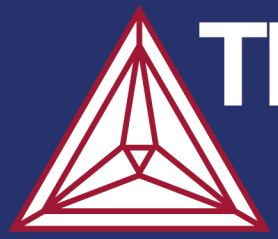

Thermo-Calc Software

Boosting the CALPHAD Modeling of Multi-component Systems by ab initio Calculations: Selected Case Studies

Giancarlo Trimarchi and Qing Chen
Thermo-Calc Software AB
Solna, Sweden

TMS 2020, San Diego, February 24, 2020

Background and objectives

- Background: DFT emerged as a crucial source of input data to build **CALPHAD** thermodynamic "**databases**" for **multi-component compounds**.

- Challenge: The number of DFT calculations required to determine the parameters of models based on the standard **Compound Energy Formalism (CEF)** increases rapidly with the number of elements and sublattices.

The CALPHAD thermodynamic modeling framework: the main idea

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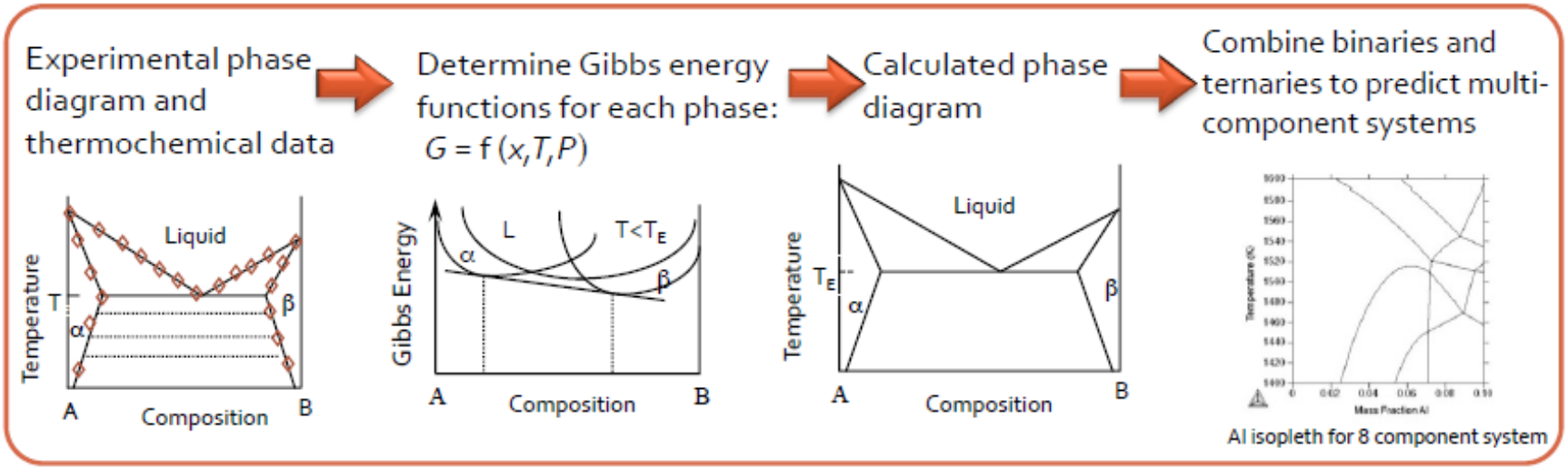
CALPHAD (CALculation of PHAse Diagrams)

- **Experimental** and **ab initio** data about the thermophysical data of an alloy are collected/geerated.
- The thermophysical data are used to fit the **Gibbs energy functions** of the phases that the alloy exhibits.
- The Gibbs energy functions are applied to calculate thermodynamic equilibrium properties including phase diagrams

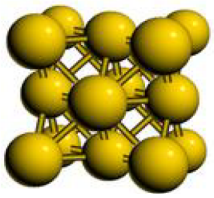


From Dr. C. Campbell, NIST, USA

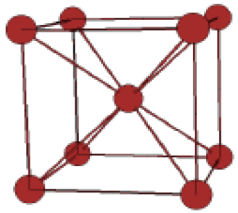
A closer look at the CALPHAD method: phases with a single sublattice

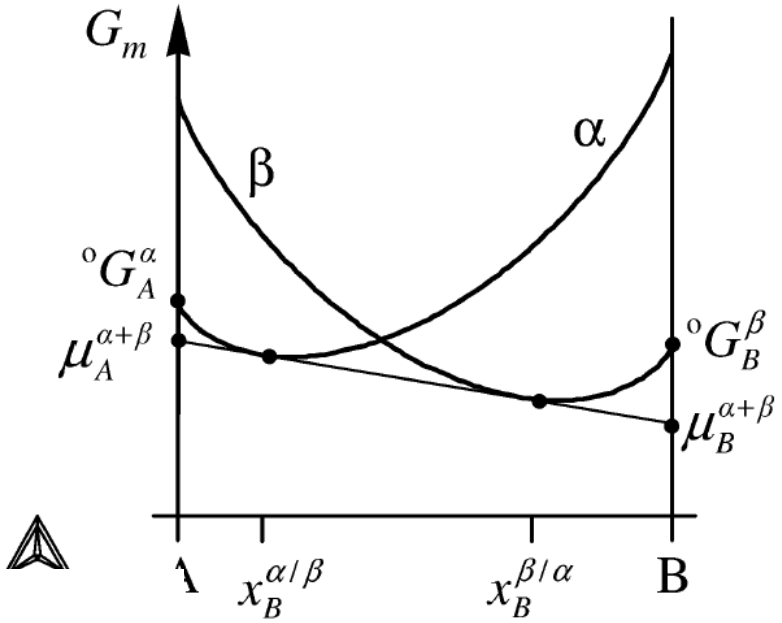
The Gibbs free energy G_m of all the phases of an $A_{1-x}B_x$ alloy is modeled across the full composition range

A



B





$$G_m(\{x_i\}, T) = {}^{\text{ref}}G + {}^{\text{id}}G + {}^{\text{E}}G$$

$$= \sum_i x_i \, {}^{\circ}G_i + RT \sum_i x_i \log(x_i) + {}^{\text{E}}G$$

$${}^{\text{E}}G = \sum_i \sum_{j>i} x_i x_j \left[\sum_\nu {}^{\nu}L_{ij}(x_i - x_j)^{\nu} \right]$$

A closer look at the CALPHAD method: multi-sublattice phases

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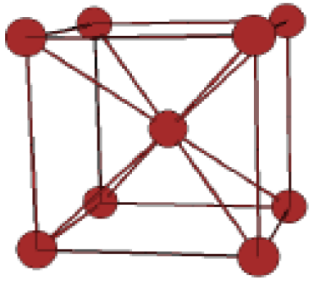
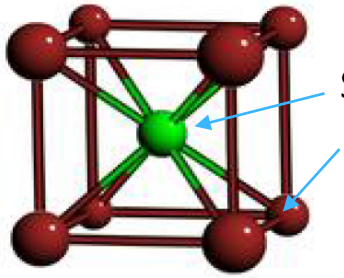
Single sublattice,
e.g., BCC



Multiple sublattices,
e.g., CsCl (B2) structure



Compound energy formalism to model the Gibbs energy

$$G_m(\{y_i^{(s)}\}, T) = {}^{\text{ref}}G + {}^{\text{id}}G + {}^{\text{E}}G$$

$${}^{\text{ref}}G = \sum_i \sum_j y_i^{(1)} y_j^{(2)} {}^{\circ}G_{i:j}$$

$${}^{\text{id}}G = RT \sum_s a^{(s)} \sum_i y_i^{(s)} \log y_i^{(s)}$$

Example of binary end-members

$${}^{\circ}G_{\text{Al:Al}}$$
$${}^{\circ}G_{\text{Ni:Ni}}$$
$${}^{\circ}G_{\text{Al:Ni}}$$
$${}^{\circ}G_{\text{Ni:Al}}$$

Phases with numerous sublattices (e.g., five) are common, including in industrially relevant alloys!

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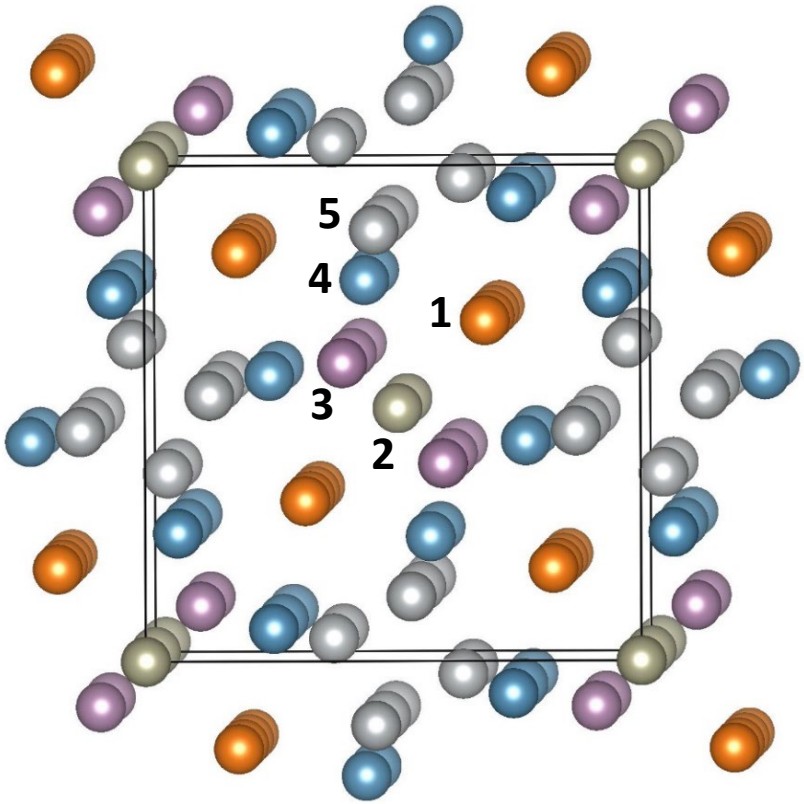
Common multi-sublattice phases: topological closed-packed (TCP) phases, e.g., σ-phase, μ-phase, χ-phase, C14, C15, etc.

σ-phase structure

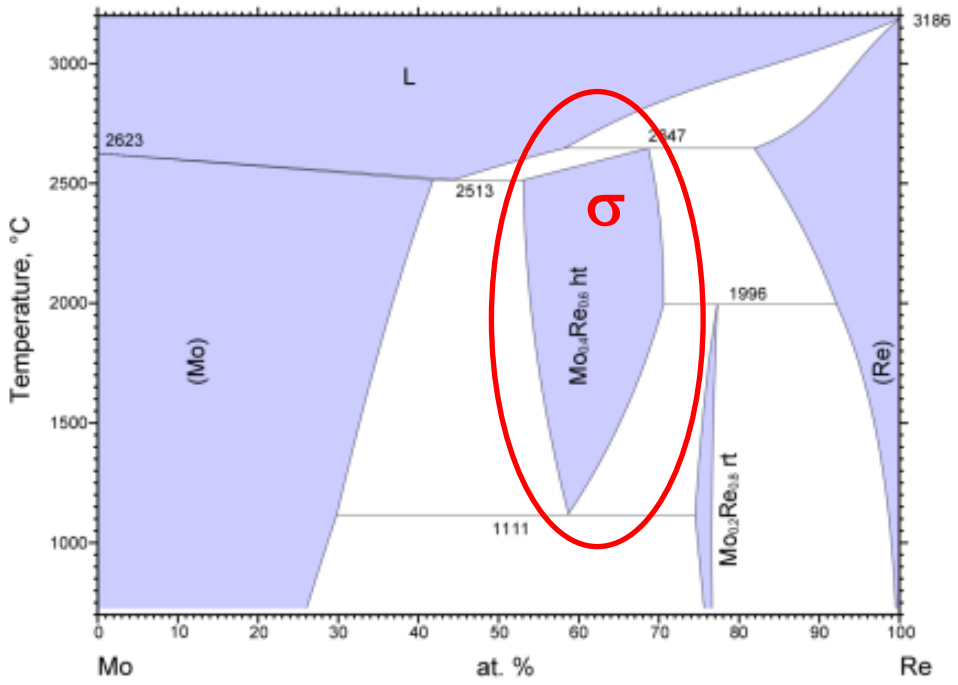


- 30 atoms in the unit cell
- 5 distinct lattice sites (Wyckoff positions)

Example of binary alloy with a σ-phase: Mo-Re

Mo-Re

Experimental phase diagram



Number of binary sigma-phase end-members: $2^5 = 32$

$${}^{\circ}G^{\sigma}_{\mathrm{Re:Mo:Mo:Mo:Mo}}$$

$${}^{\circ}G^{\sigma}_{\mathrm{Mo:Re:Mo:Mo:Mo}}$$

$${}^{\circ}G^{\sigma}_{\mathrm{Re:Re:Mo:Mo:Mo}}$$

$${}^{\circ}G^{\sigma}_{\mathrm{Mo:Mo:Mo:Re:Mo}}$$

$${}^{\circ}G^{\sigma}_{\mathrm{Mo:Mo:Re:Mo:Mo}}$$

.....

Approach to calculating the formation energies of the end-members:
Density Functional Theory!

Example of ternary alloy with a σ-phase: Mo-Ni-Re

Mo-Ni-Re phase diagram
1425 K isothermal section

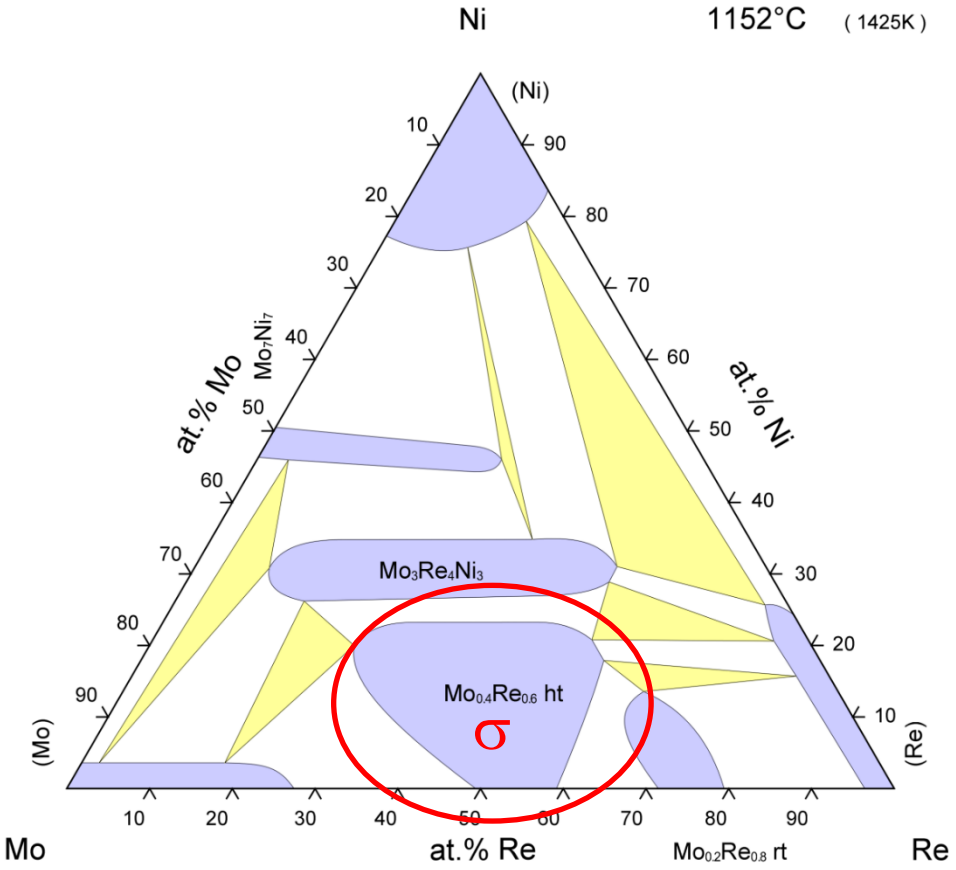


 Diagram No. 201120

Number of binary σ-phase end-members: $3^5 = 243$

- $G^{\sigma}_{\mathrm{Re:Mo:Ni:Mo:Mo}}$
- $G^{\sigma}_{\mathrm{Mo:Re:Mo:Mo:Mo}}$
- $G^{\sigma}_{\mathrm{Re:Re:Ni:Ni:Ni}}$
- $G^{\sigma}_{\mathrm{Ni:Mo:Mo:Re:Ni}}$
- $G^{\sigma}_{\mathrm{Mo:Mo:Re:Mo:Mo}}$

.....

Challenge for systematically describing the sigma phase in a real-world thermodynamic ”database”

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Elements in Thermo-Calc’s TCNI9 thermodynamic database:

Al	Ar	B	C	Ca	Co	Cr	Cu	Fe	H
Hf	Mg	Mn	Mo	N	Nb	Ni	O	Pd	Pt
Re	Ru	S	Si	Ta	Ti	V	W	Y	Zr

Some statistics about a typycal database:

- Number of elements: **30**
- Number of binary (A-B) combinations: **~ 10^2**
- Number of ternary (A-B-C) combinations: **~ 10^3**

Number of sigma end-members per element combination:

- Number of sigma **binary** end-members: **30**
- Number of sigma **ternary** end-members: **150**

Number of DFT calculations needed to model the sigma phase in a typycal database:

- Binary sigma phase: **~ 10^3**
- Number of ternary A-B-C combinations: **~ 10^5**

The effective bond energy formalism (EBEF): the main idea

Thermo-Calc Software

Dupin, Kattner, Sundman, Palumbo, and Fries
J. Res. Natl. Inst. Stan. **123,** 123020 (2018)

- Expand the end-member energies into binary terms featuring only element pairs

→ Example of expansion of the energy for a **binary** end-member

$$\Delta G^{\phi}_{\mathrm{Mo:Re:Mo:Mo:Mo}} = \Gamma_{\mathrm{Mo:Re:*:*:*}} + \Gamma_{\mathrm{*:Re:Mo:*:*}} + \Gamma_{\mathrm{*:Re:*:Mo:*}} + \Gamma_{\mathrm{*:Re:*:*:Mo}}$$

→ Example of expansion of the energy for a **ternary** end-member

$$\Delta G^{\phi}_{\mathrm{Mo:Mo:Mo:Re:Ni}} = \Gamma_{\mathrm{Mo:*:*:Re:*}} + \Gamma_{\mathrm{Mo:*:*:*:Ni}} + \Gamma_{\mathrm{*:Mo:*:Re:*}} + \Gamma_{\mathrm{*:Mo:*:*:Ni}} + \Gamma_{\mathrm{*:*:Mo:Re:*}} + \Gamma_{\mathrm{*:*:Mo:*:Ni}} + \Gamma_{\mathrm{*:*:*:Re:Ni}}$$

- **Interesting observation:** <u>these expansions involve only binary terms.</u>

The effective bond energy formalism (EBEF): non-uniqueness of the solution and a remedy to this problem

Thermo-Calc Software

Dupin, Kattner, Sundman, Palumbo, and Fries
J. Res. Natl. Inst. Stan. **123** 123020 (2018)

→ Expand the end-member energies into binary terms featuring only element pairs

$$\Delta G^{\phi}_{i:j:k:l:m} = \sum_i \sum_{j \neq i} \Big(y_i^{(1)} y_j^{(2)} \Gamma_{i:j:*:*:*} + y_i^{(1)} y_j^{(3)} \Gamma_{i:*:j:*:*} + y_i^{(1)} y_j^{(4)} \Gamma_{i:*:*:j:*} + y_i^{(1)} y_j^{(5)} \Gamma_{i:*:*:*:j} + y_i^{(2)} y_j^{(3)} \Gamma_{*:i:j:*:*} + y_i^{(2)} y_j^{(4)} \Gamma_{*:i:*:j:*} + y_i^{(2)} y_j^{(5)} \Gamma_{*:i:*:*:j} + y_i^{(3)} y_j^{(4)} \Gamma_{*:*:i:j:*} + y_i^{(3)} y_j^{(5)} \Gamma_{*:*:i:*:j} + y_i^{(4)} y_j^{(5)} \Gamma_{*:*:*:i:j} \Big)$$

The determination of the EBEF parameters is a linear regression problem:

$$y_i^{(s_1)} y_j^{(s_2)} \longrightarrow x_p$$

$$\Gamma_{i:j:*:*:*} \longrightarrow \beta_p$$

$$\Delta G^{\phi}_{i:j:k:l:m} \longrightarrow y_e$$

$$\mathbf{y} = \mathbf{X}\beta$$

$$\hat{\beta} = (\mathbf{X}^T\mathbf{X})^{-1}\mathbf{X}^T\mathbf{y}$$

Warning: $\det(\mathbf{X}^T\mathbf{X}) = 0$

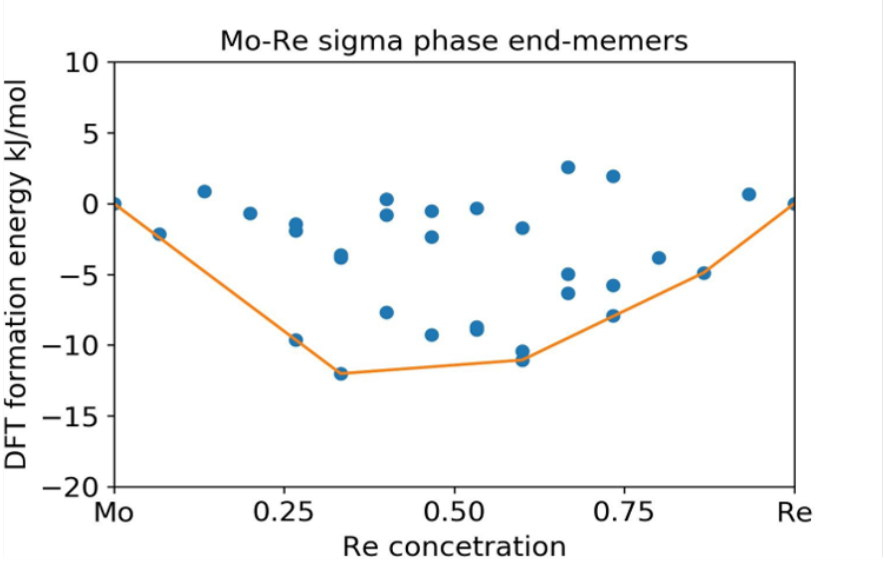
hence, there are infinite solutions

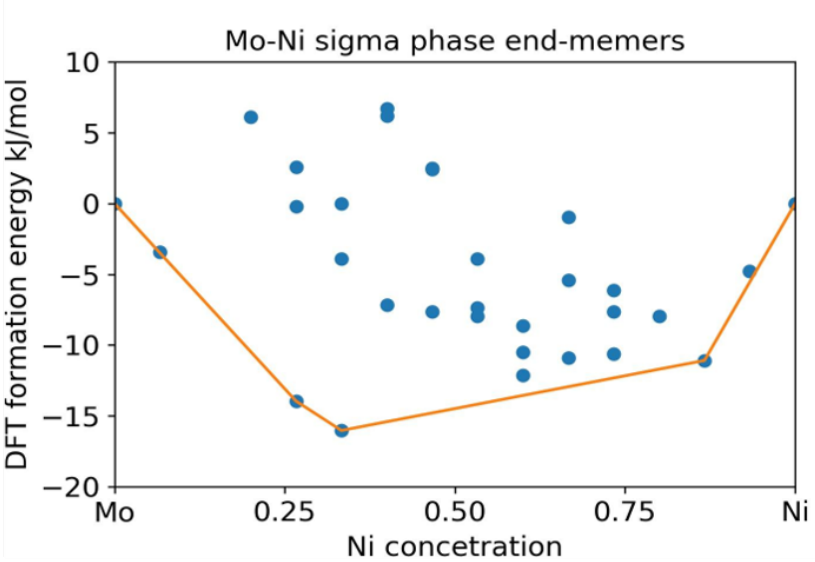
$$\hat{\beta}_{\mathrm{SVD}} = \mathbf{V}\mathbf{\Sigma}^{-1}\mathbf{U}^T\mathbf{y}$$

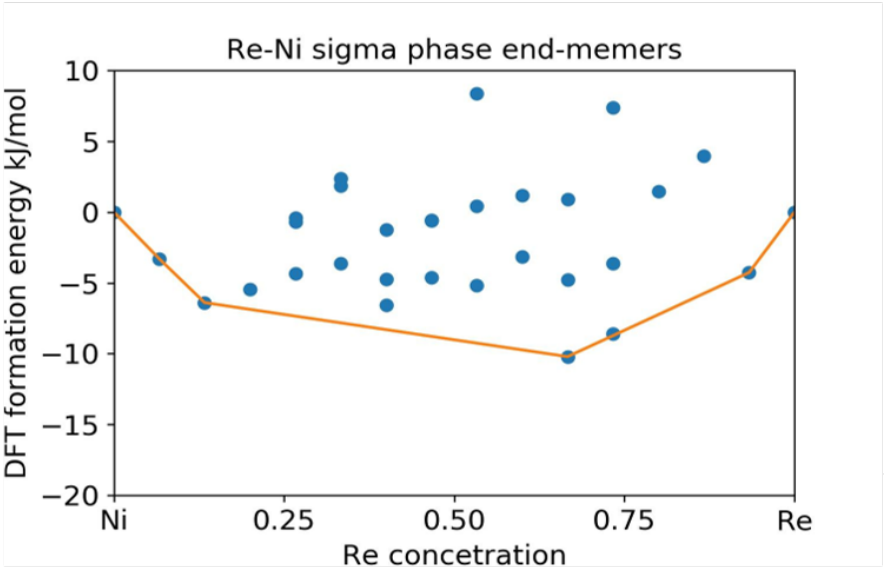
The **singular value decomposition (SVD)** gives the **minimum norm solution** which is **unique**

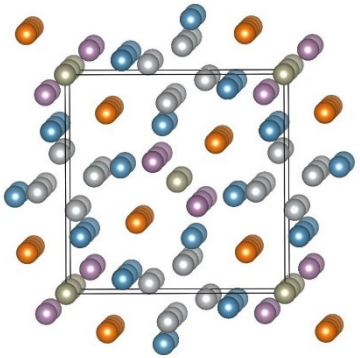
Mo-Ni-Re: DFT convex hulls for the binaries

- DFT formation energies of the binary sigma end-members.
- The references are the total energies of the elements in the sigma phase.









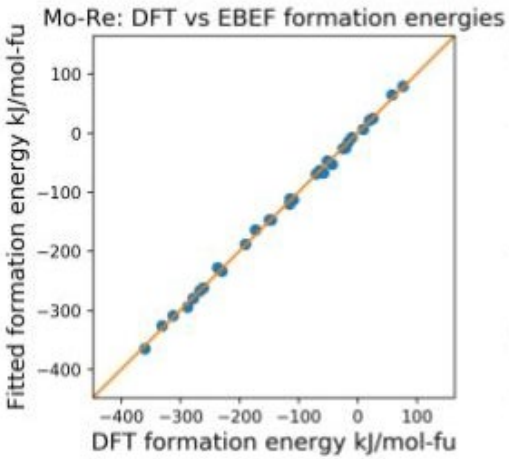
DFT total energies for the sigma endmembers from Yaqoob, Inorganic Chemistry **51**, 3071 (2012)

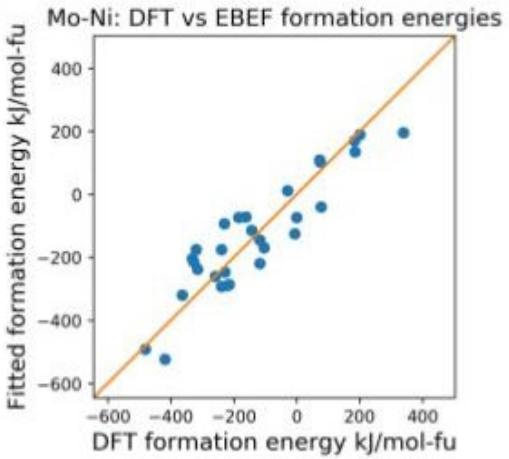
The EBEF applied to Mo-Ni-Re: performance of the proposed implementation

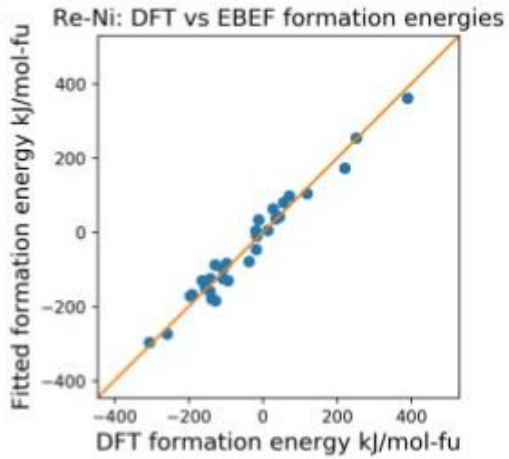
Thermo-Calc Software

Mo-Re | **Mo-Ni** | **Re-Ni**

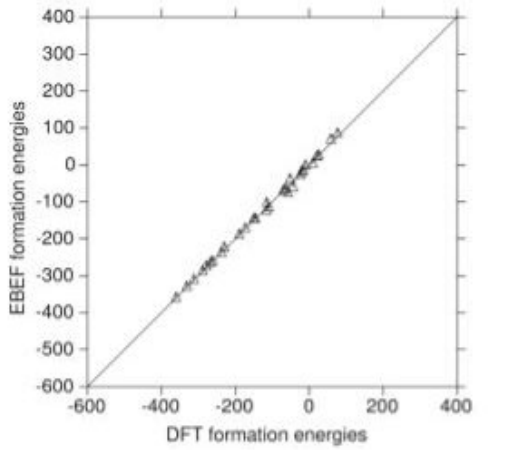
Present work

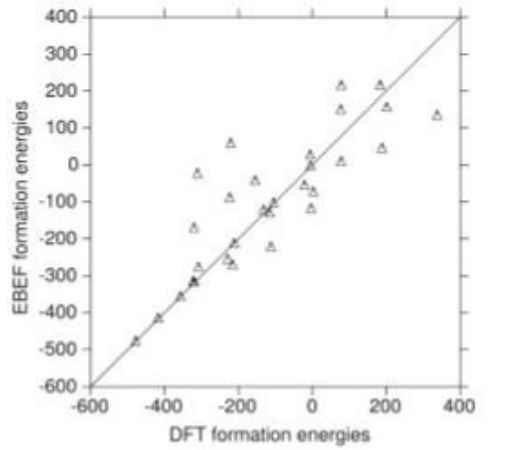


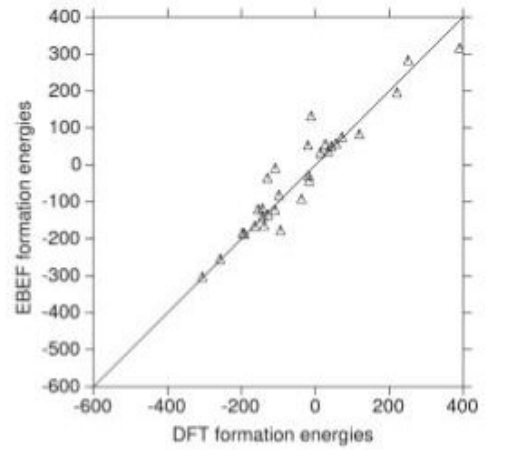




Dupin et al.

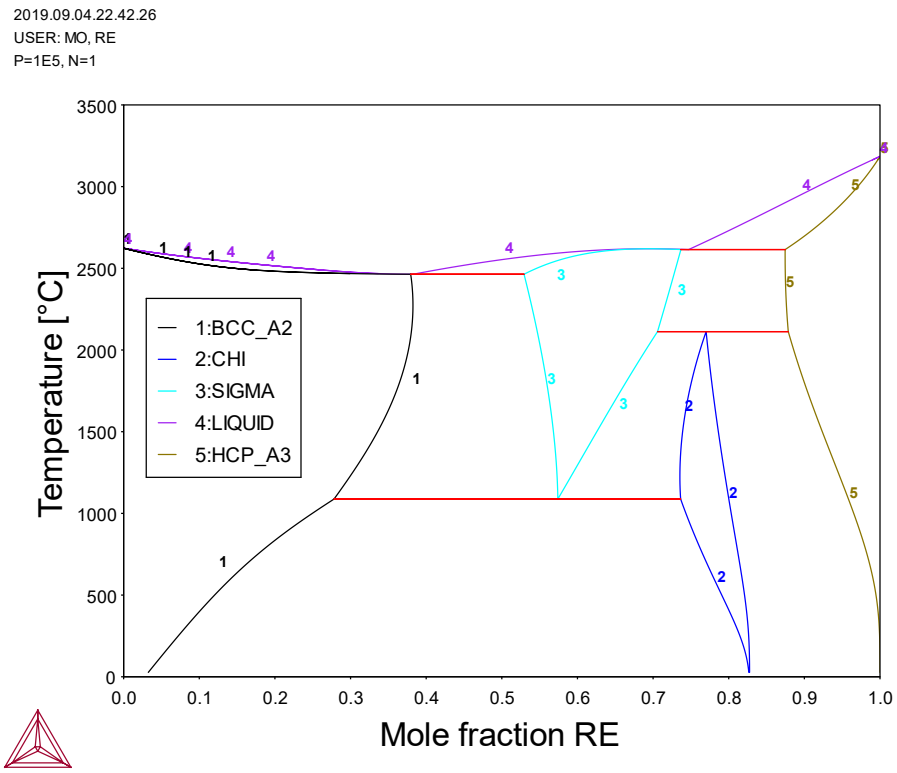




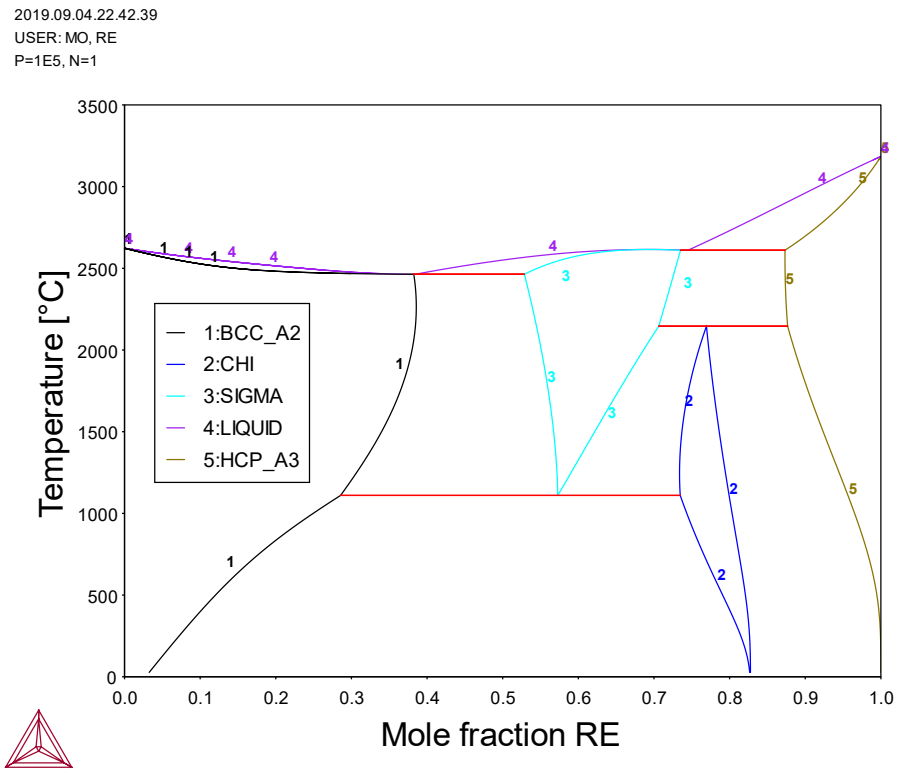


EBEF description of Mo-Re

Published EBEF parameters



EBEF parameters obtained here



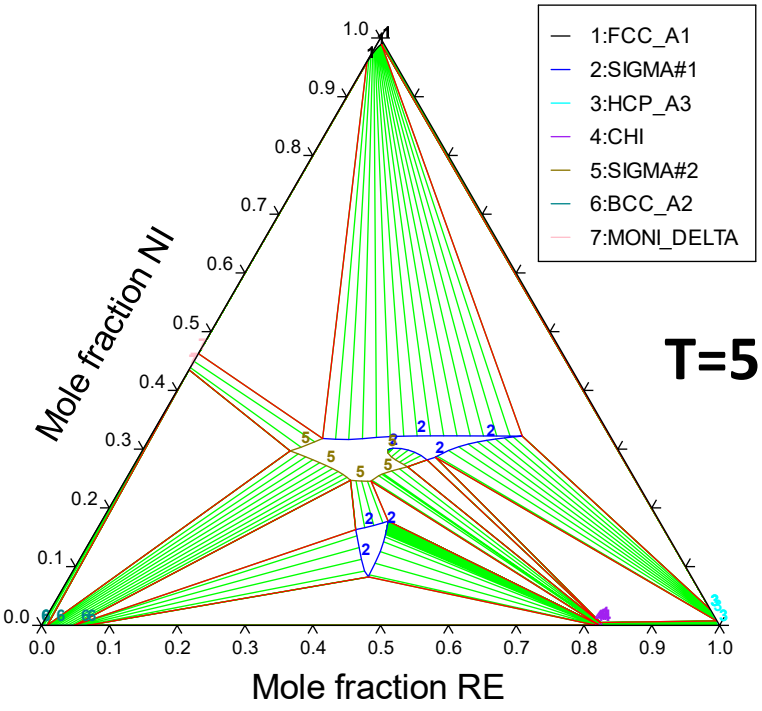
DFT total energies for the sigma endmembers from Yaqoob, Inorganic Chemistry 51, 3071 (2012)

EBEF description of Mo-Ni-Re: performance of the proposed implementation

Thermo-Calc Software

Published EBEF parameters

2019.09.03.22.00.37
USER: MO, NI, RE
T=500, N=1, P=1E5



T=500 K

EBEF parameters obtained here

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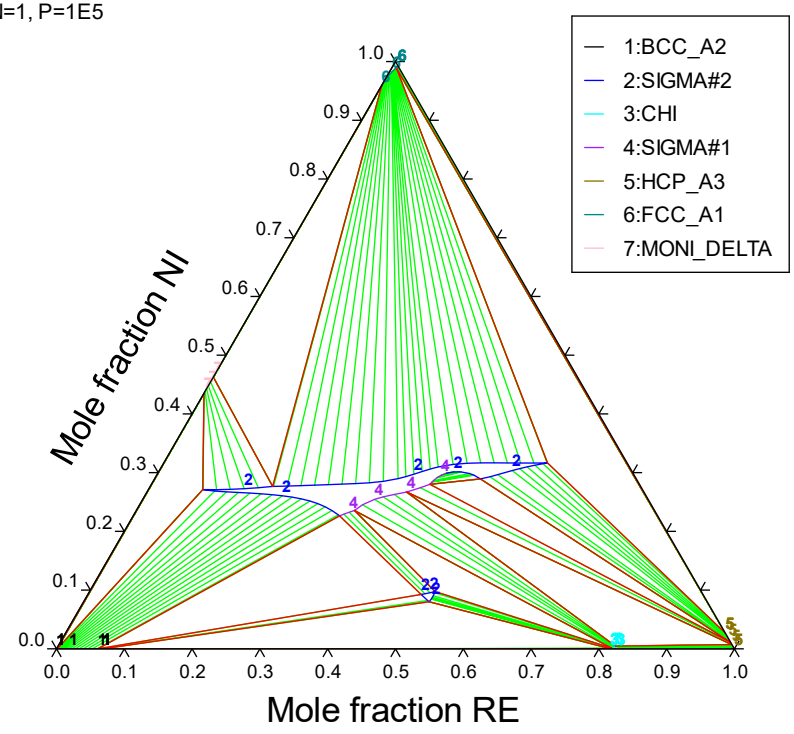

EBEF description of Mo-Ni-Re: performance of the proposed implementation

Thermo-Calc Software

Published EBEF parameters

2019.09.03.22.01.48
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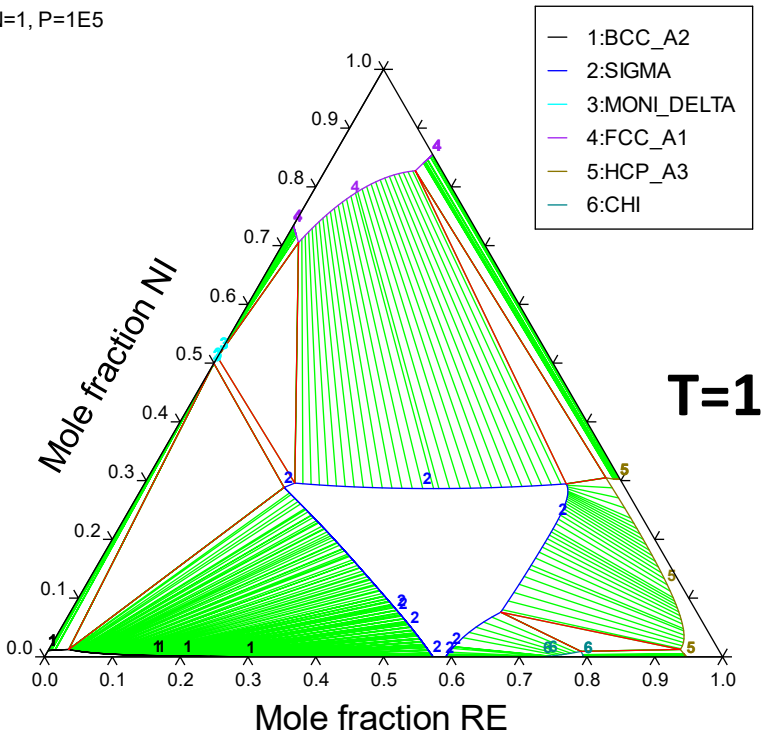

T=1500 K

EBEF parameters obtained here

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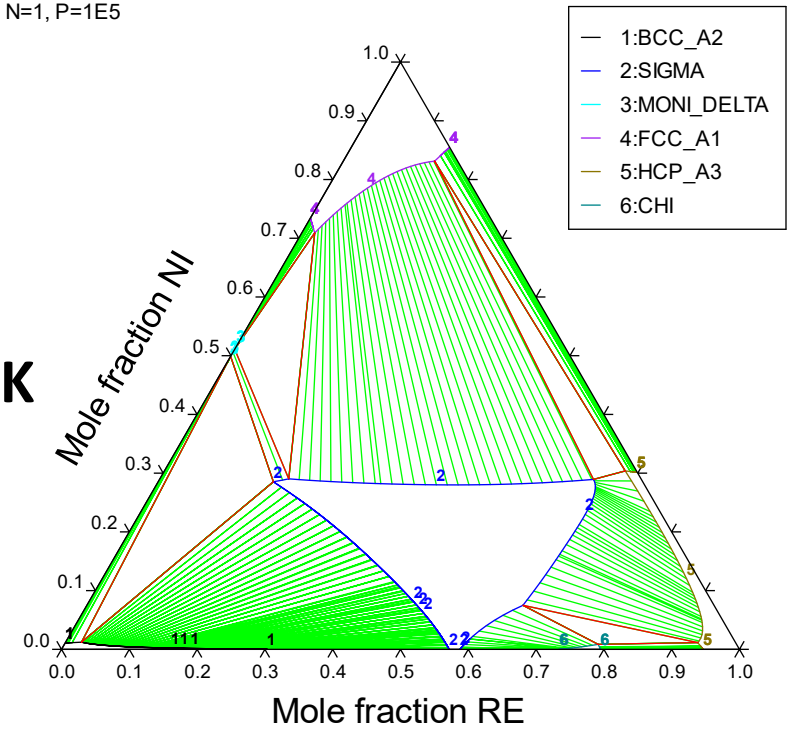
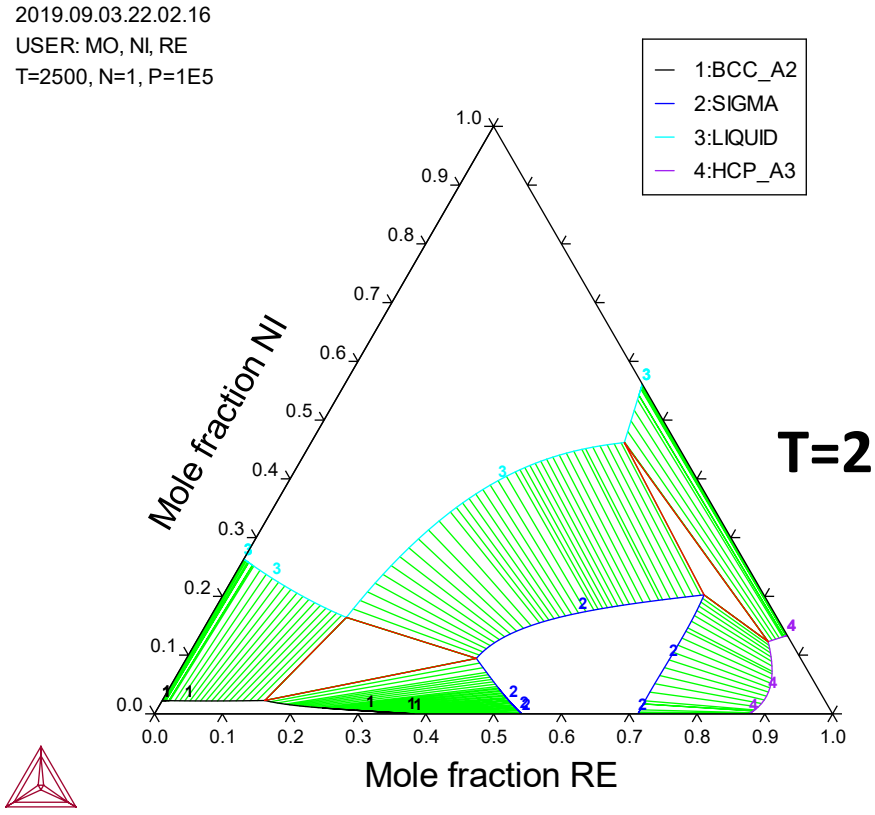
T=1500, N=1, P=1E5



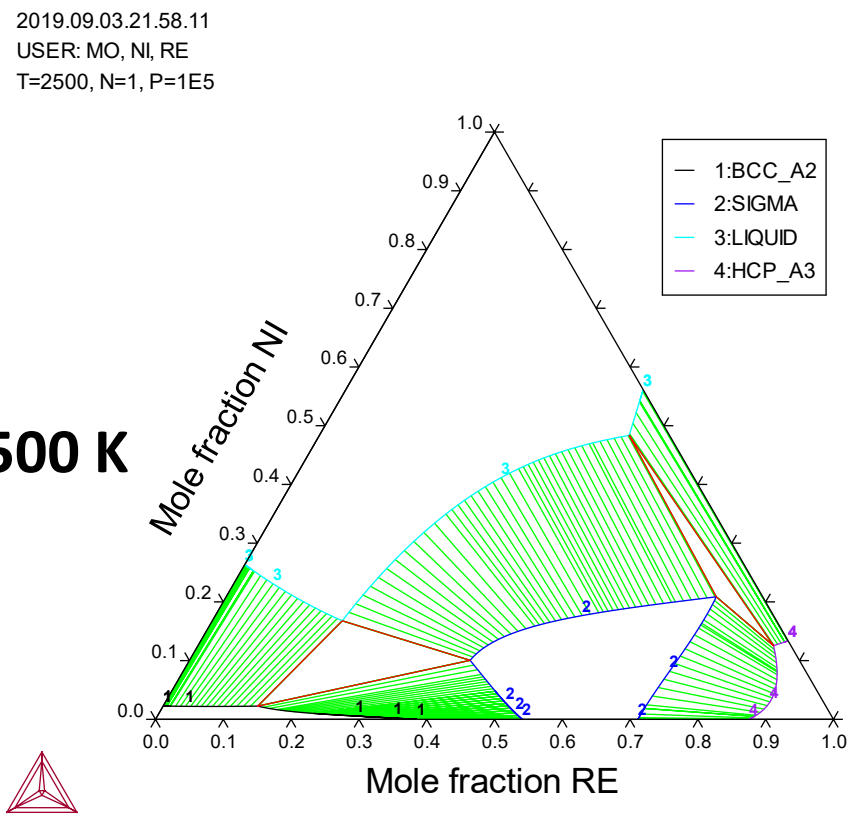
EBEF description of Mo-Ni-Re: performance of the proposed implementation

Published EBEF parameters



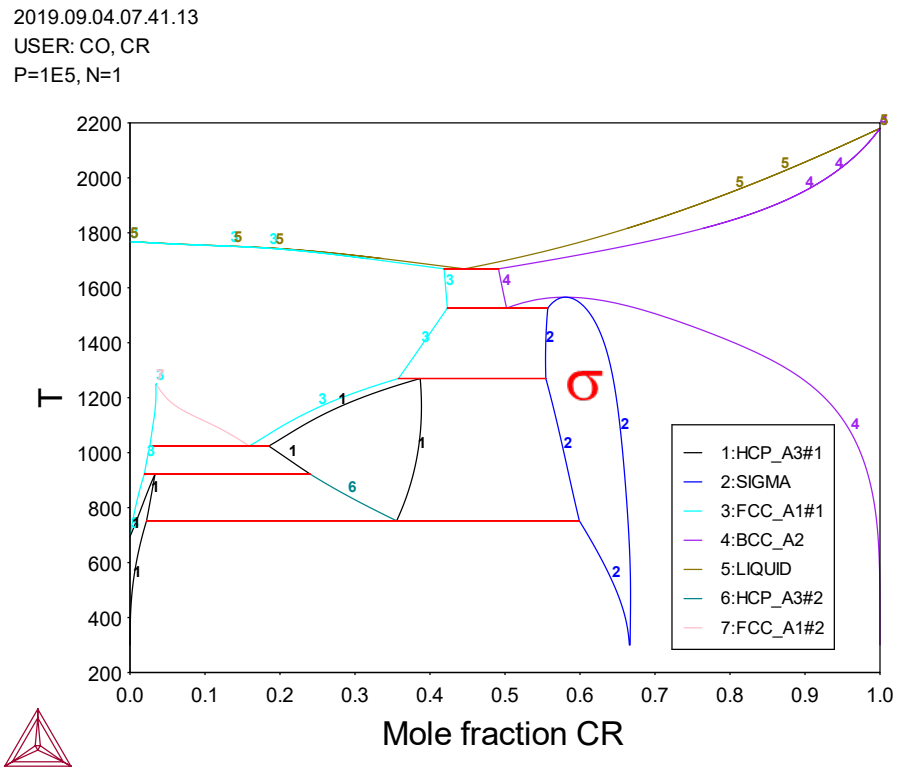
T=2500 K

EBEF parameters obtained here

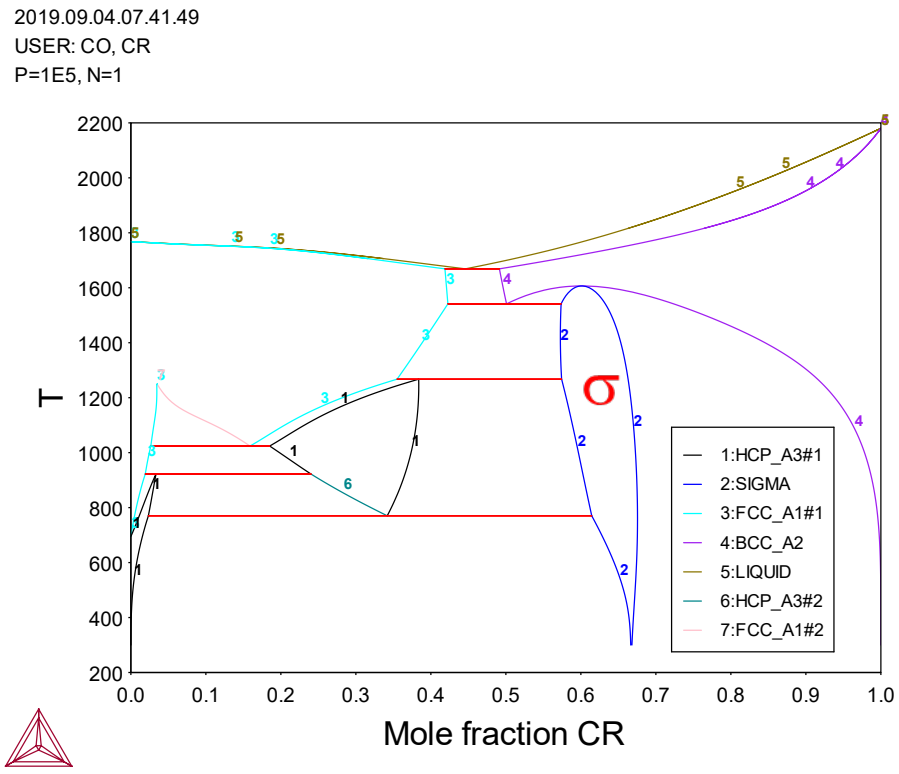


EBEF description of Co-Cr

DFT-based CEF



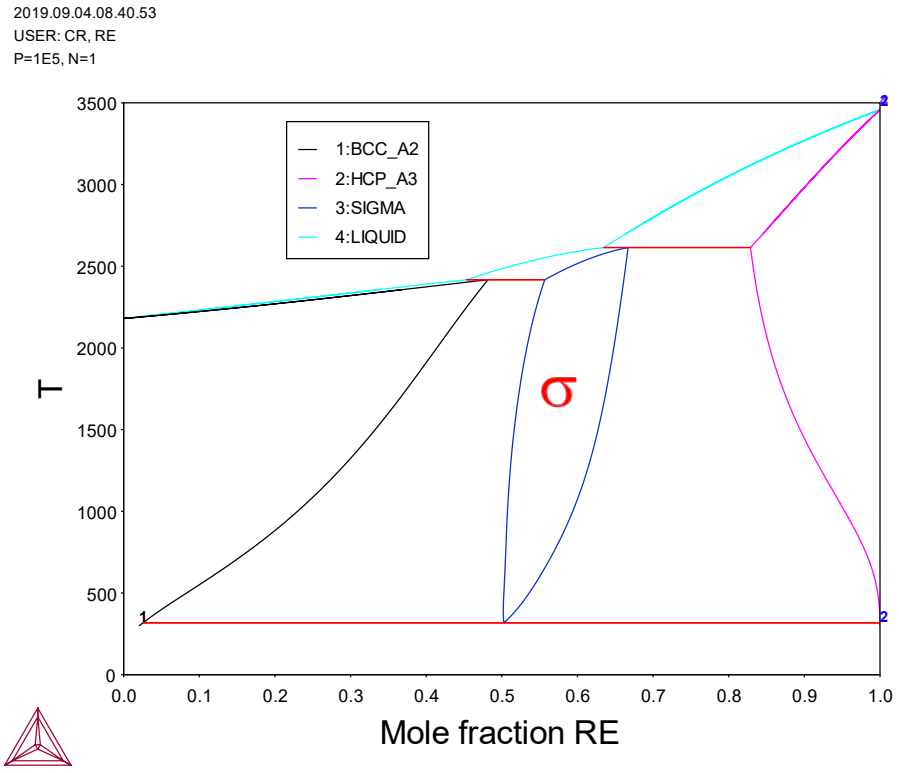
DFT-based EBEF



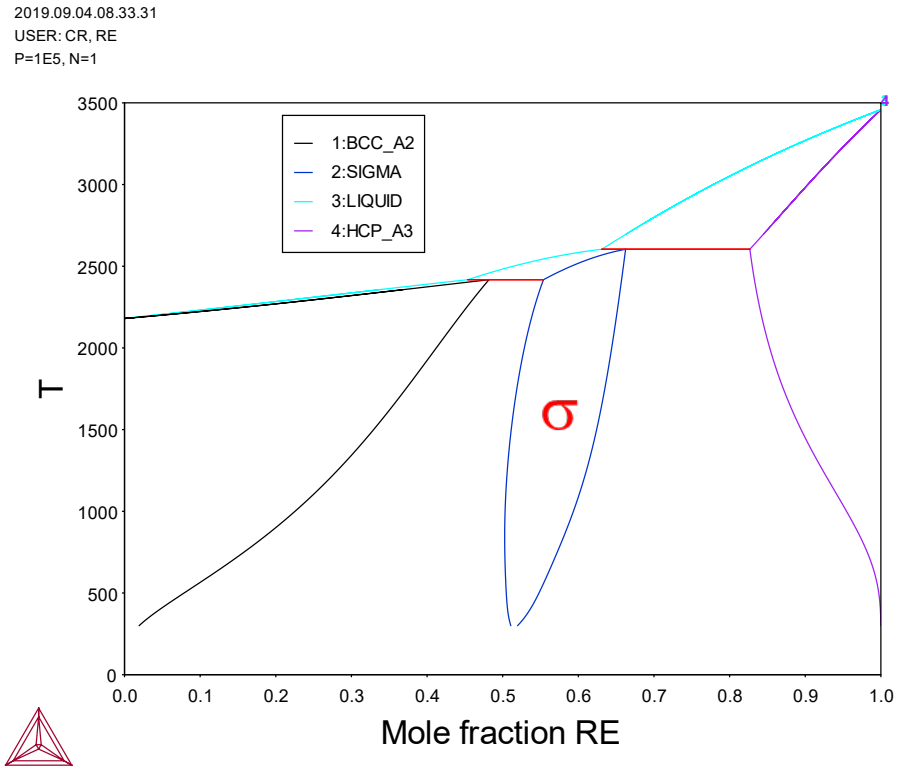
Original thermodynamic database and DFT data for the sigma endmembers from Li, Mao, Korzhavyi, and Selleby, CALPHAD **34**, 495 (2010)

EBEF description of Cr-Re

DFT-based CEF



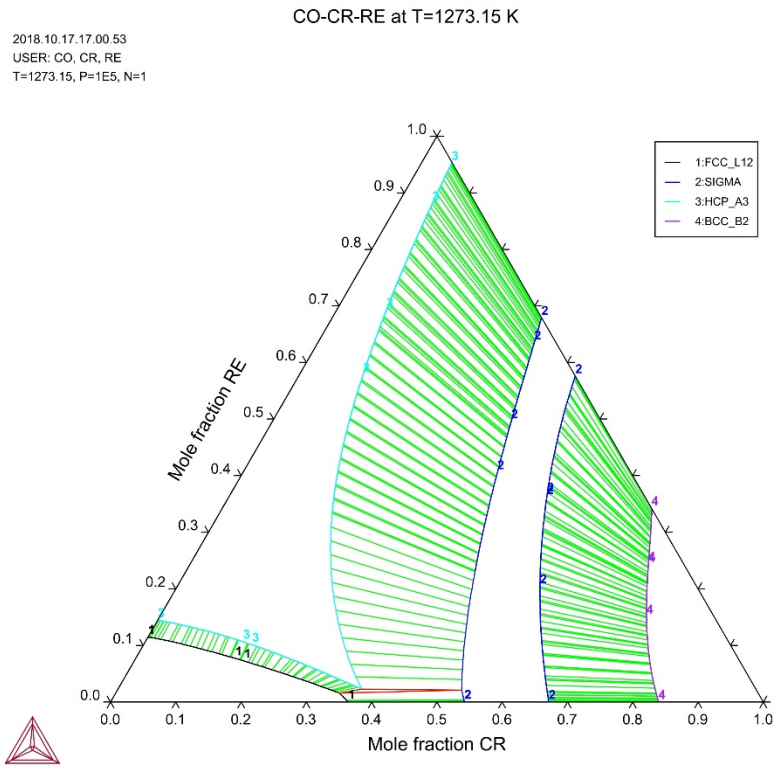
DFT-based EBEF



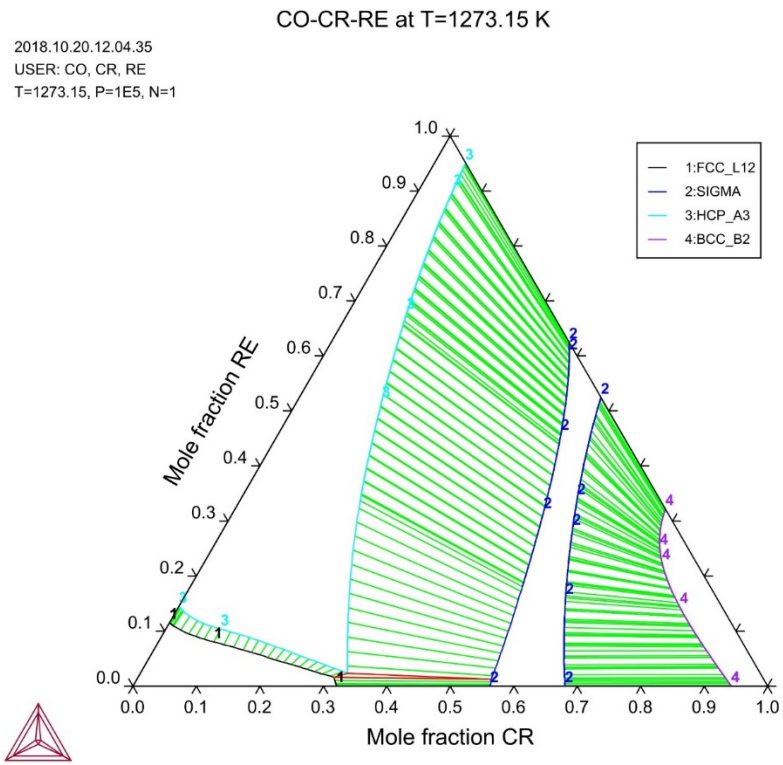
DFT data for the sigma endmembers from Palumbo et al., CALPHAD **34**, 495 (2010)

Co-Cr-Re: Compound energy formalism vs Effective Bond Energy Formalism

TCNI8



DFT-based EBEF



Where we are and outlook....

- Presented an assessment of the EBEF approach.
- Performed further tests of the performance of the EBEF on selected topologically close-packed phases.
- EBEF does emerge as a way to obtain a reasonable description of a ternary multi-sublattice phase at the cost of DFT calculations for the binary end-members.
- The fitting algorithm that we propose for the EBEs allows to deal with the non-uniqueness of the solution according