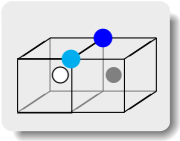
Interstitials

Metallic ordering

Interstitial and metallic ordering

Conclusion

bcc ordering



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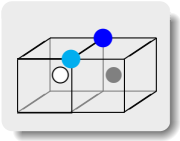
Interstitials

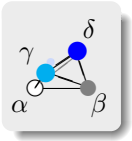
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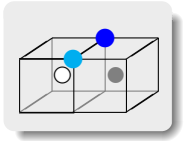
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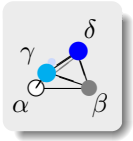
Metallic ordering

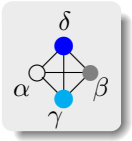
Interstitial and metallic ordering

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bcc ordering







Outline

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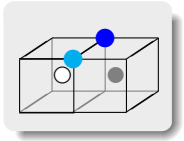
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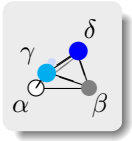
Metallic ordering

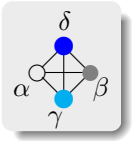
Interstitial and metallic ordering

Conclusion

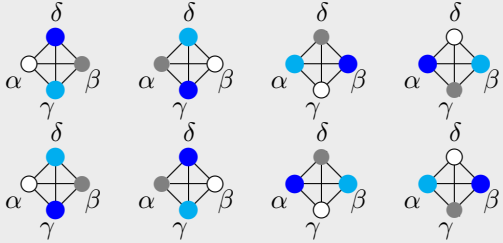
bcc ordering







From crystallographic symmetry,
the following configurations are equivalent.



Outline

Same structure means same model

One model describes ≠ structures

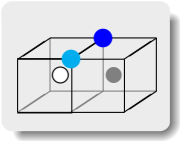
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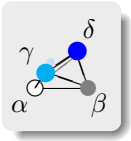
Metallic ordering

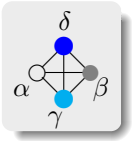
Interstitial and metallic ordering

Conclusion

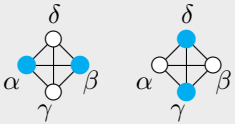
bcc ordering







From crystallographic symmetry,
the following configurations are equivalent.



B2 configurations

Outline

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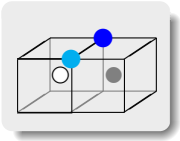
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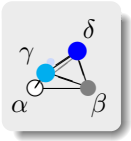
Metallic ordering

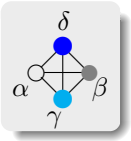
Interstitial and metallic ordering

Conclusion

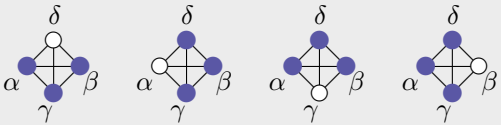
bcc ordering







From crystallographic symmetry,
the following configurations are equivalent.



$D0_3$ configurations

Outline

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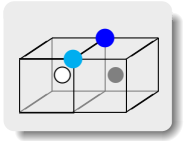
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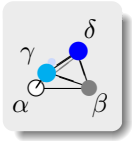
Metallic ordering

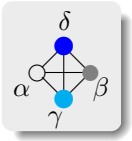
Interstitial and metallic ordering

Conclusion

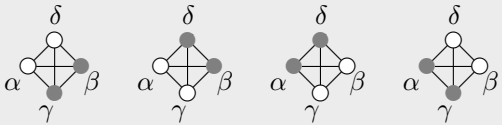
bcc ordering





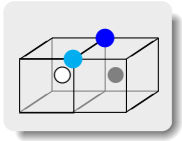


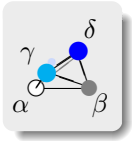
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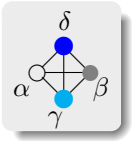


B32 configurations

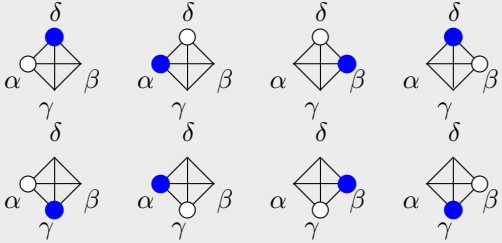
bcc ordering







From crystallographic symmetry,
the equivalence actually stands on the bonds.



Outline

Same structure means same model

One model describes ≠ structures

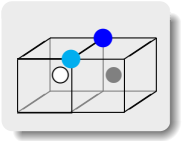
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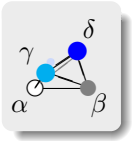
Metallic ordering

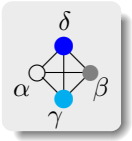
Interstitial and metallic ordering

Conclusion

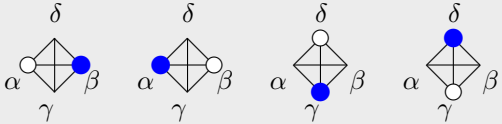
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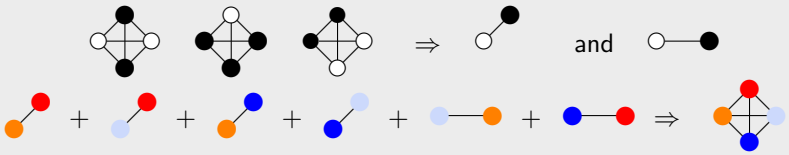
Interstitial and metallic ordering

Conclusion

bcc ordering

Giving 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, the **B option** sets automatically the equality of the Gibbs energy of the equivalent configurations for the bcc lattice.

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



The EBEF allows to apply this approximation using directly Effective Bond Energies rather that the energy of all the compounds.

https://doi.org/10.6028/jres.123.020

Outline

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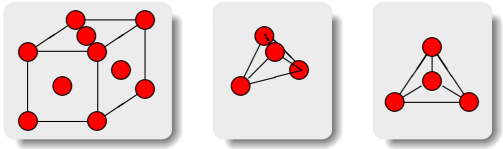
Metallic ordering

Interstitial and metallic ordering

Conclusion

fcc ordering

The 4SL fcc ordering is more simple as the lattice is built on regular tetrahedra.



Outline

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Interstitials

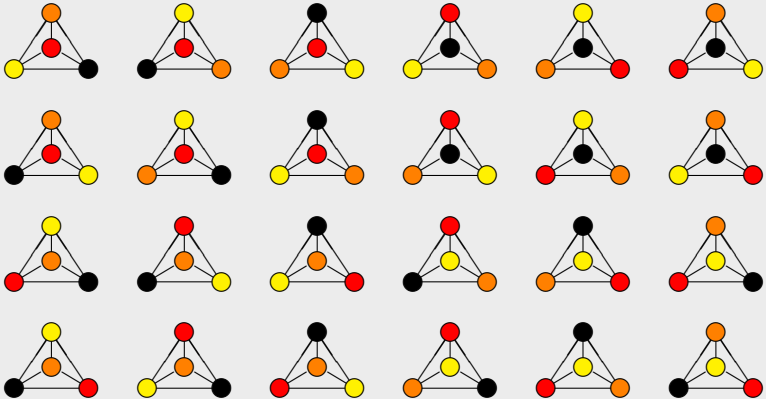
Metallic ordering

Interstitial and metallic ordering

Conclusion

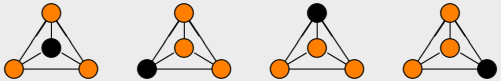
fcc ordering

From crystallographic symmetry, the following configurations are equivalent.
In Thermo-Calc, the symmetry of the phase can be set by the **F option**.



fcc ordering

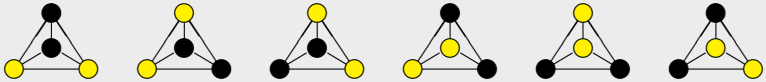
From crystallographic symmetry, the following configurations are equivalent.
In Thermo-Calc, the symmetry of the phase can be set by the **F option**.



$L1_2$ configurations

fcc ordering

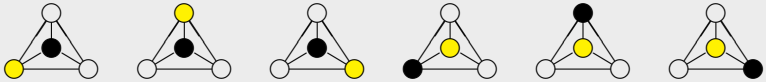
From crystallographic symmetry, the following configurations are equivalent.
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$L1_0$ configurations

fcc ordering

From crystallographic symmetry, the following configurations are equivalent.
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Bond equivalence

Outline

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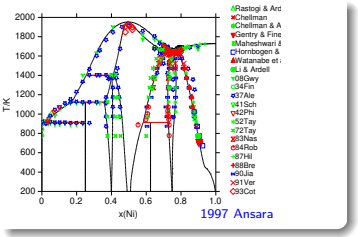
Interstitials

Metallic ordering

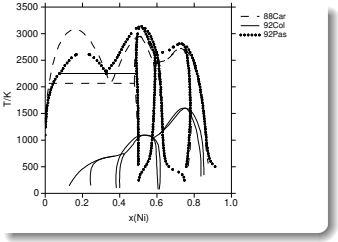
Interstitial and metallic ordering

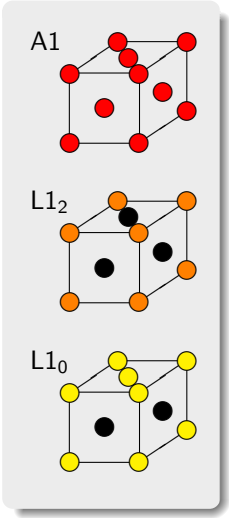
Conclusion

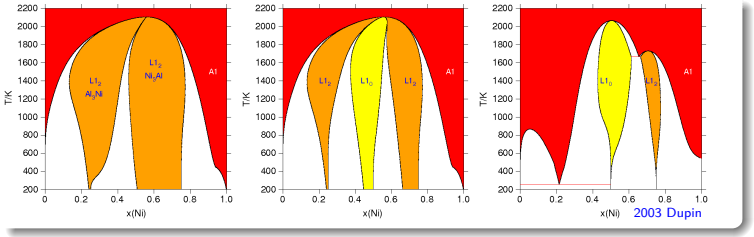
A1/L12 modelling



1997 Ansara







2003 Dupin

Outline

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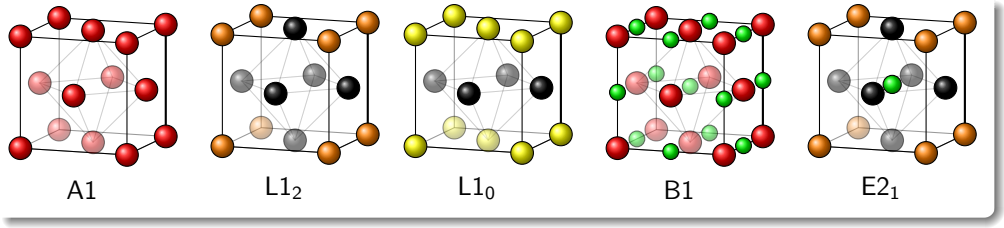
Interstitials

Metallic ordering

Interstitial and metallic ordering

Conclusion

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.

Take home

The knowledge of the crystallography of the phases is key for their 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 assessment of the parameters can be tremendously simplified by the use of DFT estimates for metastable configurations.