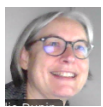
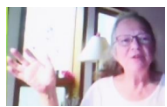
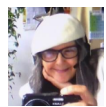
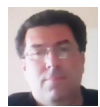
# What can the Effective Bond Energy Formalism do better ?

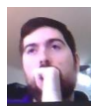
Nathalie Dupin  Daniela Ivanova  Ursula R. Kattner
Suzana G. Fries  Bo Sundman  Mauro Palumbo
Thomas Hammerschmidt  Sean Griesemer

IM2021 - October 5, 2021

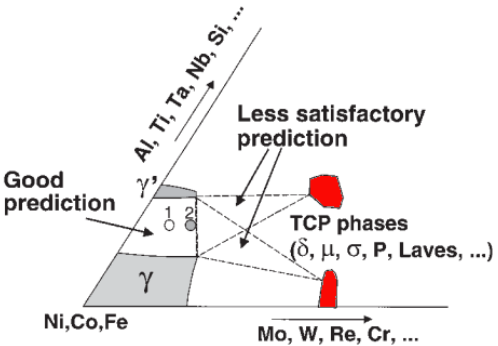


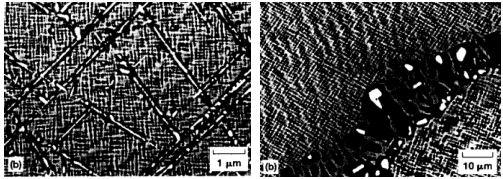




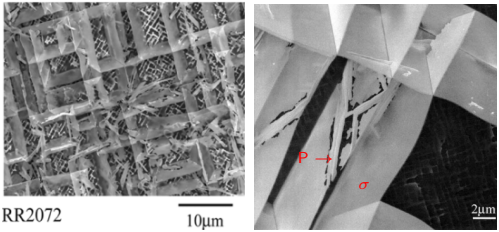
# TCP phases




Calphad - Is It Ready for Superalloy Design ?
Zhao and Henry, Advanced Engineering Materials 2002, **4** (7), 501-508



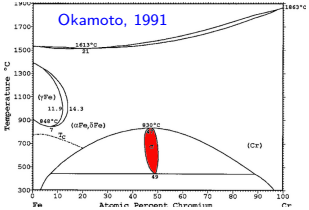

Ritzert, Arenas, Keller and Vasudevan, NASA/TM-1998-206622

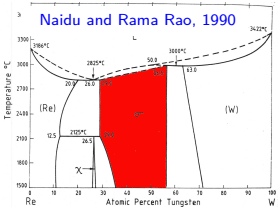


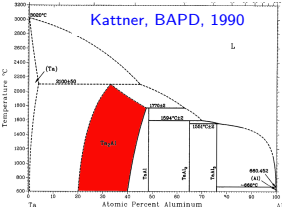

Rae and Reed, Acta mater. (2001) 4113-4125

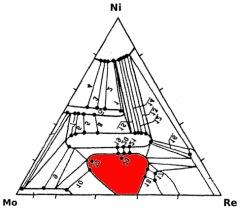
# The $\sigma$ phase

Not a stoichiometric phase!

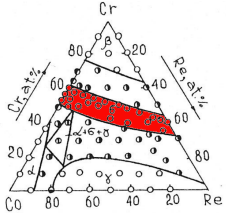


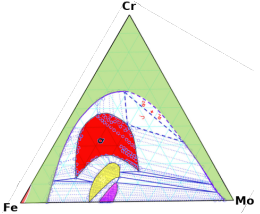




Slyusarenko et al., 1998

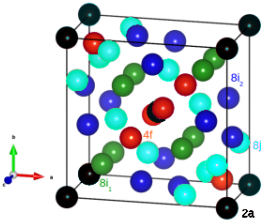



Sokolovskaya et al., 1986




Cao and Zhao, 2016

# The $\sigma$ phase

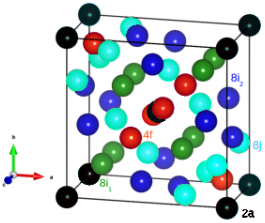



$(A,B)_2(A,B)_4(A,B)_8(A,B)_8(A,B)_8$

CN12 CN15 CN14 CN12 CN14

Prototype: FeCr,
StrukturBericht: $D8_b$,
Pearson: tP30,
Space Group: $P4_2/mnm$

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CN12 CN15 CN14 CN12 CN14

PanNickel CEF

$(Al\ Co\ Fe\ Mn\ Ni\ Re\ Ru\ Si)_8$
$(Co\ Cr\ Mo\ Nb\ Ni\ Ta\ Ti\ V\ W)_4$
$(Al\ Co\ Cr\ Fe\ Mn\ Mo\ Nb\ Ni\ Re\ Ru\ Si\ Ta\ Ti\ V\ W)_{18}$

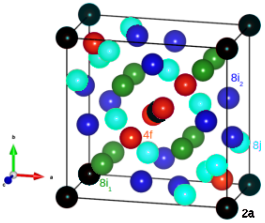
TCFE11 CEF

$(Al\ Co\ Cr\ Fe\ Mn\ Ni\ Ru\ Ta\ V)_{10}$
$(Cr\ Mo\ Nb\ Ta\ Ti\ V\ W)_4$
$(Al\ Co\ Cr\ Fe\ Mn\ Mo\ Nb\ Ni\ Ru\ Si\ Ta\ Ti\ V\ W)_{16}$

TCNI11 ECEF

$(Al\ Co\ Cr\ Fe\ Mn\ Mo\ Nb\ Ni\ Pd\ Pt\ Re\ Ru\ Si\ Ta\ Ti\ V\ W)_{10}$
$(Al\ Co\ Cr\ Fe\ Mn\ Mo\ Nb\ Ni\ Pd\ Pt\ Re\ Ru\ Si\ Ta\ Ti\ V\ W)_4$
$(Al\ Co\ Cr\ Fe\ Mn\ Mo\ Nb\ Ni\ Pd\ Pt\ Re\ Ru\ Si\ Ta\ Ti\ V\ W)_{16}$

# The $\sigma$ phase




Prototype: FeCr,
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CN12 CN15 CN14 CN12 CN14

10 16

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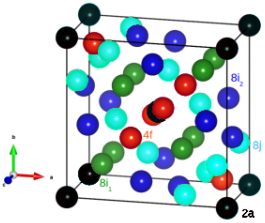
TCFE11 CEF

$(Al\ Co\ Cr\ Fe\ Mn\ Ni\ Ru\ Ta\ V)_{10}$
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$(Al\ Co\ Cr\ Fe\ Mn\ Mo\ Nb\ Ni\ Ru\ Si\ Ta\ Ti\ V\ W)_{16}$

TCNI11 ECEF

$(Al\ Co\ Cr\ Fe\ Mn\ Mo\ Nb\ Ni\ Pd\ Pt\ Re\ Ru\ Si\ Ta\ Ti\ V\ W)_{10}$
$(Al\ Co\ Cr\ Fe\ Mn\ Mo\ Nb\ Ni\ Pd\ Pt\ Re\ Ru\ Si\ Ta\ Ti\ V\ W)_4$
$(Al\ Co\ Cr\ Fe\ Mn\ Mo\ Nb\ Ni\ Pd\ Pt\ Re\ Ru\ Si\ Ta\ Ti\ V\ W)_{16}$

# The $\sigma$ phase




Prototype: FeCr,
StrukturBericht: $D8_b$,
Pearson: tP30,
Space Group: $P4_2/mnm$

$(A,B)_2(A,B)_4(A,B)_8(A,B)_8(A,B)_8$

CN12 CN15 CN14 CN12 CN14

10 16

PanNickel CEF

$(Al\ Co\ Fe\ Mn\ Ni\ Re\ Ru\ Si)_8$ fcc or hcp elements + Si
$(Co\ Cr\ Mo\ Nb\ Ni\ Ta\ Ti\ V\ W)_4$ bcc elements + Co + Ni
$(Al\ Co\ Cr\ Fe\ Mn\ Mo\ Nb\ Ni\ Re\ Ru\ Si\ Ta\ Ti\ V\ W)_{18}$

TCFE11 CEF

$(Al\ Co\ Cr\ Fe\ Mn\ Ni\ Ru\ Ta\ V)_{10}$ fcc or hcp elements + Cr + Ta + V
$(Cr\ Mo\ Nb\ Ta\ Ti\ V\ W)_4$ bcc elements
$(Al\ Co\ Cr\ Fe\ Mn\ Mo\ Nb\ Ni\ Ru\ Si\ Ta\ Ti\ V\ W)_{16}$

TCNI11 ECEF

$(Al\ Co\ Cr\ Fe\ Mn\ Mo\ Nb\ Ni\ Pd\ Pt\ Re\ Ru\ Si\ Ta\ Ti\ V\ W)_{10}$
$(Al\ Co\ Cr\ Fe\ Mn\ Mo\ Nb\ Ni\ Pd\ Pt\ Re\ Ru\ Si\ Ta\ Ti\ V\ W)_4$
$(Al\ Co\ Cr\ Fe\ Mn\ Mo\ Nb\ Ni\ Pd\ Pt\ Re\ Ru\ Si\ Ta\ Ti\ V\ W)_{16}$

# Calphad - modelling of the phase Gibbs energy

- Stoichiometric compounds $G = f(T)$
- Substitutional solutions $G = f(T, x_i)$

$$G_M = \sum_i x_i \, G_i(T) + R\,T \sum_i x_i \ln x_i + {}^{ex}G(T, x_i) + {}^{mag}G(T, x_i)$$

If pure *i* not stable, lattice stability to be defined

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- Compound Energy Formalism $G = f(T, y_i^s)$

$$G = \sum_I \prod_s y_i^s\ G_I(T) + R\,T \sum_s a^s \sum_i y_i^s \ln y_i^s + {}^{ex}G(T, y_i^s) + {}^{mag}G(T, y_i^s)$$

when e.g. $I$ = A:B:C:D:E, $\quad \prod_s y_i^s = y_A^{(1)}\ y_B^{(2)}\ y_C^{(3)}\ y_D^{(4)}\ y_E^{(5)}$

# Calphad - modelling of the phase Gibbs energy

- Compound Energy Formalism (CEF)

$$G^{\sigma} = \sum_l \prod_s y_i^s \; G_l^{\sigma} + R\,T \sum_s a^s \sum_i y_i^s \ln y_i^s + {}^{ex}G^{\sigma}(y_i^s) + {}^{mag}G^{\sigma}(y_i^s)$$

# Calphad - modelling of the phase Gibbs energy

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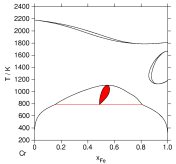
- Extended CEF (ECEF)

$$G^{\sigma} = n_f^{\sigma} \sum_i x_i \; G_i^{\sigma} + {}^{ex}G^{\sigma}(x_i) + {}^{mag}G^{\sigma}(x_i)$$
$$+ \sum_I \prod_s y_i^s \; \Delta G_I^{\sigma} + RT \sum_s a^s \sum_i y_i^s \ln y_i^s + {}^{ex}G^{\sigma}(y_i^s) + {}^{mag}G^{\sigma}(y_i^s)$$

with $n_f^{\sigma} = \sum_s a^s$ *i.e.* the total number of atoms in the formula unit *i.e.* 30 for the $\sigma$ phase

$\Delta G_I^{\sigma} = G_I^{\sigma} - \sum_s a^s \, G_i^{\sigma}$
is the ordering energy of compound *I* from the pure element in the phase

# The $\sigma$ phase CEF

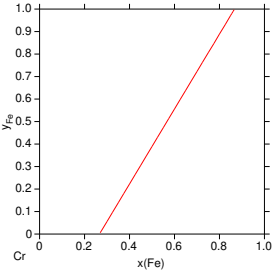


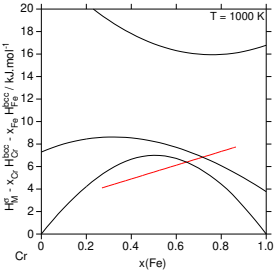

$$(Fe)_8(Cr)_4(Cr,Fe)_{18}$$

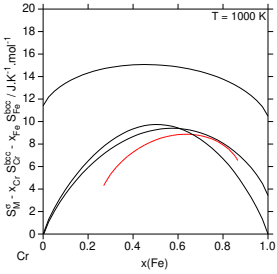
$$G^{\sigma} = y_{Cr}\, G^{\sigma}_{Fe:Cr:Cr} + y_{Fe}\, G^{\sigma}_{Fe:Cr:Fe} + 18\,RT\,(y_{Cr} \ln y_{Cr} + y_{Fe} \ln y_{Fe})$$

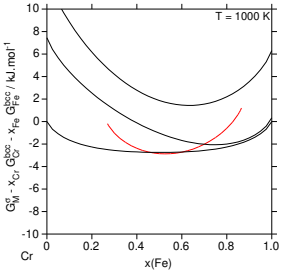
$$G^{\sigma}_{Fe:Cr:Cr} = 8\,G^{fcc}_{Fe} + 22\,G^{bcc}_{Cr} + 92300 - 95.6\,T$$
$$G^{\sigma}_{Fe:Cr:Fe} = 8\,G^{fcc}_{Fe} + 4\,G^{bcc}_{Cr} - 18\,G^{bcc}_{Fe} + 117300 - 95.6\,T$$

Andersson and Sundman, Calphad, **11**, 83-92, 1987

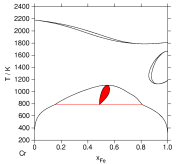


# The $\sigma$ phase CEF



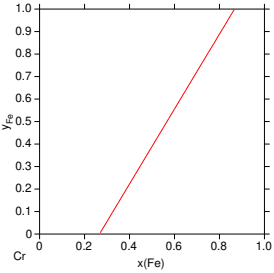

$$(Fe)_8(Cr)_4(Cr,Fe)_{18}$$

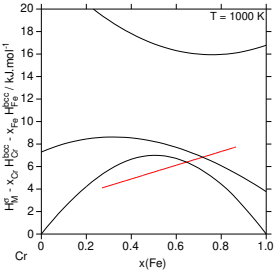
$$G^{\sigma} = y_{Cr}\, G^{\sigma}_{Fe:Cr:Cr} + y_{Fe}\, G^{\sigma}_{Fe:Cr:Fe} + 18\,RT\,(y_{Cr} \ln y_{Cr} + y_{Fe} \ln y_{Fe})$$

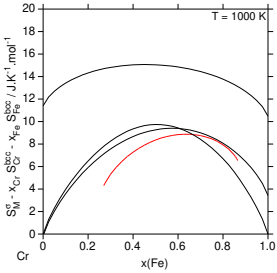
$$G^{\sigma}_{Fe:Cr:Cr} = 8\,G^{fcc}_{Fe} + 22\,G^{bcc}_{Cr} + 92300 - 95.6\,T$$
$$G^{\sigma}_{Fe:Cr:Fe} = 8\,G^{fcc}_{Fe} + 4\,G^{bcc}_{Cr} - 18\,G^{bcc}_{Fe} + 117300 - 95.6\,T$$

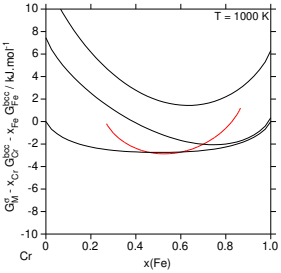
End-members far from the stable composition of the phase optimised from experiments

Andersson and Sundman, Calphad, **11**, 83-92, 1987

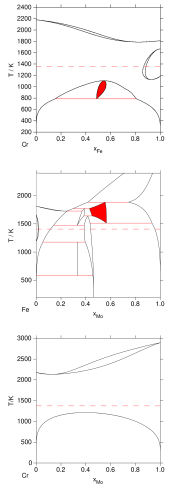


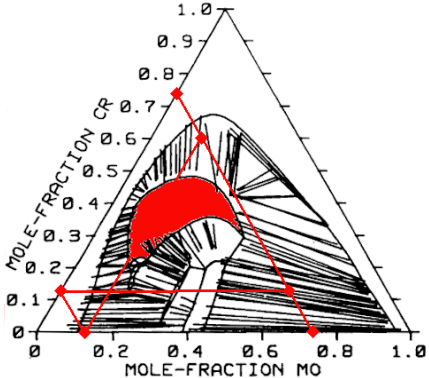



# The $\sigma$ phase CEF



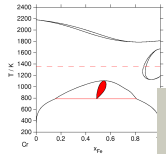

$$(Fe)_8(Cr,Mo)_4(Cr,Fe,Mo)_{18}$$

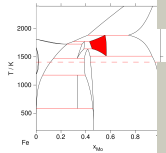
$$G^{\sigma} = \sum_j \sum_k y_j^{(2)} y_k^{(3)} G^{\sigma}_{Fe:j:k} + RT\left(4\sum_i y_i^{(2)} \ln y_i^{(2)} + 18\sum_i y_i^{(3)} \ln y_i^{(3)}\right) + {}^{ex}G^{\sigma}$$

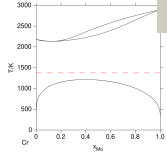



Andersson and Lange, Met. Trans. A, **19A**, 1385-1394, 1988

# The $\sigma$ phase CEF




$$(Fe)_8(Cr,Mo)_4(Cr,Fe,Mo)_{18}$$

$$G^{\sigma} = \sum_j \sum_k y_j^{(2)} y_k^{(3)} G^{\sigma}_{Fe:j:k} + RT\left(4\sum_i y_i^{(2)} \ln y_i^{(2)} + 18 \sum_i y_i^{(3)} \ln y_i^{(3)}\right) + {}^{ex}G^{\sigma}$$

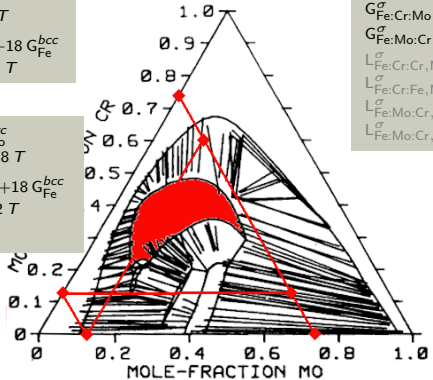
$G^{\sigma}_{Fe:Cr:Cr} = 8\,G^{fcc}_{Fe} + 22\,G^{bcc}_{Cr} + 92300 - 95.6\,T$

$G^{\sigma}_{Fe:Cr:Fe} = 8\,G^{fcc}_{Fe} + 4\,G^{bcc}_{Cr} + 18\,G^{bcc}_{Fe} + 117300 - 95.6\,T$

$G^{\sigma}_{Fe:Mo:Mo} = 8\,G^{fcc}_{Fe} + 22\,G^{bcc}_{Mo} + 83326 - 69.618\,T$

$G^{\sigma}_{Fe:Mo:Fe} = 8\,G^{fcc}_{Fe} + 4\,G^{bcc}_{Mo} + 18\,G^{bcc}_{Fe} - 1813 - 27.272\,T$

$L^{\sigma}_{Fe:Mo:Fe,Mo} = +222909$




$G^{\sigma}_{Fe:Cr:Mo} = 8\,G^{fcc}_{Fe} + 4\,G^{bcc}_{Cr} + 18\,G^{bcc}_{Mo} + 312580 - 260\,T$

$G^{\sigma}_{Fe:Mo:Cr} = 8\,G^{fcc}_{Fe} + 4\,G^{bcc}_{Mo} + 18\,G^{bcc}_{Cr} + 488480 - 360\,T$

$L^{\sigma}_{Fe:Cr:Cr,Mo} = -148000$

$L^{\sigma}_{Fe:Cr:Fe,Mo} = +175400 + 200\,T$

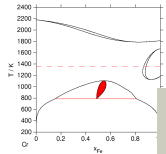
$L^{\sigma}_{Fe:Mo:Cr,Mo} = +121000$

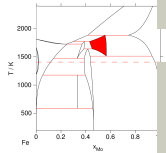
$L^{\sigma}_{Fe:Mo:Cr,Fe} = -195950 + 150\,T$

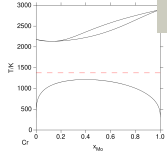
Few end-members but many excess terms

Andersson and Lange, Met. Trans. A, **19A**, 1385-1394, 1988

# The $\sigma$ phase CEF




$$(Fe)_8(Cr,Mo)_4(Cr,Fe,Mo)_{18}$$

$$G^{\sigma} = \sum_j \sum_k y_j^{(2)} y_k^{(3)} G^{\sigma}_{Fe:j:k} + RT\left(4\sum_i y_i^{(2)} \ln y_i^{(2)} + 18 \sum_i y_i^{(3)} \ln y_i^{(3)}\right) + {}^{ex}G^{\sigma}$$

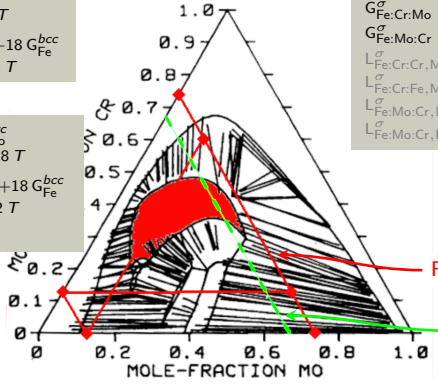
$G^{\sigma}_{Fe:Cr:Cr} = 8\,G^{fcc}_{Fe} + 22\,G^{bcc}_{Cr} + 92300 - 95.6\,T$

$G^{\sigma}_{Fe:Cr:Fe} = 8\,G^{fcc}_{Fe} + 4\,G^{bcc}_{Cr} + 18\,G^{bcc}_{Fe} + 117300 - 95.6\,T$

$G^{\sigma}_{Fe:Mo:Mo} = 8\,G^{fcc}_{Fe} + 22\,G^{bcc}_{Mo} + 83326 - 69.618\,T$

$G^{\sigma}_{Fe:Mo:Fe} = 8\,G^{fcc}_{Fe} + 4\,G^{bcc}_{Mo} + 18\,G^{bcc}_{Fe} - 1813 - 27.272\,T$

$L^{\sigma}_{Fe:Mo:Fe,Mo} = +222909$




Andersson and Lange, Met. Trans. A, **19A**, 1385-1394, 1988

$G^{\sigma}_{Fe:Cr:Mo} = 8\,G^{fcc}_{Fe} + 4\,G^{bcc}_{Cr} + 18\,G^{bcc}_{Mo} + 312580 - 260\,T$

$G^{\sigma}_{Fe:Mo:Cr} = 8\,G^{fcc}_{Fe} + 4\,G^{bcc}_{Mo} + 18\,G^{bcc}_{Cr} + 488480 - 360\,T$

$L^{\sigma}_{Fe:Cr:Cr,Mo} = -148000$

$L^{\sigma}_{Fe:Cr:Fe,Mo} = +175400 + 200\,T$

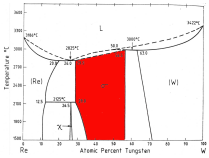
$L^{\sigma}_{Fe:Mo:Cr,Mo} = +121000$

$L^{\sigma}_{Fe:Mo:Cr,Fe} = -195950 + 150\,T$

Few end-members but many excess terms

$(B)_{10}(A)_4(A,B)_{16}$ unable to describe experimental range

# The $\sigma$ phase - FP-CEF

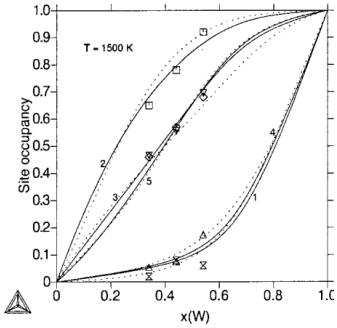



$$(Re,W)_2(Re,W)_4(Re,W)_8(Re,W)_8(Re,W)_8$$

$$G^\sigma = \sum_l \prod_s y_i^s \; G_l^\sigma + RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

With the progress of computers and FP, models closer to the crystallography became possible.

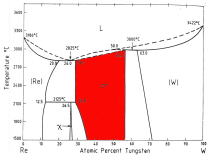
DFT




... CVM
___ FP-CEF
symbols experiments

Fries and Sundman, PRB, **66**, 012203 (2002)

# The $\sigma$ phase - FP-CEF

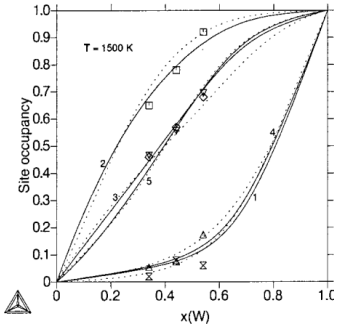



$$(Re,W)_2(Re,W)_4(Re,W)_8(Re,W)_8(Re,W)_8$$

$$G^{\sigma} = \sum_I \prod_s y_i^s \; G_I^{\sigma} + RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

With the progress of computers and FP, models closer to the crystallography became possible.

DFT

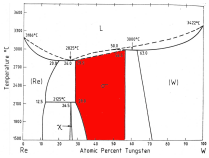



... CVM
___ FP-CEF
symbols experiments

CEF Good approximation if all end-members well estimated

Fries and Sundman, PRB, **66**, 012203 (2002)

# The $\sigma$ phase - FP-CEF

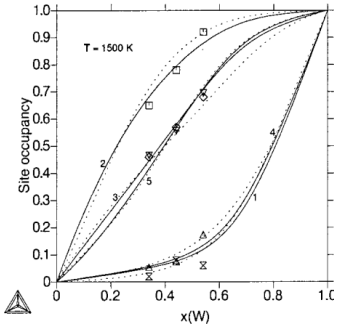



$$(Re,W)_2(Re,W)_4(Re,W)_8(Re,W)_8(Re,W)_8$$

$$G^\sigma = \sum_l \prod_s y_i^s \; G_l^\sigma + RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

DFT

With the progress of computers and FP, models closer to the crystallography became possible.



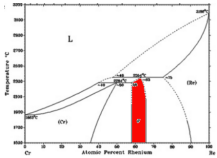

... CVM
___ FP-CEF
symbols experiments

CEF Good approximation if all end-members well estimated

$(Re,W)_{10}(Re,W)_4(Re,W)_{16}$
Good approximation !

Fries and Sundman, PRB, **66**, 012203 (2002)

# The $\sigma$ phase - FP-CEF

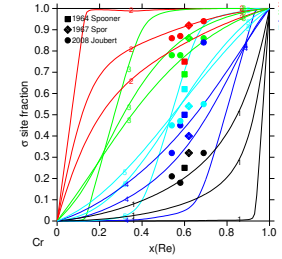


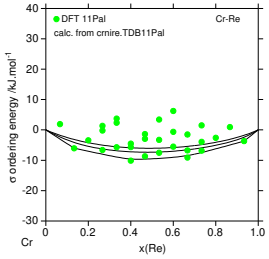

$$(Cr,Re)_2(Cr,Re)_4(Cr,Re)_8(Cr,Re)_8(Cr,Re)_8$$

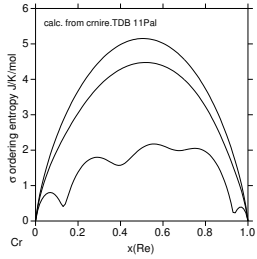
$$G^{\sigma} = \sum_l \prod_s y_i^s G_l^{\sigma} + RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

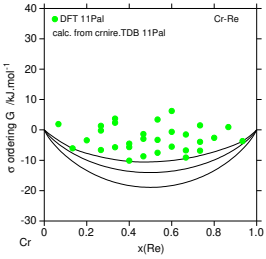
DFT

Palumbo, Abe, Fries and Pasturel, PRB, **83**, 144109 (2011)

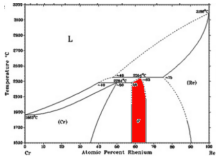


# The $\sigma$ phase - FP-CEF

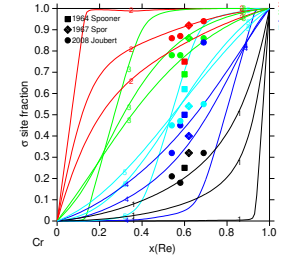


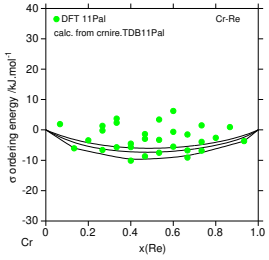

$$(Cr,Re)_2(Cr,Re)_4(Cr,Re)_8(Cr,Re)_8(Cr,Re)_8$$

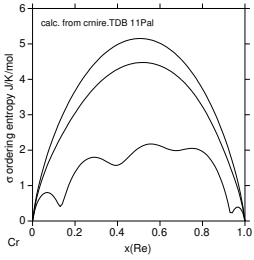
$$G^{\sigma} = \sum_I \prod_s y_i^s G_I^{\sigma} + RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

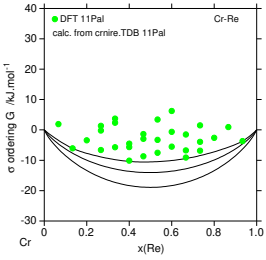
DFT

Palumbo, Abe, Fries and Pasturel, PRB, **83**, 144109 (2011)



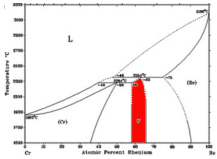




The evolution of the degree of order with temperature impact the thermodynamic functions.

# The $\sigma$ phase - FP-CEF

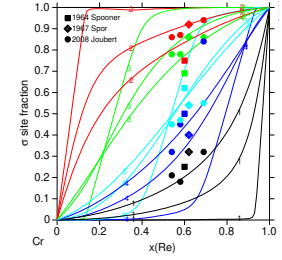


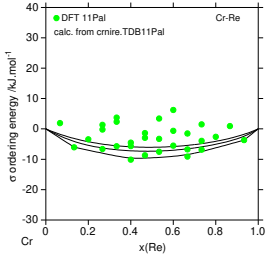

$$(Cr,Re)_2(Cr,Re)_4(Cr,Re)_8(Cr,Re)_8(Cr,Re)_8$$

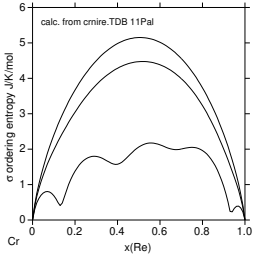
$$G^{\sigma} = \sum_l \prod_s y_i^s G_l^{\sigma} + RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

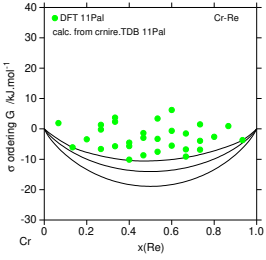
DFT

Palumbo, Abe, Fries and Pasturel, PRB, **83**, 144109 (2011)




$(Cr,Re)_{10}(Cr,Re)_4(Cr,Re)_{16}$
Bad approximation !

The evolution of the degree of order with temperature impact the thermodynamic functions.

# The $\sigma$ phase - FP-ECEF

$H_i^\sigma - T\,S_i^\sigma$ — DFT

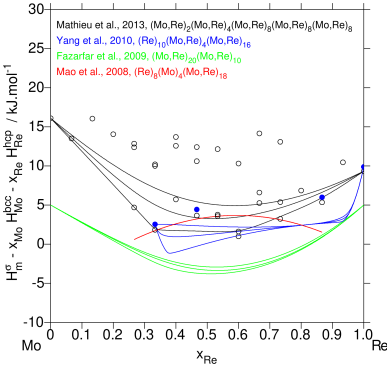
The model used strongly constrains the thermodynamic functions behavior.

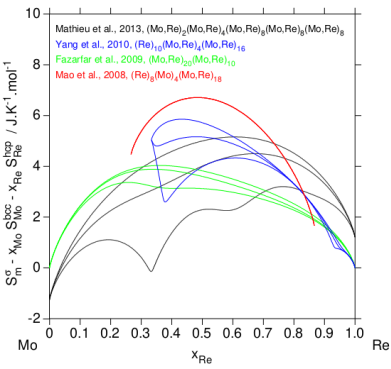
$$(Mo,Re)_2(Mo,Re)_4(Mo,Re)_8(Mo,Re)_8(Mo,Re)_8$$

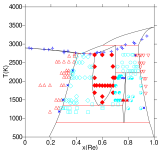
$$G^\sigma = 30\ x_i\ G_i^\sigma + \sum_I \prod_s y_i^s\ \Delta G_I^\sigma + RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

Phase diagram is not the only quality criterion.

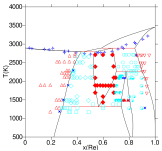
Mathieu, Dupin, Crivello, Yaqoob, Breidi *et al.*, Calphad, 2013



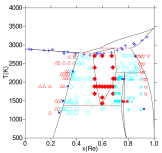



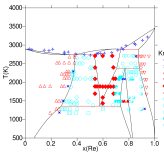

Mao et al., 2008




Farzadfar et al., 2009




Yang et al., 2010




Mathieu et al, 2013

# EBEF

18Dup Dupin, Kattner, Sundman, Palumbo, Fries, doi.org/10.6028/jres.123.020

- CEF

$$G = \sum_I \prod_s y_i^s \; G_I + RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

- ECEF

$$G = n_f \sum_i x_i \; G_i + \sum_I \prod_s y_i^s \; \Delta G_I + RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

- EBEF

$$G = n_f \sum_i x_i \; G_i \; + \sum_s \sum_{r>s} \sum_i \sum_{j \neq i} y_i^s \; y_j^r \; E_{ij}^{sr} \; + RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

$E_{ij}^{sr}$ effective bond energy when $i$ in $s$ and $j$ in $r$

$$= (a^s + a^r) \, e_{ij}^{sr} - a^s \, e_{ii}^{sr} - a^r \, e_{jj}^{sr}$$

# EBEF

18Dup Dupin, Kattner, Sundman, Palumbo, Fries, doi.org/10.6028/jres.123.020

- CEF

$$G = \sum_I \prod_s y_i^s \; G_I + RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

- ECEF

$$G = n_f \sum_i x_i \; G_i + \sum_I \prod_s y_i^s \; \Delta G_I + RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

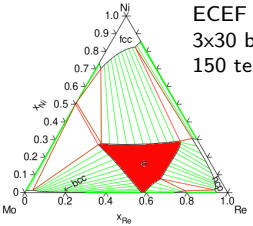
- EBEF

$$G = n_f \sum_i x_i \; G_i \; + \sum_s \sum_{r>s} \sum_i \sum_{j \neq i} y_i^s \; y_j^r \; E_{ij}^{sr} \; + RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

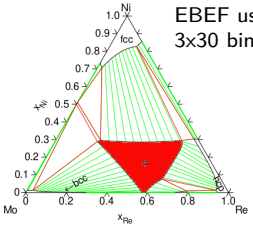
EBEF = CEF when $G_I = \sum_{s,i} a^s \, G_i + \sum_{s,i} \sum_{r>s, j \neq i} E_{ij}^{sr}$

*i.e. e.g.* when $G_{ijklm}^{\sigma} = 2\,G_i^{\sigma} + 4\,G_j^{\sigma} + 8\,G_k^{\sigma} + 8\,G_l^{\sigma} + 8\,G_m^{\sigma} + E_{ij}^{12} + E_{ik}^{13} + E_{il}^{14} + E_{im}^{15} + E_{jk}^{23} + E_{jl}^{24} + E_{jm}^{25} + E_{kl}^{34} + E_{km}^{35} + E_{lm}^{45}$

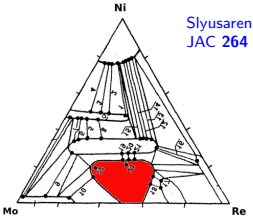
# The $\sigma$ phase - EBEF



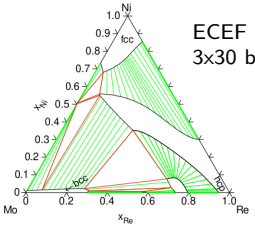

ECEF using
3x30 binary and
150 ternary DFT




EBEF using
3x30 binary DFT




Slyusarenko et al.,
JAC **264** 180-189
(1998)




ECEF using
3x30 binary DFT

# The $\sigma$ phase - DFT $\Rightarrow$ EBEF

In each binary system, the Gibbs energy of formation from the pure elements in the $\sigma$ phase is expressed for 30 $\sigma$ stoichiometric compounds using the EBE, $E^{sr}_{ij}$, with $E^{sr}_{ii} = 0$

$$\Delta G_{A:B:C:D:E} = E^{12}_{AB} + E^{13}_{AC} + E^{14}_{AD} + E^{15}_{AE} + E^{23}_{BC} + E^{24}_{BD} + E^{25}_{BE} + E^{34}_{CD} + E^{35}_{CE} + E^{45}_{DE}$$

e.g. $\Delta G_{\mathrm{Ni:Re:Re:Ni:Re}} = E^{12}_{\mathrm{NiRe}} + E^{13}_{\mathrm{NiRe}} + E^{15}_{\mathrm{NiRe}} + E^{24}_{\mathrm{ReNi}} + E^{25}_{\mathrm{ReNi}} + E^{34}_{\mathrm{ReNi}} + E^{35}_{\mathrm{ReNi}} + E^{45}_{\mathrm{NiRe}}$

The 20 EBE are determined in order to fit the DFT values for the 30 compounds using

- PARROT
- Matrix inversion

In OpenCalphad or in Thermo-Calc, $E^{12}_{AB}$ is `G(SIGMA,A:B:*:*:*;0)`, $E^{12}_{BA}$ is `G(SIGMA,B:A:*:*:*;0)`, $\cdots$
They contribute to the Gibbs energy of the phase being multiplied respectively by $y^{(1)}_A\, y^{(2)}_B$, $y^{(1)}_B\, y^{(2)}_A$, $\cdots$

# The $\sigma$ phase - DFT $\Rightarrow$ EBEF using PARROT

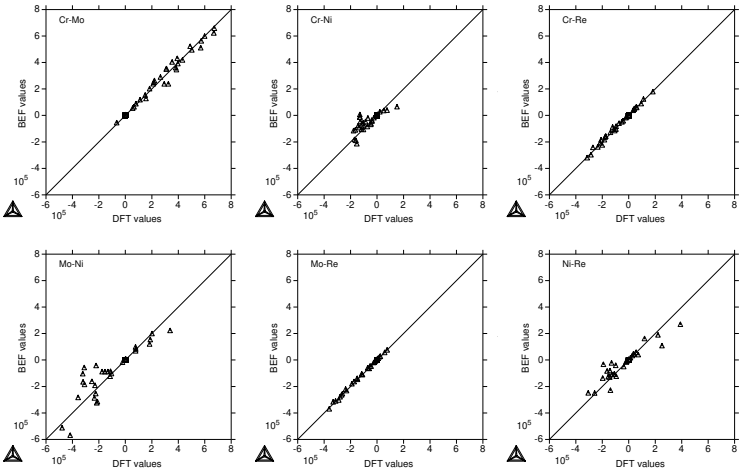
```
enter-phase SIG10 , 5 2 4 8 8 8
   NI ; RE ; RE ; NI ; RE ; N N
enter-parameter G(SIG10,NI:RE:RE:NI:RE;0) „
   + NI1RE2 + NI1RE3 + NI1RE5 + RE2NI4 + RE3NI4 + NI4RE5 ;„ N

CREATE 10,1
CHANGE_STATUS PHASE SIG10 =ENT 1
 SET_REFERENCE Ni SIG_BEF„„
 SET_REFERENCE Re SIG_BEF„„
 SET_CONDITION p=1E5 t=300 n(Ni)=10 n(Re)=20
 COMMENT        -306236 n(Re)=20 NI:RE:RE:NI:RE
 EXPERIMENT HR= -306235.99:1%
```

The optimised value for `NI1RE2` will be used for the parameter

`G(SIG_BEF,NI:RE:*:*:*:;0)`

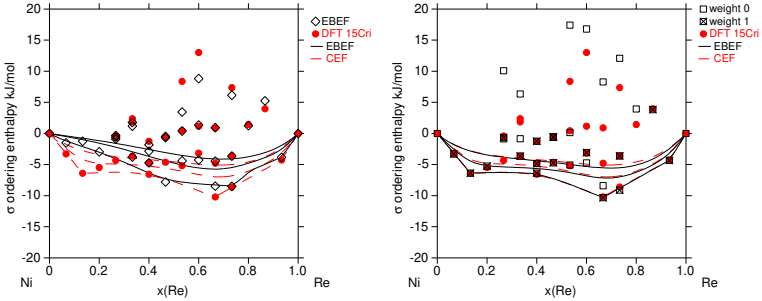
# Optimisation for the binary systems of Cr-Mo-Ni-Re




The EBEF approximation is fairly good or very good depending on the systems.

DFT values : 15Cri Crivello, Souques, Breidi, Bourgeois and Joubert, Calphad, **51** 233-240 (2015)

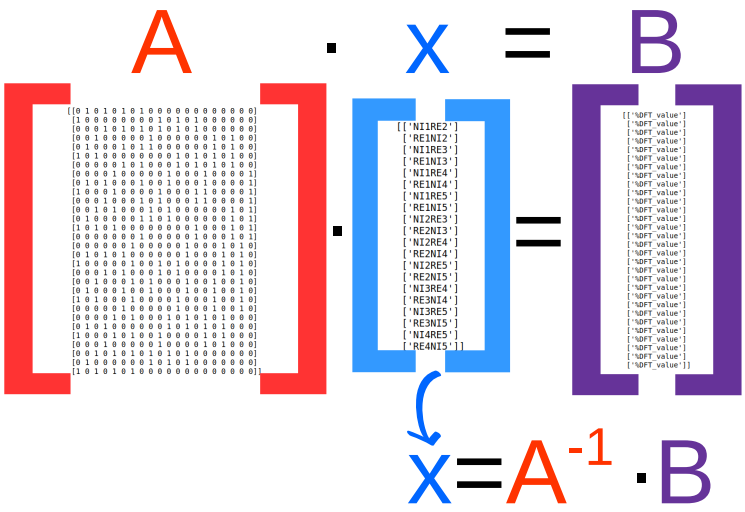
# Advanced optimisation




When the optimisation using all the configurations is not highly satisfactory, disregarding some configuration of higher energy may allow to get EBEF description closer to CEF.

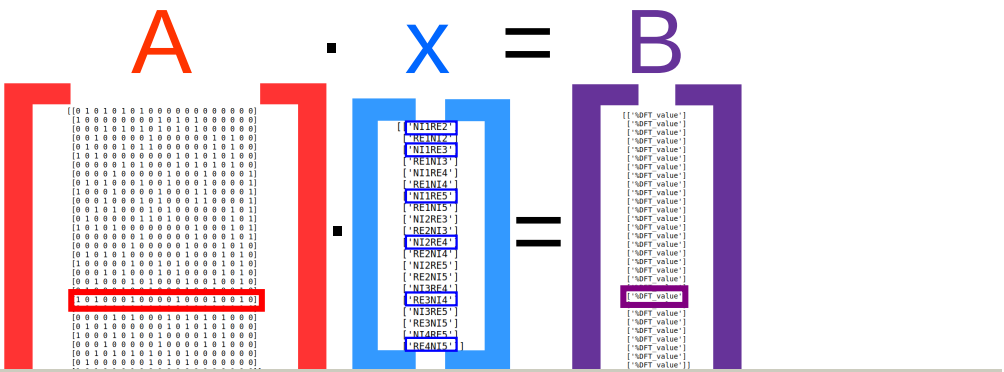
# Matrix inversion

Ivanova, Fries, Hammerschmidt, 2019

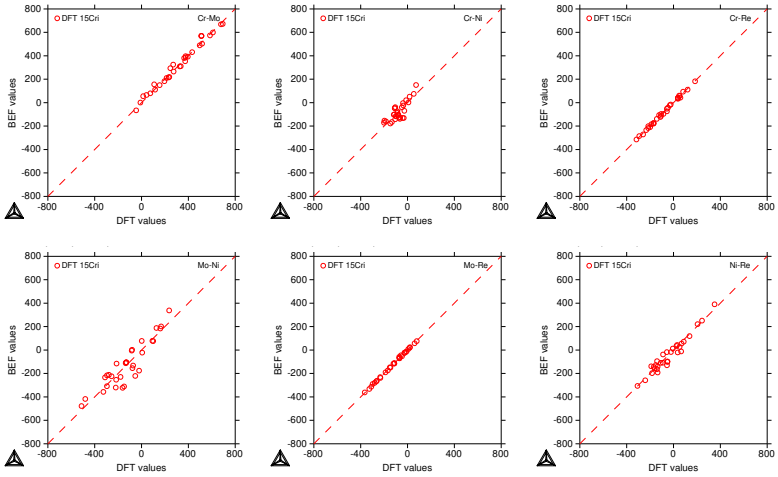

A
·
x
=
B
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['RE1NI2']
['N1RE3']
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# Matrix inversion

Ivanova, Fries, Hammerschmidt, 2019

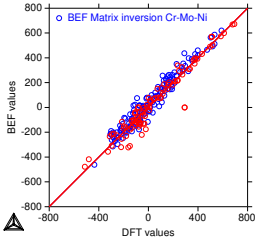


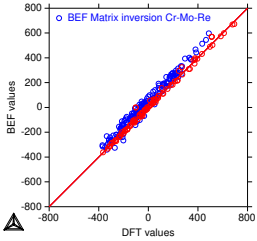
# Matrix inversion in Cr-Mo-Ni-Re

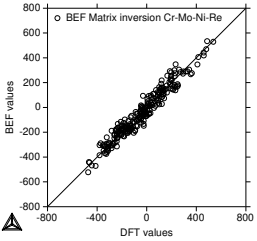


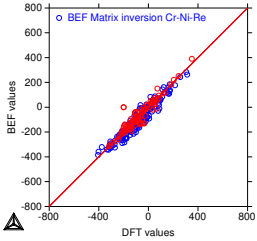

The same fairly good and very good agreements as with Parrot are obtained for the different binary systems.

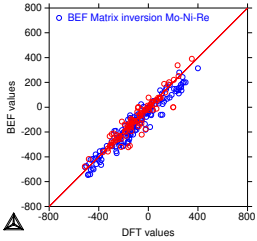
# Matrix inversion in Cr-Mo-Ni-Re



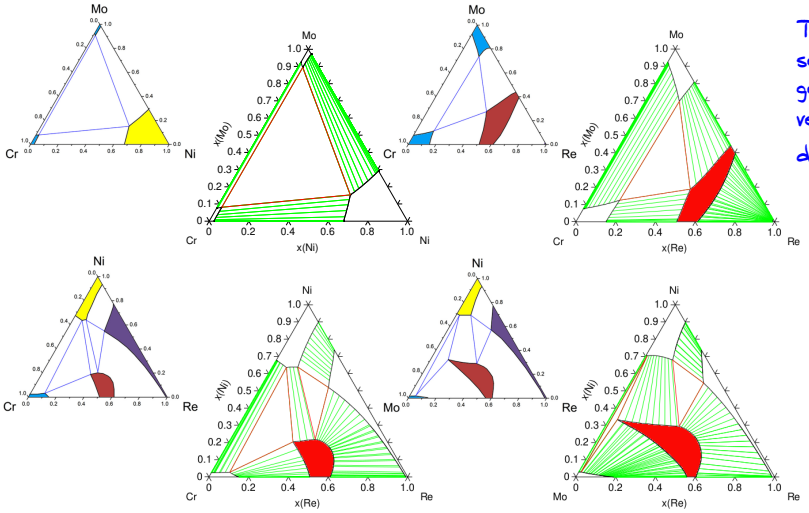




The strong correlation obtained for the ternary and quaternary compounds between the EBEF approximation and the values calculated by DFT shows the interest of using the EBEF for multicomponent phases.

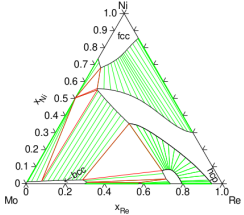
# Matrix inversion in Cr-Mo-Ni-Re



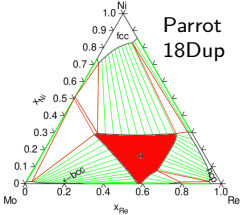

The EBEF approximation seems good enough to get ternary extrapolations very close to the CEF descriptions.

15Cri CEF TDB 1143 lines
/ EBEF TDB 253 lines

# Mo-Ni-Re from 3x30 binary DFT, changing only Ni-Re

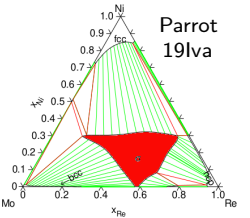



ECEF / 15Cri



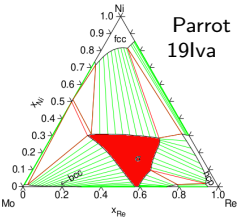

Parrot 18Dup

EBEF / 15Cri




Parrot 19Iva

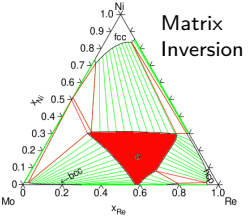
EBEF / 15Cri




Parrot 19Iva

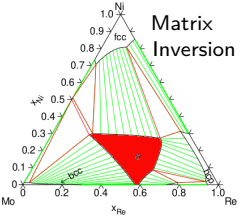
EBEF / 11Pal

Whatever the approach used, EBEF extrapolates much better than CEF.




Matrix Inversion

EBEF / 15Cri




Matrix Inversion

EBEF / 11Pal

# Thermodynamic modeling is alive !

Thermodynamic modeling is alive !

Thank you for your attention !