THE EFFECTIVE BOND ENERGY FORMALISM

Nathalie Dupin

Calcul Thermodynamique
nathdupin@cthermo.fr

Ackownledgements to Bo Sundman, Ursula R. Kattner, Suzana G. Fries, Mauro Palumbo, Jean-Claude Crivello, Thomas Hammerschmidt, Daniela Ivanova, Júlio César Pereira dos Santos, Olivier Dezellus, Christine Guéneau

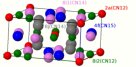
TOFA 2024 Lyon

2024.09.26

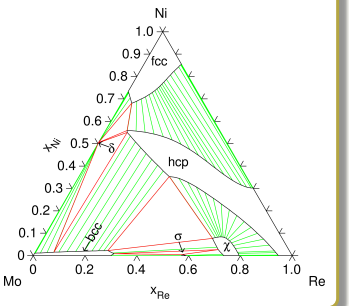
Outline

- ⇝ Appealing results for the sigma phase
- ⇝ The formalism
- ⇝ Applying EBEF to the mu phase
- ⇝ Summary

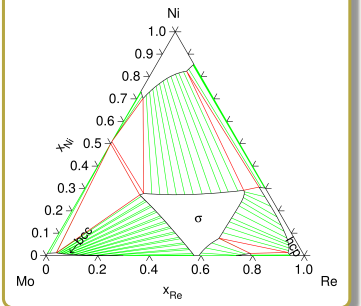
Describing σ phase with 5SL in Mo-Ni-Re



σ CEF using 93 DFT results (elements and binary)

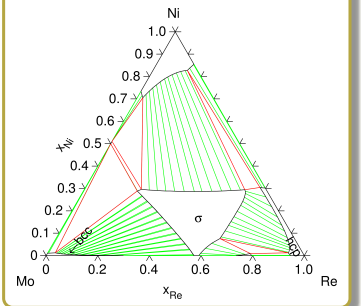


σ CEF using 243 DFT results (elements, binary and ternary)



If 10 elements, 10^5 DFT results needed!

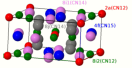
σ EBEF using 93 DFT results (elements and binary)



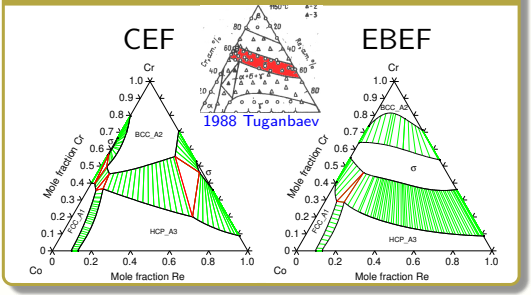
If 10 elements, 1360 DFT results needed

2018 - Implementation of the Effective Bond Energy Formalism in the Multicomponent Calphad Approach, Dupin, Kattner, Sundman, Palumbo, Fries, https://doi.org/10.6028/jres.123.020

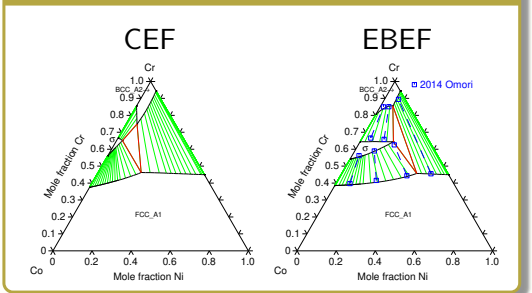
Describing σ phase with 5SL



Co-Cr-Re @ 1150°C without ternary parameters



Co-Cr-Ni @ 1000°C without ternary parameters



Ability to extrapolate from only binary information confirmed with different phase diagram topologies

2023 Applying the Effective Bond Energy Formalism (EBEF) to Describe (σ) the Sigma Phase in the Co-Cr-Ni-Re System, J. Pereira dos Santos *et al.* https://doi.org/10.1007/s11669-023-01079-3

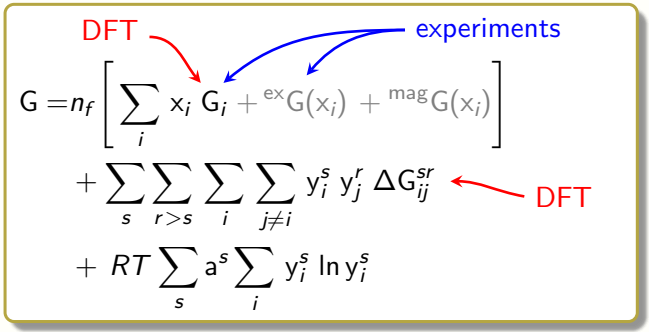
The formalism

DFT

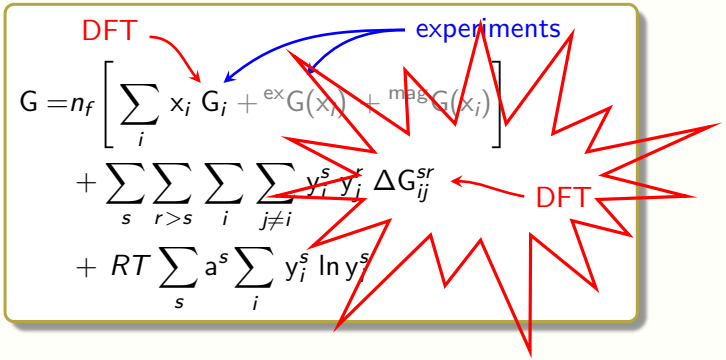
$$G = n_f \left[\sum_i x_i \, G_i + {}^{ex}G(x_i) + {}^{mag}G(x_i) \right]$$
$$+ \sum_s \sum_{r>s} \sum_i \sum_{j \neq i} y_i^s \, y_j^r \, \Delta G_{ij}^{sr}$$
$$+ RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

DFT

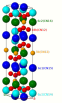
The formalism



The formalism



Applying EBEF to the μ phase

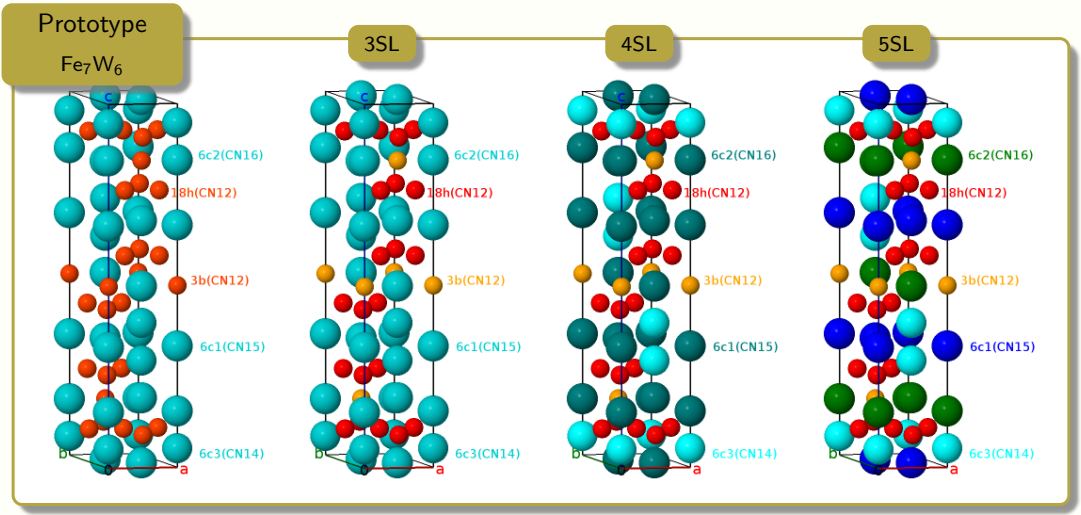


The μ phase

What is the physical meaning of the EBE?

Getting close to CEF

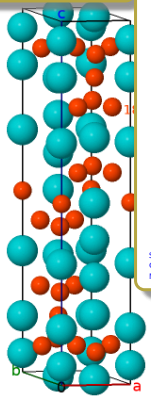
The μ phase


Prototype
Fe_7W_6
3SL
4SL
5SL
c
b
a
6c2(CN16)
18h(CN12)
3b(CN12)
6c1(CN15)
6c3(CN14)

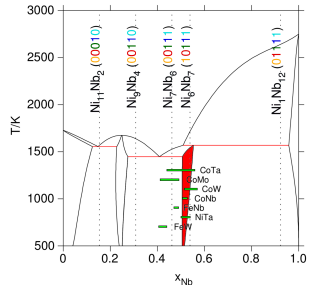
The μ phase

Prototype

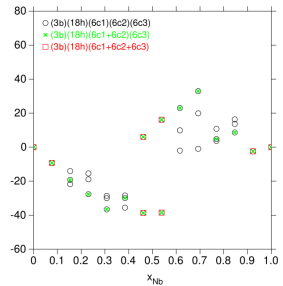
Fe_7W_6



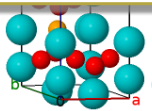
Ni-Nb

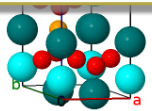


Study of the μ phase of Ni-Nb Rietveld analysis, First principle calculations and Calphad approach, N. Dupin, J.-M. Joubert, B. Sundman, S. G. Fries, A. Pasturel, M. Sluiter, 2002 Calphad Stockholm

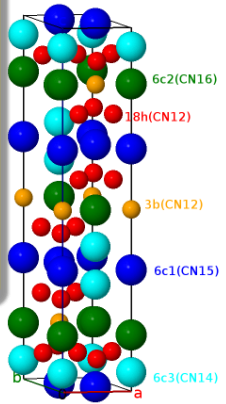


Using first-principles results to calculate finite-temperature thermodynamic properties of the Nb–Ni μ phase in the Bragg–Williams approximation, Dupin *et al.*, 2006 Phil. Mag., https://doi.org/10.1080/14786430500437488

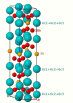




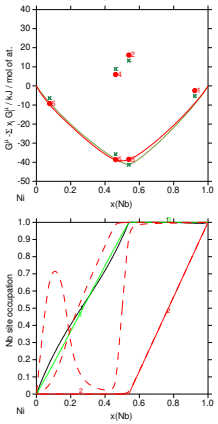
5SL



Meaning of the EBE - 3SL (3b)(18h)(6c1+6c2+6c3)



Ni-Nb 3SL @ 1500 K



CEF from DFT

$\Delta G_{Ni:Nb:Nb} = -31863$ (1)
$\Delta G_{Nb:Nb:Ni} = +209976$ (2)
$\Delta G_{Nb:Ni:Nb} = -499993$ (3)
$\Delta G_{Ni:Nb:Ni} = +78403$ (4)
$\Delta G_{Ni:Ni:Nb} = -502632$ (5)
$\Delta G_{Nb:Ni:Ni} = -120172$ (6)

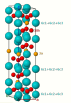
EBEF

$\Delta G_{Ni:Nb:*} = +40875$
$\Delta G_{Nb:Ni:*} = -181360$
$\Delta G_{Ni:*:Nb} = -109825$
$\Delta G_{Nb:*:Ni} = +98275$
$\Delta G_{*:Ni:Nb} = -355720$
$\Delta G_{*:Nb:Ni} = +74615$

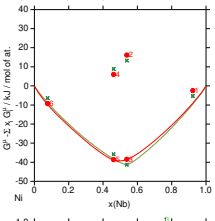
CEF = EBEF (/DFT)

$\Delta G_{Ni:Nb:Nb} = -68950$ (+116%)
$\Delta G_{Nb:Nb:Ni} = +172890$ (−17%)
$\Delta G_{Nb:Ni:Nb} = -537080$ (+7%)
$\Delta G_{Ni:Nb:Ni} = +115490$ (+47%)
$\Delta G_{Ni:Ni:Nb} = -465545$ (−7%)
$\Delta G_{Nb:Ni:Ni} = -83085$ (−31%)

Meaning of the EBE - 3SL (3b)(18h)(6c1+6c2+6c3)



Ni-Nb 3SL @ 1500 K



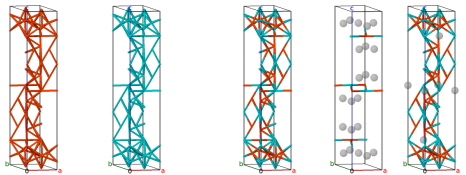
CEF from DFT

$\Delta G_{Ni:Nb:Nb} = -31863$ (1)
$\Delta G_{Nb:Nb:Ni} = +209976$ (2)
$\Delta G_{Nb:Ni:Nb} = -499993$ (3)
$\Delta G_{Ni:Nb:Ni} = +78403$ (4)
$\Delta G_{Ni:Ni:Nb} = -502632$ (5)
$\Delta G_{Nb:Ni:Ni} = -120172$ (6)

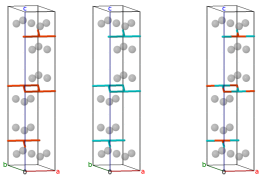
EBEF

$\Delta G_{Ni:Nb:*} = +40875$
$\Delta G_{Nb:Ni:*} = -181360$
$\Delta G_{Ni:*:Nb} = -109825$
$\Delta G_{Nb:*:Ni} = +98275$
$\Delta G_{*:Ni:Nb} = -355720$
$\Delta G_{*:Nb:Ni} = +74615$

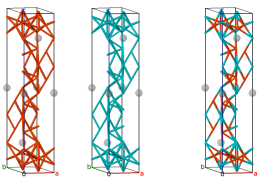
$\frac{1}{2}$ Ni:Ni:Ni + $\frac{1}{2}$ Nb:Nb:Nb $\xrightarrow[\Delta G_{Ni:Ni:Nb}]{}$ Ni:Ni:Nb = Ni:*:Nb + *:Ni:Nb



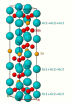
$\frac{1}{2}$ Ni:*:Ni + $\frac{1}{2}$ Nb:*:Nb $\xrightarrow[\Delta G_{Ni:*:Nb}]{}$ Ni:*:Nb



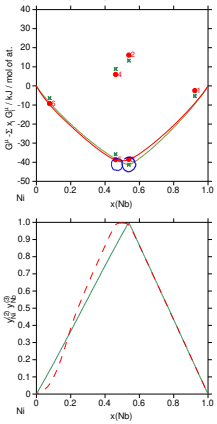
$\frac{1}{2}$ *:Ni:Ni + $\frac{1}{2}$ *:Nb:Nb $\xrightarrow[\Delta G_{*:Ni:Nb}]{}$ *:Ni:Nb



Meaning of the EBE - 3SL (3b)(18h)(6c1+6c2+6c3)



Ni-Nb 3SL @ 1500 K



CEF from DFT

$\Delta G_{Ni:Nb:Nb} = -31863$ (1)
$\Delta G_{Nb:Nb:Ni} = +209976$ (2)
$\Delta G_{Nb:Ni:Nb} = -499993$ (3)
$\Delta G_{Ni:Ni:Nb} = -502632$ (5)
$\Delta G_{Nb:Ni:Ni} = -120172$ (6)

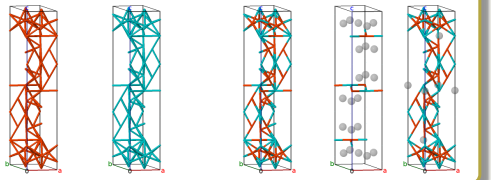
EBEF

$\Delta G_{Ni:Nb:*} = +40875$
$\Delta G_{Nb:Ni:*} = -181360$
$\Delta G_{Ni:*:Nb} = -109825$
$\Delta G_{Nb:*:Ni} = +98275$
$\Delta G_{*:Ni:Nb} = -355720$
$\Delta G_{*:Nb:Ni} = +74615$

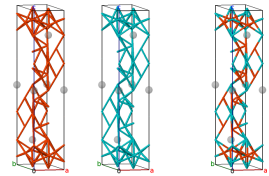
CEF = EBEF (/DFT)

$\Delta G_{Ni:Nb:Nb} = -68950$ (+116%)
$\Delta G_{Nb:Nb:Ni} = +172890$ (−17%)
$\Delta G_{Nb:Ni:Nb} = -537080$ (+7%)
$\Delta G_{Ni:Ni:Nb} = +115490$ (+47%)
$\Delta G_{Ni:Ni:Nb} = -465545$ (−7%)
$\Delta G_{Nb:Ni:Ni} = -83085$ (−31%)

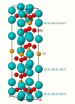
$\frac{1}{2}$ Ni:Ni:Ni + $\frac{1}{2}$ Nb:Nb:Nb $\xrightarrow{\Delta G_{Ni:Ni:Nb}}$ Ni:Ni:Nb = Ni:*:Nb + *:Ni:Nb



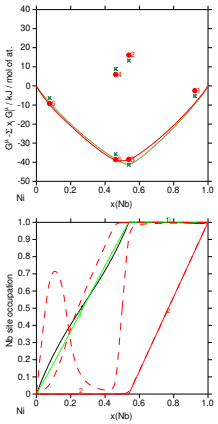
$\frac{1}{2}$ *:Ni:Ni + $\frac{1}{2}$ *:Nb:Nb $\xrightarrow{\Delta G_{*:Ni:Nb}}$ *:Ni:Nb



Meaning of the EBE - 3SL (3b)(18h)(6c1+6c2+6c3)



Ni-Nb 3SL @ 1500 K



CEF from DFT

$\Delta G_{Ni:Nb:Nb} = -31863$ (1)
$\Delta G_{Nb:Nb:Ni} = +209976$ (2)
$\Delta G_{Nb:Ni:Nb} = -499993$ (3)
$\Delta G_{Ni:Nb:Ni} = +78403$ (4)
$\Delta G_{Ni:Ni:Nb} = -502632$ (5)
$\Delta G_{Nb:Ni:Ni} = -120172$ (6)

EBEF

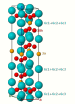
$\Delta G_{Ni:Nb:*} = +40875$
$\Delta G_{Nb:Ni:*} = -181360$
$\Delta G_{Ni:*:Nb} = -109825$
$\Delta G_{Nb:*:Ni} = +98275$
$\Delta G_{*:Ni:Nb} = -355720$
$\Delta G_{*:Nb:Ni} = +74615$

CEF = EBEF (/DFT)

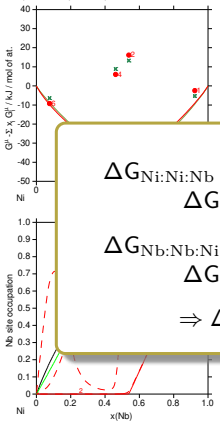
$\Delta G_{Ni:Nb:Nb}$	-68950	$(+116\%)$
$\Delta G_{Nb:Nb:Ni}$	$+172890$	(-17%)
$\Delta G_{Nb:Ni:Nb}$	-537080	$(+7\%)$
$\Delta G_{Ni:Nb:Ni}$	$+115490$	$(+47\%)$
$\Delta G_{Ni:Ni:Nb}$	-465545	(-7%)
$\Delta G_{Nb:Ni:Ni}$	-83085	(-31%)

Same number of parameters in the CEF and EBEF but the conversion doesn't provide the same description. Why?

Meaning of the EBE - 3SL (3b)(18h)(6c1+6c2+6c3)



Ni-Nb 3SL @ 1500 K



CEF from DFT

$\Delta G_{\mathrm{Ni:Nb:Nb}} = -31863$ (1)
$\Delta G_{\mathrm{Nb:Nb:Ni}} = +209976$ (2)
$\Delta G_{\mathrm{Nb:Ni:Nb}} = -499993$ (3)
$\Delta G_{\mathrm{Ni:Nb:Ni}} = +78403$ (4)
$\Delta G_{\mathrm{Ni:Ni:Nb}} = -502632$ (5)
$\Delta G_{\mathrm{Nb:Ni:Ni}} = -120172$ (6)

EBEF

$\Delta G_{\mathrm{Ni:Nb:*}} = +40875$
$\Delta G_{\mathrm{Nb:Ni:*}} = -181360$
$\Delta G_{\mathrm{Ni:*:Nb}} = -109825$
$\Delta G_{\mathrm{Nb:*:Ni}} = +98275$
$\Delta G_{\mathrm{*:Ni:Nb}} = -355720$
$\Delta G_{\mathrm{*:Nb:Ni}} = +74615$

CEF = EBEF (/DFT)

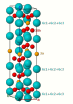
$\Delta G_{\mathrm{Ni:Nb:Nb}}$	$= -68950$	$(+116\%)$
$\Delta G_{\mathrm{Nb:Nb:Ni}}$	$= +172890$	(-17%)
$\Delta G_{\mathrm{Nb:Ni:Nb}}$	$= -537080$	$(+7\%)$
$\Delta G_{\mathrm{Ni:Nb:Ni}}$	$= +115490$	$(+47\%)$
$\Delta G_{\mathrm{Ni:Ni:Nb}}$	$= -465545$	(-7%)
$\Delta G_{\mathrm{Nb:Ni:Ni}}$	$= -83085$	(-31%)

$$\Delta G_{\mathrm{Ni:Ni:Nb}} + \Delta G_{\mathrm{Ni:Nb:Ni}} + \Delta G_{\mathrm{Nb:Ni:Ni}} = \Delta G_{\mathrm{Ni:*:Nb}} + \Delta G_{\mathrm{*:Ni:Nb}} + \Delta G_{\mathrm{Ni:Nb:*}} + \Delta G_{\mathrm{*:Nb:Ni}} + \Delta G_{\mathrm{Nb:Ni:*}} + \Delta G_{\mathrm{Nb:*:Ni}}$$

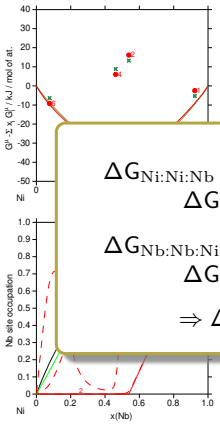
$$\Delta G_{\mathrm{Nb:Nb:Ni}} + \Delta G_{\mathrm{Nb:Ni:Nb}} + \Delta G_{\mathrm{Ni:Nb:Nb}} = \Delta G_{\mathrm{Nb:*:Ni}} + \Delta G_{\mathrm{*:Nb:Ni}} + \Delta G_{\mathrm{Nb:Ni:*}} + \Delta G_{\mathrm{*:Ni:Nb}} + \Delta G_{\mathrm{Ni:Nb:*}} + \Delta G_{\mathrm{Ni:*:Nb}}$$

$$\Rightarrow \Delta G_{\mathrm{Nb:Ni:Ni}} + \Delta G_{\mathrm{Ni:Nb:Ni}} + \Delta G_{\mathrm{Ni:Ni:Nb}} = \Delta G_{\mathrm{Nb:Nb:Ni}} + \Delta G_{\mathrm{Nb:Ni:Nb}} + \Delta G_{\mathrm{Ni:Nb:Nb}}$$

Meaning of the EBE - 3SL (3b)(18h)(6c1+6c2+6c3)



Ni-Nb 3SL @ 1500 K



CEF from DFT

$\Delta G_{Ni:Nb:Nb} = -31863$ (1)
$\Delta G_{Nb:Nb:Ni} = +209976$ (2)
$\Delta G_{Nb:Ni:Nb} = -499993$ (3)
$\Delta G_{Ni:Nb:Ni} = +78403$ (4)
$\Delta G_{Ni:Ni:Nb} = -502632$ (5)
$\Delta G_{Nb:Ni:Ni} = -120172$ (6)

EBEF

$\Delta G_{Ni:Nb:*} = +40875$
$\Delta G_{Nb:Ni:*} = -181360$
$\Delta G_{Ni:*:Nb} = -109825$
$\Delta G_{Nb:*:Ni} = +98275$
$\Delta G_{*:Ni:Nb} = -355720$
$\Delta G_{*:Nb:Ni} = +74615$

CEF = EBEF (/DFT)

$\Delta G_{Ni:Nb:Nb}$	$= -68950$	$(+116\%)$
$\Delta G_{Nb:Nb:Ni}$	$= +172890$	(-17%)
$\Delta G_{Nb:Ni:Nb}$	$= -537080$	$(+7\%)$
$\Delta G_{Ni:Nb:Ni}$	$= +115490$	$(+47\%)$
$\Delta G_{Ni:Ni:Nb}$	$= -465545$	(-7%)
$\Delta G_{Nb:Ni:Ni}$	$= -83085$	(-31%)

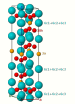
$$\Delta G_{Ni:Ni:Nb} + \Delta G_{Ni:Nb:Ni} + \Delta G_{Nb:Ni:Ni} = \Delta G_{Ni:*:Nb} + \Delta G_{*:Ni:Nb} + \Delta G_{Ni:Nb:*} + \Delta G_{*:Nb:Ni} + \Delta G_{Nb:Ni:*} + \Delta G_{Nb:*:Ni}$$

$$\Delta G_{Nb:Nb:Ni} + \Delta G_{Nb:Ni:Nb} + \Delta G_{Ni:Nb:Nb} = \Delta G_{Nb:*:Ni} + \Delta G_{*:Nb:Ni} + \Delta G_{Nb:Ni:*} + \Delta G_{*:Ni:Nb} + \Delta G_{Ni:Nb:*} + \Delta G_{Ni:*:Nb}$$

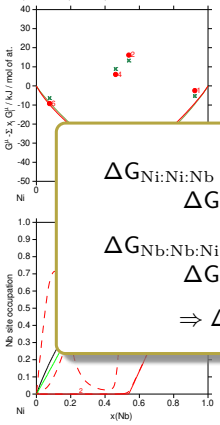
$$\Rightarrow \Delta G_{Nb:Ni:Ni} + \Delta G_{Ni:Nb:Ni} + \Delta G_{Ni:Ni:Nb} = \Delta G_{Nb:Nb:Ni} + \Delta G_{Nb:Ni:Nb} + \Delta G_{Ni:Nb:Nb}$$

If the CEF values do not respect this constraint the EBEF cannot be strictely equivalent.

Meaning of the EBE - 3SL (3b)(18h)(6c1+6c2+6c3)



Ni-Nb 3SL @ 1500 K



CEF from DFT

$\Delta G_{Ni:Nb:Nb} = -31863$ (1)
$\Delta G_{Nb:Nb:Ni} = +209976$ (2)
$\Delta G_{Nb:Ni:Nb} = -499993$ (3)
$\Delta G_{Ni:Nb:Ni} = +78403$ (4)
$\Delta G_{Ni:Ni:Nb} = -502632$ (5)
$\Delta G_{Nb:Ni:Ni} = -120172$ (6)

EBEF

$\Delta G_{Ni:Nb:*} = +40875$
$\Delta G_{Nb:Ni:*} = -181360$
$\Delta G_{Ni:*:Nb} = -109825$
$\Delta G_{Nb:*:Ni} = +98275$
$\Delta G_{*:Ni:Nb} = -355720$
$\Delta G_{*:Nb:Ni} = +74615$

CEF = EBEF (/DFT)

$\Delta G_{Ni:Nb:Nb} = -68950$ (+116%)
$\Delta G_{Nb:Nb:Ni} = +172890$ (−17%)
$\Delta G_{Nb:Ni:Nb} = -537080$ (+7%)
$\Delta G_{Ni:Nb:Ni} = +115490$ (+47%)
$\Delta G_{Ni:Ni:Nb} = -465545$ (−7%)
$\Delta G_{Nb:Ni:Ni} = -83085$ (−31%)

$$\Delta G_{Ni:Ni:Nb} + \Delta G_{Ni:Nb:Ni} + \Delta G_{Nb:Ni:Ni} = \Delta G_{Ni:*:Nb} + \Delta G_{*:Ni:Nb} + \Delta G_{Ni:Nb:*} + \Delta G_{*:Nb:Ni} + \Delta G_{Nb:Ni:*} + \Delta G_{Nb:*:Ni}$$

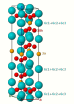
$$\Delta G_{Nb:Nb:Ni} + \Delta G_{Nb:Ni:Nb} + \Delta G_{Ni:Nb:Nb} = \Delta G_{Nb:*:Ni} + \Delta G_{*:Nb:Ni} + \Delta G_{Nb:Ni:*} + \Delta G_{*:Ni:Nb} + \Delta G_{Ni:Nb:*} + \Delta G_{Ni:*:Nb}$$

$$\Rightarrow \Delta G_{Nb:Ni:Ni} + \Delta G_{Ni:Nb:Ni} + \Delta G_{Ni:Ni:Nb} = \Delta G_{Nb:Nb:Ni} + \Delta G_{Nb:Ni:Nb} + \Delta G_{Ni:Nb:Nb}$$

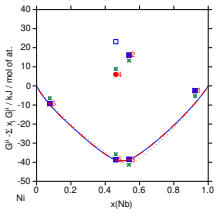
$$-120172 + 78403 - 502632 \stackrel{?}{=} +209976 - 499993 - 31863$$

$$-544401 \stackrel{?}{=} -321880$$

Getting closer to CEF - 3SL (3b)(18h)(6c1+6c2+6c3)



Ni-Nb 3SL @ 1500 K



CEF from DFT

$\Delta G_{Ni:Nb:Nb} = -31863$ (1)
$\Delta G_{Nb:Nb:Ni} = +209976$ (2)
$\Delta G_{Nb:Nb:Nb} = -499993$ (3)
$\Delta G_{Ni:Nb:Ni} = +78403$ (4)
$\Delta G_{Ni:Ni:Nb} = -502632$ (5)
$\Delta G_{Nb:Ni:Ni} = -120172$ (6)

EBEF ignoring (4)

$\Delta G_{Ni:Nb:*} = +133592$
$\Delta G_{Nb:Ni:*} = -162816$
$\Delta G_{Ni:*:Nb} = -165455$
$\Delta G_{Nb:*:Ni} = +42644$
$\Delta G_{*:Ni:Nb} = -337177$
$\Delta G_{*:Nb:Ni} = +167332$

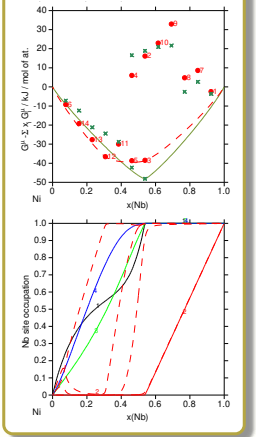
CEF = EBEF (/DFT)

$\Delta G_{Ni:Nb:Nb} = -31863$ (0%)
$\Delta G_{Nb:Nb:Ni} = +209976$ (0%)
$\Delta G_{Nb:Ni:Nb} = -499993$ (0%)
$\Delta G_{Ni:Nb:Ni} = +300924$ (+283%)
$\Delta G_{Ni:Ni:Nb} = -502632$ (0%)
$\Delta G_{Nb:Ni:Ni} = -120172$ (0%)

Disregarding one of the compound with high positive ordering energy ⇒ EBEF description closer to CEF.

Getting closer to CEF - 4SL (3b)(18h)(6c1+6c2)(6c3)

Ni-Nb 4SL @ 1500 K



CEF from DFT

$$\Delta G_{Ni:Nb:Nb:Nb} = -31863 \quad (1)$$
$$\Delta G_{Nb:Nb:Ni:Ni} = +209976 \quad (2)$$
$$\Delta G_{Nb:Ni:Nb:Nb} = -499993 \quad (3)$$
$$\Delta G_{Ni:Nb:Ni:Ni} = +78403 \quad (4)$$
$$\Delta G_{Ni:Ni:Nb:Nb} = -502632 \quad (5)$$
$$\Delta G_{Nb:Ni:Ni:Ni} = -120172 \quad (6)$$
$$\Delta G_{Nb:Nb:Nb:Ni} = +112138 \quad (7)$$
$$\Delta G_{Ni:Nb:Nb:Ni} = +62218 \quad (8)$$
$$\Delta G_{Nb:Nb:Ni:Nb} = +428246 \quad (9)$$
$$\Delta G_{Ni:Nb:Ni:Nb} = +298662 \quad (10)$$
$$\Delta G_{Nb:Ni:Nb:Ni} = -389350 \quad (11)$$
$$\Delta G_{Nb:Ni:Ni:Ni} = -475527 \quad (12)$$
$$\Delta G_{Nb:Ni:Ni:Nb} = -359372 \quad (13)$$
$$\Delta G_{Ni:Ni:Ni:Nb} = -250120 \quad (14)$$

EBEF

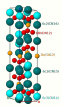
$$\Delta G_{Ni:Nb:*:*} = +49176$$
$$\Delta G_{Nb:Ni:*:*} = -172863$$
$$\Delta G_{Ni:*:Nb:*} = -87913$$
$$\Delta G_{Nb:*:Ni:*} = +50397$$
$$\Delta G_{Ni:*:*:Nb} = -8476$$
$$\Delta G_{Nb:*:*:Ni} = +28842$$
$$\Delta G_{*:Ni:Nb:*} = -214705$$
$$\Delta G_{*:Nb:Ni:*} = +145644$$
$$\Delta G_{*:Ni:*:Nb} = -238500$$
$$\Delta G_{*:Nb:*:Ni} = +20856$$
$$\Delta G_{*:*:Ni:Nb} = +85743$$
$$\Delta G_{*:*:Nb:Ni} = -15249$$

CEF = EBEF (/DFT)

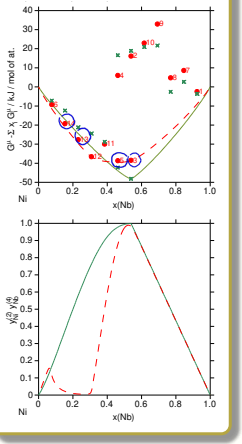
$$\Delta G_{Ni:Nb:Nb:Nb} = -47213 \quad (+48\%)$$
$$\Delta G_{Nb:Nb:Ni:Ni} = +245739 \quad (+17\%)$$
$$\Delta G_{Nb:Ni:Nb:Nb} = -626068 \quad (+25\%)$$
$$\Delta G_{Ni:Nb:Ni:Ni} = +215676 \quad (+175\%)$$
$$\Delta G_{Ni:Ni:Nb:Nb} = -549594 \quad (+9\%)$$
$$\Delta G_{Nb:Ni:Ni:Ni} = -93624 \quad (-22\%)$$
$$\Delta G_{Nb:Nb:Nb:Ni} = +34449 \quad (-69\%)$$
$$\Delta G_{Ni:Nb:Nb:Ni} = -33130 \quad (-153\%)$$
$$\Delta G_{Nb:Nb:Ni:Nb} = +281784 \quad (-34\%)$$
$$\Delta G_{Ni:Nb:Ni:Nb} = +272087 \quad (-9\%)$$
$$\Delta G_{Nb:Ni:Nb:Ni} = -373975 \quad (-4\%)$$
$$\Delta G_{Ni:Ni:Nb:Ni} = -317867 \quad (-33\%)$$
$$\Delta G_{Nb:Ni:Ni:Nb} = -275223 \quad (-23\%)$$
$$\Delta G_{Ni:Ni:Ni:Nb} = -161233 \quad (-35\%)$$

The default inversion is not as good as in the case of 3SL.

Getting closer to CEF - 4SL (3b)(18h)(6c1+6c2)(6c3)



Ni-Nb 4SL @ 1500 K



CEF from DFT

$$\Delta G_{Ni:Nb:Nb:Nb} = -31863 \quad (1)$$
$$\Delta G_{Nb:Nb:Ni:Ni} = +209976 \quad (2)$$
$$\Delta G_{Nb:Ni:Nb:Nb} = -499993 \quad (3)$$
$$\Delta G_{Ni:Nb:Ni:Ni} = +78403 \quad (4)$$
$$\Delta G_{Ni:Ni:Nb:Nb} = -502632 \quad (5)$$
$$\Delta G_{Nb:Ni:Ni:Ni} = -120172 \quad (6)$$
$$\Delta G_{Nb:Nb:Nb:Ni} = +112138 \quad (7)$$
$$\Delta G_{Ni:Nb:Nb:Ni} = +62218 \quad (8)$$
$$\Delta G_{Nb:Nb:Ni:Nb} = +428246 \quad (9)$$
$$\Delta G_{Ni:Nb:Ni:Nb} = +298662 \quad (10)$$
$$\Delta G_{Nb:Ni:Nb:Ni} = -389350 \quad (11)$$
$$\Delta G_{Ni:Ni:Nb:Ni} = -475527 \quad (12)$$
$$\Delta G_{Nb:Ni:Ni:Nb} = -359372 \quad (13)$$
$$\Delta G_{Ni:Ni:Ni:Nb} = -250120 \quad (14)$$

EBEF

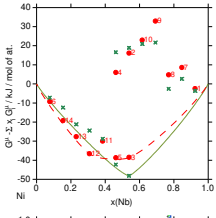
$$\Delta G_{Ni:Nb:*:*} = +49176$$
$$\Delta G_{Nb:Ni:*:*} = -172863$$
$$\Delta G_{Ni:*:Nb:*} = -87913$$
$$\Delta G_{Nb:*:Ni:*} = +50397$$
$$\Delta G_{Ni:*:*:Nb} = -8476$$
$$\Delta G_{Nb:*:*:Ni} = +28842$$
$$\Delta G_{*:Ni:Nb:*} = -214705$$
$$\Delta G_{*:Nb:Ni:*} = +145644$$
$$\Delta G_{*:Ni:*:Nb} = -238500$$
$$\Delta G_{*:Nb:*:Ni} = +20856$$
$$\Delta G_{*:*:Ni:Nb} = +85743$$
$$\Delta G_{*:*:Nb:Ni} = -15249$$

CEF = EBEF (/DFT)

$$\Delta G_{Ni:Nb:Nb:Nb} = -47213 \quad (+48\%)$$
$$\Delta G_{Nb:Nb:Ni:Ni} = +245739 \quad (+17\%)$$
$$\Delta G_{Nb:Ni:Nb:Nb} = -626068 \quad (+25\%)$$
$$\Delta G_{Ni:Nb:Ni:Ni} = +215676 \quad (+175\%)$$
$$\Delta G_{Ni:Ni:Nb:Nb} = -549594 \quad (+9\%)$$
$$\Delta G_{Nb:Ni:Ni:Ni} = -93624 \quad (-22\%)$$
$$\Delta G_{Nb:Nb:Nb:Ni} = +34449 \quad (-69\%)$$
$$\Delta G_{Ni:Nb:Nb:Ni} = -33130 \quad (-153\%)$$
$$\Delta G_{Nb:Nb:Ni:Nb} = +281784 \quad (-34\%)$$
$$\Delta G_{Ni:Nb:Ni:Nb} = +272087 \quad (-9\%)$$
$$\Delta G_{Nb:Ni:Nb:Ni} = -373975 \quad (-4\%)$$
$$\Delta G_{Ni:Ni:Nb:Ni} = -317867 \quad (-33\%)$$
$$\Delta G_{Nb:Ni:Ni:Nb} = -275223 \quad (-23\%)$$
$$\Delta G_{Ni:Ni:Ni:Nb} = -161233 \quad (-35\%)$$

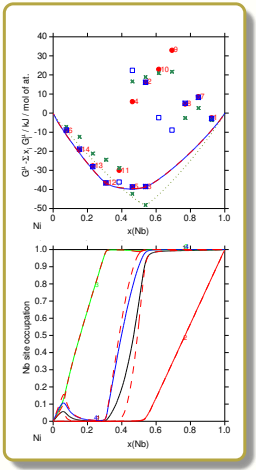
Getting closer to CEF - 4SL (3b)(18h)(6c1+6c2)(6c3)

Ni-Nb 4SL @ 1500 K



EBEF
default inversion

$\Delta G_{Ni:Nb:*:*} = +49176$
$\Delta G_{Nb:Ni:*:*} = -172863$
$\Delta G_{Ni:*:Nb:*} = -87913$
$\Delta G_{Nb:*:Ni:*} = +50397$
$\Delta G_{Ni:*:*:Nb} = -8476$
$\Delta G_{Nb:*:*:Ni} = +28842$
$\Delta G_{*:Ni:Nb:*} = -214705$
$\Delta G_{*:Nb:Ni:*} = +145644$
$\Delta G_{*:Ni:*:Nb} = -238500$
$\Delta G_{*:Nb:*:Ni} = +20856$
$\Delta G_{*:*:Ni:Nb} = +85743$
$\Delta G_{*:*:Nb:Ni} = -15249$



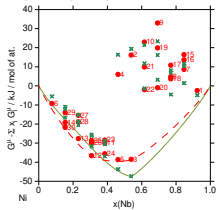
EBE ignoring
(4), (9), (10), (11)

$\Delta G_{Ni:Nb:*:*} = +91712$
$\Delta G_{Nb:Ni:*:*} = -125765$
$\Delta G_{Ni:*:Nb:*} = -95945$
$\Delta G_{Nb:*:Ni:*} = -25605$
$\Delta G_{Ni:*:*:Nb} = -32459$
$\Delta G_{Nb:*:*:Ni} = +36028$
$\Delta G_{*:Ni:Nb:*} = -269563$
$\Delta G_{*:Nb:Ni:*} = +18254$
$\Delta G_{*:Ni:*:Nb} = -104665$
$\Delta G_{*:Nb:*:Ni} = +181300$
$\Delta G_{*:*:Ni:Nb} = -108166$
$\Delta G_{*:*:Nb:Ni} = -110019$

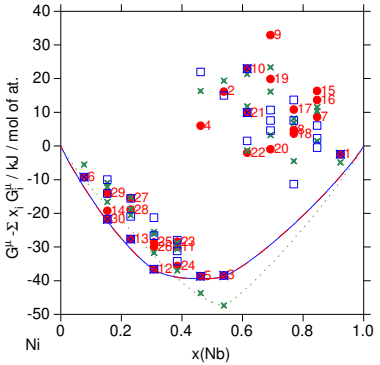
Disregarding 4 DFT
⇒ EBEF very close to the original CEF description.

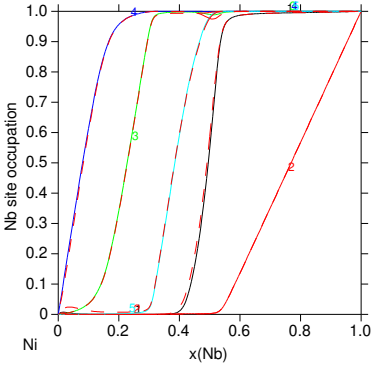
Getting closer to CEF - 5SL (3b)(18h)(6c1)(6c2)(6c3)

EBEF default inversion



EBEF using only compounds (6), (30), (13), (12), (5), (3), (1), (21) and (10)





Summary

- ⇝ EBEF has a great ability to extrapolate from binary information.
- ⇝ The determination of the EBE
  - is key,
  - can be tricky,
  - can be performed using DFT results.
- ⇝ Using only some of the DFT results can help to get closer to CEF.
- ⇝ Comparison to the CEF description based on all the binary DFT results is strongly recommanded.