CALPHAD Modeling of Homogeneity Ranges

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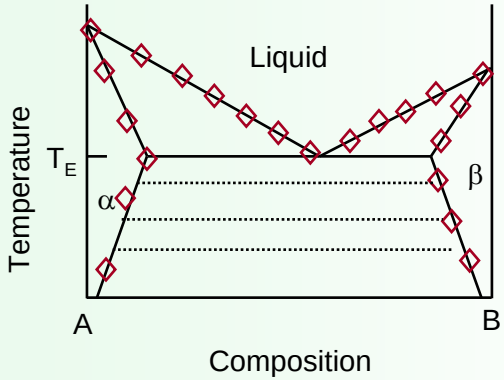
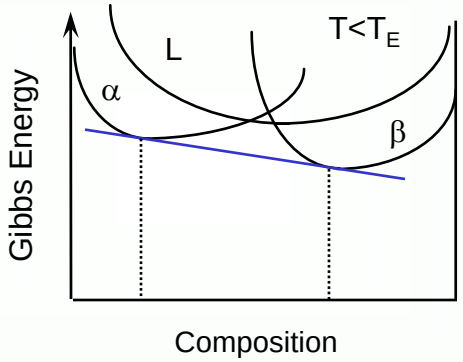
CALPHAD Approach

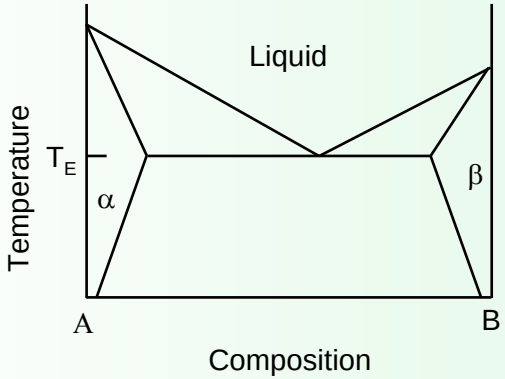
Experimental phase diagram and thermochemical data

Determine Gibbs energy functions for each phase: $G = f(x,T,P)$

Calculated phase diagram







$$G^{\phi} = G^{0} + G^{ideal} + G^{excess}$$

Binaries → Ternaries → Quaternaries → n^{th} order Systems

Model Descriptions

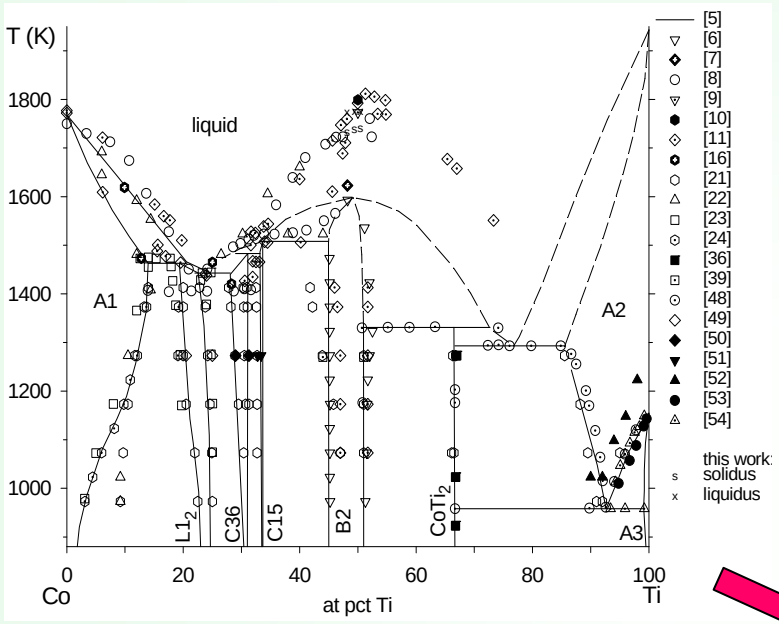
- Stoichiometric model
  - solids with fixed concentration
- Regular solution type model
  - liquids
  - disordered substitutional solid solutions
- Associate model
  - liquids with short range order
  - gas phase
- Sublattice model
  - interstitial solid solutions
  - ordered phases with homogeneity ranges

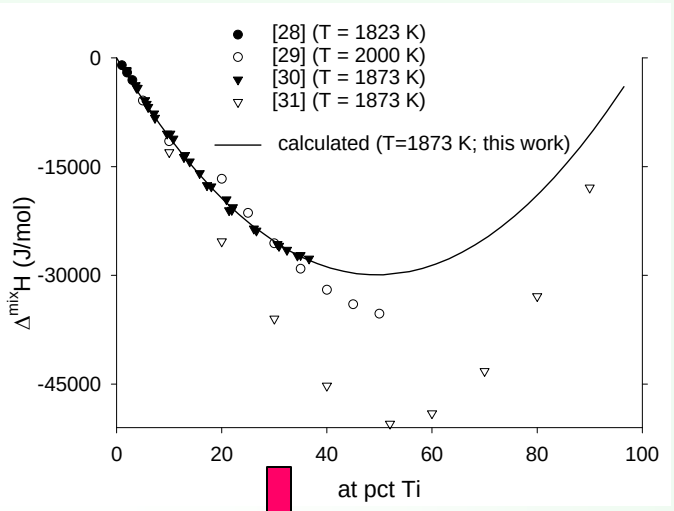
Each model allows expansion to multicomponent descriptions

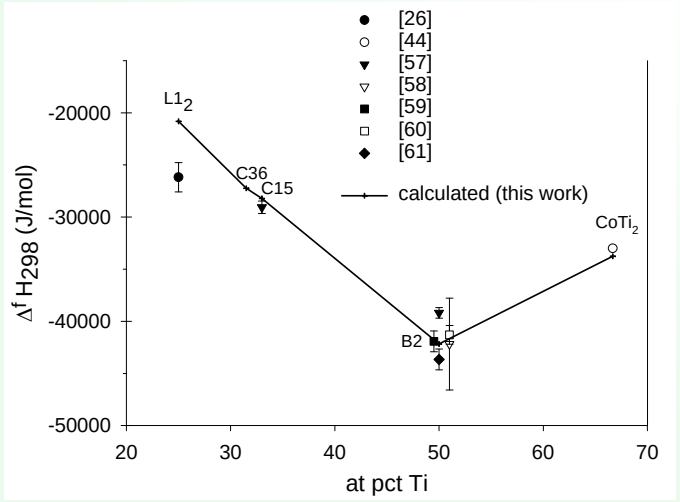
Experimental Data for Parameter Optimization

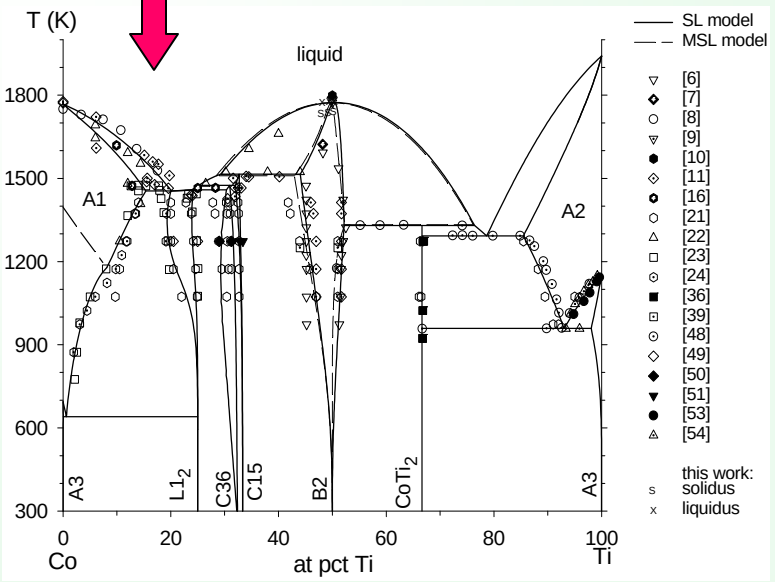
- Phase diagram data
  - Phase boundaries: liquidus, solidus, solvus
    - Thermal analysis, microstructures, X-ray
  - Temperatures of invariant equilibria
    - Thermal analysis
- Thermochemical data
  - Enthalpies (mixing, formation)
    - Calorimetry (solution, bomb)
  - Heat capacities
    - Calorimetry (drop)
  - Chemical potentials
    - Vapor pressure, electromotive force measurements

Systems with Plenty Experimental Data









CALPHAD Methodology

$$G = \sum x_i G_i^0 + R\,T\,x_i \ln x_i + G^{xs}$$

binary — Assessment: G^{xs}_{bin}

ternary — Extrapolation $(\sum G^{xs}_{bin})$ + Assessment: G^{xs}_{ter}

quaternary — Extrapolation $(\sum G^{xs}_{bin} + \sum G^{xs}_{ter})$ + Assessment: G^{xs}_{quat}

True quaternary phases are rare in metallic systems

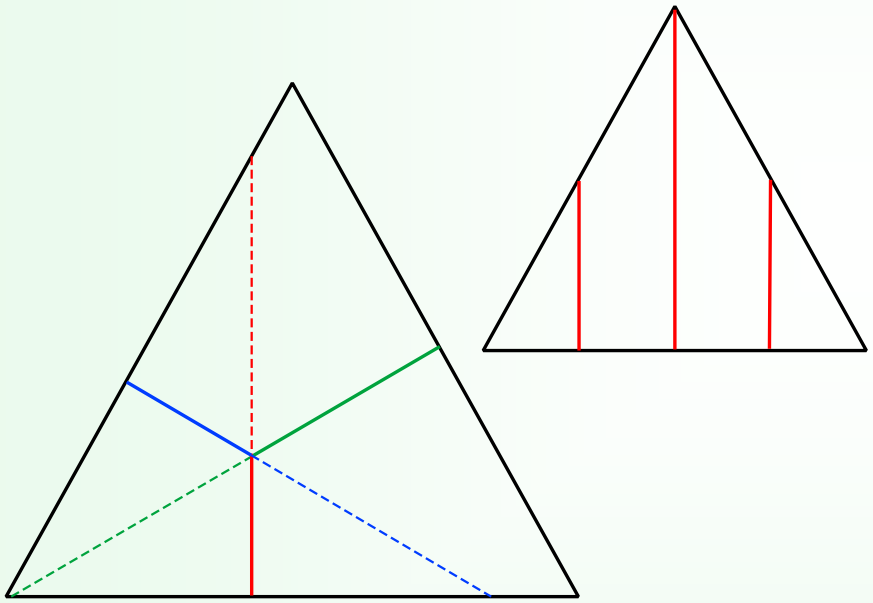
$\Rightarrow$ **Assessment of ternary systems is usually sufficient for the description of a multicomponent system**

The same approach can be used for the assessment of other properties

Extrapolation of Multicomponent Systems

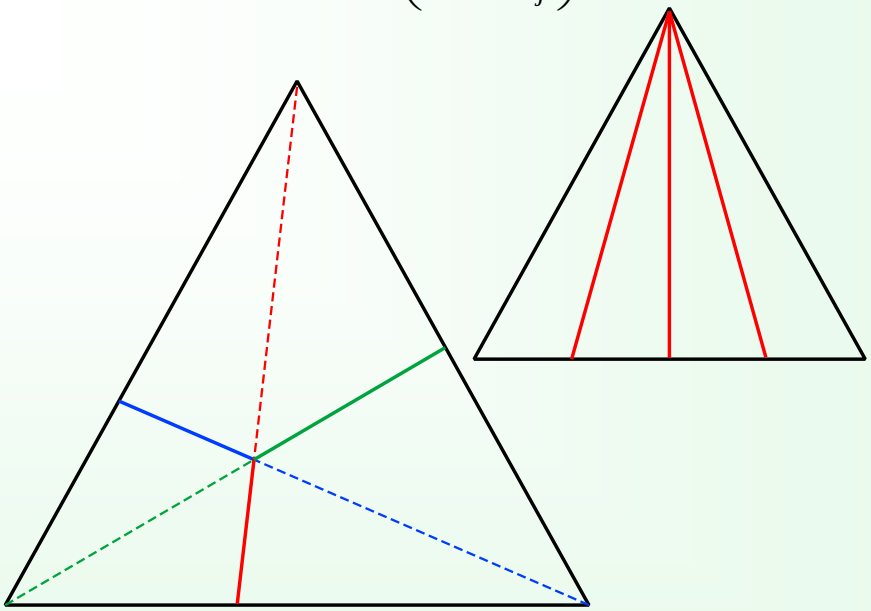
Muggianu formalism:

$$^{ex}G = \sum_{m}^{\frac{n(n-1)}{2}} x_i x_j \sum_{k}^{l_{ij}} L_k^{ij} \left(x_i - x_j\right)^k$$



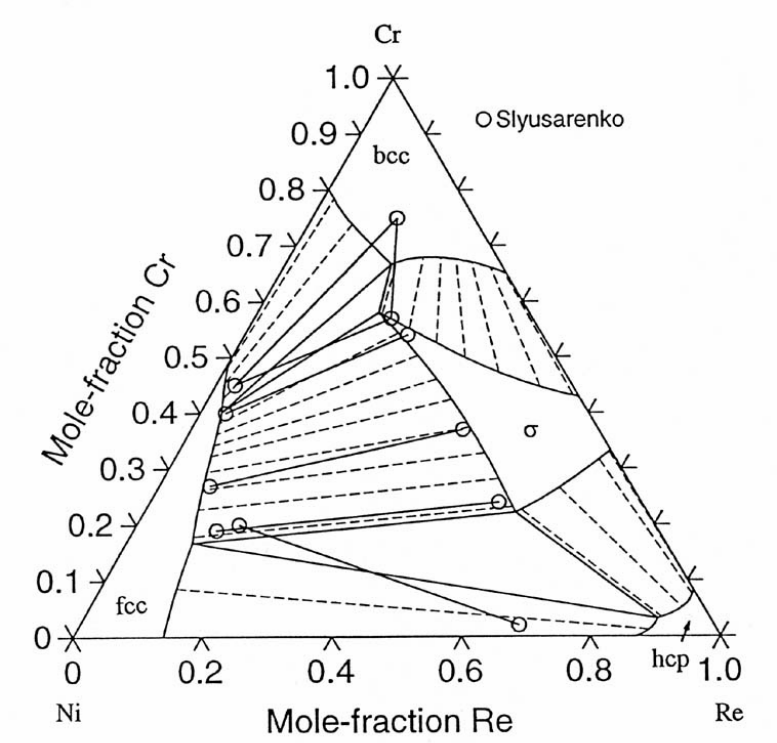
Kohler formalism:

$$^{ex}G = \sum_{m}^{\frac{n(n-1)}{2}} x_i x_j \sum_{k}^{l_{ij}} L_k^{ij} \left(\frac{x_i - x_j}{x_i + x_j}\right)^k$$

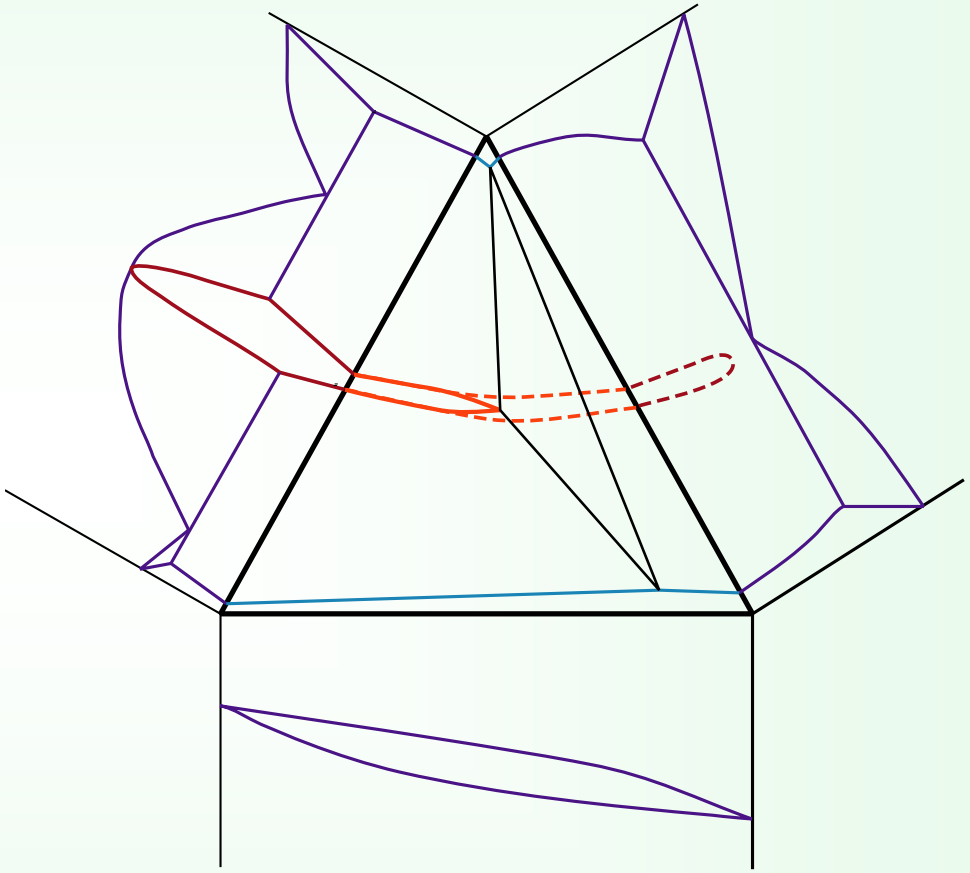


Muggianu formalism is most commonly used because it is easily generalized

Extrapolation of Homogeneity Ranges



Huang and Chang
J. Alloys & Compds. 274 (1998) 209



Parameters are needed to describe hypothetical metastable end-member phases

stable binary
metastable binary
stable ternary
metastable ternary

Extrapolation Requirements and Results

$$G^{\varphi} = y'_A y''_A G^{\circ}_{AA} + y'_A y''_B G^{\circ}_{AB} + y'_B y''_A G^{\circ}_{BA} + y'_B y''_B G^{\circ}_{BB} +$$

$$RT\{a'(y'_A \ln y'_A + y'_B \ln y'_B) + a''(y''_A \ln y''_A + y''_B \ln y''_B)\} +$$

$$y'_A y'_B y''_A \sum_{i=0}^{n_1} L_i^1 (y'_A - y'_B)^i + y'_A y'_B y''_B \sum_{i=0}^{n_2} L_i^2 (y'_A - y'_B)^i + y'_A y''_A y''_B \sum_{i=0}^{n_3} L_i^3 (y''_A - y''_B)^i + y'_B y''_A y''_B \sum_{i=0}^{n_4} L_i^4 (y''_A - y''_B)^i + y'_A y'_B y''_A y''_B L^5$$

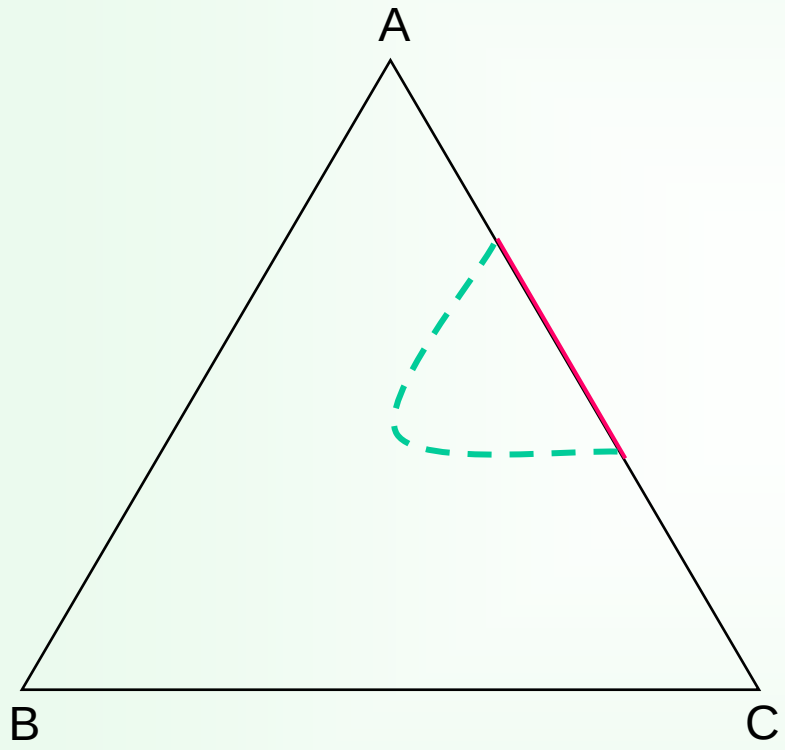
Requirements:

- Identical description of unaries
- Compatible descriptions of solution and intermediate phases

Results:

- “Draft” of higher component system
- Comparison with experimental data determines whether the description needs adjustments
- Provide roadmap for critical experiments if no experimental data exist
- In many cases, sufficiently accurate prediction of phase equilibria for systems with more than 3 components

Modeling of Substitutional Solutions



$$G^{\varphi} = x_A G_A^{\circ} + x_B G_B^{\circ} + x_C G_C^{\circ} +$$

$$RT \sum_k x_k \ln(x_k) +$$

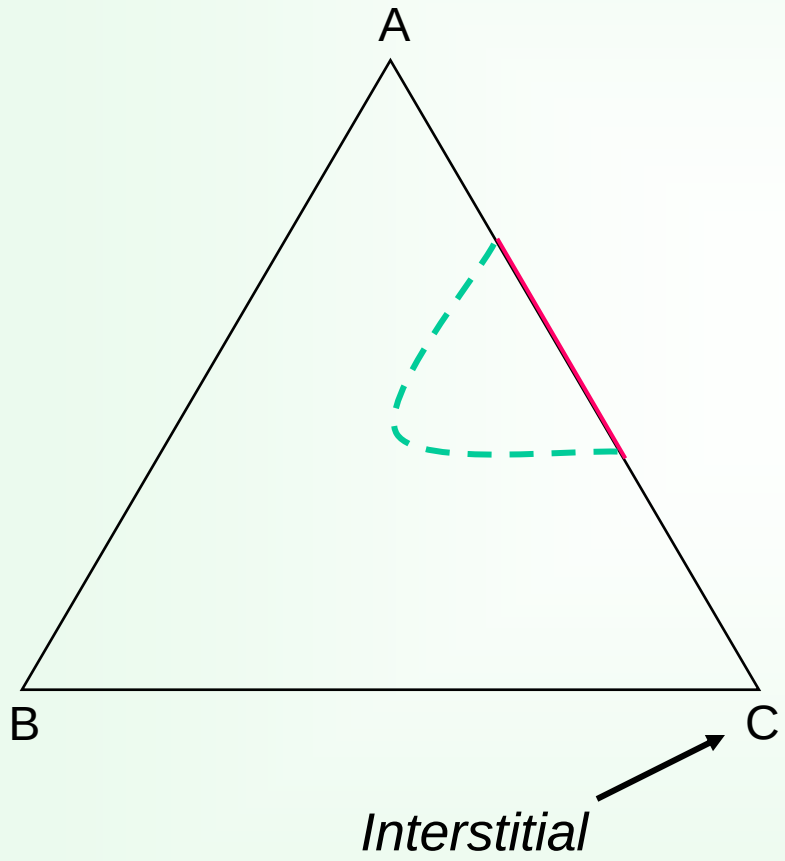
$$x_A x_B \sum_i (x_A - x_B)^i {}^i L_{AB} +$$

$$x_A x_C \sum_i (x_A - x_C)^i {}^i L_{AC} +$$

$$x_B x_C \sum_i (x_B - x_C)^i {}^i L_{BC} +$$

$$x_A x_B x_C \sum_k x_k {}^k L$$

Modeling of Interstial Solutions



$$G^{\varphi} = y_A y_{Va} G^{\circ}_{A:Va} + y_A y_C G^{\circ}_{A:C} +$$

$$y_B y_{Va} G^{\circ}_{B:Va} + y_B y_C G^{\circ}_{B:C} +$$

$$RT \sum_s a_s \sum_k y_k \ln(y_k) +$$

$$y_A y_B y_{Va} \sum_i (y_A - y_B)^{i\,i} L_{AB:Va} +$$

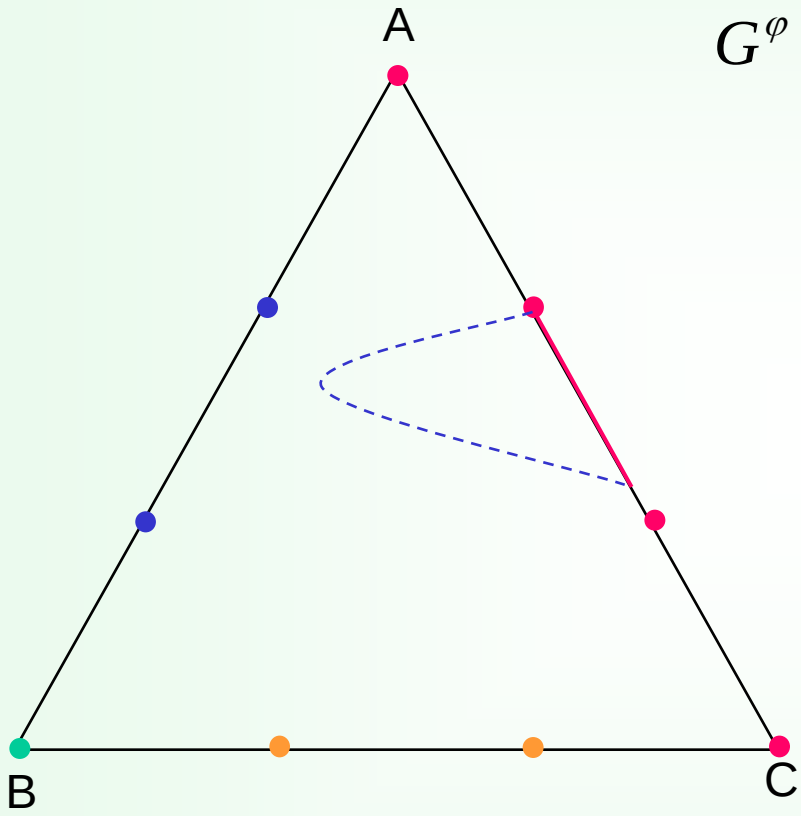
$$y_A y_B y_C \sum_i (y_A - y_B)^{i\,i} L_{AB:C} +$$

$$y_A y_C y_{Va} \sum_i (y_C - y_{Va})^{i\,i} L_{A:CVa} +$$

$$y_B y_C y_{Va} \sum_i (y_C - y_{Va})^{i\,i} L_{B:CVa} +$$

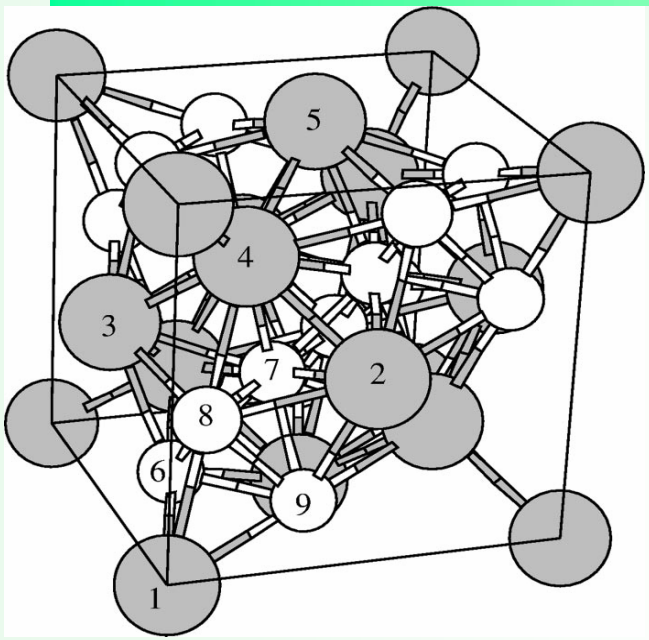
$$y_A y_B y_C y_{Va} L_{AB:CVa}$$

Modeling of Ordered Phases



$$G^{\varphi} = y'_A y''_A G^{\circ}_{A:A} + y'_B y''_B G^{\circ}_{B:B} + y'_C y''_C G^{\circ}_{C:C} +$$
$$y'_A y''_B G^{\circ}_{A:B} + y'_B y''_A G^{\circ}_{B:A} +$$
$$y'_A y''_C G^{\circ}_{A:C} + y'_C y''_A G^{\circ}_{C:A} +$$
$$y'_B y''_C G^{\circ}_{B:C} + y'_C y''_B G^{\circ}_{C:B} +$$
$$RT\left\{\begin{matrix} a'\left(y'_A \ln y'_A + y'_B \ln y'_B\right)+ \\ a''\left(y''_A \ln y''_A + y''_B \ln y''_B\right) \end{matrix}\right\} +$$
$$y'_A y'_B \sum_{k''} y''_A \sum_i L_i^k \left(y'_A - y'_B\right)^i +$$
$$y''_A y''_B \sum_{k'} y'_B \sum_i L_i^k \left(y''_A - y''_B\right)^i$$

H in C15 AB_2 as in (Ti,Zr) (V, Cr, Mn, Fe, Co, Ni)$_2$



Hong & Fu, Phys. Rev. B 66(2002) 094109

The C15 Laves phase structure

- large atoms are *A* (Zr,Ti)
- small atoms are *B* (V, Cr, Mn, Fe, Co, Ni)
- 2*A*2*B* tetrahedral site is formed by the atoms labeled 2, 4, 7, and 8
- 1*A*3*B* site by atoms 1, 6, 8, and 9;
- 4*B* site by atoms 6, 7, 8, and 9.

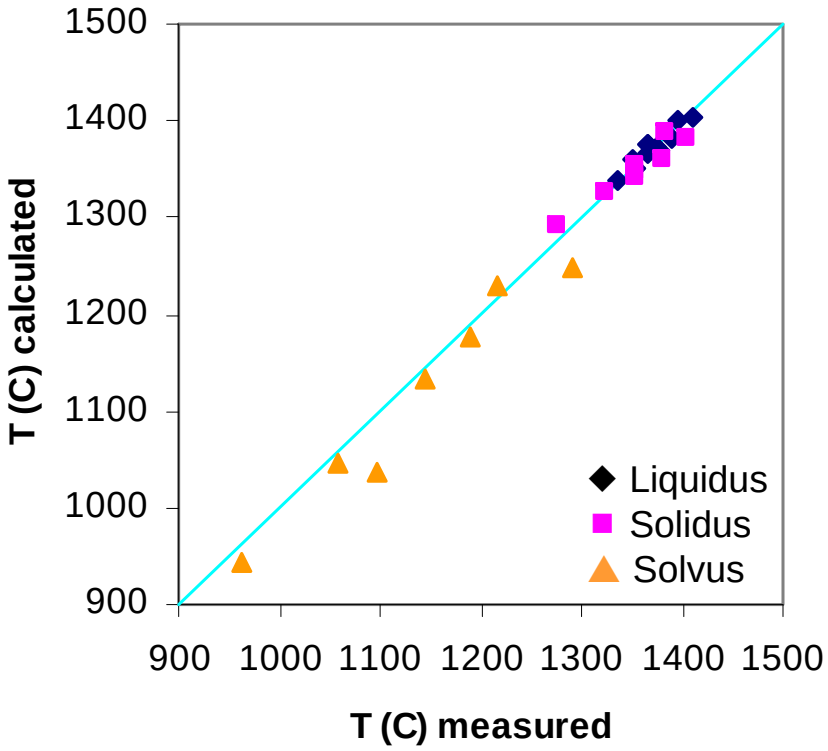
Space Group 227; Fd3m

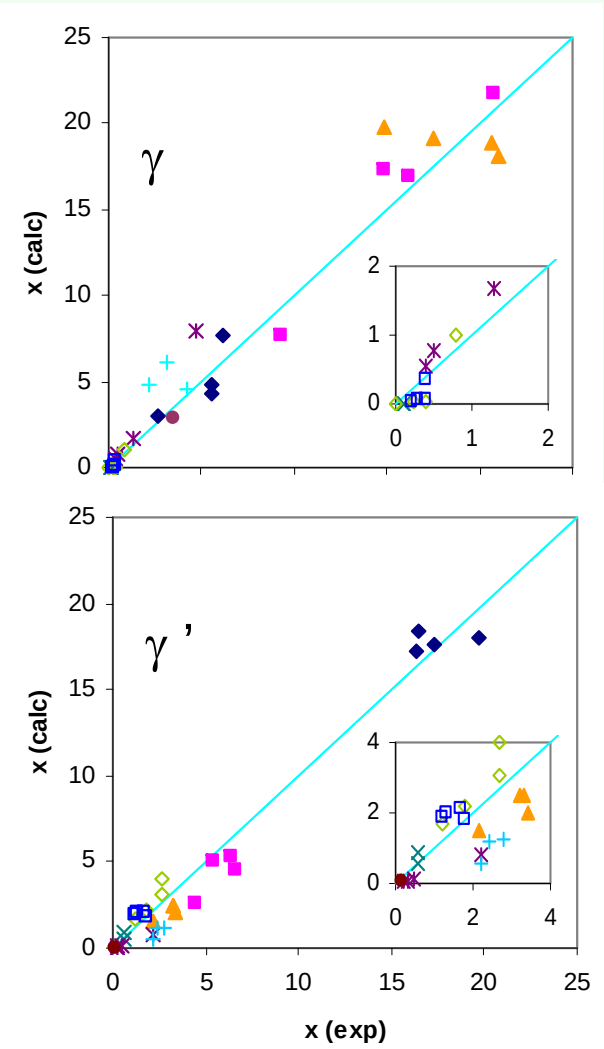
8a	Ti,Zr
16 d	V, Cr, Mn, Fe, Co, Ni
8b	4B tetrahedral hole ; very little H
32e	1A3B tetrahedral hole; can be ~¼ filled with H
96g	2A2B tetrahedral hole; can be ~¼ filled with H

H-H distance is too close if holes are more filled

Calculations of Phase Equilibria for 10-Component Superalloys

Experimental and calculated liquidus, solidus and solvus temperatures and γ/γ' tie lines





Phase-based Functions for Other Properties

The CALPHAD method uses functions of temperature, composition and pressure to describe the Gibbs energy of ***individual phases***. This method could also be applied for the description of other properties.

- Physical Properties
  - Volume
  - Elastic Constants
  - Electrical properties
  - Thermal conductivity
  - Viscosity
  - …
- Kinetic Properties
  - Diffusion
  - Nucleation
  - …

CALPHAD and Other Computational Methods

- The CALPHAD method is a very powerful tool for dealing with commercial alloys because of their multicomponent nature
- The CALPHAD method needs quantities that cannot be easily obtained from experimental data
- Data from atomistic simulations and DFT calculations are an extremely valuable supplement to experimental data for CALPHAD input
- Only with cooperation of all computational methods and experimental methods the progress needed for the development of new materials and process designs will be enabled

End