Modelling σ phase with the help of DFT
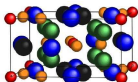
Nathalie Dupin [1]   Jean-Marc Joubert[2]   Jean-Claude Crivello[2]
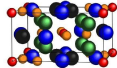Khurram Yaqoob[2]   Abed Breidi[2]   Jean-Marc Fiorani[3]

[1]Calcul Thermodynamique

[2]Institut de Chimie et des Matériaux Paris-Est

[3]Institut Jean Lamour

Calphad XLI, 2012 june 6th

Introduction

▶ After decades using models considering models of the type $A_a(A,B)_c B_b$ derived in order to decrease as much as possible the number of end compounds to describe the σ phase, the pioneer work of Fries and Sundman on Re-W justified the use of DFT total energies within the CEF to describe the thermodynamic properties of this phase.

▶ Since, different studies, often focussed on binary systems, were reported. They are in general either DFT studies that do not propose a description allowing to describe the phase diagram in agreement with experiments or Calphad description where DFT calculations are used with some freedom.

▶ The purpose of this study is to use DFT results as directly as possible to describe the thermodynamic properties of the σ phase in order to calculate accurately phase diagram in multicomponent systems.
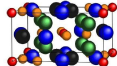
Outline
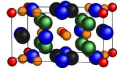
- Mo-Re
  - $(A,B)_2(A,B)_4(A,B)_8(A,B)_8(A,B)_8$
  - Simplifications to 4, 3 and 2 SL
  - Simplifications with excess interactions
  - Ignoring some ordering
  - The old model $(A)_{10}(B)_4(A,B)_{16}$
- Mo-Ni-Re

σ phase

Based on the crystallographic structure of the phase

	$(A,B)_2$	$(A,B)_4$	$(A,B)_8$	$(A,B)_8$	$(A,B)_8$
s	2a	4f	$8i_1$	$8i_2$	8j
a^s	2	4	8	8	8

$$G^{\sigma} = \sum_{ABCDE} y_A^{2a} \, y_B^{4f} \, y_C^{8i_1} \, y_D^{8i_2} \, y_E^{8j} \, G_{ABCDE}^{\sigma} + RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

$$G_{ABCDE}^{\sigma} - \sum_s a^s G_i^{SER} = E_{ABCDE}^{\sigma} - \sum_s a^s E_i^{SER} + T \sum_s a^s \Delta S_i^{\sigma}$$

E_{ABCDE}^{σ} and E_i^{SER} total energies from DFT[*]

ΔS_i^{σ} assessed from phase diagram information, does not affect the ordering as their contribution depend linearly on the composition.

[*]For more details on DFT calculations, poster Me8 : Systematic DFT Investigation of χ and σ Phases in Transition Metal – Re Binary Systems, **Jean-Claude Crivello**, et al.
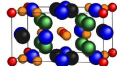
Disordered contribution

The CEF has actually been used within the following formalism

$$G^{\sigma} = \sum_s a_s \ G^{dis-\sigma}(x) + \Delta G^{ord-\sigma}(y)$$

$$G^{dis-\sigma}(x) = \sum_i x_i \, G_i^{\sigma} + \sum_{i,j} x_i \, x_j L_{i,j}^{\sigma}$$
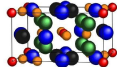
$$\Delta G^{ord-\sigma}(x) = \sum_{ABCDE} y_A^{2a} \, y_B^{4f} \, y_C^{8i_1} \, y_D^{8i_2} \, y_E^{8j} \, \Delta G_{ABCDE}^{\sigma}$$

$$+ RT \sum_s a^s \sum_i y_i^s \ln y_i^s$$

with $\Delta G_{ABCDE}^{\sigma} = E_{ABCDE}^{\sigma} - \sum_s a^s \, E_i^{\sigma}$

$\frac{G_i^{\sigma}}{\sum_s a_s} - G_i^{SER} = \frac{E_i^{\sigma}}{\sum_s a_s} - E_i^{SER} + T \, \Delta S_i^{\sigma}$

$\Delta G^{ord-\sigma}(y)$ only from DFT.

Assessed ΔS_i^{σ} only in $G^{dis-\sigma}(x)$.

Phase diagram

and σ properties at 500, 1500 and 2500K
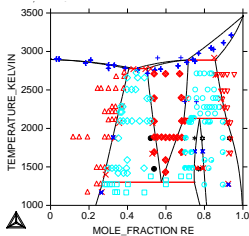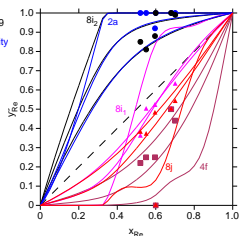
$$L_{Mo,Re}^{liq.,0} = -1130 - 4.138\,T$$
$$L_{Mo,Re}^{liq.,1} = -53870 + 16.67\,T$$

$$L_{Mo,Re}^{bcc,0} = +1666 - 4.138\,T$$
$$L_{Mo,Re}^{bcc,1} = -57100 + 16.67\,T$$

$$L_{Mo,Re}^{hcp,0} = +24197 - 10.75\,T$$
$$L_{Mo,Re}^{hcp,1} = -10495$$

$$\Delta S_{Mo}^{\sigma} = 3.9 \quad \Delta S_{Re}^{\sigma} = 1.024$$

$$\Delta S_{Mo}^{\chi} = 5.35 \quad \Delta S_{Re}^{\chi} = -0.216$$
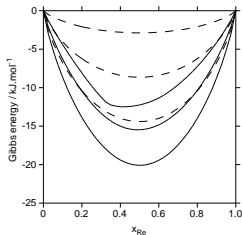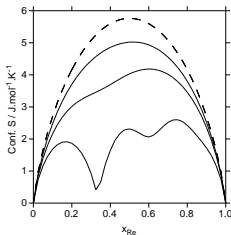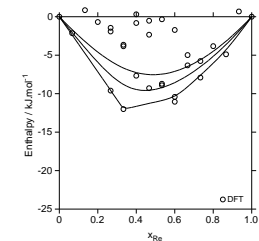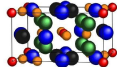
σ simplifications based on site occupancies

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

CN12   CN15   CN14   CN12   CN14

4SL $(A,B)_{10}(A,B)_4(A,B)_8(A,B)_8$ $G^{4SL}_{ABCD} = G^{5SL}_{ABCAD}$

3SL $(A,B)_{10}(A,B)_4(A,B)_{16}$ $G^{3SL}_{ABC} = G^{5SL}_{ABCAC}$

2SL $(A,B)_{10}(A,B)_{20}$ $G^{2SL}_{AB} = G^{5SL}_{ABBAB}$

These simplifications will be applied with different assumptions keeping unchanged the description of the other phases assessed with the 5SL DFT-CEF.
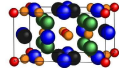
Using only DFT for the σ phase
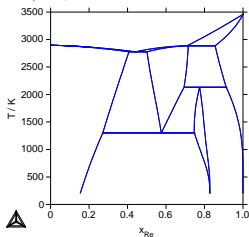
$\rightarrow (A,B)_{10}(A,B)_4(A,B)_8(A,B)_8$
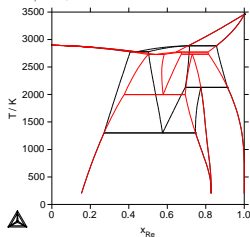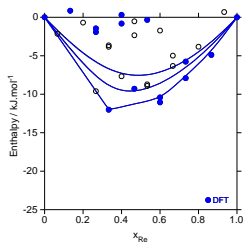
$\rightarrow (A,B)_{10}(A,B)_4(A,B)_{16}$
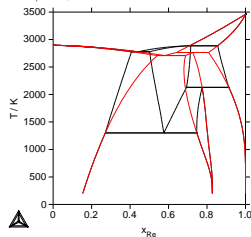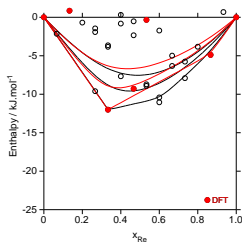
$\rightarrow (A,B)_{10}(A,B)_{20}$
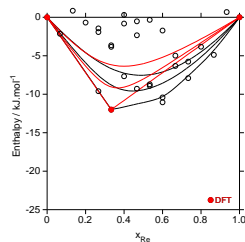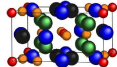
Excess interactions fitted on phase diagram

$\rightarrow (A,B)_{10}(A,B)_4(A,B)_8(A,B)_8$

L(SIGMA,MO,RE:*:*:*;0)=0

$\rightarrow (A,B)_{10}(A,B)_4(A,B)_{16}$
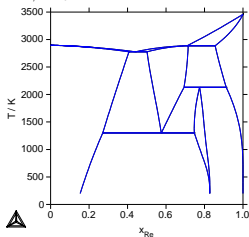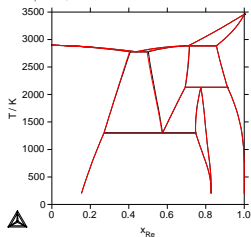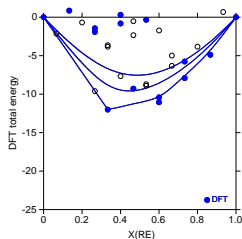
L(SIGMA,MO,RE:*:*;0)=0
L(SIGMA,*:*:MO,RE;0)=-145120
+4.377*T

$\rightarrow (A,B)_{10}(A,B)_{20}$
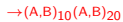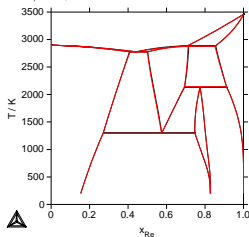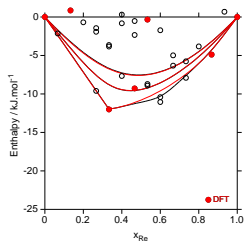
L(SIGMA,MO,RE:*;0)=0
L(SIGMA,*:MO,RE;0)=-259000
+21.3*T
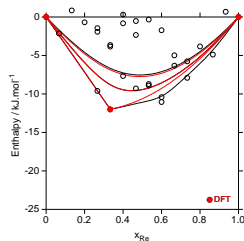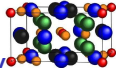
Using DFT values for most stable configurations only
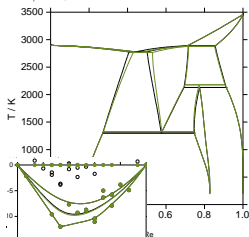
5SL 17 DFT compounds
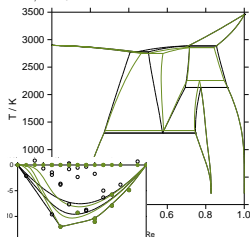
5SL 11 DFT compounds

For each phase diagram, the enthalpies of formation used are shown with solid symbols.

Ignoring the ordering of some compounds can rapidly modify the phase diagram. The selection of the most stable compounds can be difficult and depend on the system.
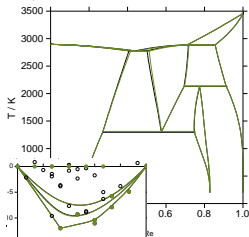
4SL 11 DFT compounds
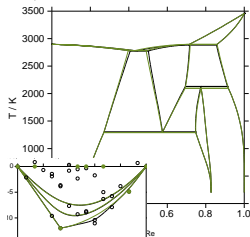
3SL 4 DFT compounds

2SL 3 DFT compounds
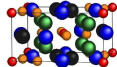
$(Re)_{10}(Mo)_4(Mo,Re)_{16}$

with previous excess
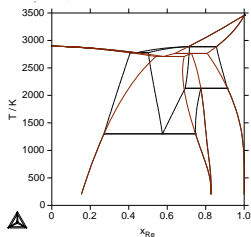
This "classical" model has widely been used. Its main drawback is that some σ compositions cannot be described. Moreover, it largely underestimates the configurational entropy. This flaw should be compensated by introducing an extra entropy of formation actually accounting for the configuration entropy not described by this model.

5SL DFT-CEF

500K

1500K

2500K

Mo-Ni (K. Frisk)

Mo-Re

Ni-Re (TCNI)

5SL DFT-CEF

500K

1500K

2500K

Mo-Ni

Mo-Re

Ni-Re
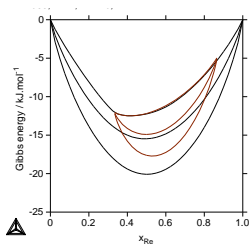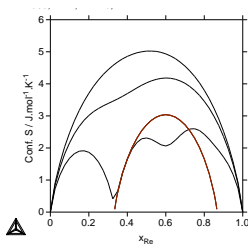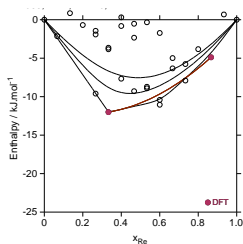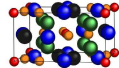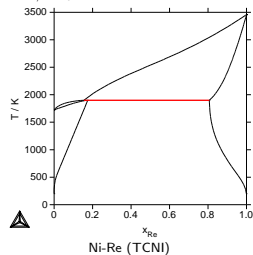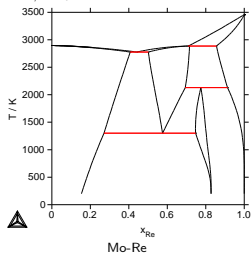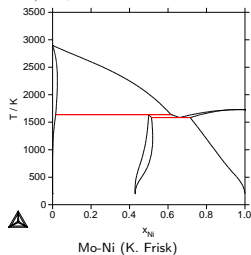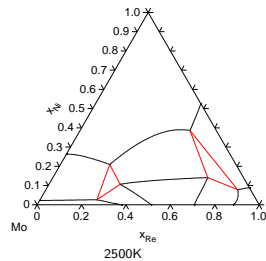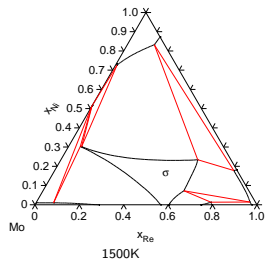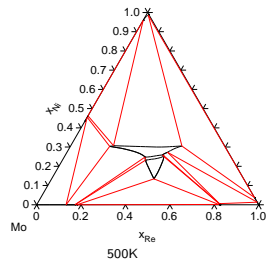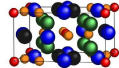
5SL DFT-CEF

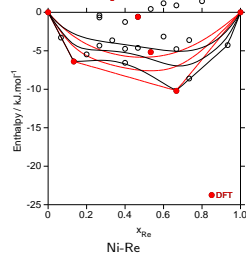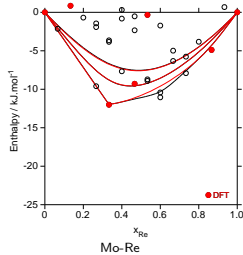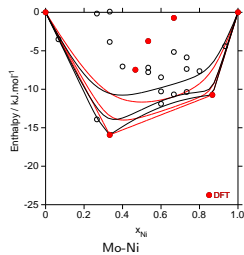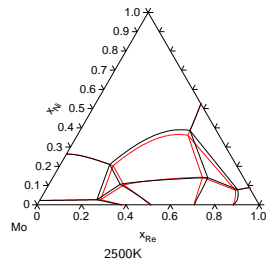$\Delta S^{\sigma}_{Ni} = -6$ roughly assessed from experimental phase diagram.

4SL DFT-CEF

500K

1500K

2500K

Mo-Ni

Mo-Re

Ni-Re

3SL DFT-CEF

500K

1500K

2500K

Mo-Ni

Mo-Re

Ni-Re

2SL DFT-CEF

500K

1500K

2500K
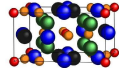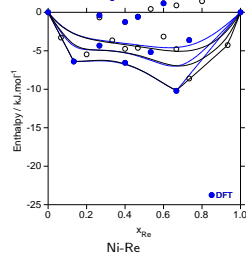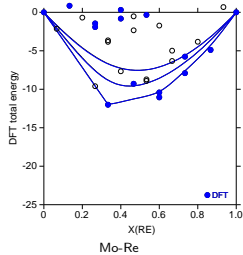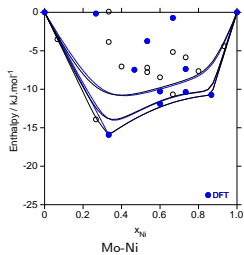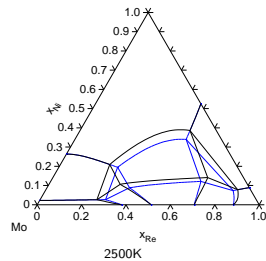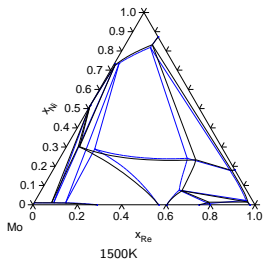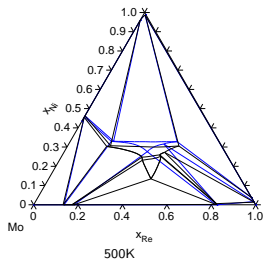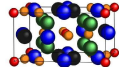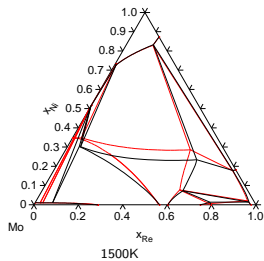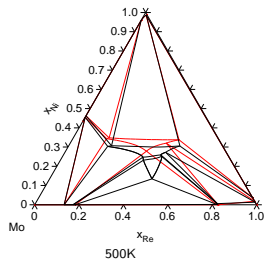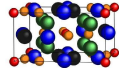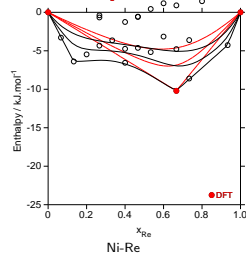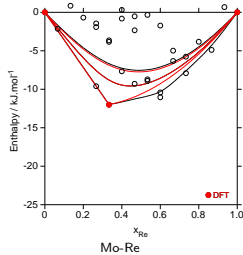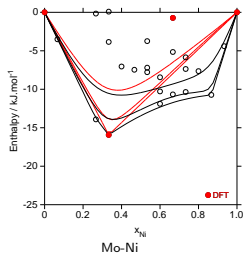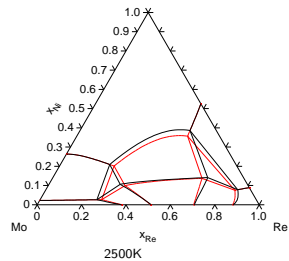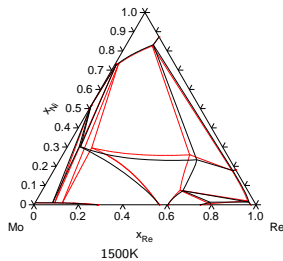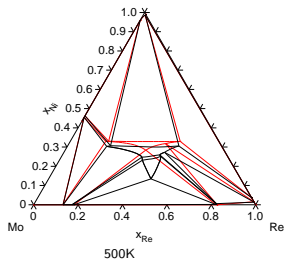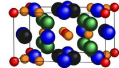
Mo-Ni

Mo-Re

Ni-Re

DFT-CEF with only binary DFT

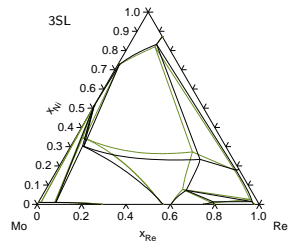$\Delta G^{\sigma}_{Mo_a Ni_b Re_c} = 0$
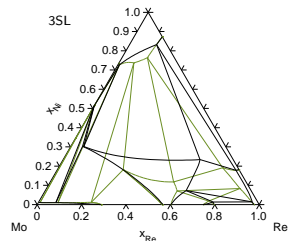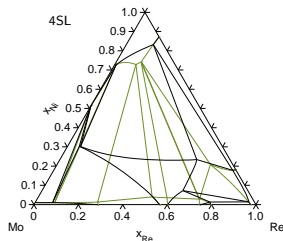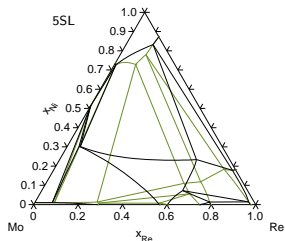
$\Delta G^{\sigma}_{Mo_a Ni_b Re_c} = \frac{a}{a+c} \Delta G^{\sigma}_{Mo_a Ni_b Mo_c} + \frac{c}{a+c} \Delta G^{\sigma}_{Re_a Ni_b Re_c}$
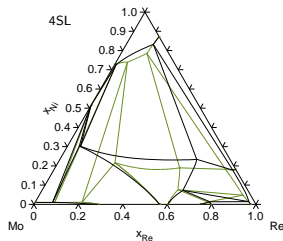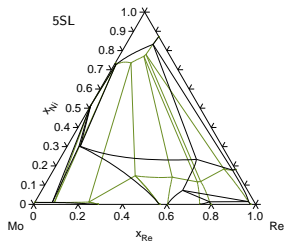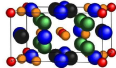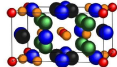
Conclusion and perspectives

- ▶ Good Mo-Re and Mo-Ni-Re phase diagram with reduced number of assessed parameters with 5SL DFT-CEF.
- ▶ Ignoring some compounds ... bad idea.
- ▶ All the elements in all sublattices.
- ▶ Need of common lattice stabilities.
- ▶ 2SL very appealing but bad at low temperatures
- ▶ to be done : other binary systems, Co-Cr-Re, ...

Ackownledgement