Introduction to the CALPHAD approach (CALculation of PHAse Diagram)

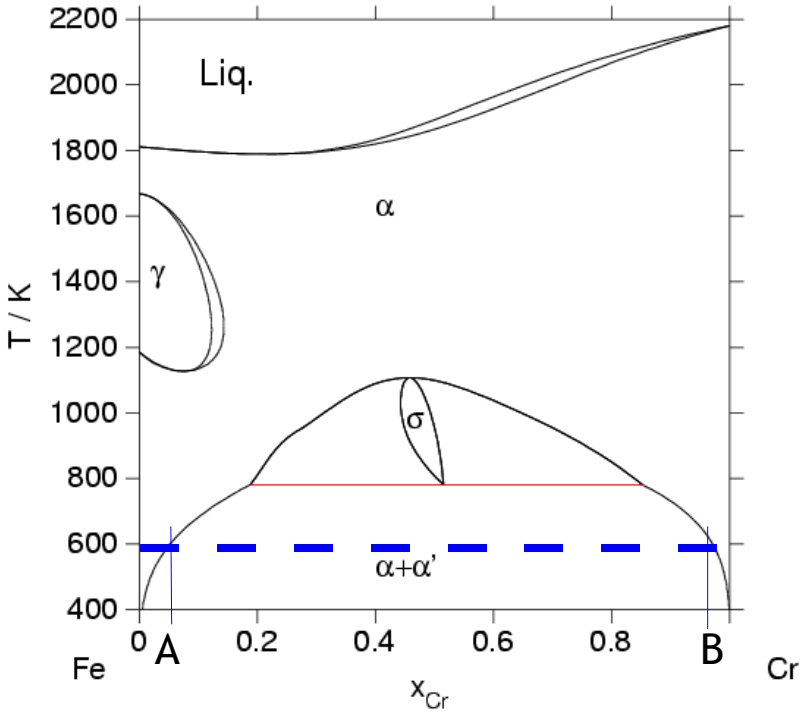
Nathalie Dupin

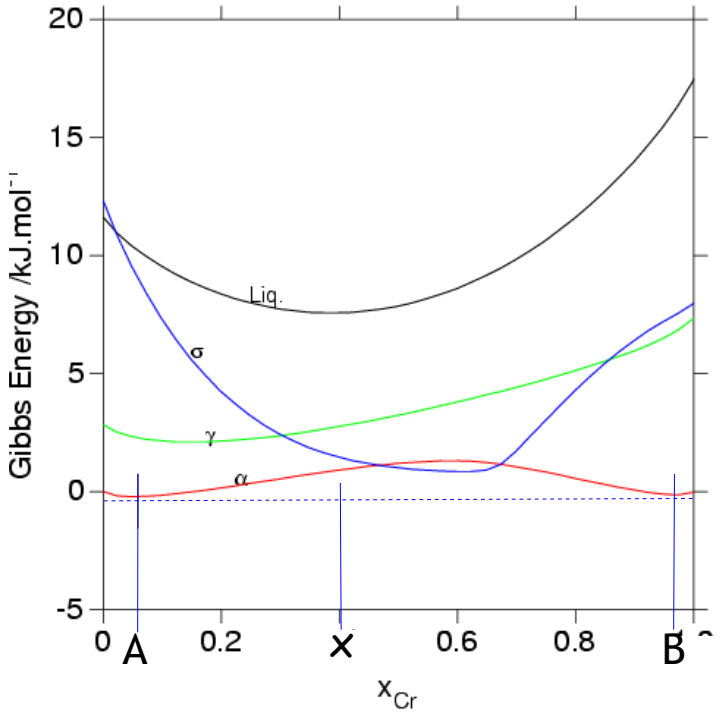
Calcul Thermodynamique
3 rue de l'avenir 63670 Orcet

The Calphad approach aims to calculate
phase equilibria from the Gibbs energy
description of all the phases using parametric models
assessed from experimental and theoretical information
and stored in thermodynamic databases
that can be used by general software codes.

Phase equilibria from Gibbs Energy

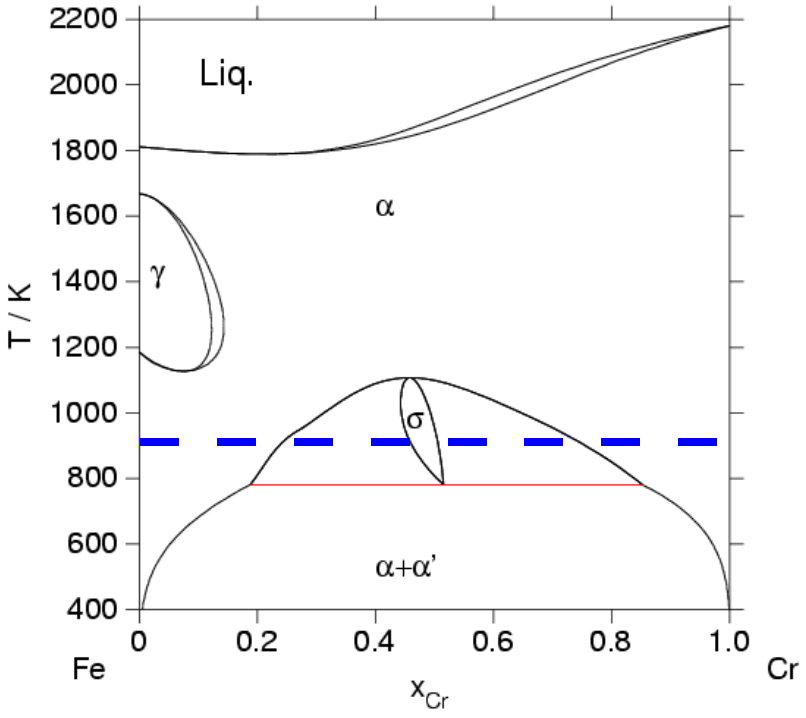
The phase equilibrium is defined
by the Gibbs energy minimum.

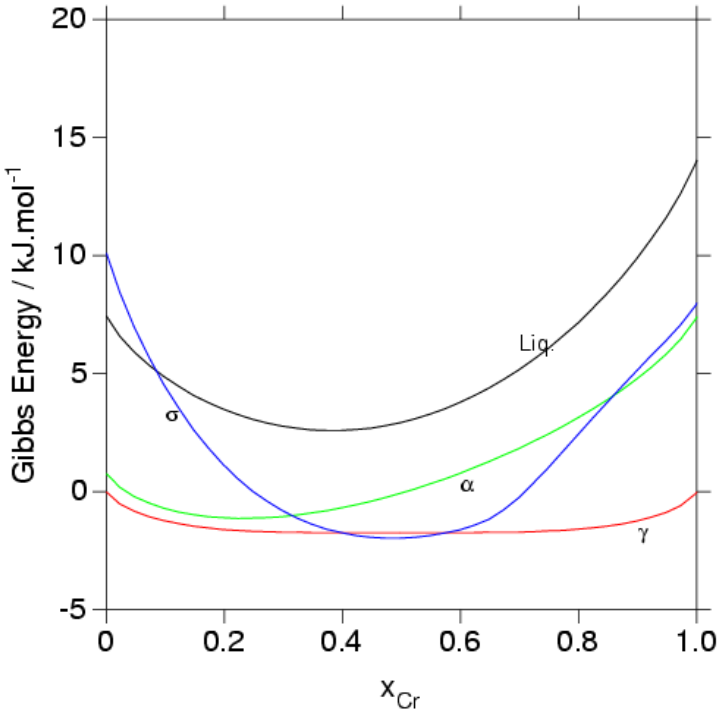




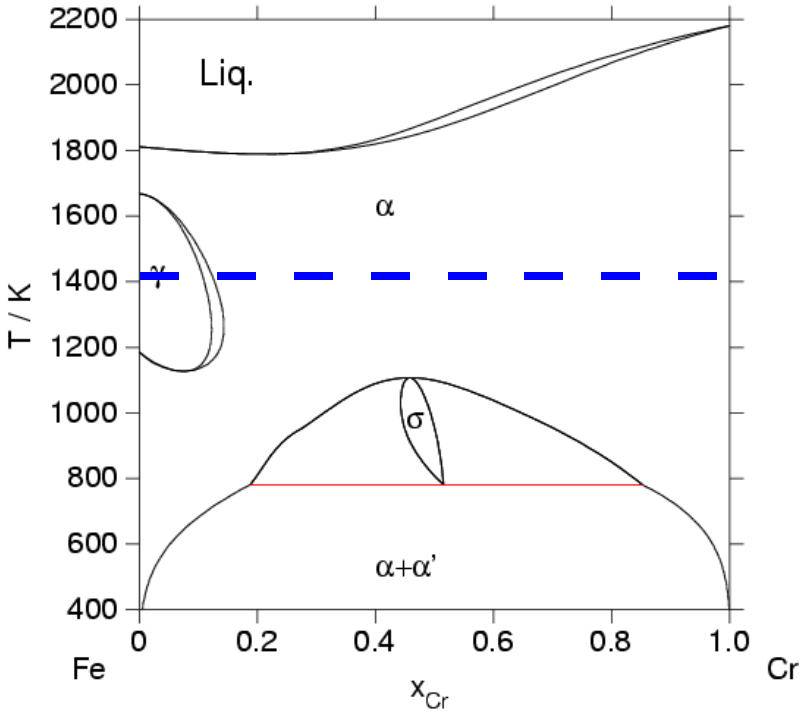
$f^{\alpha} = xB/AB$

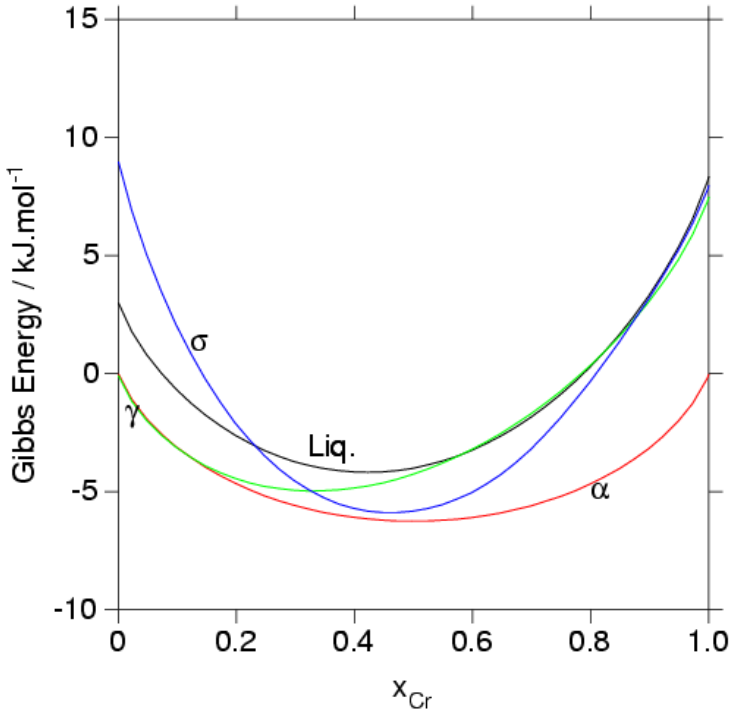
Phase equilibria from Gibbs Energy



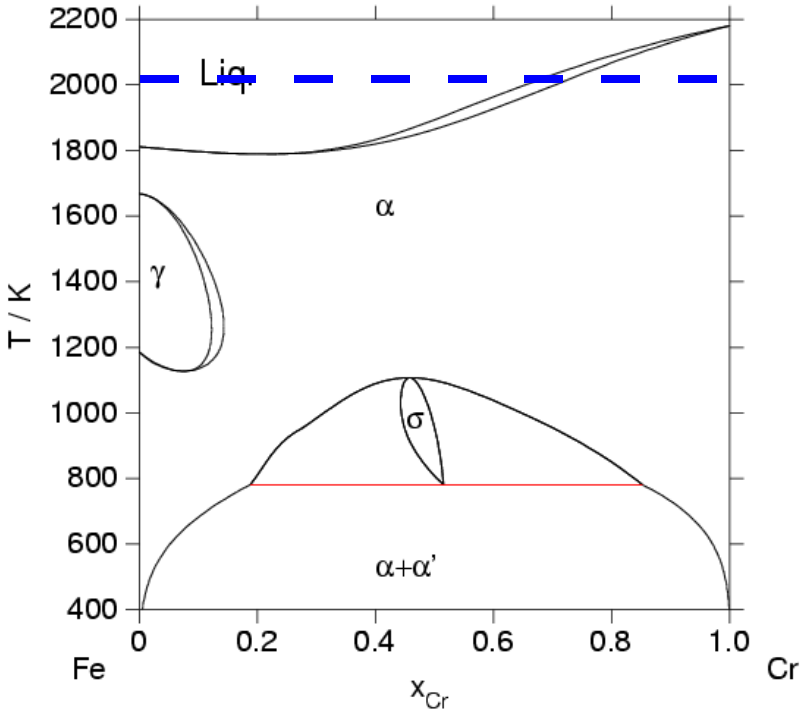


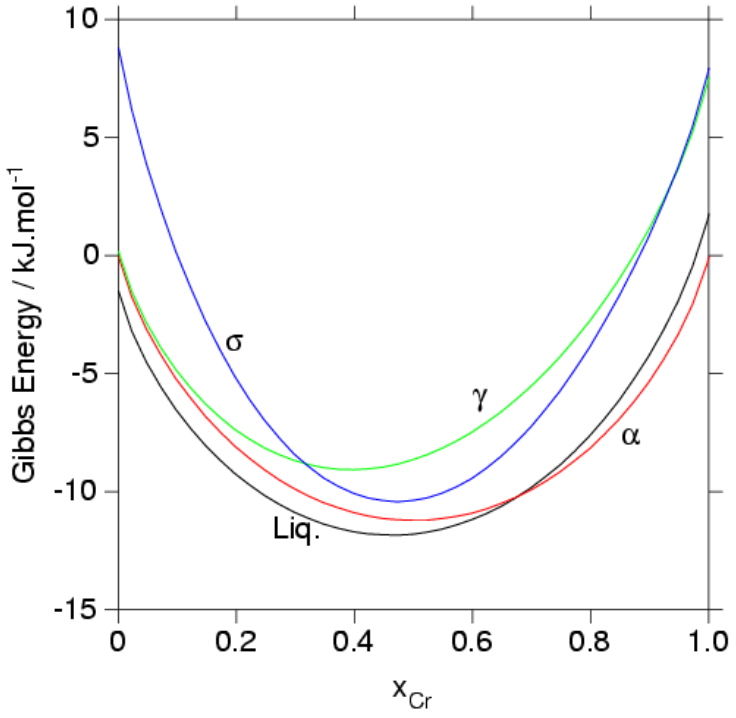
Phase equilibria from Gibbs Energy





Phase equilibria from Gibbs Energy





Phase equilibria from Gibbs Energy

In 1957, Meijering applied this method to the thermodynamic analysis of the Cr-Cu-Ni system.

The development of computers hardware and software has allowed the extension of this approach, its application to multicomponent systems provided there are available Gibbs energy descriptions.

Information on some different Gibbs energy minimisation codes can be found at

www.thermocalc.com
www.factsage.com
www.npl.co.uk/mtdata
thermodata.online.fr

Parametric Thermodynamic Models

- G=f(T)
  - . Elements
  - . Stoichiometric compounds
  - . Parameter determination

- G=f(x)
  - . Substitutional solutions
  - . Associate model
  - . Compound Energy Formalism
    - Generalities
    - Intertitial solutions
    - None-stoichiometric compounds
    - Ordering

- G=f(P)

Parametric Thermodynamic Models - G=f(T)

- Elements

$$G_i^{\varphi}(T) - H_i^{SER}(T_0) = a + b\ T + c\ T \ln T + \sum_n d_n\ T^n$$

$$\Rightarrow \quad S_i^{\varphi}(T) = -\left(\frac{\partial G}{\partial T}\right)_P = -\ b - c - c \ln T - \sum_n n\ d_n\ T^{n-1}$$

$$\Rightarrow \quad H_i^{\varphi}(T) - H_i^{SER}(T_0) = a - c\ T - \sum_n (n-1)\ d_n\ T^n$$

$$\Rightarrow \quad Cp = \left(\frac{\partial H}{\partial T}\right)_P = -\ c - \sum_n n\ (n-1)\ d_n\ T^{n-1}$$

Parametric Thermodynamic Models - G=f(T)

- Stoichiometric compounds

$$G^{\varphi}_{Comp.}(T) - \sum x_i H_i^{SER}(T_0) = \quad a + b\,T + c\,T\ln T + \sum_n d_n\,T^n$$

- Stoichiometric compounds without Cp data available

$$G^{\varphi}_{Comp.}(T) - \sum x_i H_i^{SER}(T_0) =$$

$$\sum x_i \left(G_i^{SER}(T) - H_i^{SER}(T_0)\right) + \Delta H_f + T\Delta S_f$$

Parametric Thermodynamic Models - G=f(T)

- Determination of $a, b, c, d_n, \Delta H_f, \Delta S_f$

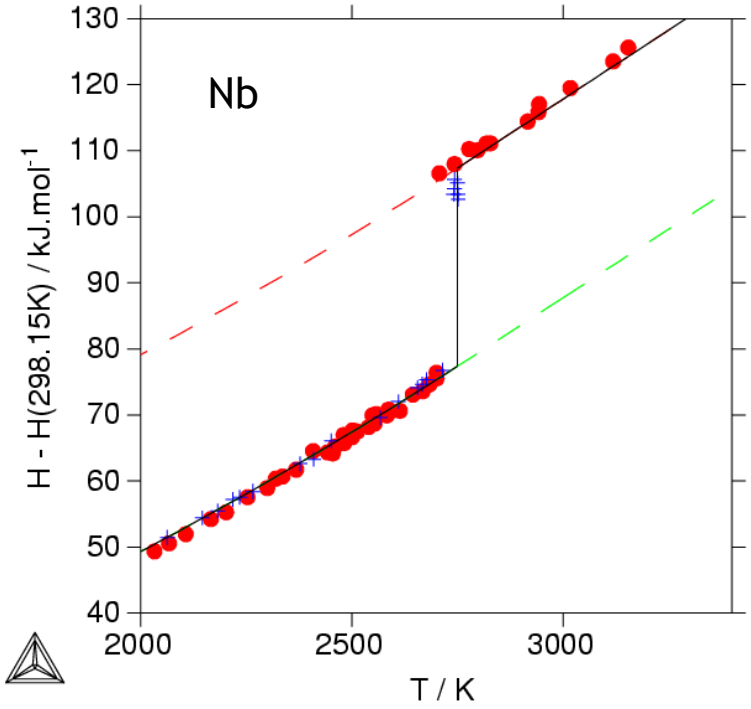
  - from experimental result (H-H(T_0), Cp, ΔH_f, P, ...)

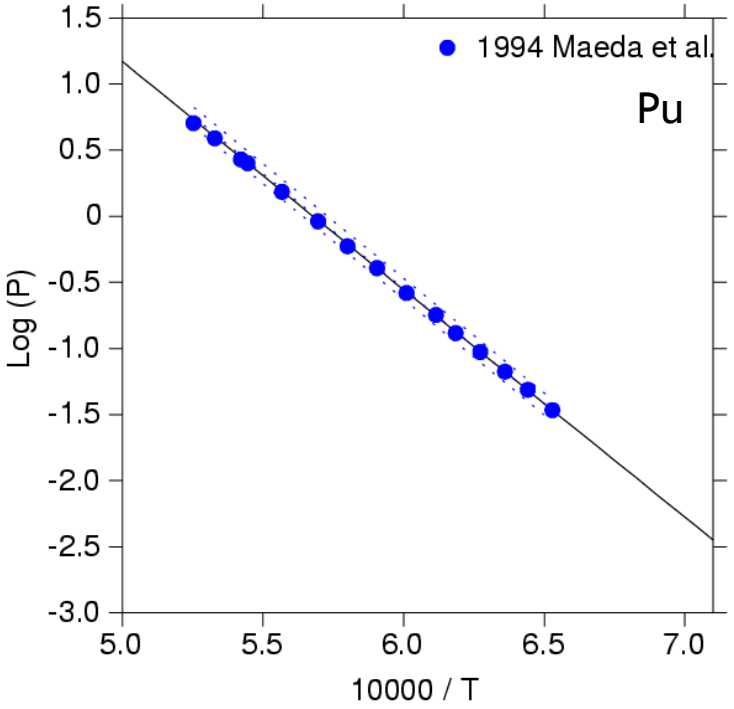
  - for metastable states

    - from other temperature range (Liq. at low T, solid at high T, β-Zr at low T, ...)
    - from extrapolation into high order systems (Cr in fcc, ...)
    - from theoritical calculations, correlations, trends

Parametric Thermodynamic Models - G=f(T)

Estimation of lattice stabilities from experiments

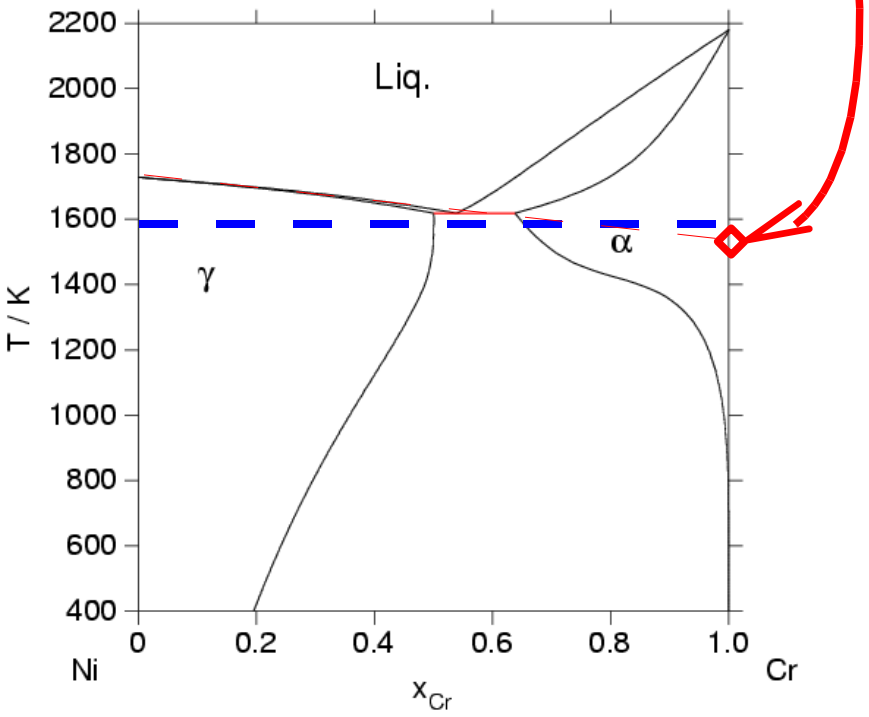




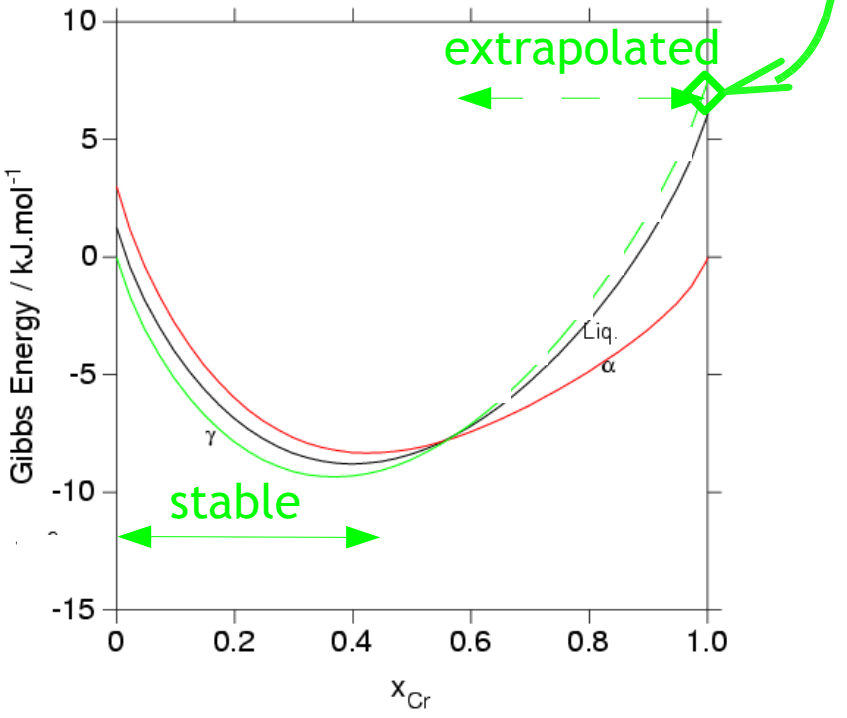
Parametric Thermodynamic Models - G=f(T)

Estimation of metastable lattice stabilities from binary systems

(Cr, fcc) melting T
extrapolated from ≠ Cr-X

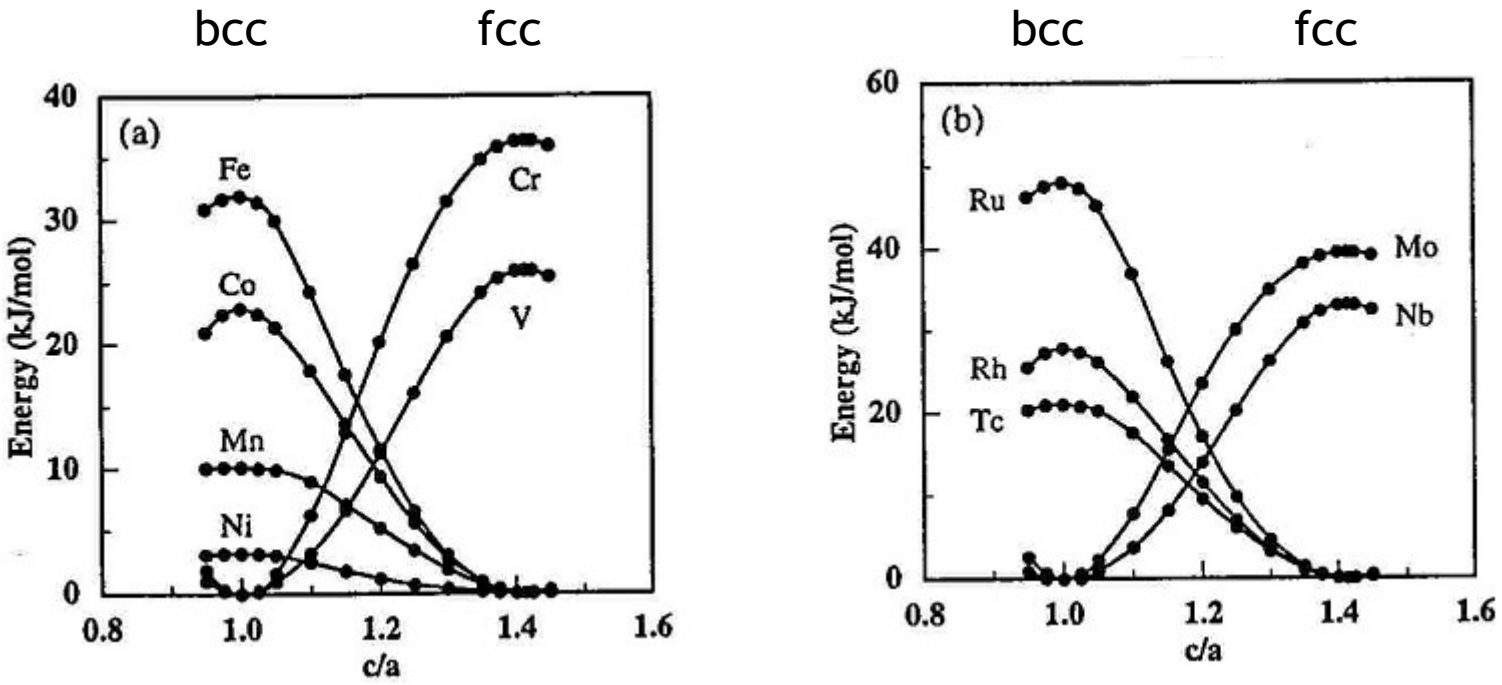


G(Cr, fcc)
extrapolated from ≠ Cr-X



Parametric Thermodynamic Models - G=f(T)

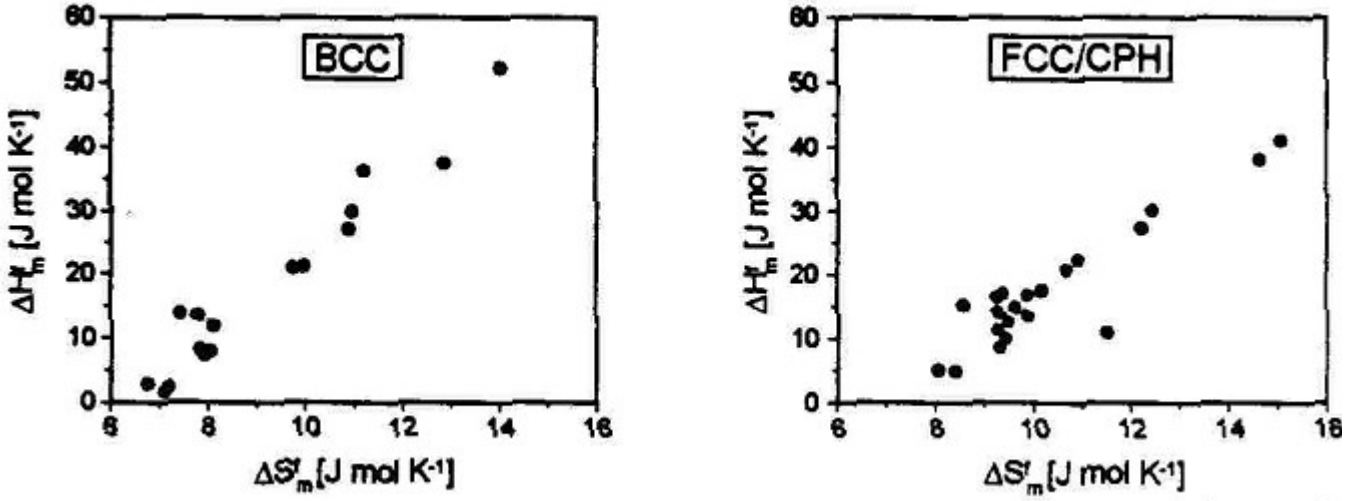
Estimation of metastable lattice stabilities from FP results



P.J. Craievich, M. Weinert, J.M. Sanchez, R.E. Watson, 1994

Parametric Thermodynamic Models - G=f(T)

Estimation of lattice stabilities from correlations



N. Saunders, A.P. Miodownik, A.T. Dinsdale, Calphad, 12 (1988)

Parametric Thermodynamic Models - G=f(T)

A widely used set of lattice stabilities for the pure elements in common structures was published by A. Dinsdale, *SGTE data for pure elements*, Calphad, **15** 317-425 (1991)

The use of a common set of lattices stabilities is required for the consistency of the description of higher order systems.

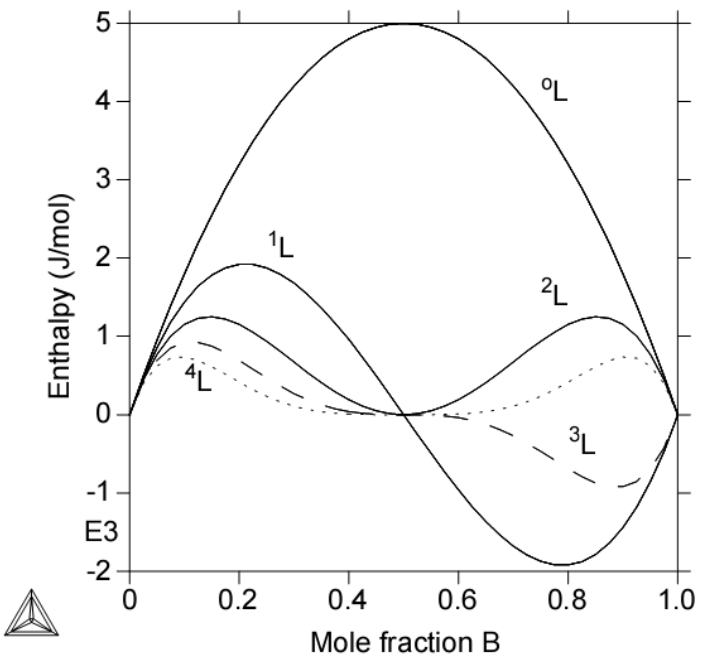
Parametric Thermodynamic Models - G=f(x)

- Substitutional solutions

$$G^{\varphi}(T) - x_i^{\varphi} H_i^{SER}(T_0) = \sum_i x_i^{\varphi} \left(G_i^{\varphi}(T) - H_i^{SER}(T_0)\right) + R\,T \sum_i x_i^{\varphi} \ln x_i^{\varphi} + \sum_i \sum_{j>i} \sum_{\nu} x_i^{\varphi} x_j^{\varphi} (x_i^{\varphi} - x_j^{\varphi})^{\nu} L_{i,j}^{\varphi,\nu} + \sum_i \sum_{j>i} \sum_{k>j} x_i^{\varphi}\, x_j^{\varphi}\, x_k^{\varphi}\, L_{i,j,k}^{\varphi}$$

Parametric Thermodynamic Models - G=f(x)

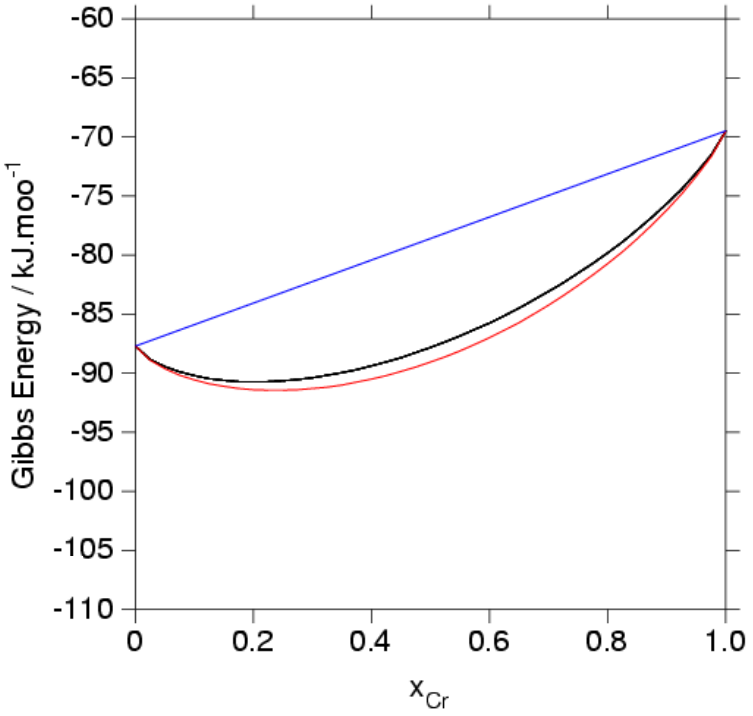
The expression of the excess Gibbs energy of mixing thanks to the Redlich-Kister polynomials allows to describe many different real cases with a large flexibility.



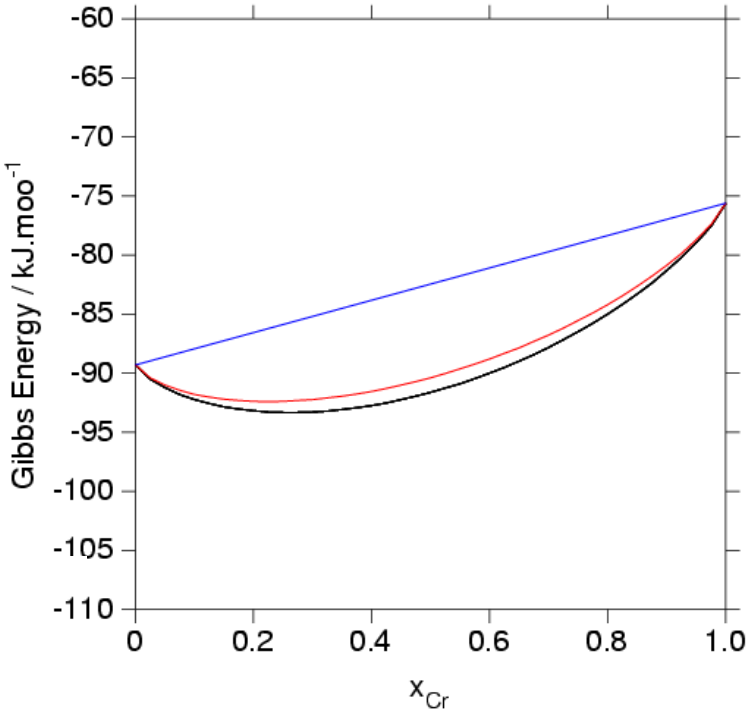
Computational Thermodynamics, Assessing Thermodynamic Data and Creating Multicom-ponent Databases using the Calphad Method, H.L. Lukas, S.G. Fries, B. Sundman http://www.cambridge.org/catalogue/catalogue.asp?isbn=0521868114

Parametric Thermodynamic Models - G=f(x)

Example : Fe-Cr, 1600K, Liquid and bcc



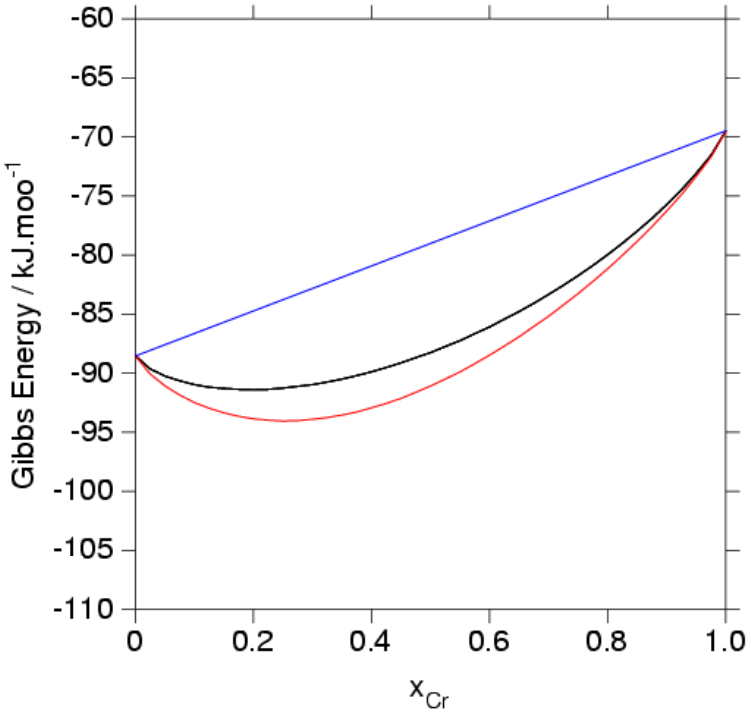
Stabilizing excess interaction

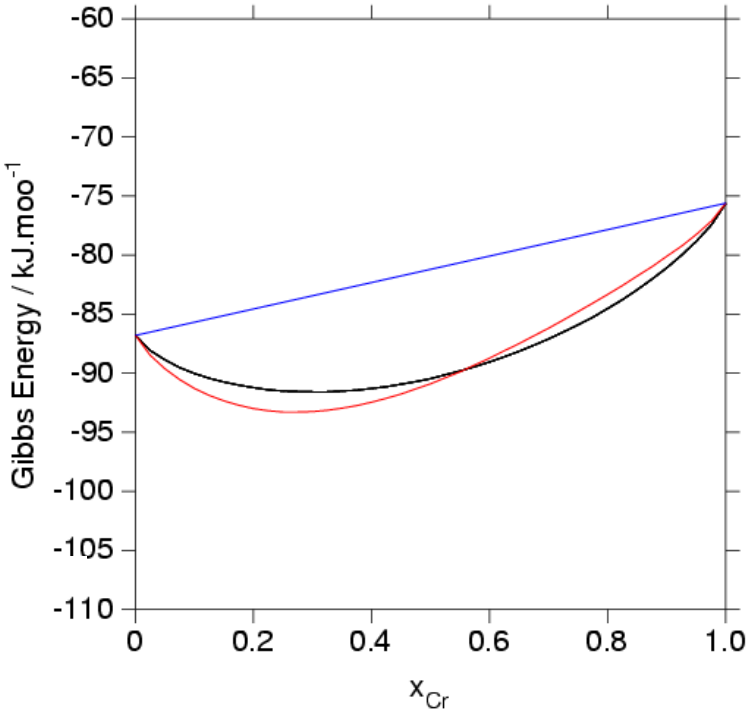


Destabilizing excess interaction

Parametric Thermodynamic Models - G=f(x)

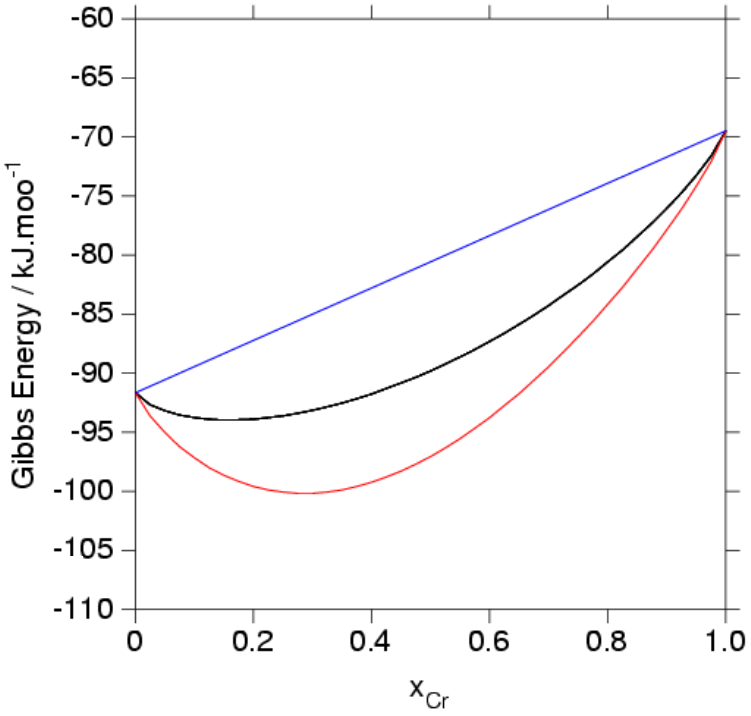
Example : Ni-Cr, 1600K, Liquid and bcc

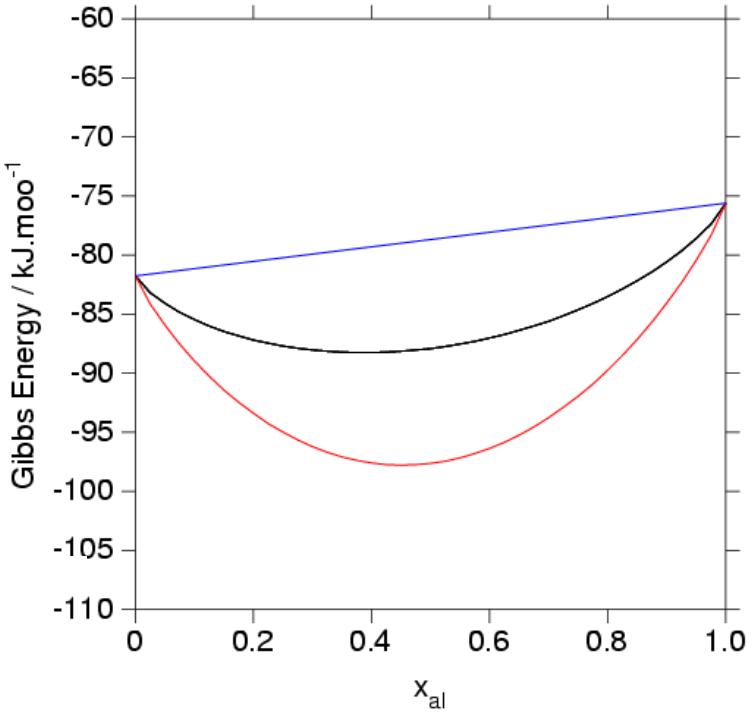




Parametric Thermodynamic Models - G=f(x)

Example : Al-Cr, 1600K, Liquid and bcc





Parametric Thermodynamic Models - G=f(x)

- Associate model

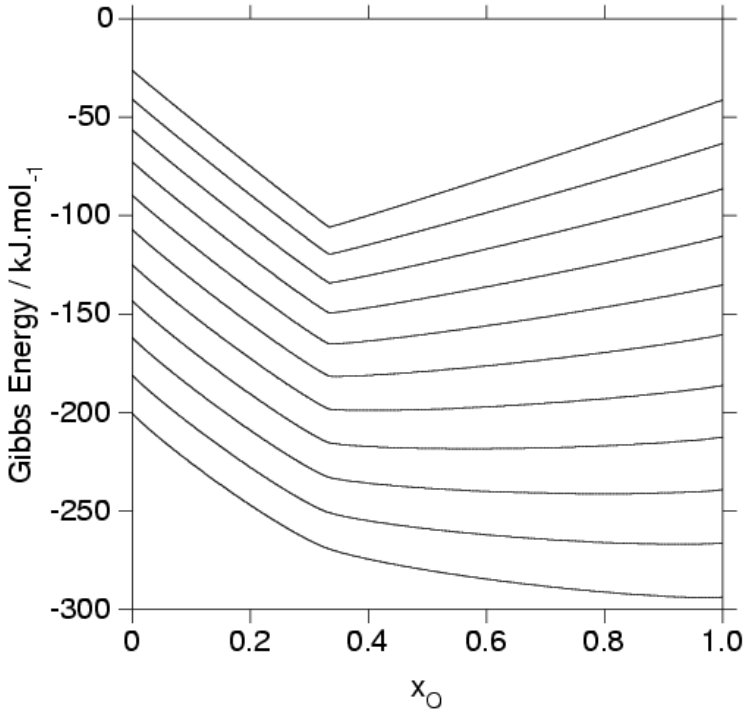
$$G^{\varphi}(T) - x_i^{\varphi} H_i^{SER}(T_0) = \sum_C y_C^{\varphi} \left(G_C^{\varphi}(T) - \sum_i x_i H_i^{SER}(T_0) \right) + R\,T \sum_C y_C^{\varphi} \ln y_C^{\varphi} + \sum_C \sum_{C'>C} \sum_{\nu} y_C^{\varphi} y_{C'}^{\varphi} (y_C^{\varphi} - y_{C'}^{\varphi})^{\nu} \; L_{C,C'}^{\varphi,\nu}$$

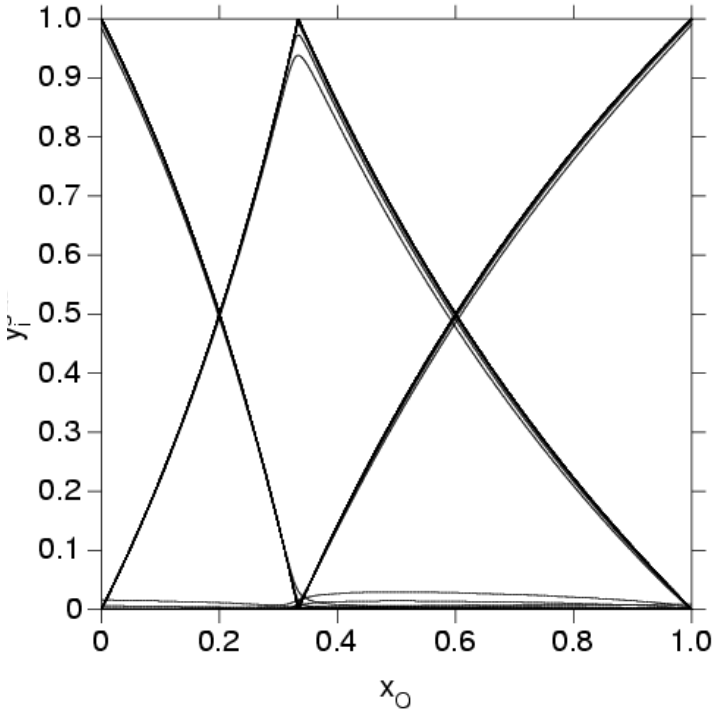
$$\sum_C y_C^{\varphi} = 1 \qquad x_i^{\varphi} = \frac{\sum_C n_i^C y_C^{\varphi}}{\sum_i \sum_C n_i^C y_C^{\varphi}}$$

$$n_H^{H_2O} = 2$$

Parametric Thermodynamic Models - G=f(x)

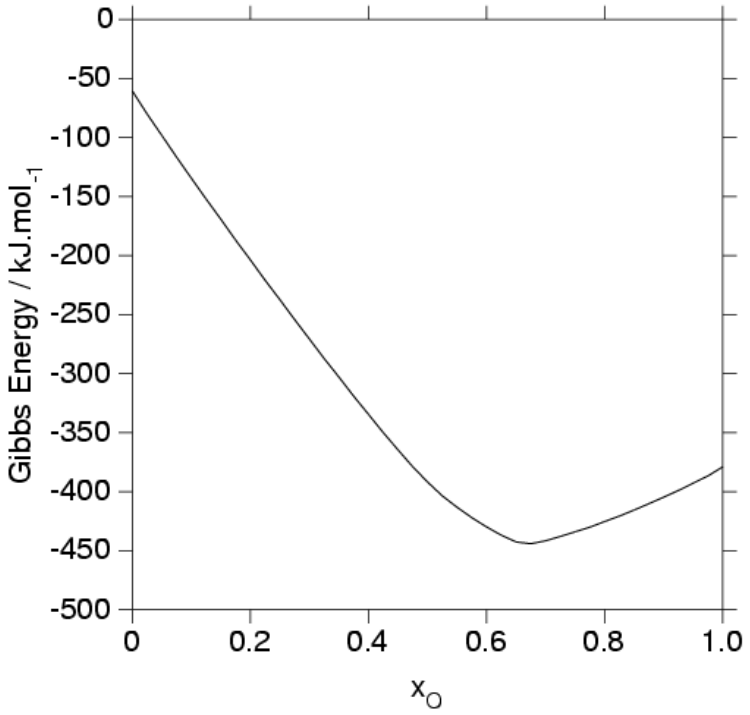
Example : H-O, 400-2400K, Gas

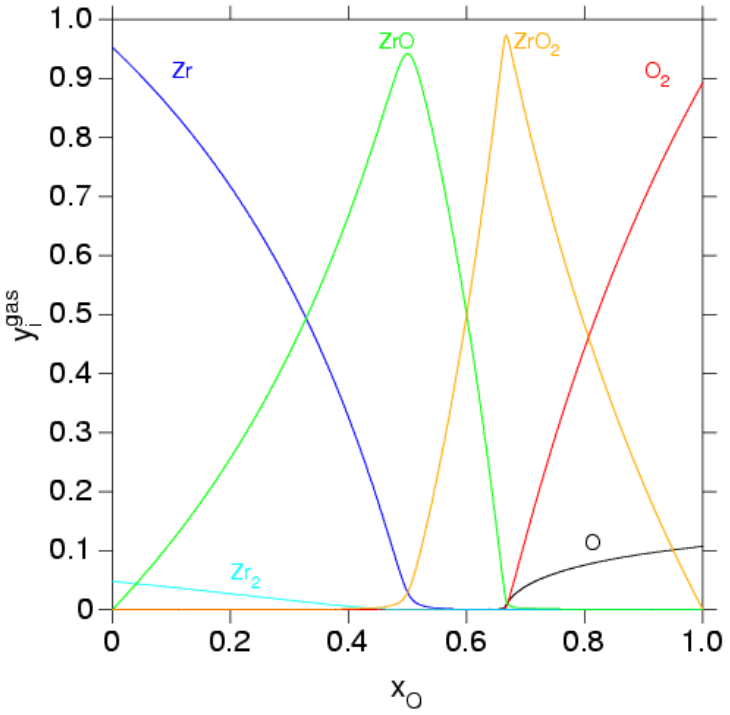




Parametric Thermodynamic Models - G=f(x)

Example : Zr-O, 3000K, Gas





Parametric Thermodynamic Models - G=f(x)

- Compound Energy Formalism - Generalities

Based on the existence of sublattices in crystalline phases, the CEF uses the sublattice fraction occupancies as composition variables used define the Gibbs Energy

n_i^s number of species i in sublattice s

n^s number of site in sublattice s $\qquad n^s = \sum_i n_i^s$

n_i total number of species i $\qquad n_i = \sum_s n_i^s$

$$y_i^s = \frac{n_i^s}{n^s}$$

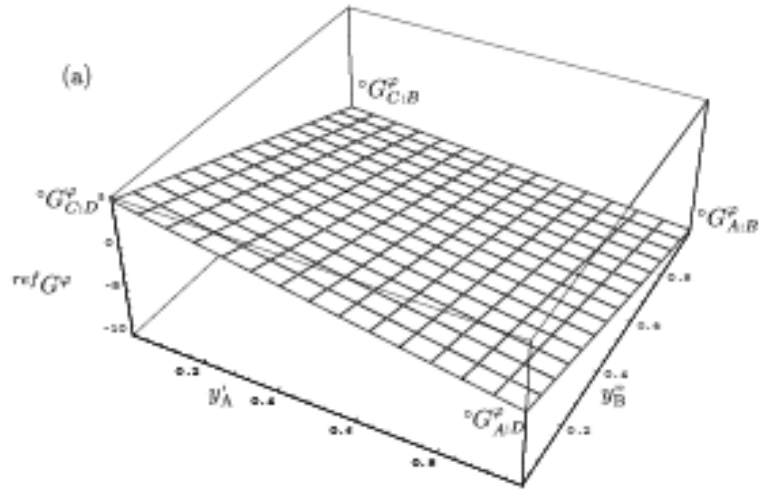
Parametric Thermodynamic Models - G=f(x)

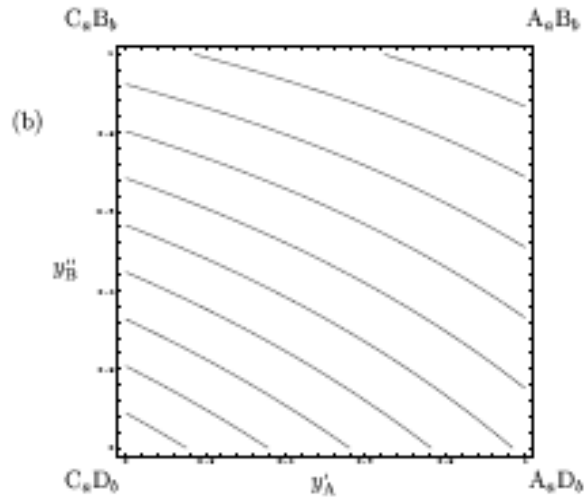
- Compound Energy Formalism - Generalities

$$(\mathrm{A,C})_a\ (\mathrm{B,D})_b$$

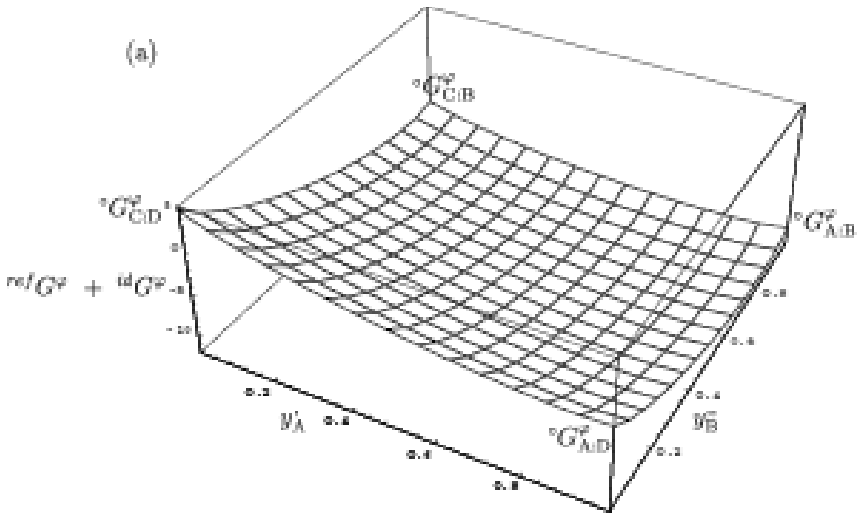
$$\begin{aligned} G_m^{\varphi}(T) \ - \ & \sum_i x_i^{\varphi}\ H_i^{SER}(T_0) \\ = \ & \sum_i \sum_j y_i^{'}\ y_j^{''}\ \left(G_{i:j}^{\varphi}(T) - a\ H_i^{SER}(T_0) - b\ H_j^{SER}(T_0)\right) \\ & + R\ T\ \left(a \sum_i y_i^{'} \ln y_i^{'} + b \sum_j y_j^{''} \ln y_j^{''}\right) \\ & + \sum_j y_A^{'}\ y_C^{'}\ y_j^{''}\ L_{A,C:j}^{\varphi} + \sum_i y_i^{'}\ y_B^{''}\ y_D^{''}\ L_{i:B,D}^{\varphi} \\ & + y_A^{'}\ y_C^{'}\ y_B^{''}\ y_D^{''}\ L_{A,C:B,D}^{\varphi} \end{aligned}$$

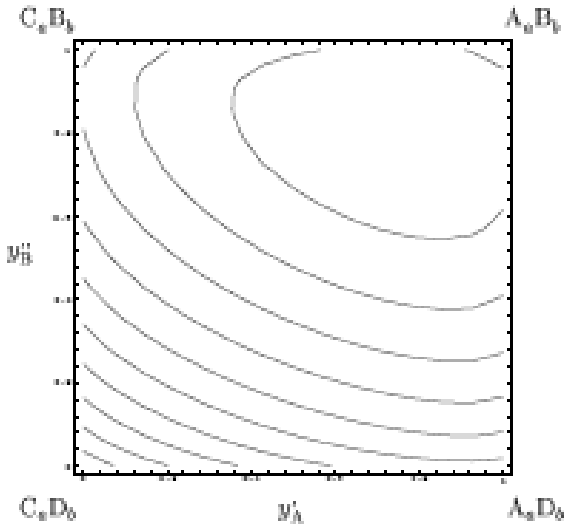
$$\sum_i \sum_j y_i' \, y_j'' \left(G^{\varphi}_{i:j}(T) - a \; H_i^{SER}(T_0) - b \; H_j^{SER}(T_0) \right)$$





$$\sum_i \sum_j y_i' \, y_j'' \left(G^{\varphi}_{i:j}(T) - a \; H_i^{SER}(T_0) - b \; H_j^{SER}(T_0) \right)$$
$$+ \; R \; T \; \left(a \sum_i y_i' \ln y_i' + b \sum_j y_j'' \ln y_j'' \right)$$





Parametric Thermodynamic Models - G=f(x)

- Compound Energy Formalism - Generalities

Substitutional solutions (only one sublattice)
and stoichiometric compounds (only one species by sublattice)
are particular cases of the CEF.
Many others can be treated, among them :

$(M)_a(C,\underline{\square})_b$	interstitial solution
$(M)_a(\underline{C},\square)$	substoichiometric compounds
$(A)_a(B)_b(B,\underline{\square})_c$	interstitial defects
$(\underline{A},B)_a(A,\underline{B})_b$	antisite defects
$(\underline{A},\square)_a(A,\underline{B})_b$	triple defects
$(A)_a(A,B)_b(B)_c$	restricted composition range
$(Na^+, K^+)(Cl^-, F^-)$	ionic reciprocal solution
$(Fe^{3+}, \underline{Fe}^{2+})_1 (\underline{Fe}^{3+}, Fe^{2+,\square})_2 (O^{2-})_4$	spinel

Parametric Thermodynamic Models - G=f(x)

Interstitial Solutions

$$(\mathrm{M})_a(\square\ ,\mathrm{C})_b$$

$$x^{\varphi}_{\mathrm{M}} = \frac{a\ y'_{\mathrm{M}}}{a + b\ (1 - y''_{\square})} \qquad x^{\varphi}_{\mathrm{C}} = \frac{b\ y''_{\mathrm{C}}}{a + b\ (1 - y''_{\square})}$$

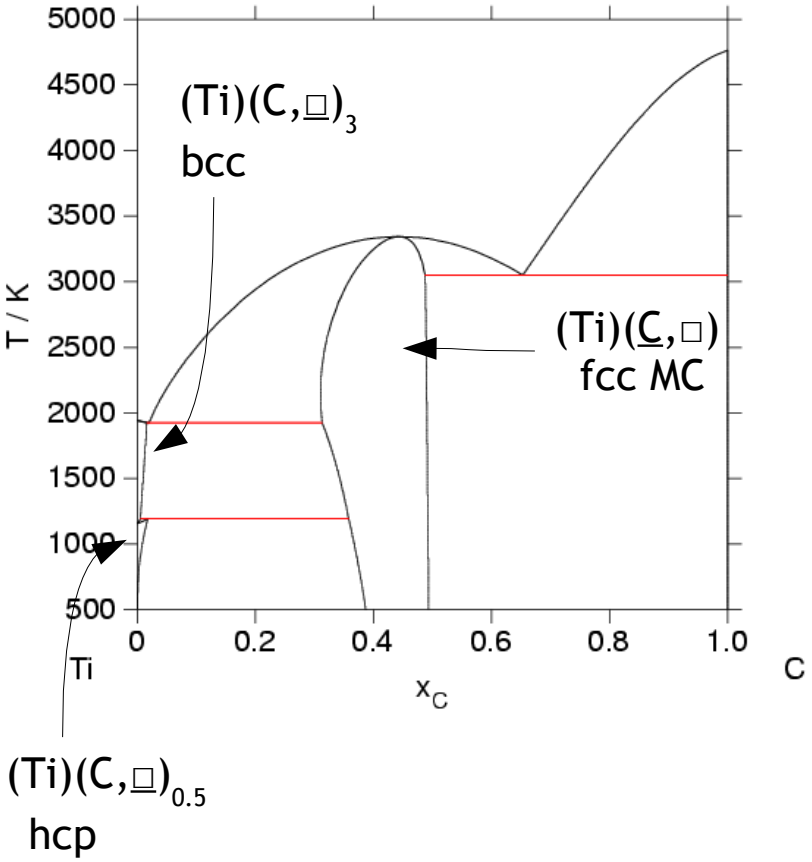
interstitial solutions	$y''_{\square} >> y''_{C}$
non stoichiometric carbides, $\cdots$	$y''_{\square} << y''_{C}$

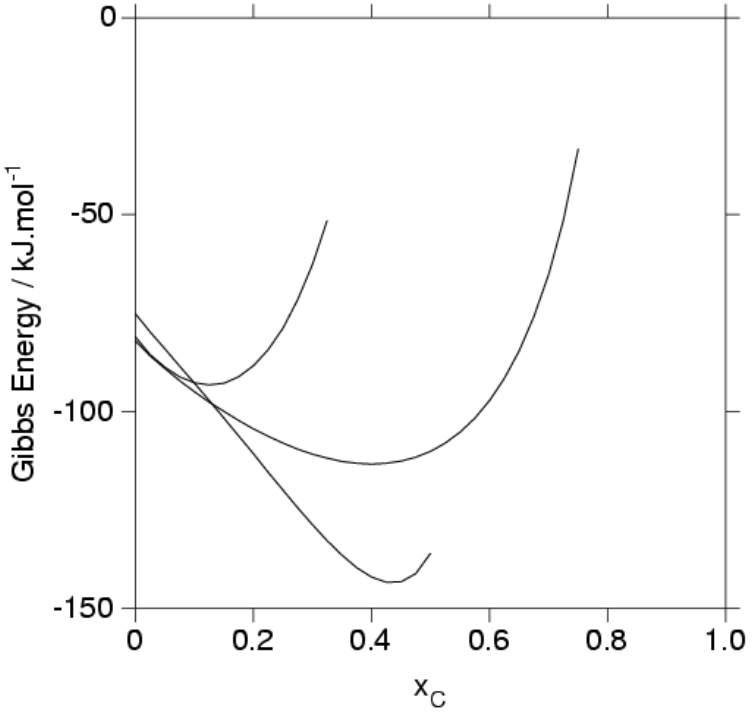
$G^{\varphi}_{\mathrm{M:C}}(T) \Rightarrow$ stoichiometric carbide

$G^{\varphi}_{\mathrm{M:}\square}(T) \Rightarrow$ pure M

Parametric Thermodynamic Models - G=f(x)

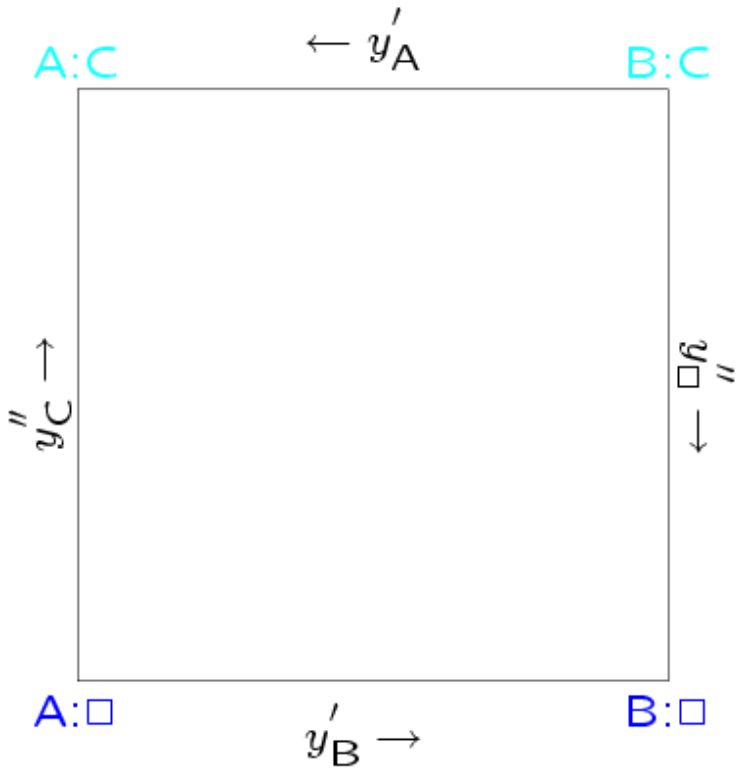
Example : Ti-C

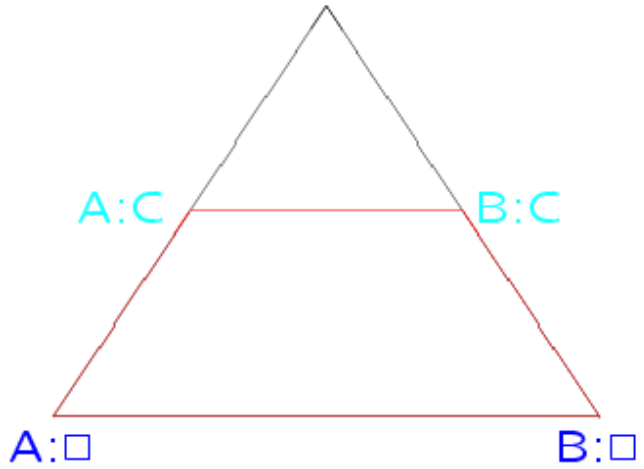




Parametric Thermodynamic Models - G=f(x)

$(A,B)_a(\square\ ,C)_b$





Parametric Thermodynamic Models - G=f(x)

Non stoichiometric compound A_aB_b

$$A_p\ (A,B)_q\ B_r$$

$$x^{\varphi}_{A} = \frac{p + q\ y_A}{p + q + r} \qquad x^{\varphi}_{B} = \frac{q\ y_B + r}{p + q + r}$$

$G^{\varphi}_{A:A:B:}(T)$ and $G^{\varphi}_{A:B:B}(T) \Rightarrow$ stoichiometric compounds

Parametric Thermodynamic Models - G=f(x)

Non stoichiometric compound A_aB_b

$$(A,B)_a(A,B)_b$$

$$x_A^{\varphi} = \frac{a\ y_A^{'} + b\ y_A^{''}}{a+b} \qquad x_B^{\varphi} = \frac{a\ y_B^{'} + b\ y_B^{''}}{a+b}$$

$G^{\varphi}_{A:B}(T) \Rightarrow$ *stable* stoichiometric compound

$G^{\varphi}_{B:A}(T) \Rightarrow$ antistructural stoichiometric compound

$G^{\varphi}_{A:A}(T)$ and $G^{\varphi}_{B:B}(T) \Rightarrow$ *metastable* pure elements A and B

Parametric Thermodynamic Models - G=f(x)

Ordering

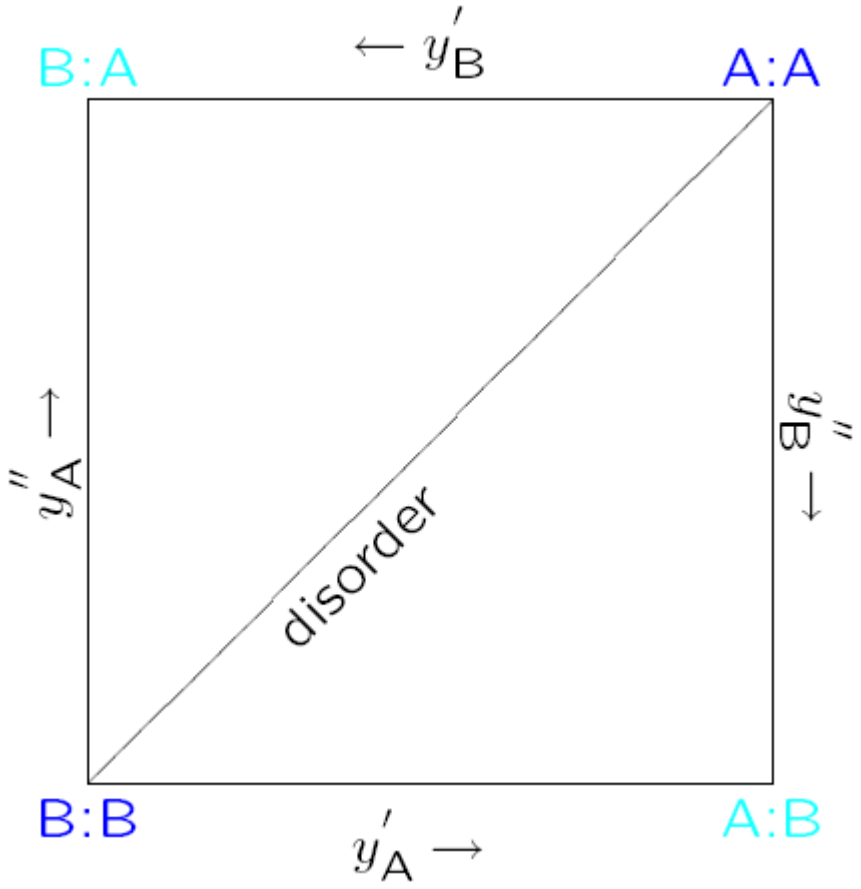
$$(\mathbf{A},\mathrm{B})_a\ (\mathrm{A},\mathbf{B})_b \quad \rightleftharpoons \quad (\mathrm{A},\mathrm{B})_{a+b}$$

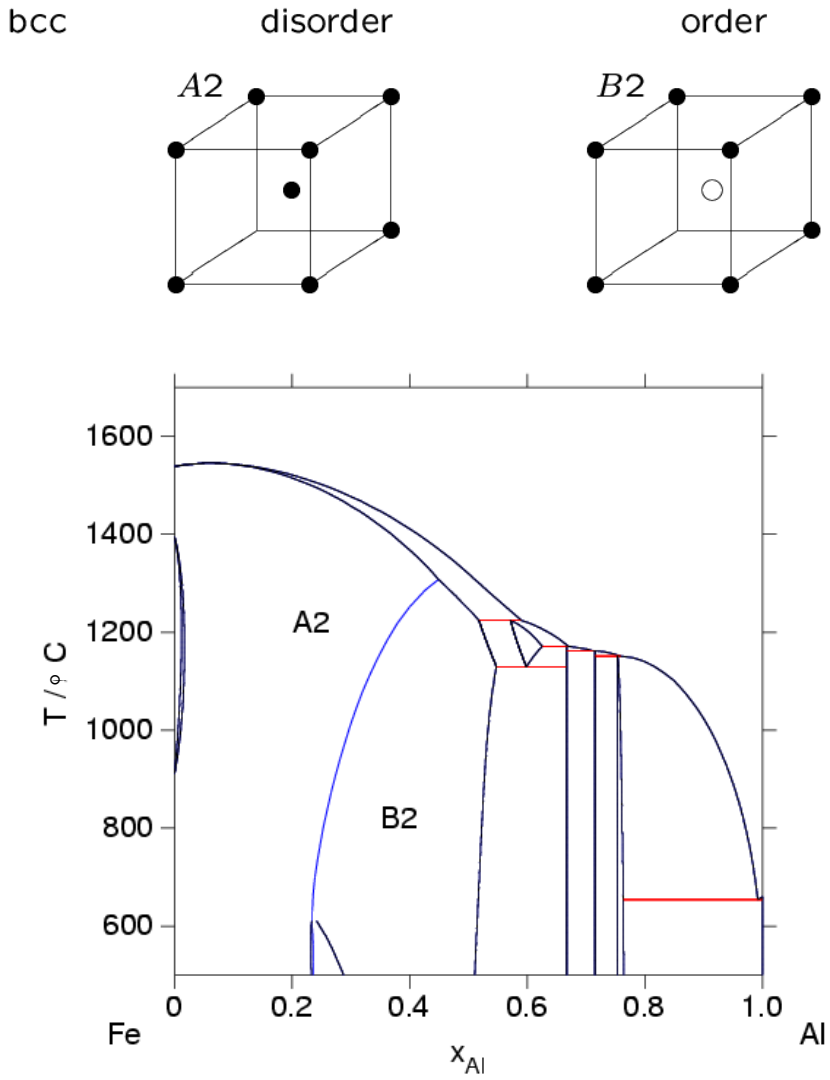
$$x_i^{\varphi} = \frac{a\ y_i^{'} + b\ y_i^{''}}{a+b} \quad \rightleftharpoons \quad x_i^{\varphi} = y_i^{'} = y_i^{''}$$

$G^{\varphi}_{\mathrm{A:B}}(T) \Rightarrow$ *stable* stoichiometric compound
$G^{\varphi}_{\mathrm{B:A}}(T) \Rightarrow$ antistructural stoichiometric compound

$G^{\varphi}_{\mathrm{A:A}}(T)$ and $G^{\varphi}_{\mathrm{B:B}}(T) \Rightarrow$ pure elements A and B

Parametric Thermodynamic Models - G=f(x)





Parametric Thermodynamic Models - G=f(P)

$$G_i^{\varphi}(P) \;=\; V_0 \; e^{\int_{298}^{T} \alpha(T)dT} \; \int_0^P e^{-\int_0^P \kappa dP} dP$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad \alpha = \frac{1}{V}\left(\frac{\partial G}{\partial T}\right)_P \qquad \kappa = \frac{1}{V}\left(\frac{\partial G}{\partial P}\right)_T$$

$$G^{\varphi}_{A_a B_b}(T,P) = G^{\varphi}_{A_a B_b}(T,P_0) + V\ (P - P_0)$$

$$G^{gas}_{A_a B_b}(T,P) = G^{gas}_{A_a B_b}(T,P_0) + RTln(P/P_0)$$

Assessment from experimental knowledge

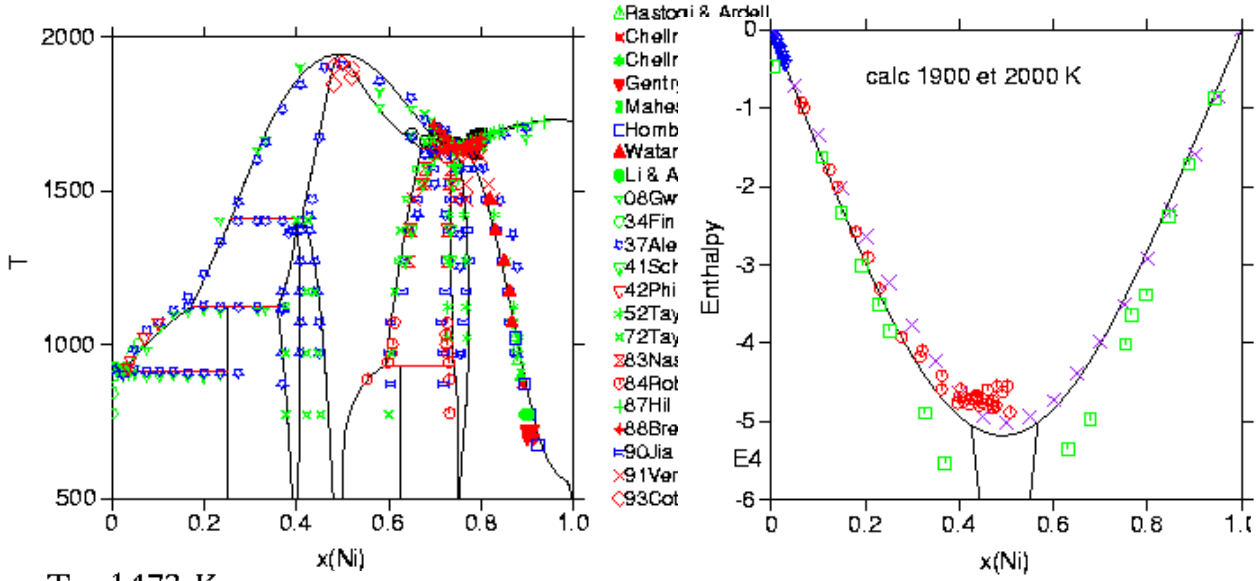
The parameters available in the models are assessed taking into account all the experimental knowledge :

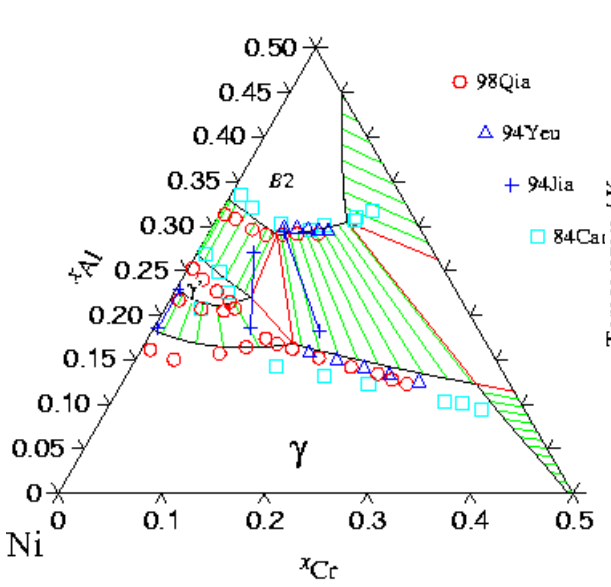
- phase diagram from
  - metallography,
  - microprobe,
  - DTA,...
- thermodynamics from
  - calorimetric measurements ($H-H(T_0)$, Cp, ΔH_f, ...),
  - mass spectrometry,
  - emf, ...
- crystallography

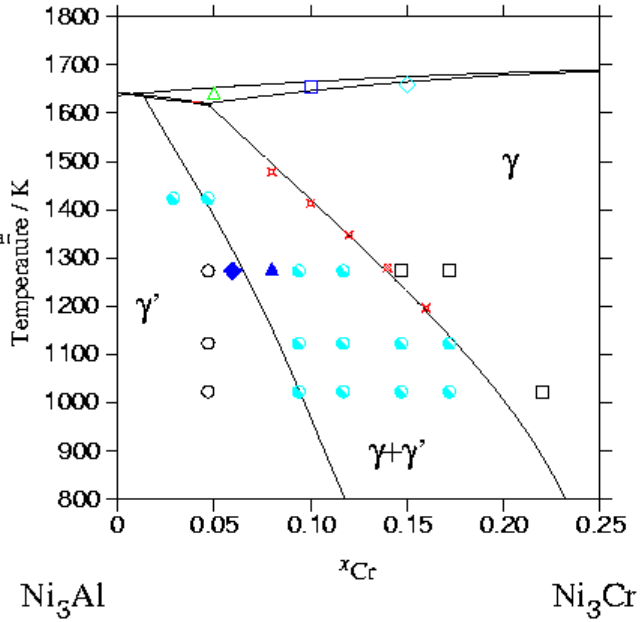
and FP results, for metastable area, unkown data :

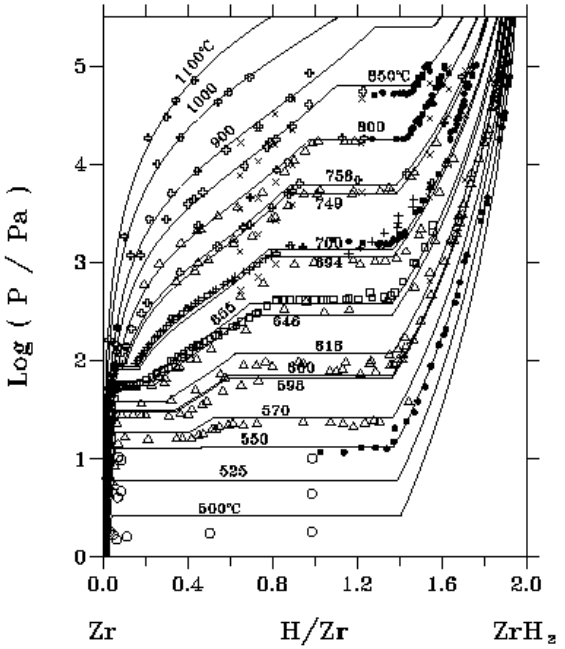
- total energy
- topology
- volume, ...

Using experimental results

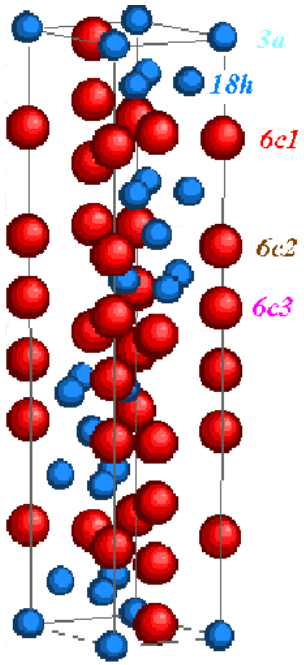






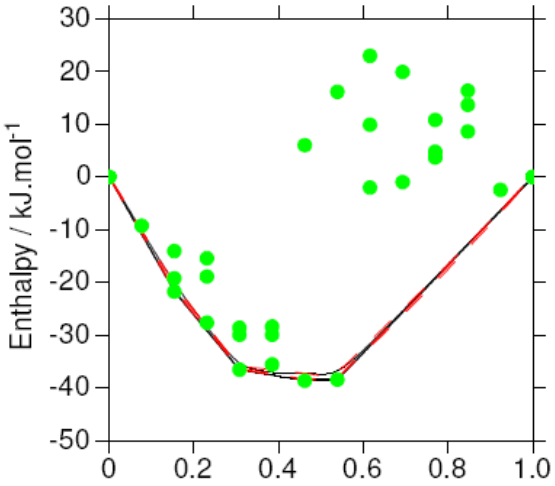


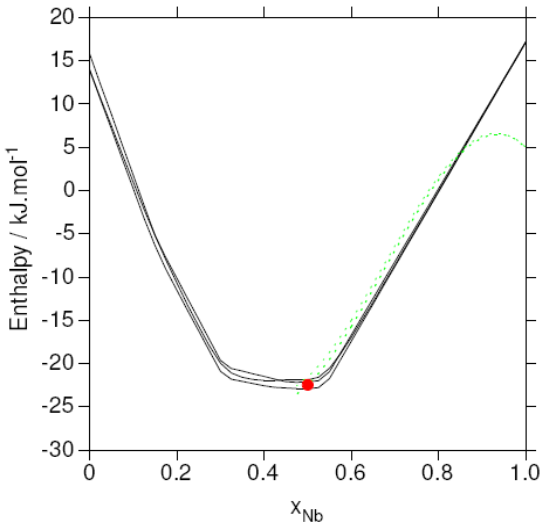
Using FP results, total energy

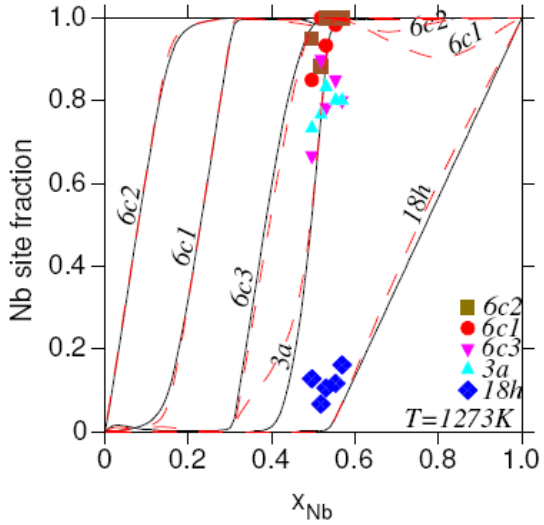


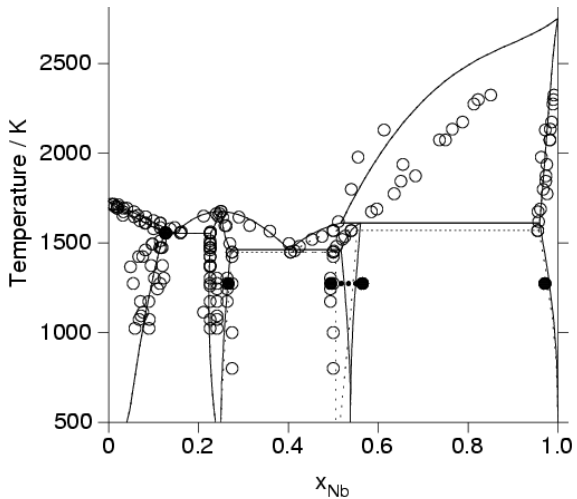
- VASP
- VASP + CVM
- VASP + CEF
- CEF without FP

$(Ni,Nb)_3\ (Ni,Nb)_{18}\ (Ni,Nb)_6\ (Ni,Nb)_6\ (Ni,Nb)_6$





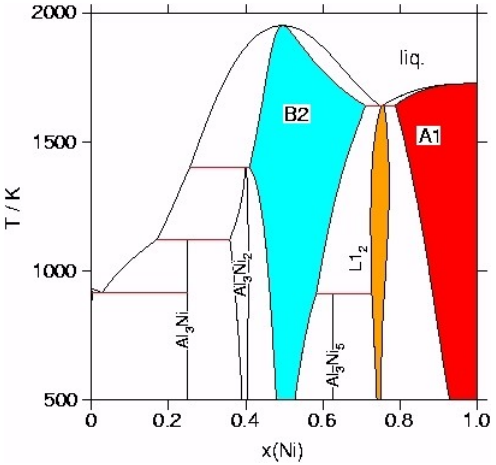




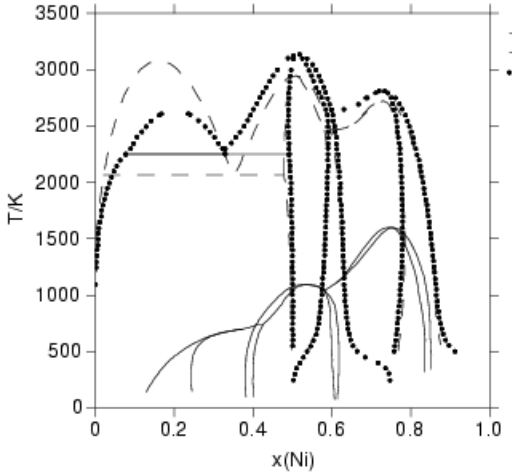
N. Dupin, S. Fries, J.M. Joubert, B. Sundman, M. Sluiter, Y. Kawazoe, A. Pasturel

Using FP results, topology

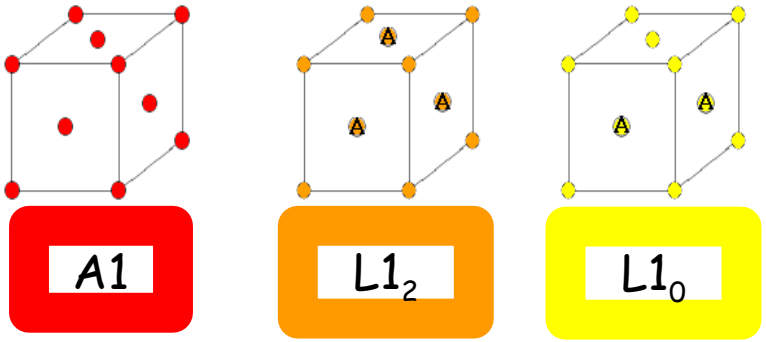
stable



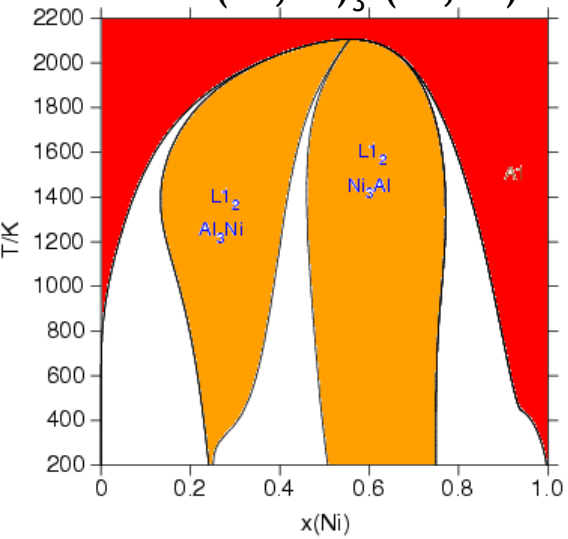
metastable, ab initio



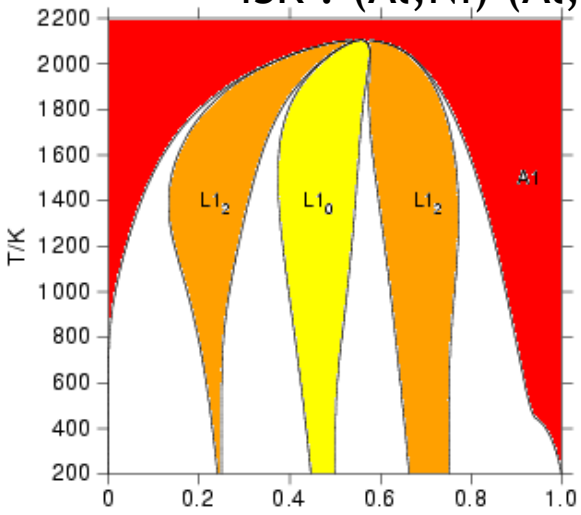
[88Car] A. E. Carlsson, et J. M. Sanchez, Solid State Commun., **65**, (6), 527-530
[92Col] C. Colinet, P. Hicter, et A. Pasturel, Phys. Rev. B, **45**, (4), 1571-1580
[92Pas] A. Pasturel, C. Colinet, A. T. Paxton, et M. van Schilfgaarde, J. Phys. Condens. Matter, **4**, (4), 942-959



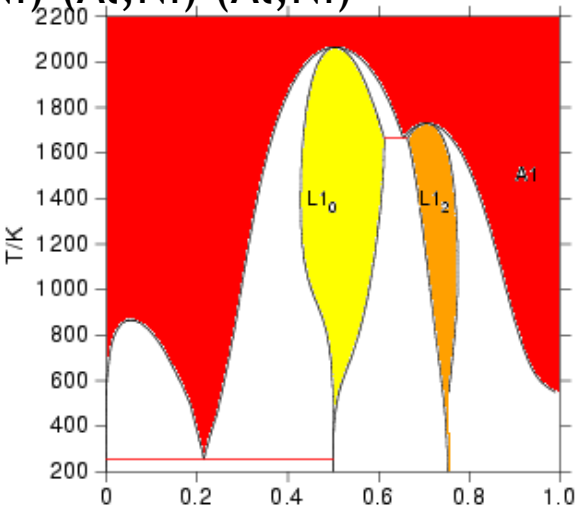
2SR : $(Al,Ni)_3$ (Al,Ni)



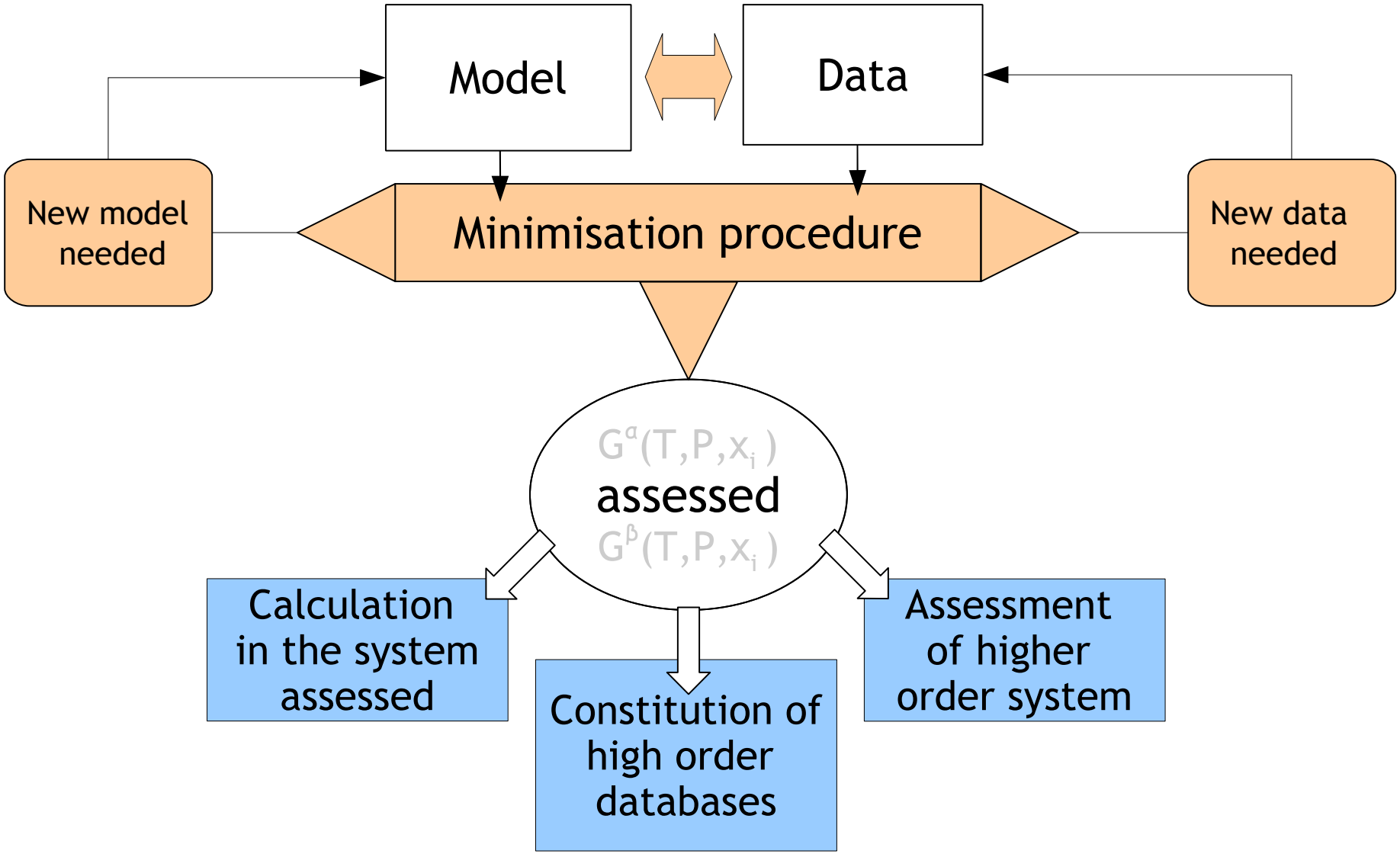
4SR : (Al,Ni) (Al,Ni) (Al,Ni) (Al,Ni)

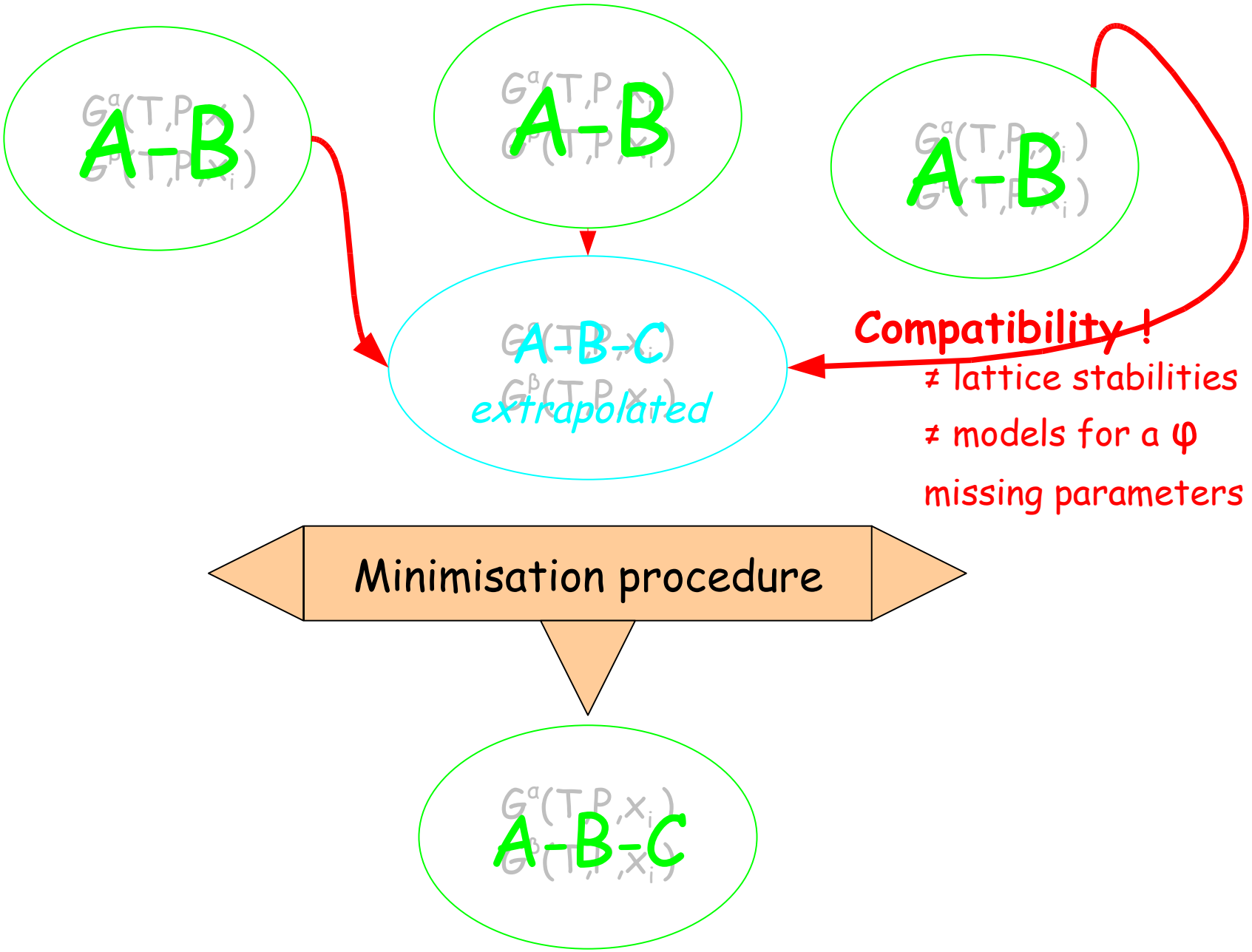


without $L^{x(Ni)}_{Al,Ni:Al,Ni}$

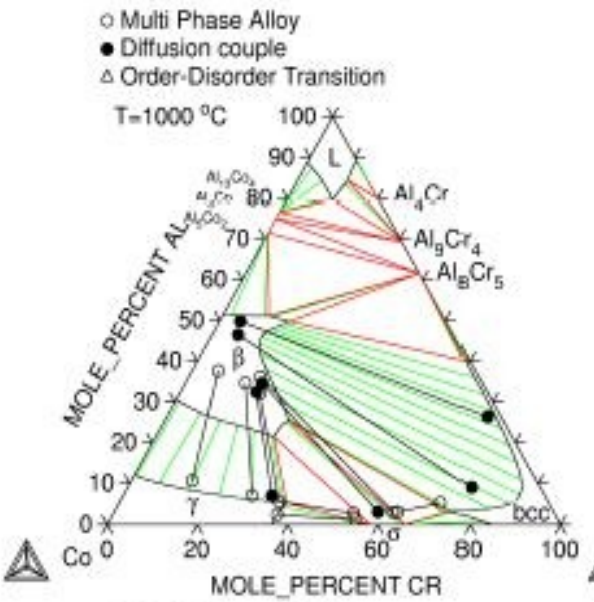


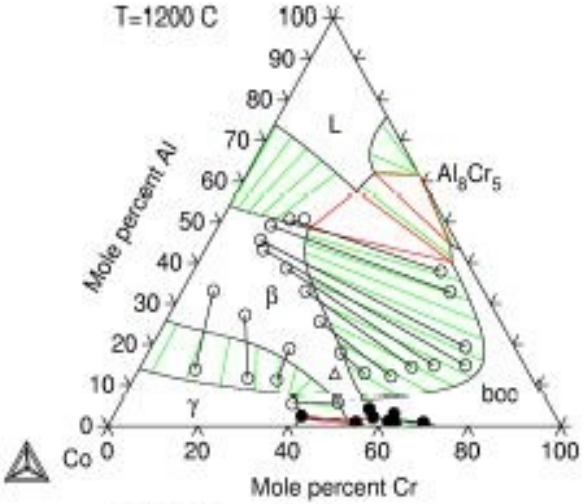
with $L^{x(Ni)}_{Al,Ni:Al,Ni}$

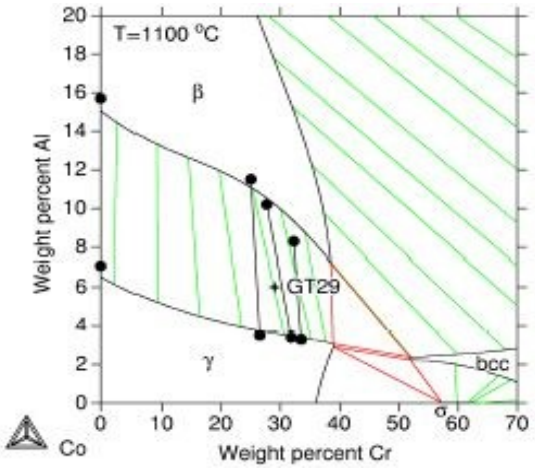

Model
Data
New model needed
Minimisation procedure
New data needed
$G^{\alpha}(T,P,x_i)$
assessed
$G^{\beta}(T,P,x_i)$
Calculation in the system assessed
Constitution of high order databases
Assessment of higher order system


A-B
A-B
A-B
A-B-C
extrapolated
Compatibility !
≠ lattice stabilities
≠ models for a φ
missing parameters
Minimisation procedure
A-B-C

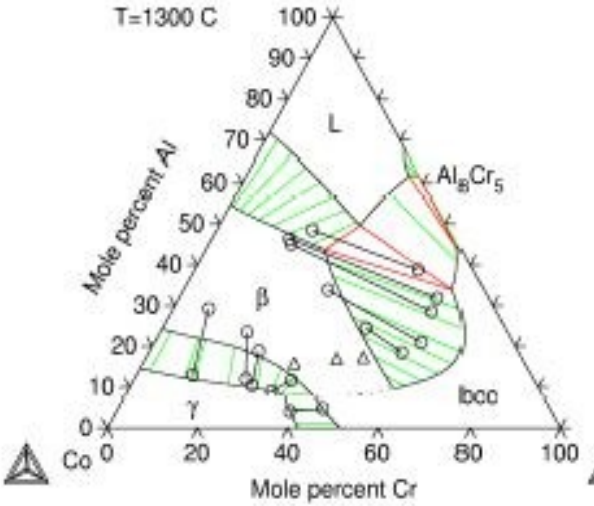
T. Gomez-Acebo et al., 2004

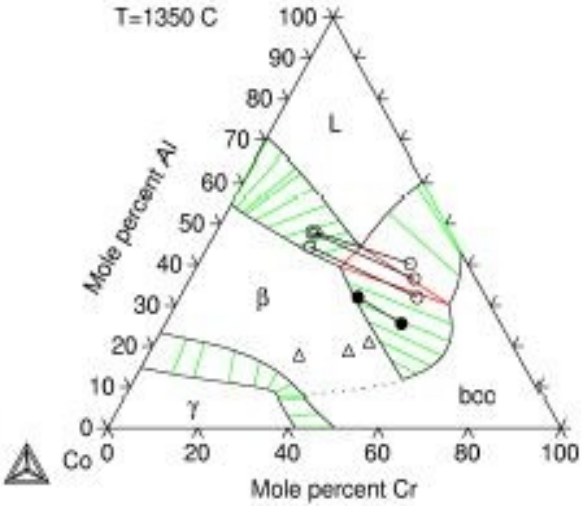






Exp. : T. Gomez-Acebo et al.





Exp. : K. Ishikawa et al., 1998

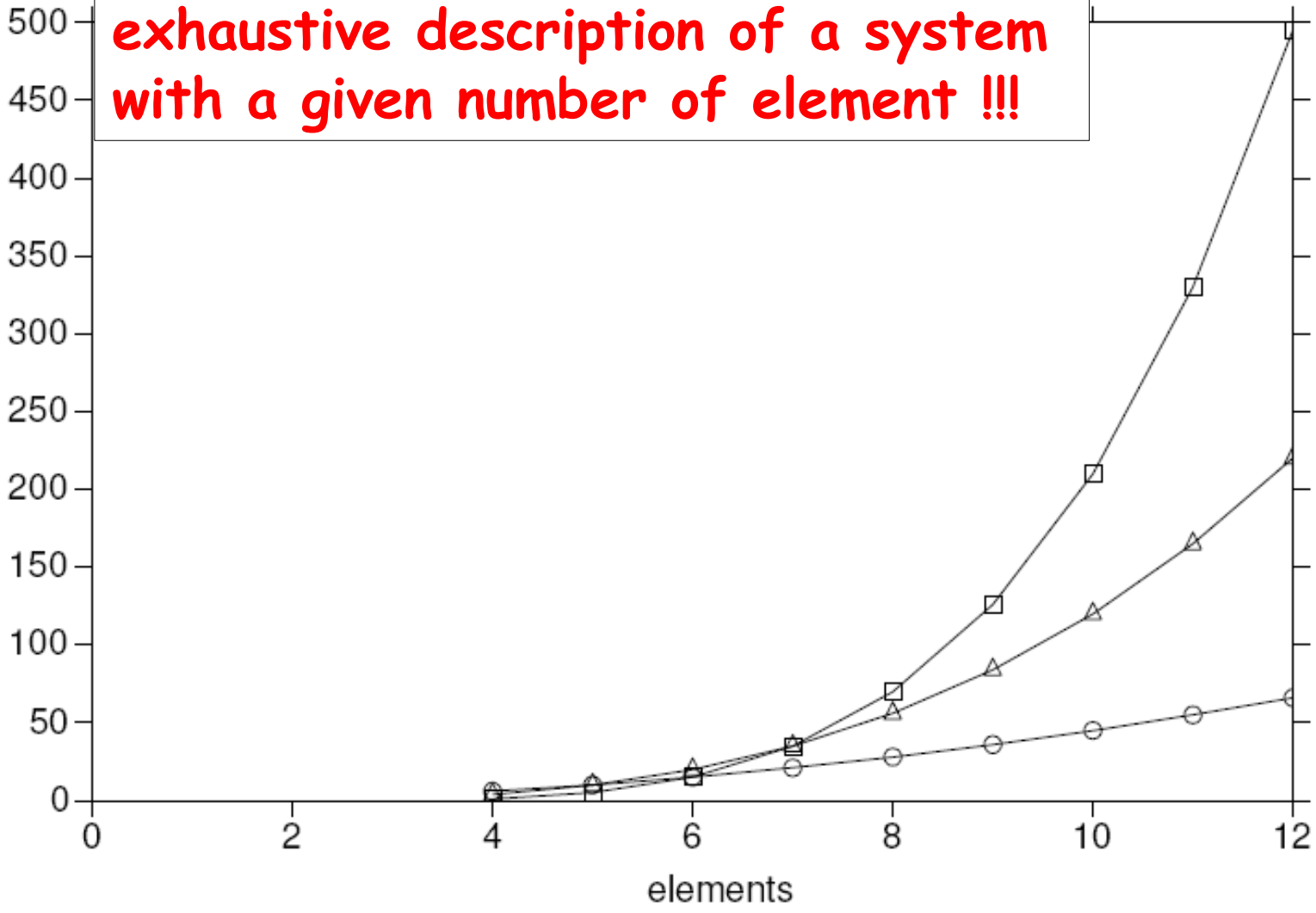
extrapolated
Al-Co-Cr
TCNI

The assessment of low order system parameters from higher order system may be missleading.

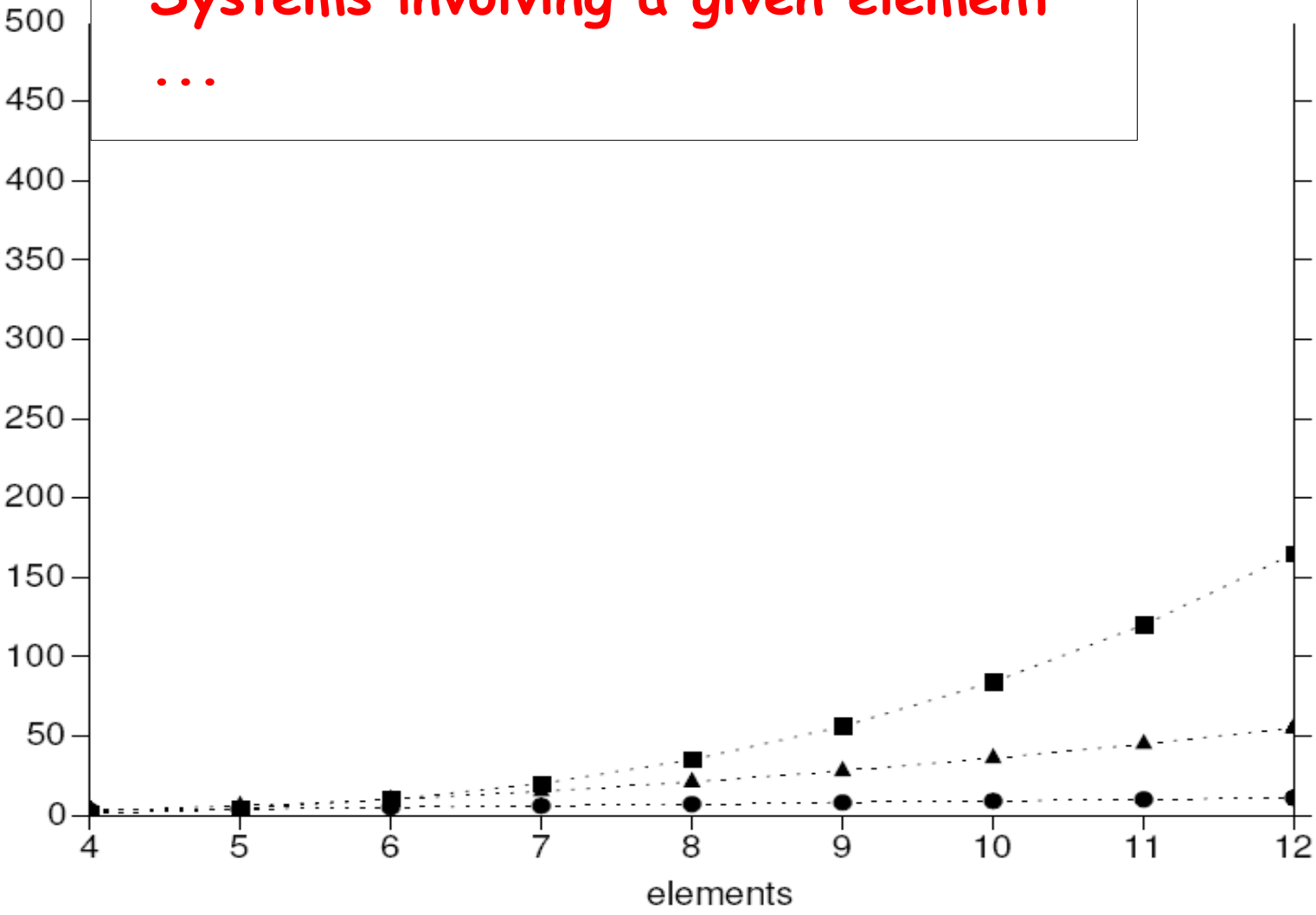
The Calphad approach is useful to critical assess experimental data.

The ability of the Calphad approach to extrapolate to higher order systems justify the constitution of high order databases of industrial and scientific interest because it is not necessary to assess all subsystems.

No of system to study for the exhaustive description of a system with a given number of element !!!



Systems involving a given element ...



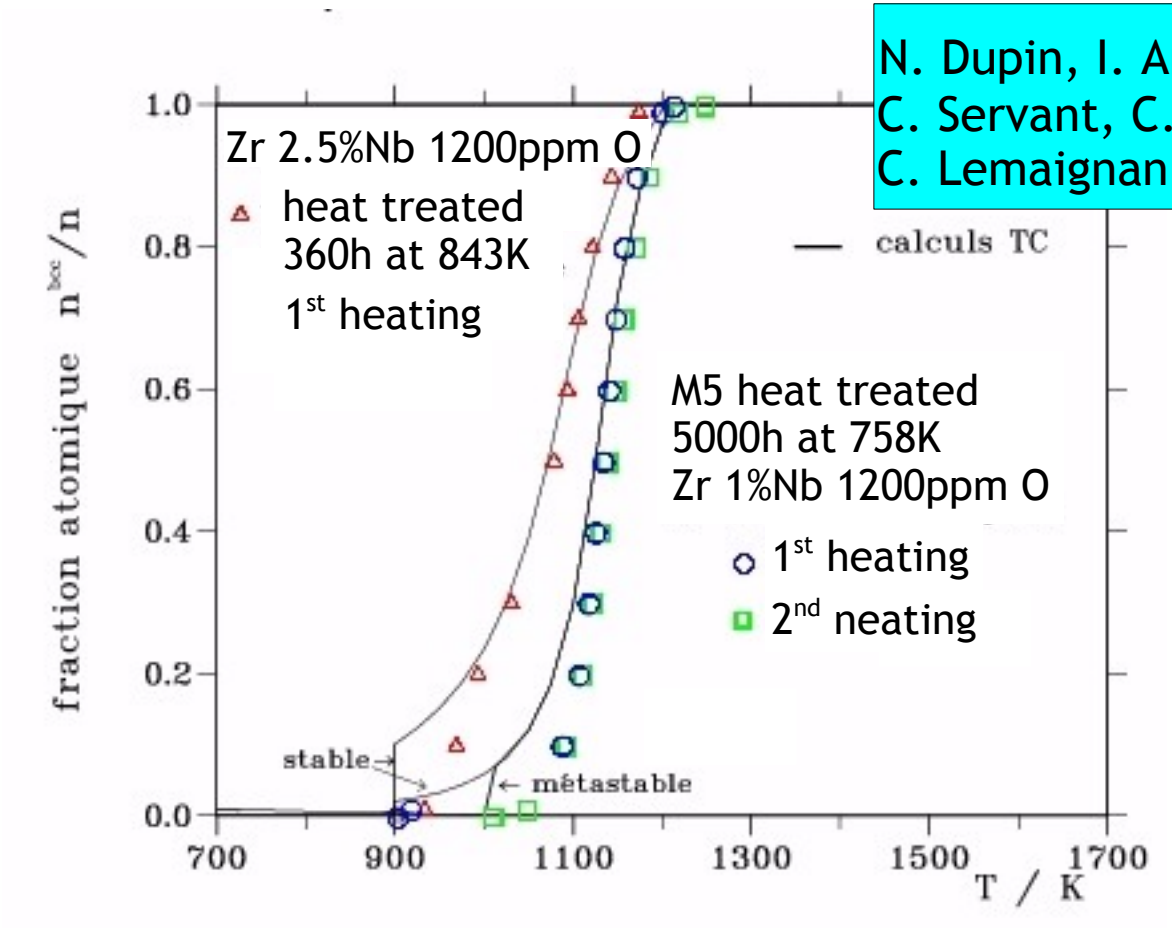
Conclusions : some limitations

- **Many systems are not described or only partially;** this can be related to scarce experimental knowledge but not only.
- Some experimental knowledge is needed.
- Calphad cannot predict the energy of formation of a compound, that is ab initio.
- Crystallography and defects are often simplified.
- Models are sometimes missused by assessors using too many parameters making extrapolation less accurate.
- The models implemented are limited.

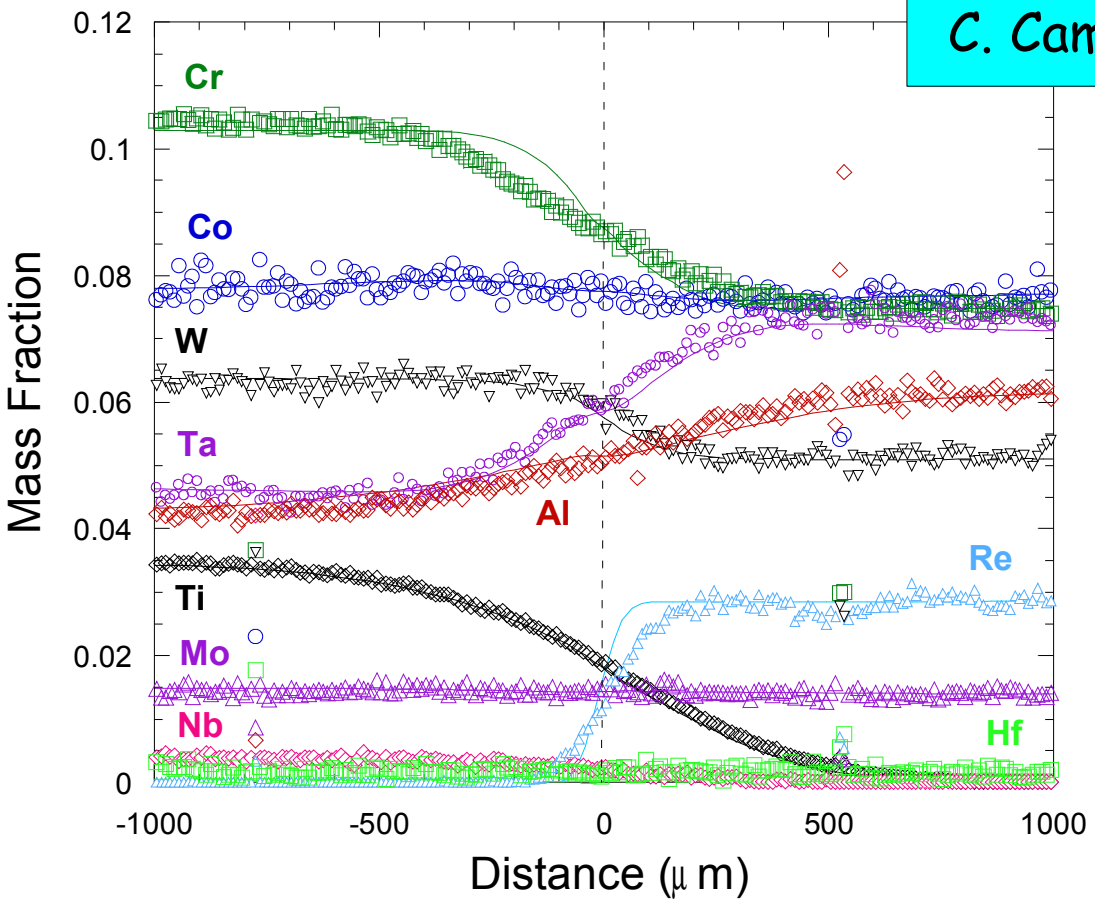
... but used everyday to

- **Critically assess many different kinds of experimental data simultaneously**
- **Verify** the consistency of **experimental results**
- **Plan** experimental studies in systems not well known
- Calculate equilibria (also metastable) and properties in **multiconstituant** systems whatever x,T,P
- Define heat **treatments**, chemical ...
- Optimise **new materials**
- Couple with **diffusion** simulation
- ...

N. Dupin, I. Ansara,
C. Servant, C. Toffolon,
C. Lemaignan, J.C. Brachet



C. Campbell


Mass Fraction
0.12
0.1
0.08
0.06
0.04
0.02
0
-1000
-500
0
500
1000
Distance (μm)
Cr
Co
W
Ta
Al
Re
Ti
Mo
Nb
Hf