A value for empty bcc in the Calphad approach

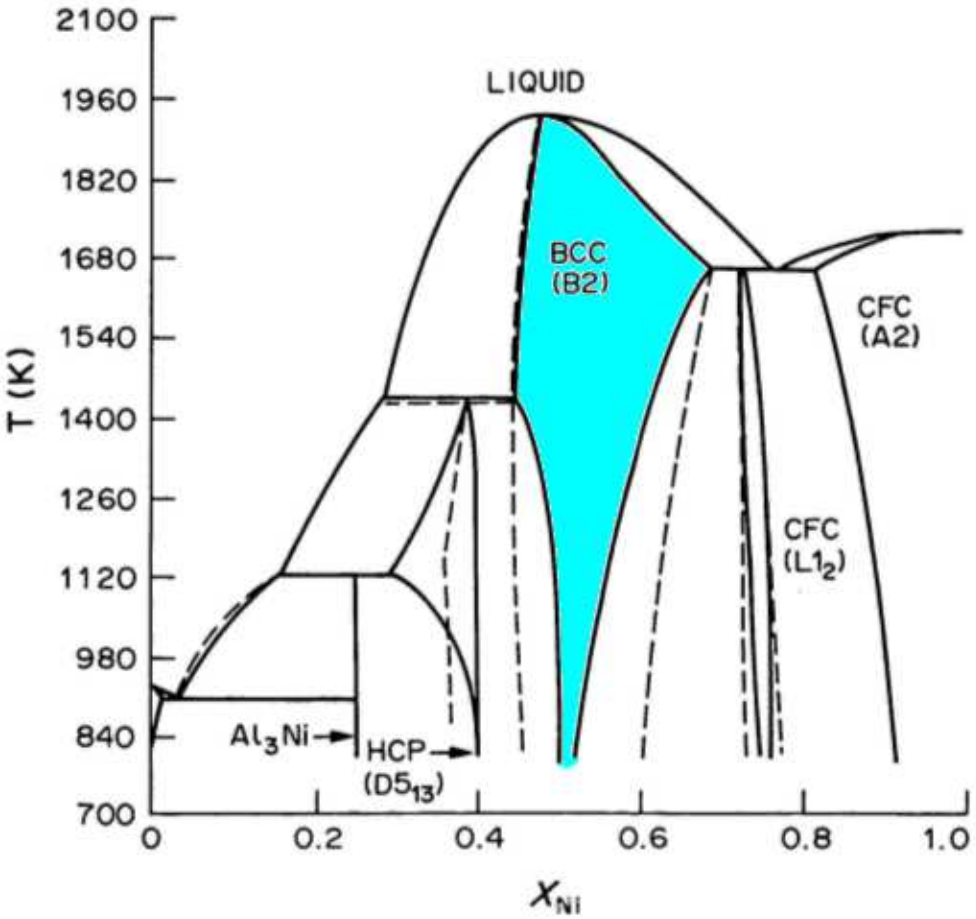
Nathalie Dupin

Calcul Thermodynamique

2016 May 29 - June 3 Awaji Island Calphad XLV

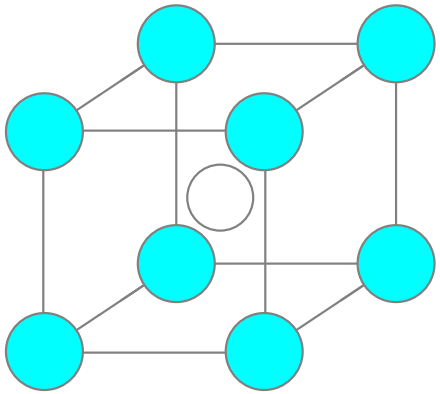
AlNi first B2 CEF description

I. Ansara et al. Acta metall. (1988) 36:977-982



B2 StrukturBericht

CsCl Prototype

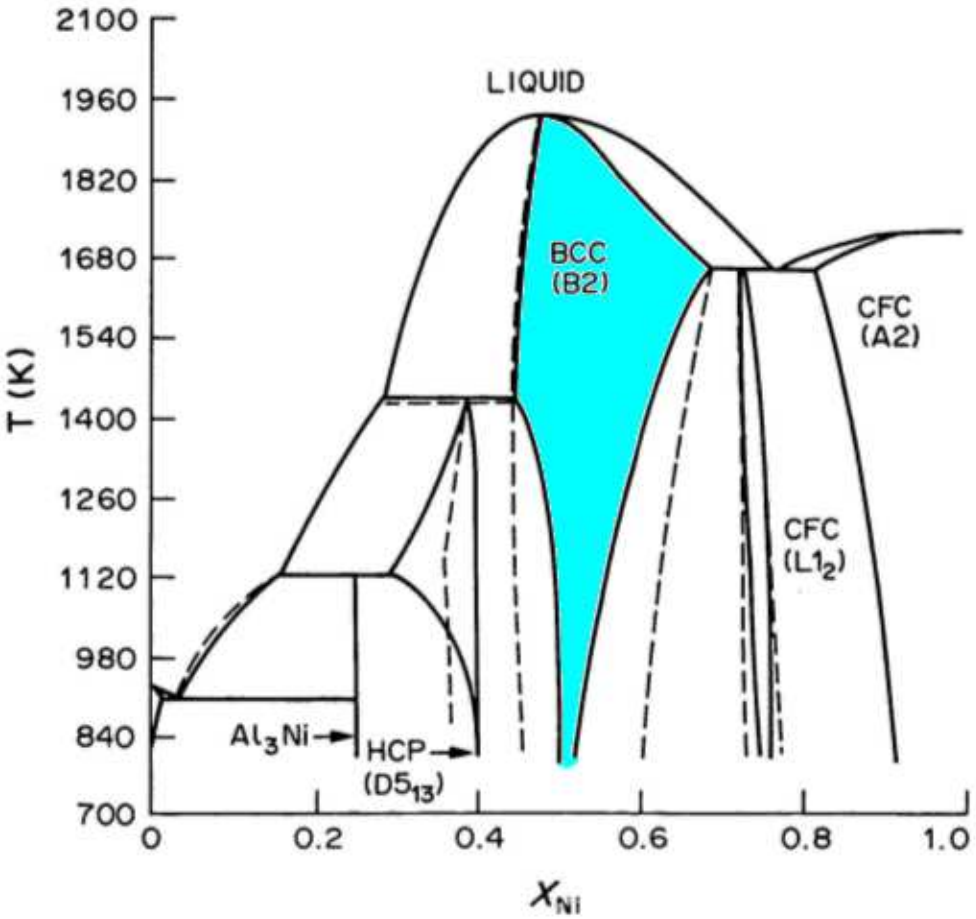


modelled

(Al,Ni)(Ni,Va)

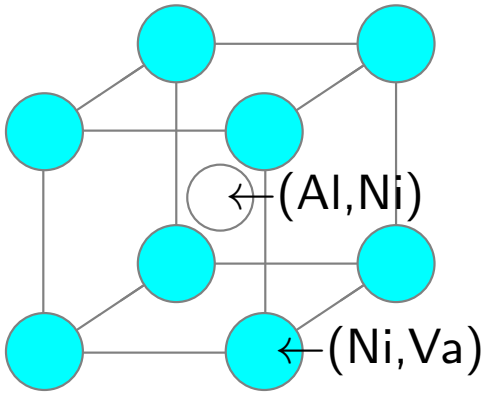
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B2 StrukturBericht

CsCl Prototype

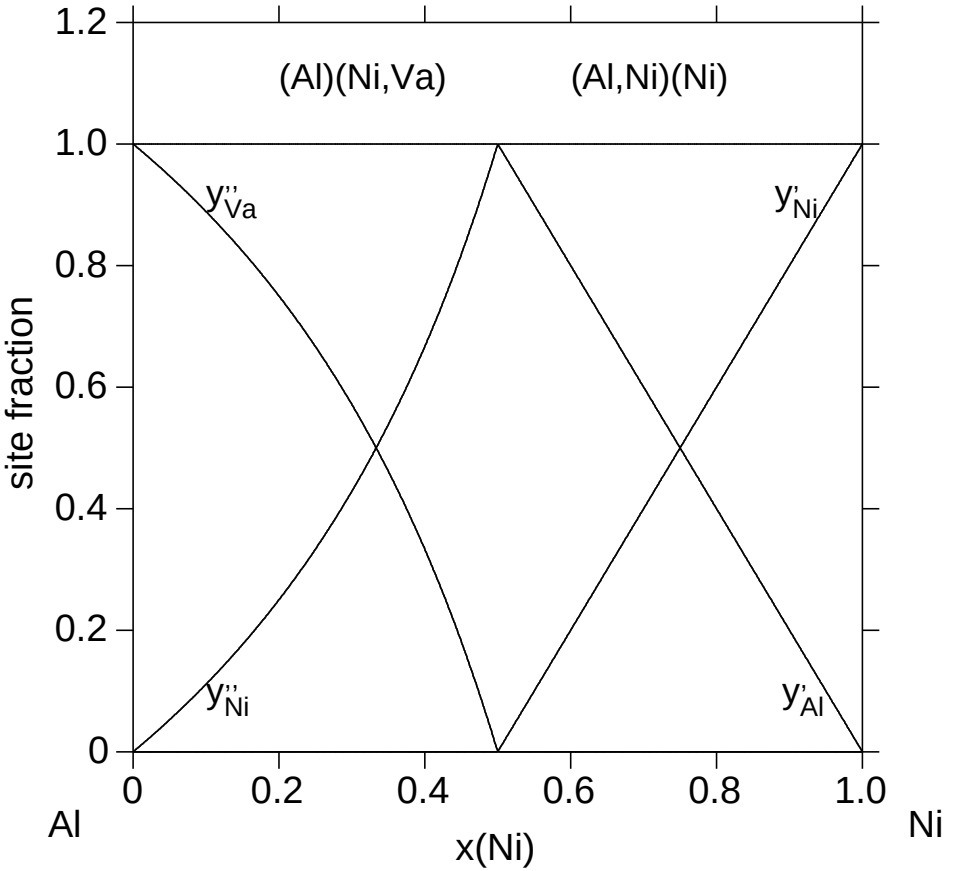


modelled

(Al,Ni)(Ni,Va)

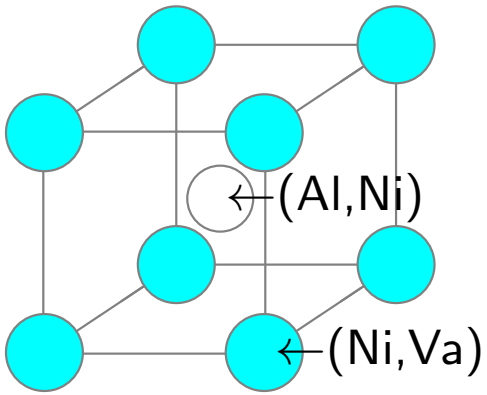
AlNi first B2 CEF description

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B2 StrukturBericht

CsCl Prototype



modelled

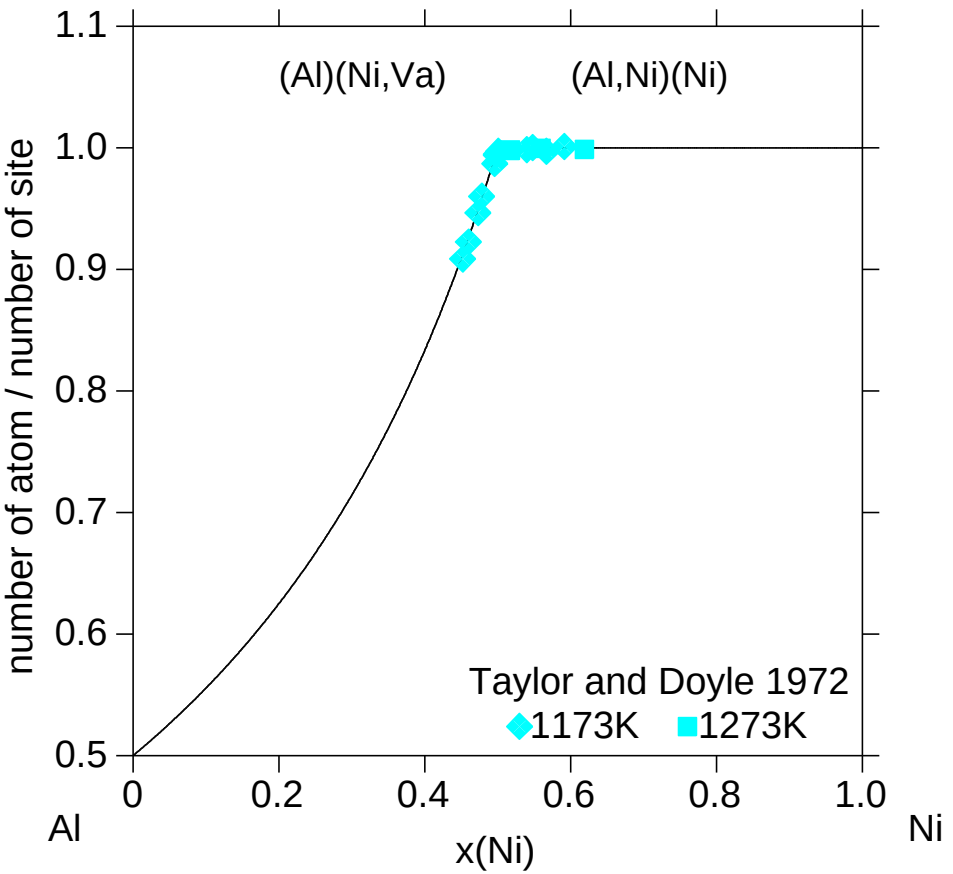
(Al,Ni)(Ni,Va)

$G^{B2}_{Al:Va} = G^{bcc}_{Al} + 10000 - T, \quad G^{B2}_{Ni:Ni} = 2G^{bcc}_{Ni}, \quad G^{B2}_{Ni:Va} = -G^{B2}_{Al:Ni} + G^{B2}_{Ni:Ni} + G^{B2}_{Al:Va}$

optimised parameters: $G^{B2}_{Al:Ni}$, $L^{B2}_{Al,Ni:Ni} = L^{B2}_{Al,Ni:Va}, L^{B2}_{Al:Ni,Va} = L^{B2}_{Ni:Ni,Va}$

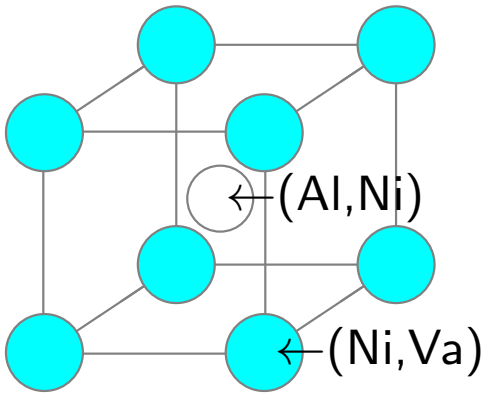
AlNi first B2 CEF description

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B2 StrukturBericht

CsCl Prototype



modelled

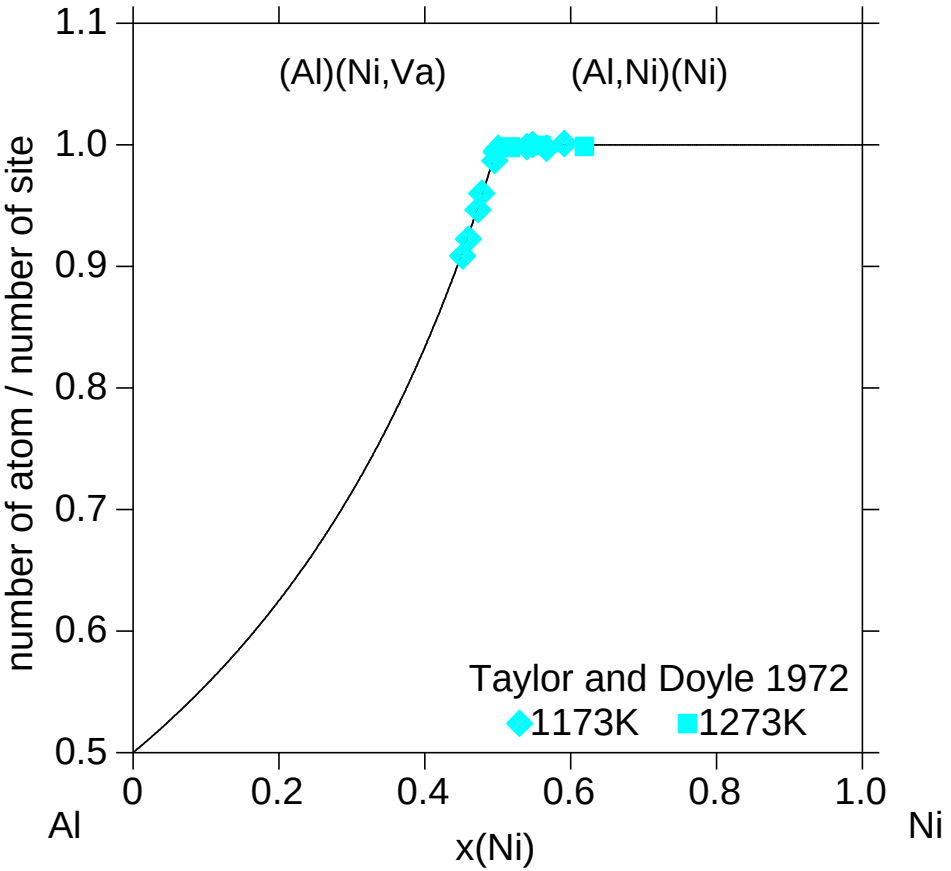
(Al,Ni)(Ni,Va)

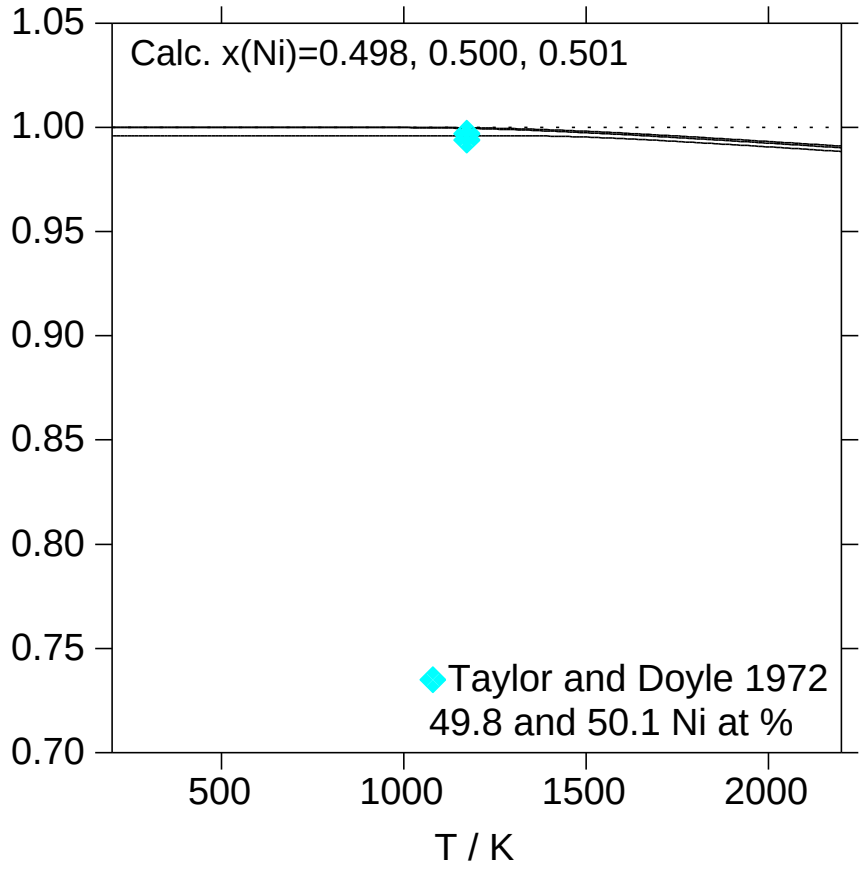
$$G^{B2}_{Al:Va} = G^{bcc}_{Al} + 10000 - T, \quad G^{B2}_{Ni:Ni} = 2G^{bcc}_{Ni}, \quad G^{B2}_{Ni:Va} = -G^{B2}_{Al:Ni} + G^{B2}_{Ni:Ni} + G^{B2}_{Al:Va}$$

optimised parameters: $G^{B2}_{Al:Ni}$, $L^{B2}_{Al,Ni:Ni} = L^{B2}_{Al,Ni:Va}, L^{B2}_{Al:Ni,Va} = L^{B2}_{Ni:Ni,Va}$

AlNi first B2 CEF description

I. Ansara et al. Acta metall. (1988) 36:977-982



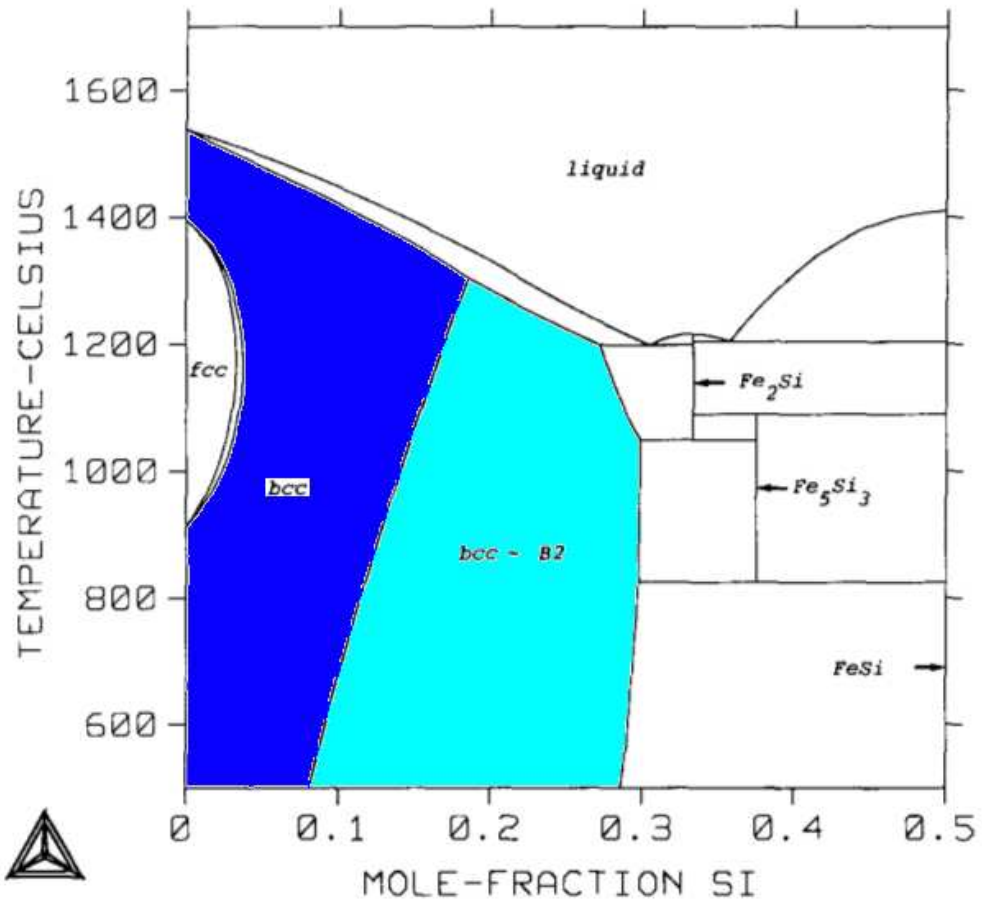


$G^{B2}_{Al:Va} = G^{bcc}_{Al} + 10000 - T, \quad G^{B2}_{Ni:Ni} = 2G^{bcc}_{Ni}, \quad G^{B2}_{Ni:Va} = -G^{B2}_{Al:Ni} + G^{B2}_{Ni:Ni} + G^{B2}_{Al:Va}$

optimised parameters: $G^{B2}_{Al:Ni}$, $L^{B2}_{Al,Ni:Ni} = L^{B2}_{Al,Ni:Va}, L^{B2}_{Al:Ni,Va} = L^{B2}_{Ni:Ni,Va}$

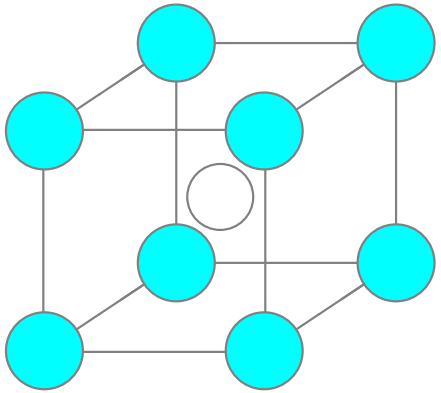
FeSi first A2/B2 CEF description

J. Lacaze et al. Met. Trans. A (1991) 22:1991-2211



B2 StrukturBericht

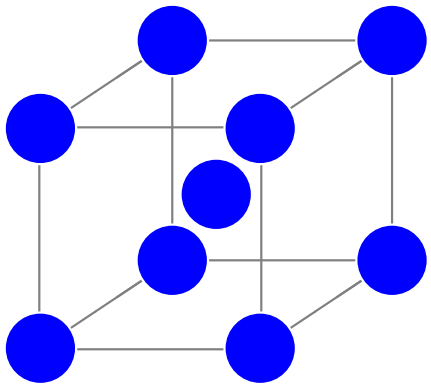
CsCl Prototype



modelled

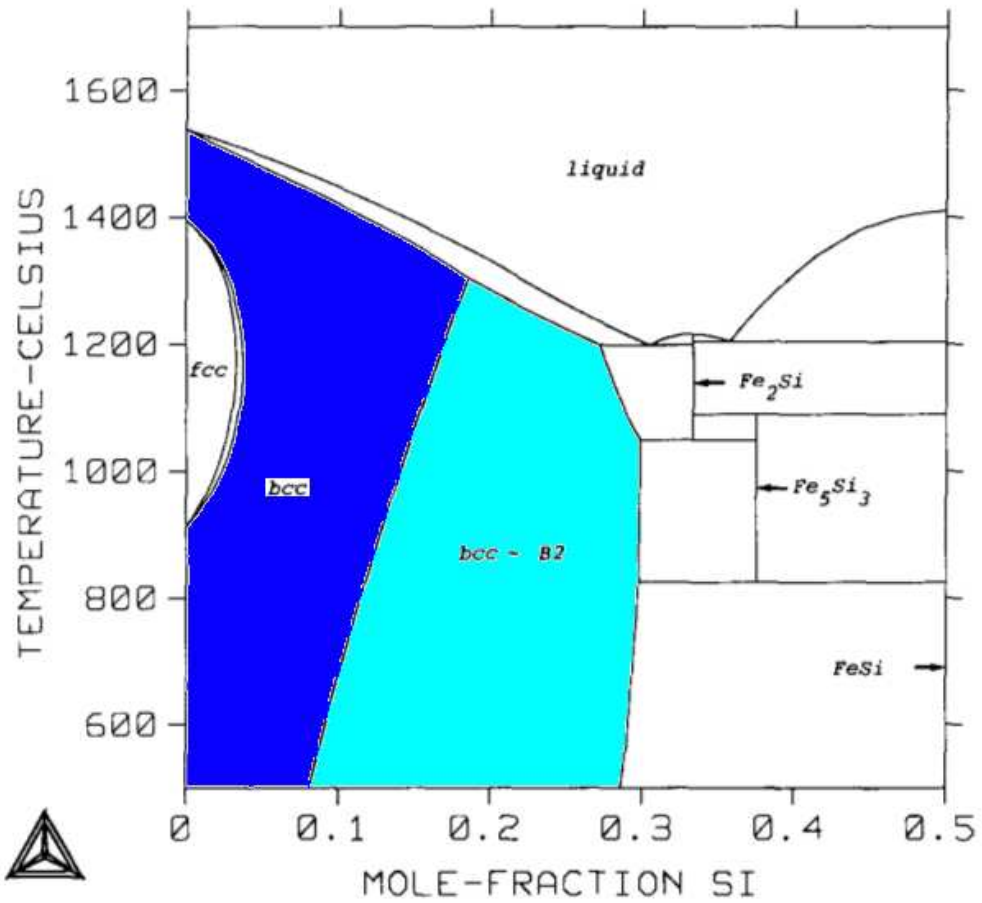
(Fe,Si)(Fe,Si)

disordering in A2



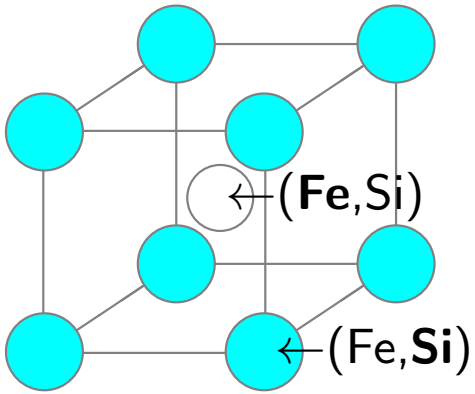
FeSi first A2/B2 CEF description

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B2 StrukturBericht

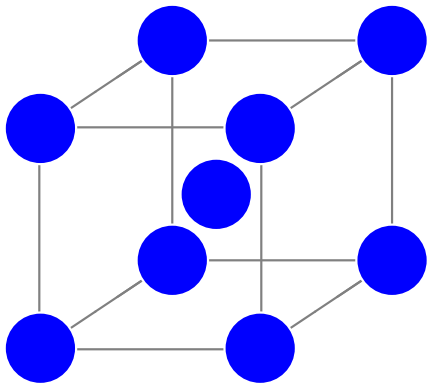
CsCl Prototype



modelled

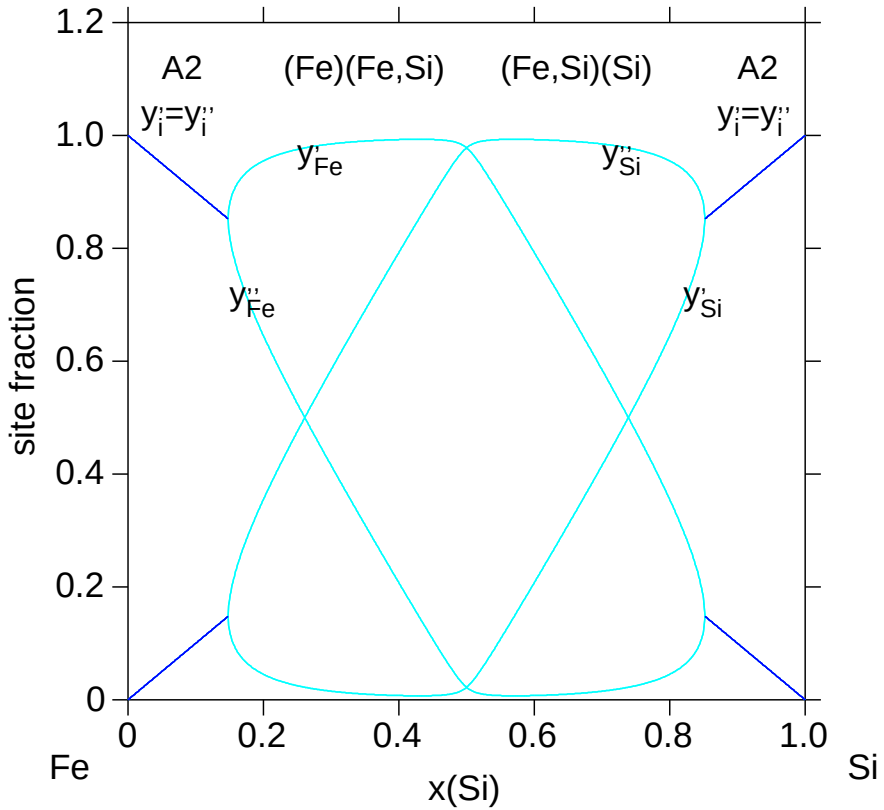
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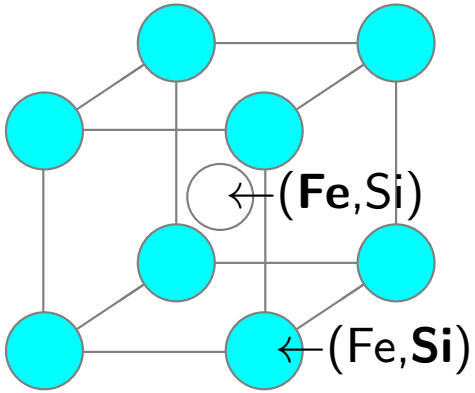
FeSi first A2/B2 CEF description

J. Lacaze et al. Met. Trans. A (1991) 22:1991-2211

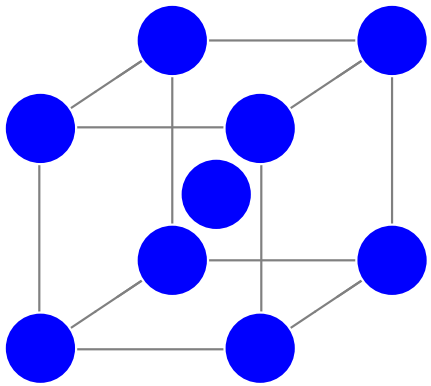


B2 StrukturBericht

CsCl Prototype



modelled (Fe,Si)(Fe,Si) disordering in A2



$$G_i^{B2} = 2G_i^{bcc}, \qquad G_{i:j}^{B2} = G_{j:j}^{B2}, \qquad L_{i,j:k}^{B2} = L_{k:i,j}^{B2}$$

General multicomponent B2 CEF description

A model able to describe the metallic B2 phases on a wide multicomponent range should be able to describe

- the triple defects exhibited by AlNi for instance and
- the second order transition with the A2 like in Fe-Si.

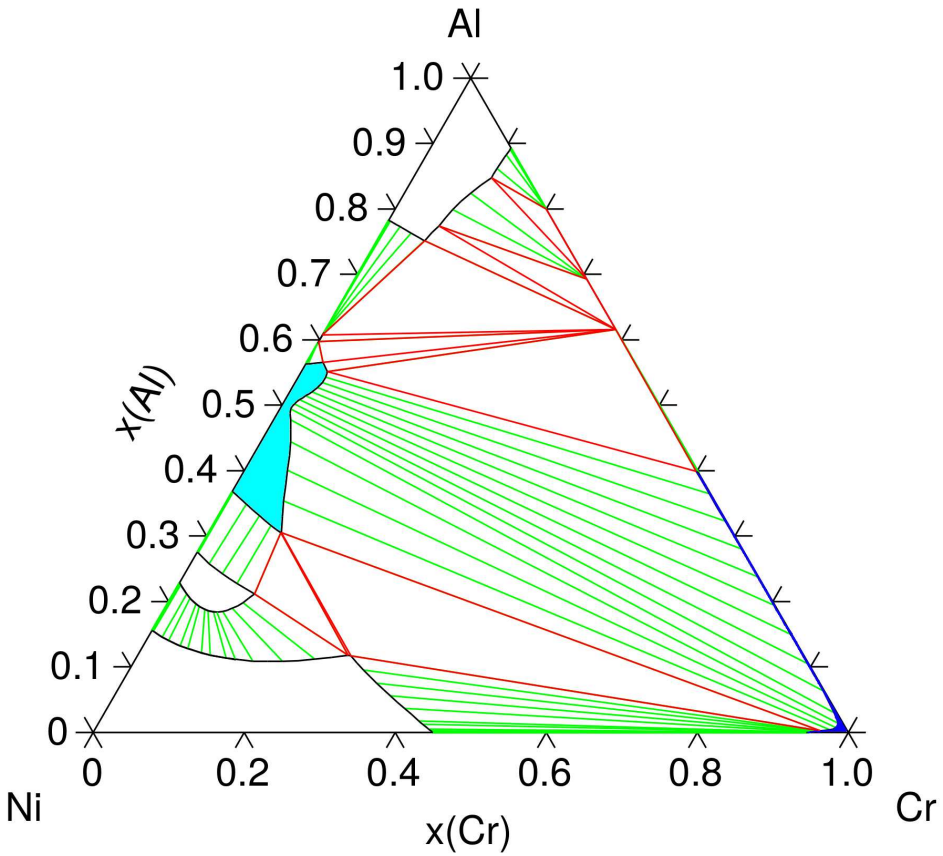
$$\Rightarrow \text{(A,B,...,Va)(A,B,...,Va)}$$

inducing to assess a parameter $G^{B2}_{Va:Va}$

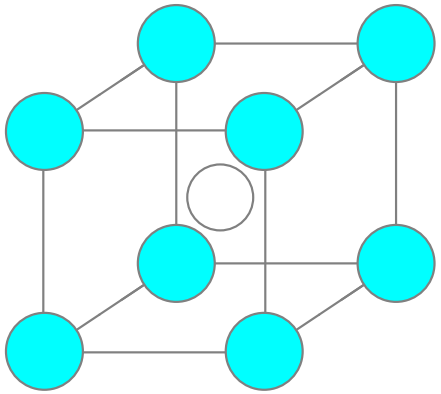
corresponding to the Gibbs energy of the empty bcc lattice.

Al-Cr-Ni first ternary symmetrical CEF description

N. Dupin et al. Calphad (2001) 25:279-298



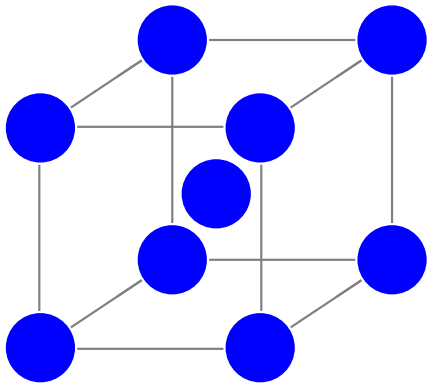
B2



modelled

(Al,Cr,Ni,Va)(Al,Cr,Ni,Va)

disordering in A2



Al-Cr-Ni first ternary symmetrical CEF description

N. Dupin et al. Calphad (2001) 25:279-298

$$G = G^{bcc}(x) + \Delta G^{B2}(y)$$

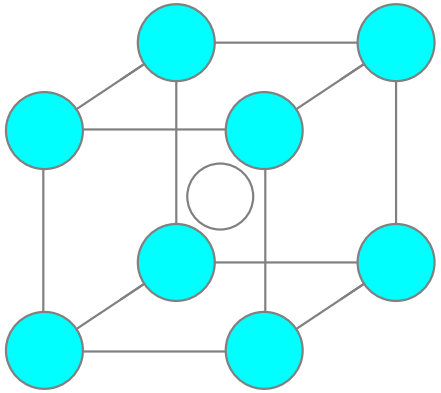
with $\Delta G^{B2}(y) = 0$ when $y_i' = y_i'' = x_i$

$\rightsquigarrow G^{bcc}_{Va} = 0$

$\rightsquigarrow L^{bcc}_{Ni,Va}$ and $L^{bcc}_{Al,Va}$ from mathematical equivalence to the previous B2 CEF

$\rightsquigarrow L^{bcc}_{Cr,Va}$ big

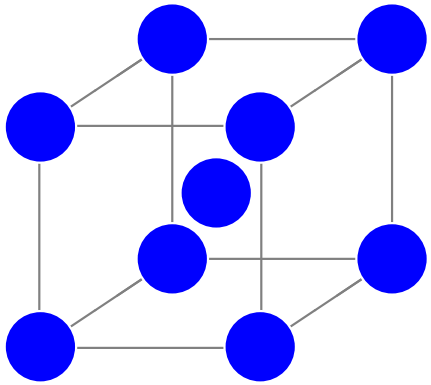
B2



modelled

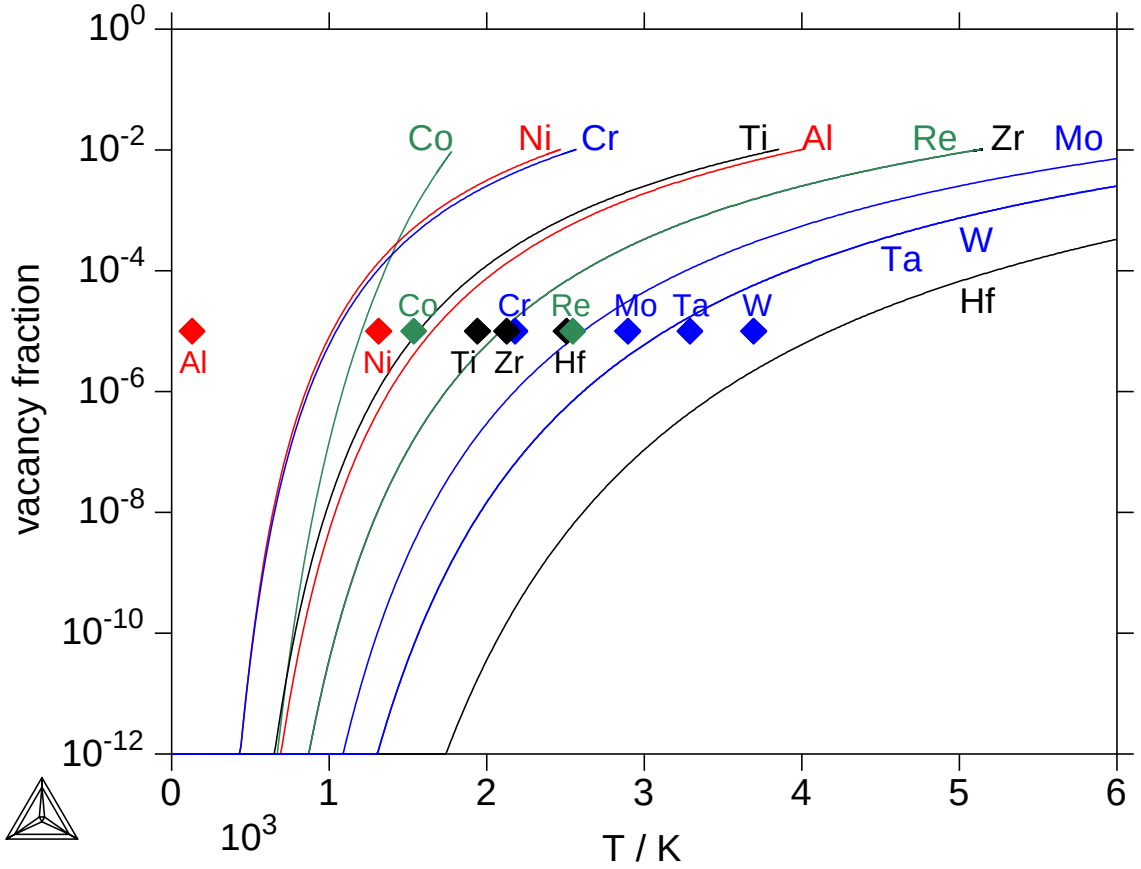
(Al,Cr,Ni,Va)(Al,Cr,Ni,Va)

disordering in A2



Va in pure bcc elements

N. Dupin, NI13-2003 based on Al-Cr-Ni 2001 ($G_{Va}^{bcc} = 0$)



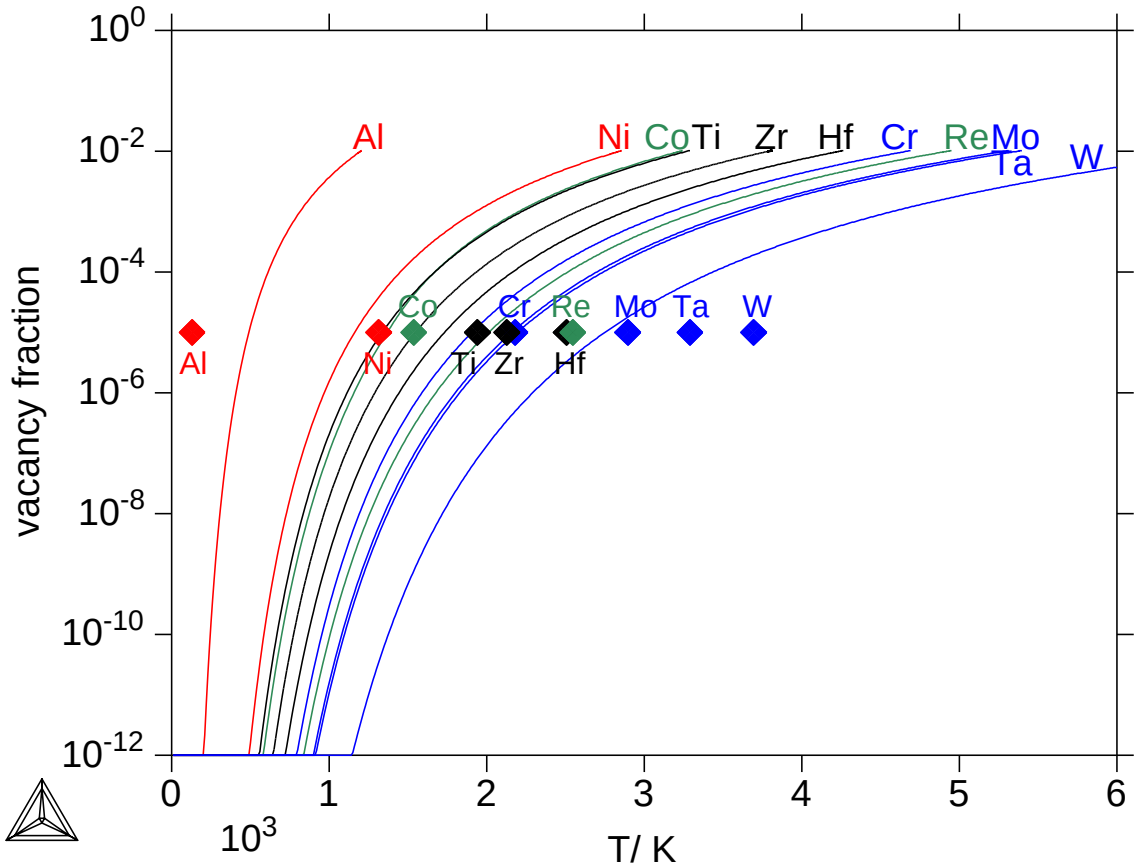
◇ indicate the bcc melting temperature

- Instability for 10^{-2} Va
- Amount of Va / melting temperature not reasonable
- High amount of Va in Cr $\Rightarrow \Delta T^{melt.} = 8K$

$\Rightarrow$ bad $L_{i,Va}^{bcc}$!

Va in pure bcc elements

N. Dupin, NI13-2006 using DFT sc/bcc for $L^{bcc}_{i,Va}$ ($G^{bcc}_{Va} = 0$)



$$L^{bcc}_{i,Va} = 2\,(E^{sc}_{i} - E^{bcc}_{i})$$

with E^{φ}_{i} from VASP in kJ/mol
XiaoGang Lu private 2003/09/29

- Reasonnable order for the amount of Va / melting temperature
- High amount of Va $\Rightarrow \Delta T^{melt.} > 0.1K$ for Ti, Zr, Hf, Re, Mo, Ta, W
- Instability for 10^{-2} Va

Substitutional solution of Va

$$G = y_A G_A + y_{Va} G_{Va} + G^{id} + y_A\, y_{Va}\, L_{A,Va}$$

Substitutional solution of Va

$$G = y_A G_A + y_{Va} G_{Va} + G^{id} + y_A\, y_{Va}\, L_{A,Va}$$

$$\Delta G/site = y_{Va} G_{Va} + G^{id} + y_A\, y_{Va}\, L_{A,Va}$$

Substitutional solution of Va

$$G = y_A G_A + y_{Va} G_{Va} + G^{id} + y_A\, y_{Va}\, L_{A,Va}$$

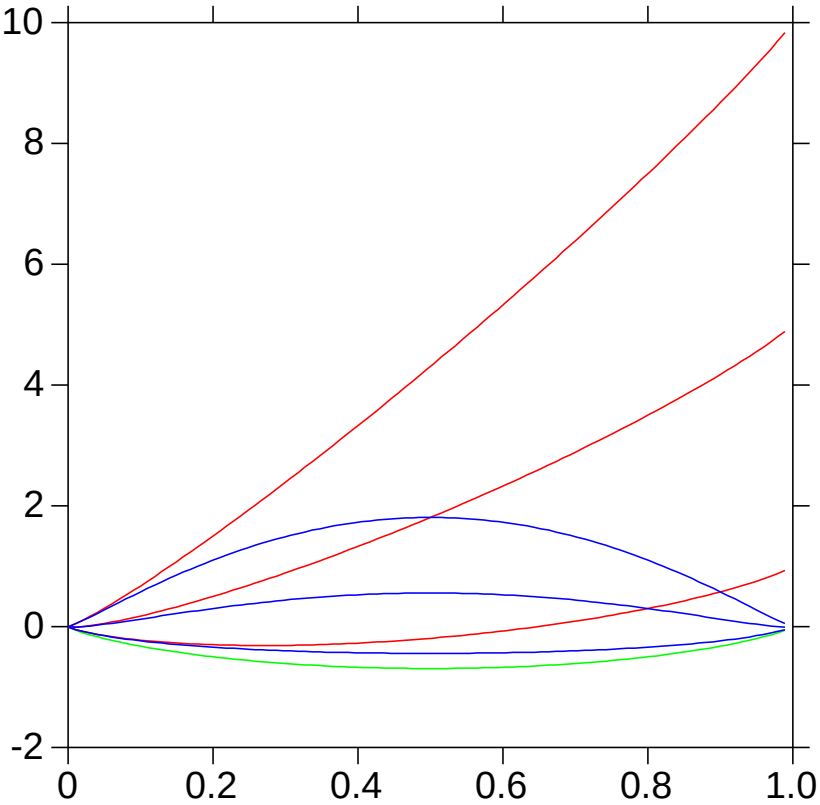
$$\Delta G/site = y_{Va} G_{Va} + G^{id} + y_A\, y_{Va}\, L_{A,Va} \qquad \Delta G/atom = y_{Va}/y_A G_{Va} + G^{id}/y_A + y_{Va}\, L_{A,Va}$$

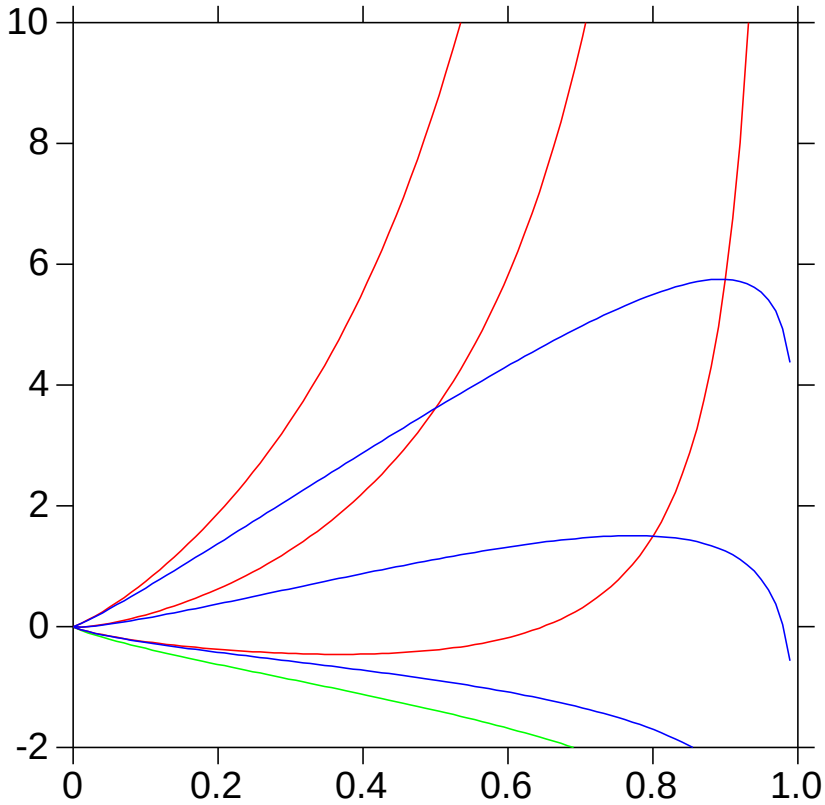
Substitutional solution of Va

$$G = y_A G_A + y_{Va} G_{Va} + G^{id} + y_A\, y_{Va}\, L_{A,Va}$$

$$\Delta G/site = y_{Va} G_{Va} + G^{id} + y_A\, y_{Va}\, L_{A,Va}$$

$$\Delta G/atom = y_{Va}/y_A\, G_{Va} + G^{id}/y_A + y_{Va}\, L_{A,Va}$$

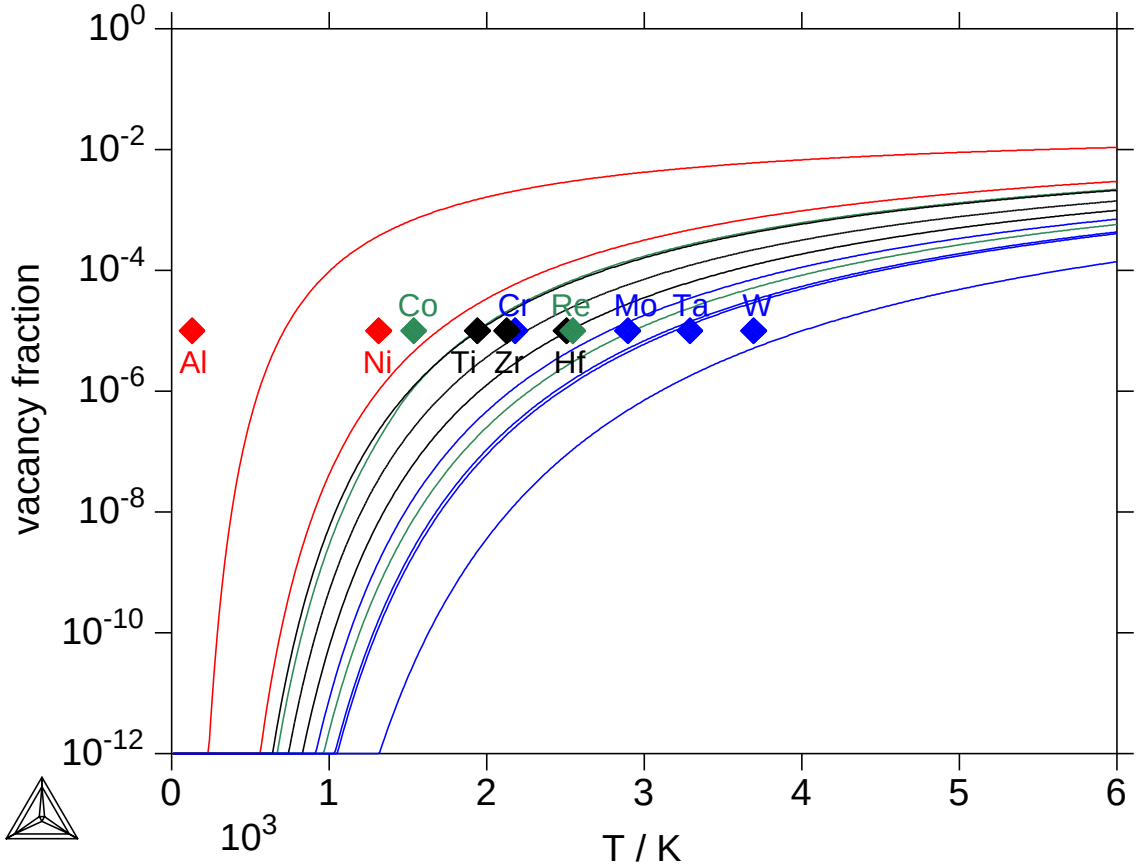




$G_{Va} = 0$ is responsible for instability

Va in pure bcc elements

Assessing G^{bcc}_{Va} using DFT sc/bcc for $L^{bcc}_{i,Va}$



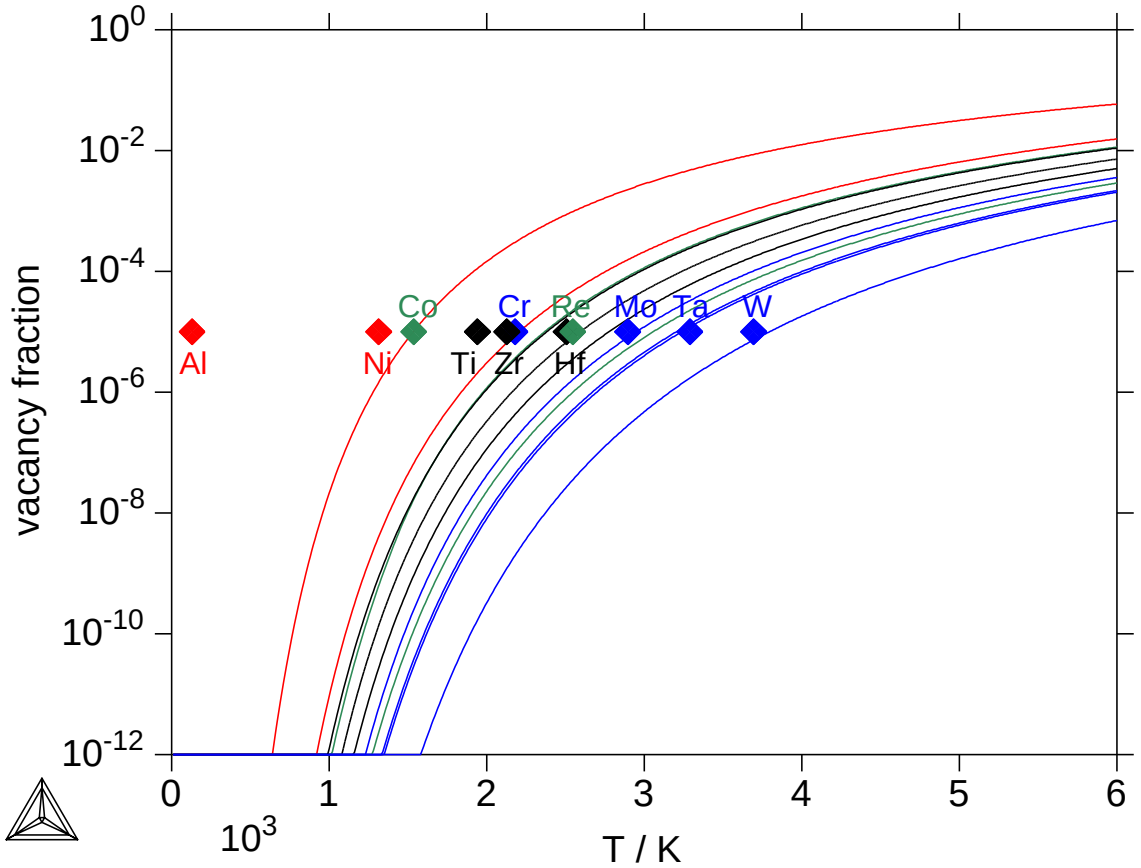
- No more instability
- Amount of Va close to 10^{-5} at $T^{melt.}$

$\Rightarrow G^{bcc}_{Va} = 30\,T$

$\rightsquigarrow$ used since in TCNI
$\rightsquigarrow$ H.L. Lukas et al., Computational Thermodynamics, IBSN 978-0-521-86811-2
$\rightsquigarrow$ A. Dinsdale et al., Mat. Sc. Tech., 30 (2014) 1715-18
$\rightsquigarrow$ used in several published binary or ternary assessments

Va in pure bcc elements

$G_{Va}^{bcc} = 100000$ and DFT sc/bcc for $L_{i,Va}^{bcc}$

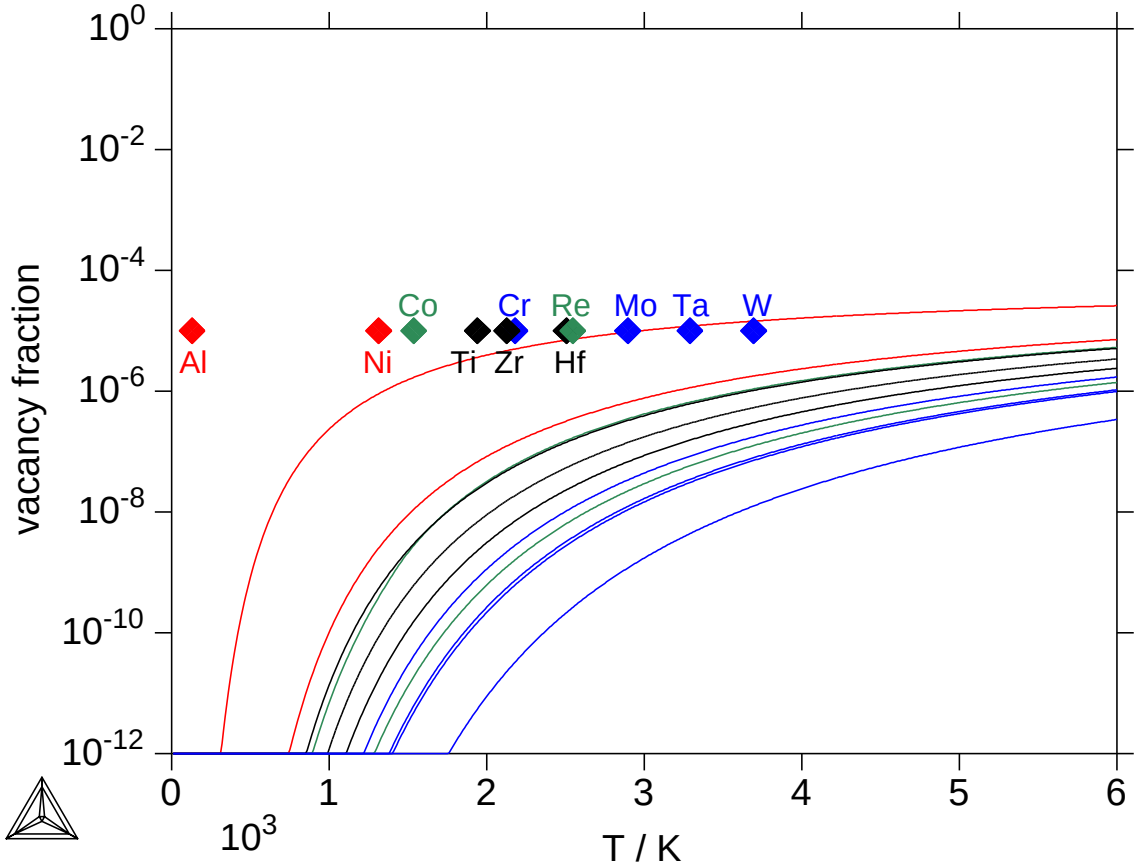


- No stability problem
- Very low amount of Va for low melting elements

$G_{Va}^{bcc} = 100000$ used in different works

Va in pure bcc elements

$G_{Va}^{bcc} = 80\,T$ and DFT sc/bcc for $L_{i,Va}^{bcc}$

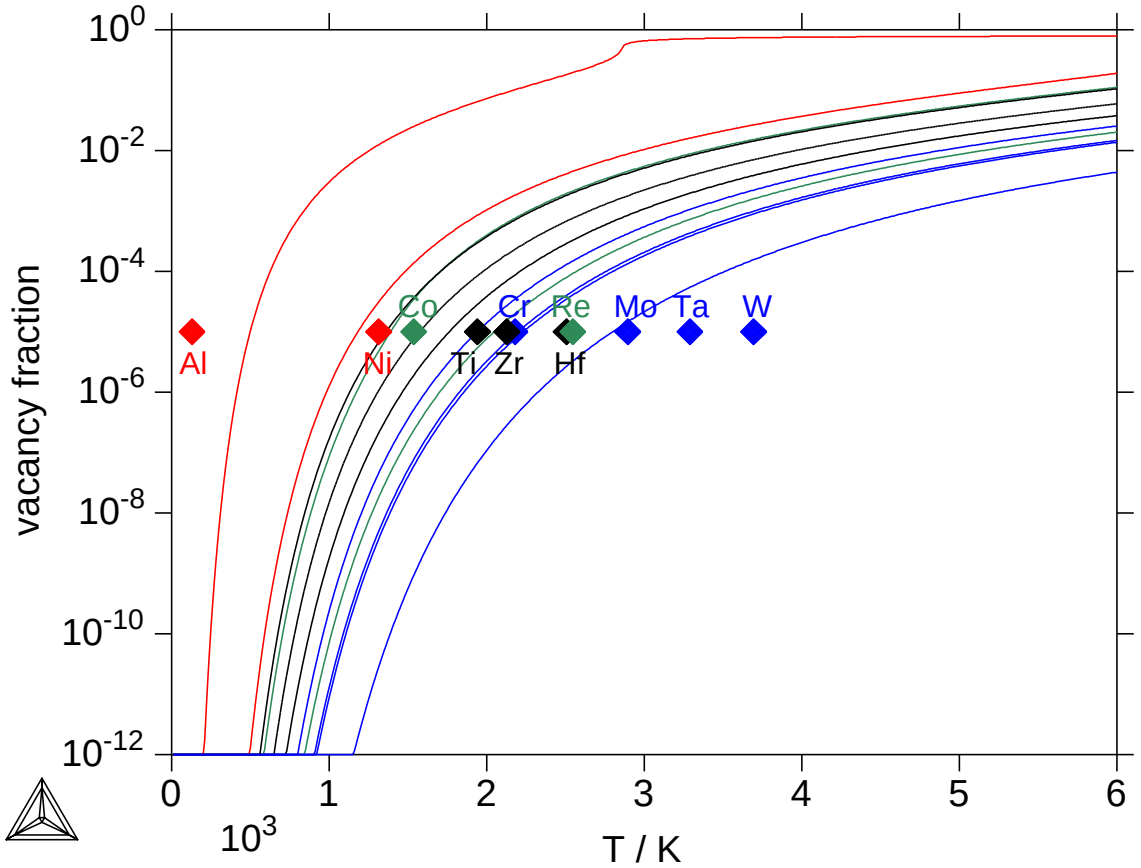


- No stability problem
- Very low Va amount

$G_{Va}^{bcc} = 80\,T$ used in different works

Va in pure bcc elements

$G_{Va}^{bcc} = 0.2RT$ and DFT sc/bcc for $L_{i,Va}^{bcc}$

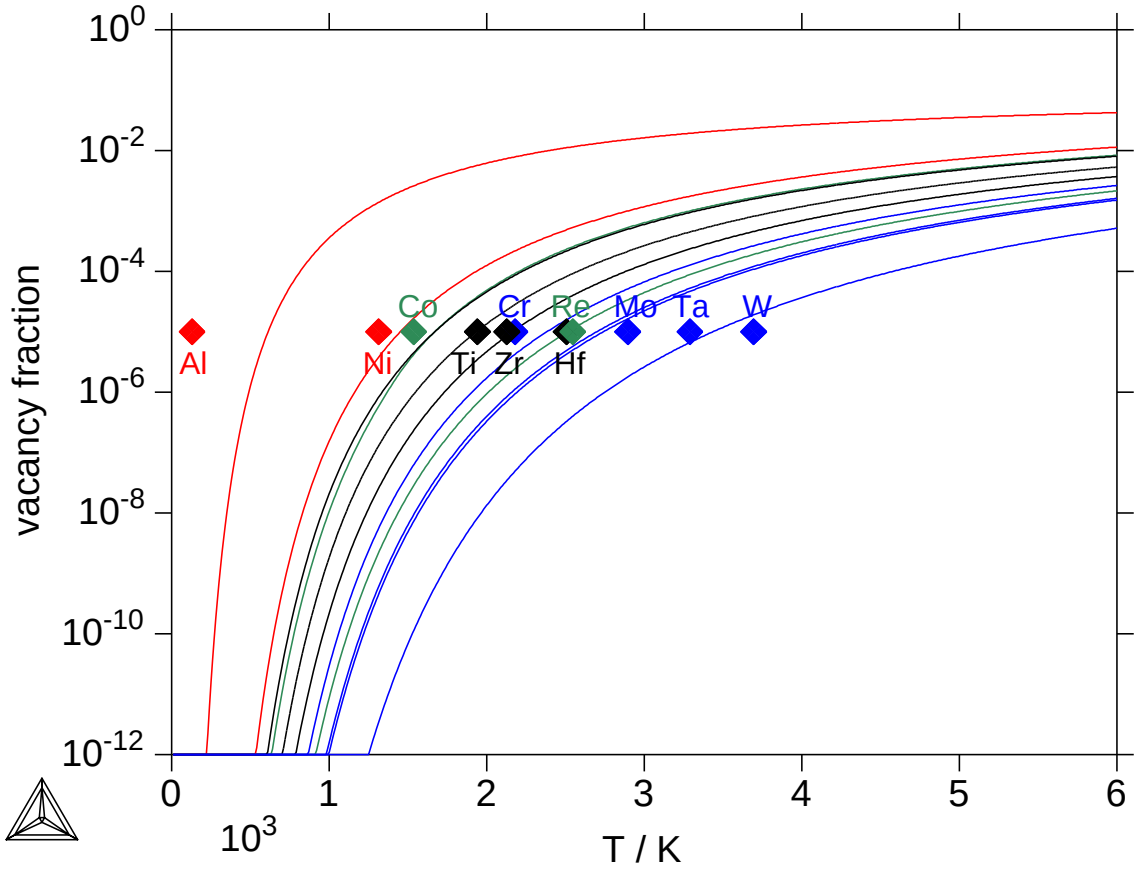


- Instability not far for low melting T elements
- Higher amount of Va $\Rightarrow L_{i,Va}^{bcc}$ to be modified

$G_{Va}^{bcc} = 0.2RT$ proposed by
P. Franke J. Ph. Eq. Diff. 35 780-87 (2014)

Va in pure bcc elements

$G_{Va}^{bcc} = 2.3RT$ and DFT sc/bcc for $L_{i,Va}^{bcc}$

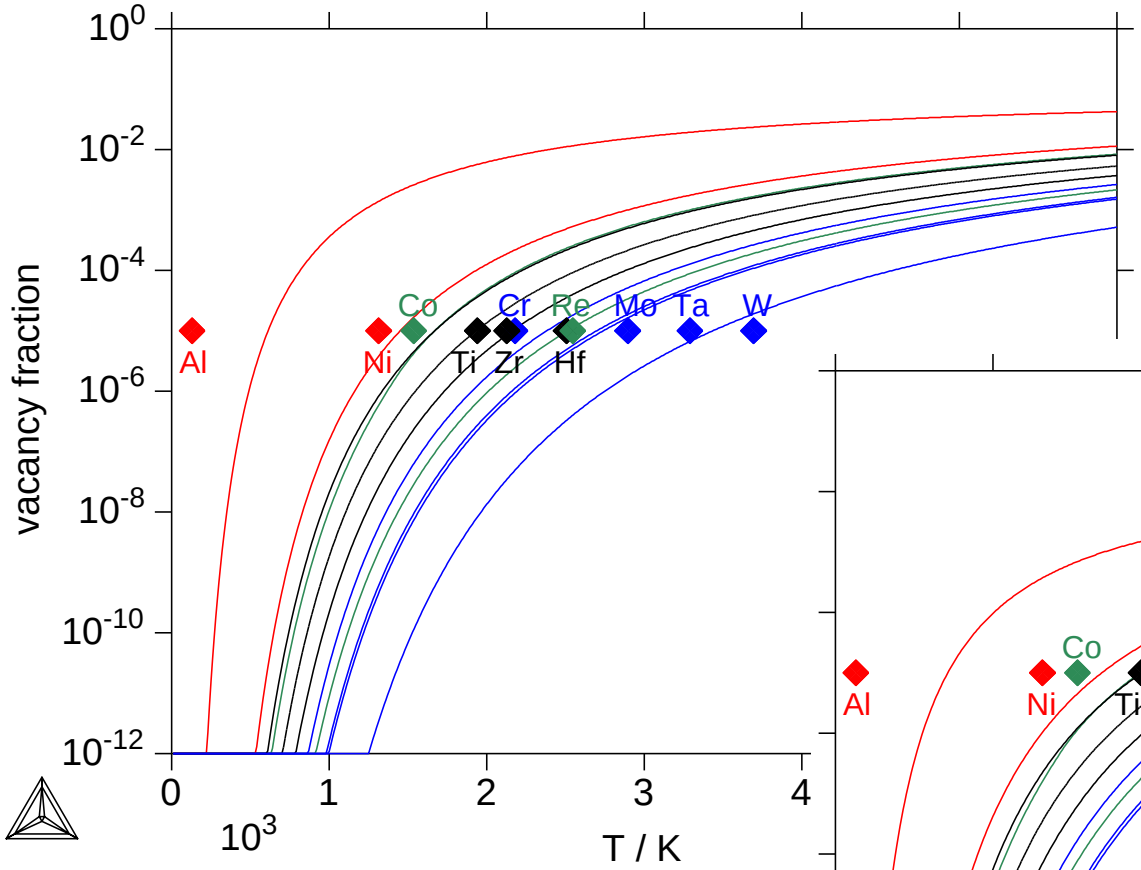


- Very close to $G_{Va}^{bcc} = 30\,T$

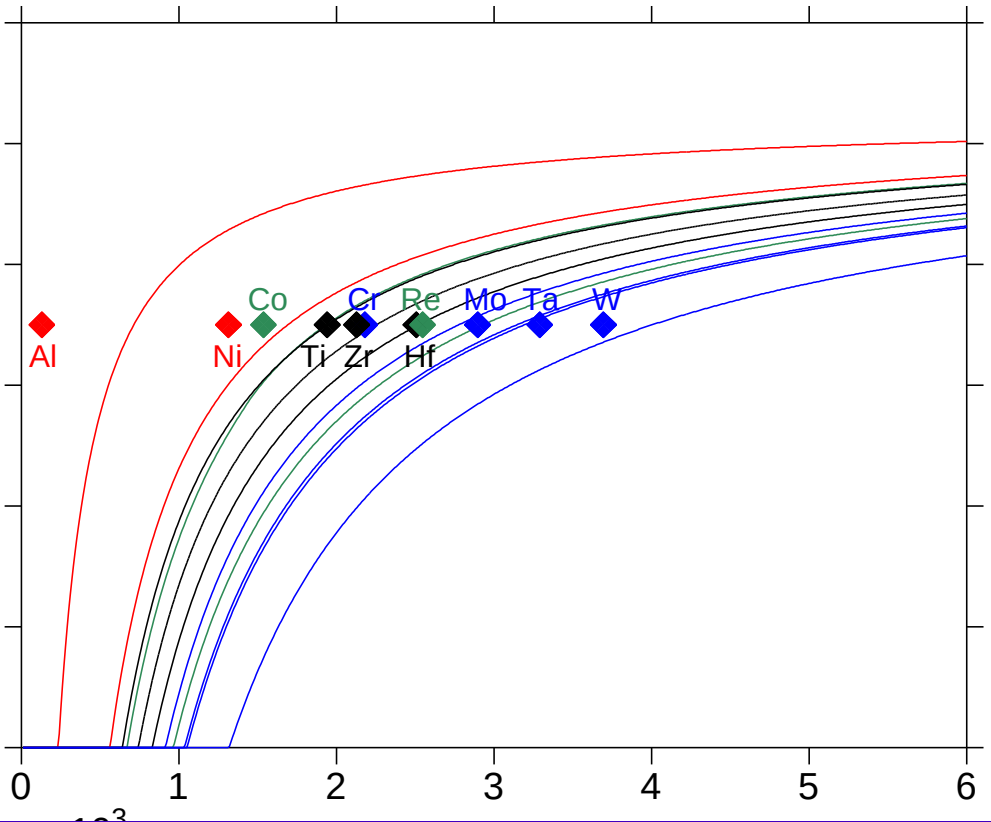
$G_{Va}^{bcc} = 2.3RT$ recommended by
Rogal et al. Phys. Status Solidi B 251 97-129 (2014)

Va in pure bcc elements

$G_{Va}^{bcc} = 2.3RT$ and DFT sc/bcc for $L_{i,Va}^{bcc}$



- Very close to $G_{Va}^{bcc} = 30\,T$



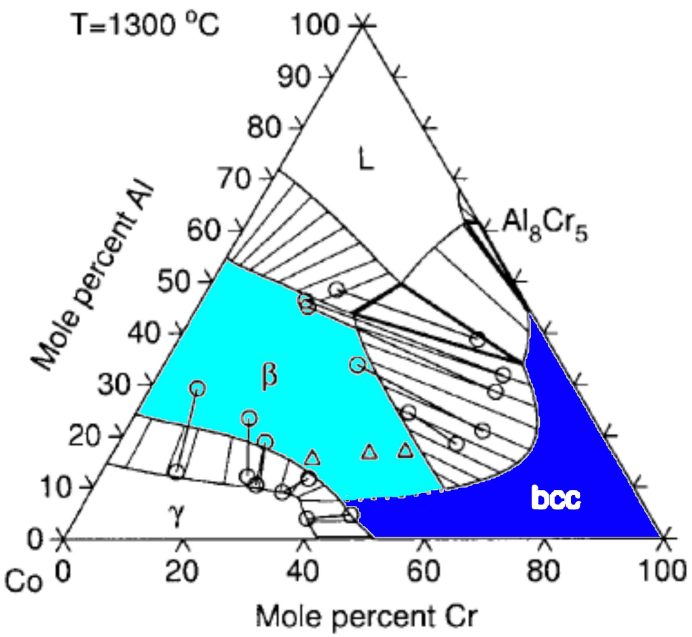
$G_{Va}^{bcc} = 2.3RT$ recommende
Rogal et al. Phys. Status S

Discussion

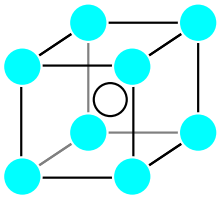
- $G_{Va}^{bcc} = 30\,T$ recommended for bcc when using the current SGTE description of the pure elements.
- There is no reason to use the same value for other phases. A similar derivation could be followed for each, using a partially empty configuration meaningful for the structure.
- Better estimated of the $L_{i,Va}^{\varphi}$ parameters could be reached from FP using several configurations with more dilute Va.
- The actual amount of vacancies should be taken into account in the next generation description of pure elements. Experimental amount of vacancy should be used for that. FP can help when they miss in particular for metastable states.

What does bring coupling B2 and A2 descriptions?

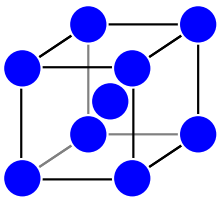
T. Gómes-Acebo et al. JPEDAV (2004) 25:237-251

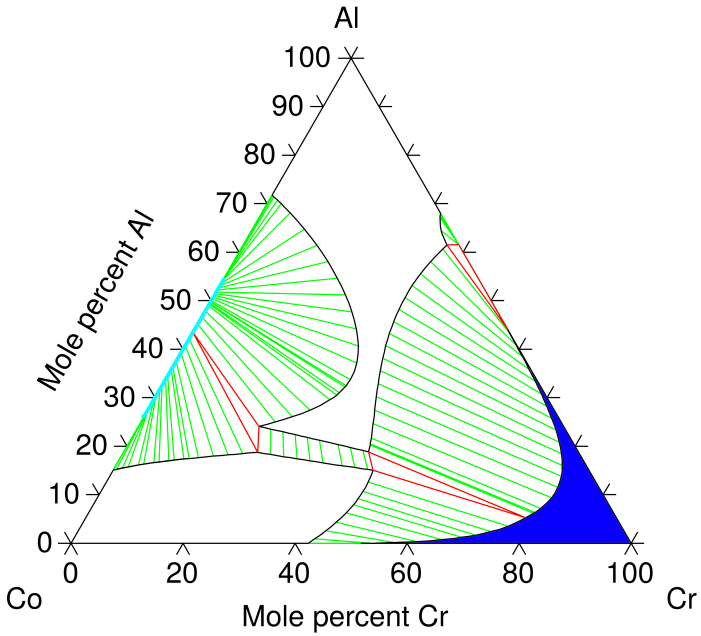


B2(β)



A2(bcc)



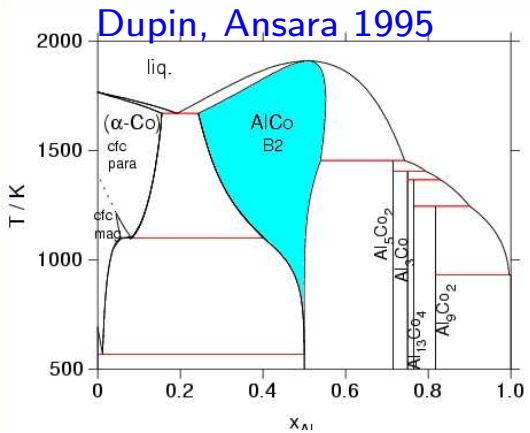


exp.: Ishikawa et al. *Ber.Bun/Phys.Chem.* **102** 1206 (1998)

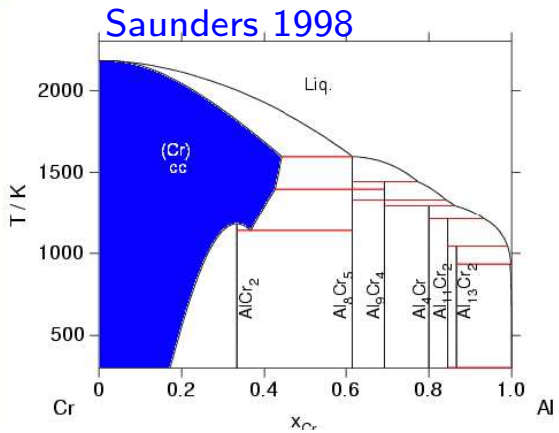
B2: (Al,Co)(Co,Va)
A2: (Al,Co,Cr)

TCNI: B2 and A2: (Al,Co,Cr,Va)(Al,Co,Cr,Va)

Dupin, Ansara 1995



Saunders 1998



Kussofsky, Jansson 1997

