Quality Assurance Concepts in Assessment and Database Construction

Ursula R. Kattner
Metallurgy Division, NIST, Gaithersburg, MD 20899

From First Principles to Multi-Scale Modeling of Materials Workshop
Rio de Janeiro, Brazil
May 31, 2011

National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Assessments and Databases

- Assessment of a system
  - Mostly binary and ternary systems
  - Selection of model descriptions for individual phases
  - Critical evaluation of experimental data
  - Adjustment of model parameters to experimental data
- Databases
  - At least 4 components (=“*multicomponent*”)
  - Selection of model descriptions for individual phases
  - Critical evaluation of available thermodynamic descriptions of constituent binary and ternary subsystems
  - In case of incompatibility reassessment of phase descriptions or entire systems
  - Adjustment of model parameters not determined by the constituent binary and ternary subsystems to experimental data

Components of a Thermodynamic Assessment

- System
  - General topology of the phase diagram
  - Solid phases and their crystal structures
  - Structure of the liquid phase
  - Gas phase stable as single phase?
- Experimental Data
  - Phase diagram data
    - Reference books: Predel, Massalski, Hansen-Elliott-Shunk, Phase Diagrams for Ceramists, …
    - Electronic databases: ASM, MSI, ACerS/NIST, …
    - Literature search
  - Thermodynamic data
    - Reference books: Hultgren, JANAF, Barin, Knacke, …
    - Electronic databases: NIST, …
    - Literature search
  - Auxiliary data
    - Computational data: DFT, MC, CVM, CAS, Miedema, ..
    - Crystal structure data: ICSD, ASM, …
    - …

Selection of models

+

Critical data evaluation

↓

Optimization of model parameters

CALPHAD Models

- Should describe phase as physically as possible
  - Long range order
  - Short range order
- Crucial for realistic extrapolation of description to higher component systems
- Crucial if thermodynamic description is to be coupled with description of other properties
  - Diffusion mobilities

- **Gibbs energy functions are not just "curves" that are fitted!**

Models for Temperature and Pressure Dependence

- Temperature dependence based on heat capacity C_P

$$C_P = -c - \sum_n n(n-1) d_n * T^{n-1}$$

$$H = a + \int_T C_P dT \quad and \quad S = -b + \int_T \frac{C_P}{T} dT$$

$$G = H - ST = a + bT + cT\ln(T) + \sum_n d_n * T^n$$

  - Contributions from magnetism
- Pressure dependence
  - Gas species $G = G(T) + RT\ln\left(\frac{f}{P_0}\right)$
    - ideal $f = P$
    - non-ideal $\ln\frac{f}{P} = \sum_{i=1}^{n} a_i P^i \quad \text{with} \quad a_i = \sum_{j=1}^{m} \frac{\alpha_{ij}}{T^m}$
  - Condensed phases: only needed for very high pressure and is rarely used because of lack of data

Models for Concentration Dependence - Sublattice Model

- General model with great versatility
- Many of the other models are actually special cases

$(A,B,C)_k(F,G)_m(S,T,V)_n$

$$G^{\varphi} = \sum_{i_k} y_{i_k}^{k} \sum_{i_m} y_{i_m}^{m} \sum_{i_n} y_{i_n}^{n} G_{i_k i_m i_n}^{\circ}$$

frame of reference

$$+ RT \left\{ \sum_{s} a^{s} \sum_{i_s} y_{i_s}^{s} \ln y_{i_s}^{s} \right\}$$

configurational entropy

$$\left. \begin{aligned} &+ \sum_{i_k} y_{i_k}^{k} \sum_{i_m} y_{i_m}^{m} \left(y_S^n y_T^n \sum_{j=0} L_j^{n_v} \left(y_S^n - y_T^n\right)^j + y_S^n y_V^n \sum_{j=0} L_j^{n_T} \left(y_S^n - y_V^n\right)^j + y_T^n y_V^n \sum_{j=0} L_j^{n_S} \left(y_T^n - y_V^n\right)^j \right) \\ &+ \sum_{i_k} y_{i_k}^{k} \sum_{i_m} y_{i_m}^{m} \left(y_S^n y_T^n y_V^n \sum_{i_n} L_{i_n} y_{i_n}^{n} \right) \\ &+ \ldots \\ &+ \prod_{i_k} y_{i_k}^{k} \prod_{i_m} y_{i_m}^{m} \prod_{i_n} y_{i_n}^{n} L_{kmn} \end{aligned} \right]$$

excess energy

Models for Concentration Dependence - Gas Phase and Liquid Phase

- Gas phase $G^{\varphi} = \sum_i y_i \, G_i^{\circ} + RT \sum_i y_i \ln y_i$
- Liquid phase
  - Without short range order
    - Regular solution type model *(A,B,C)*

$$G^{\varphi} = \sum_i x_i G_i^{\circ} + RT \sum_i x_i \ln(x_i) + x_i x_{j>i} \sum_n L_{ij}^n (x_i - x_{j>i})^n + \ldots$$

  - With short range order
    - Associate model *(A,B,A_mB_n)*

$$G^{\varphi} = \sum_i y_i \, G_i^{\circ} + RT \sum_i y_i \ln y_i + y_i y_{j>i} \sum_n L_{ij}^n (y_i - y_{j>i}) + \ldots$$

      - May not extrapolate well to higher order systems
    - Ionic liquid sublattice model *$(A^{+n})_P(B^{+m},Va)_Q$*
    - Modified quasichemical model *(A–A)+(B–B) = 2(A–B)+ΔG_{AB}*
      - Coordination numbers of *A* and *B* result in pair fractions → G^{φ}

Models for Concentration Dependence - Solid Phases

- Stoichiometric model *$A_m C_n$*
  - Solids with fixed concentration $G^{\varphi} = x_A^{\circ} G_A^{\circ} + x_C^{\circ} G_C^{\circ} + \Delta G^{f}$
  - Can be translated into semi-stoichiometric model *$(A,B)_m C_n$*

    $$G^{\varphi} = y_A G_{AC}^{\varphi} + y_B G_{BC}^{\varphi} + y_A y_B G^{ex}$$
- Regular solution type model *(A,B,C)*
  - Disordered substitutional solid solutions

    $$G^{\varphi} = \sum_i x_i G_i^{\circ} + RT \sum_i x_i \ln(x_i) + x_i x_{j>i} \sum_n L_{ij}^n (x_i - x_{j>i})^n + \ldots$$
- Sublattice model
  - Interstitial solutions, ordered phases with homogeneity ranges
  - Phases with order/disorder transformations

    $$G^{\varphi} = G^{ord}(y_i) - G^{ord}(y_i = x_i) + G^{dis}(x_i)$$
- Cluster site approximation
  - Phases with order/disorder transformations
  - Tetrahedral clusters sharing corners
  - Cluster partition function, cluster and site probabilities → ΔG^{φ}

Criteria for Model Selection

- Liquid phase
  - Significant difference in electronegativity of elements
  - Strong minima
    - Enthalpy of mixing
    - Electric and thermal conductivity
  - Strong maxima
    - Viscosity
- Solid phases
  - Width of homogeneity range
  - Different phases belonging to the same structure family → existence/possibility of order/disorder transformations
  - Crystal structure data
    - Provide basic information for sublattice model description

Selection, Combination and Simplification of Sublattice Descriptions

- Selection based on crystal structure (Wyckoff sites) and site occupation
- Simplifications for structures with many different Wyckoff sites
  - Combination of sublattices to reduce number of end-member phases
  - Disallow substitution on certain sublattices
- Combination of sublattices is based on similar features of the crystallographic sites
  - Coordination number
  - Point symmetry and coordination polyhedra
  - Site occupation on deviation from stoichiometry
- Choice of model is of great importance for constructing multicomponent databases

Example: C14 Laves Phase ($MgZn_2$)

- Current Practices in C14 Modeling

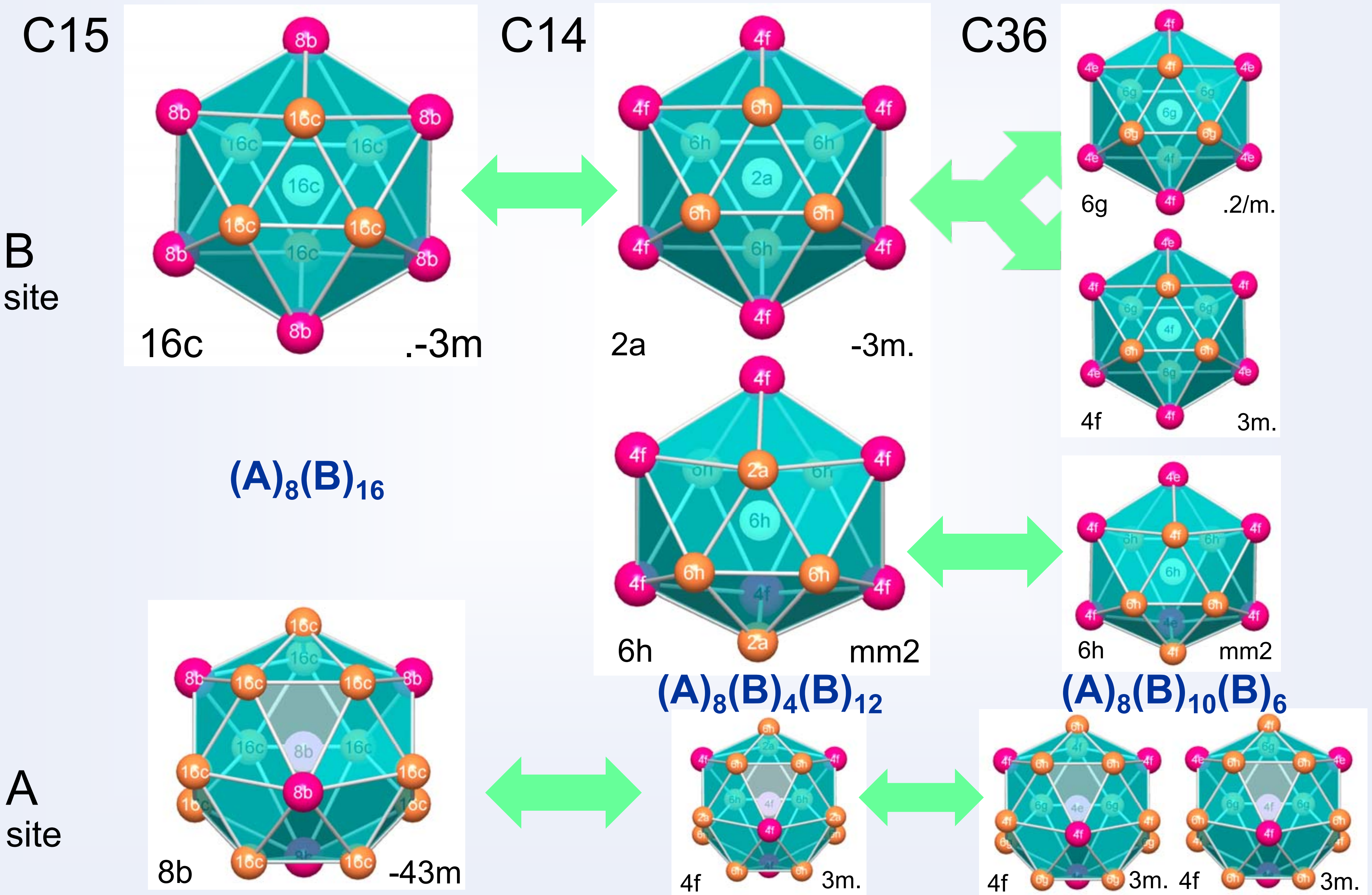
Author	Model
Ansara et al., CAPHAD 21 (1997) 171	$(A,B)_2(A,B)$
Ferro & Cacciamani, CALPHAD 26 (2002) 537	$(A,B)_2(A,B)$
Pavlů et al., CALPHAD 33 (2009) 382	$(A,B)_6B_2(A,B)_4$
Rigaud et al., CALPHAD 33 (2009) 442	$(A,B)_2(A,B)$
De Keyzer et al., CALPHAD 33 (2009) 108	$(A,B)_6(A,B)_2(A,B)_4$ but with constraints
Mathon et al., CALPHAD 33 (2009) 136	$(A,B)_2(A,B)$

- Different sublattice model descriptions create compatibility issues in the construction of multicomponent databases

Crystal Structure of Laves Phases

Prototype	C15		C14			C36				
Space Group	Fd-3m		$P6_3/mmc$			$P6_3/mmc$				
Pearson Symbol	cF24		hP12			hP24				
Wyckoff Position	8a	16d	4f	2a	6h	4e	4f	4f	6g	6h
Point Symmetry	-43m	-3m	3m	-3m	mm	3m	3m	3m	2/m	mm
Occupation	**A**	**B**	**A**	**B**	**B**	**A**	**A**	**B**	**B**	**B**
Coordination Number	16	12	16	12	12	16	16	12	12	12
Nearest Neighbors	4 **A** 12 **B**	6 **A** 6 **B**	4 **A** 12 **B**	6 **A** 6 **B**	6 **A** 6 **B**	4 **A** 12 **B**	4 **A** 12 **B**	6 **A** 6 **B**	6 **A** 6 **B**	6 **A** 6 **B**

Coordination Polyhedra in Laves Phases



C15

C14

C36

B site

A site

$(A)_8(B)_{16}$

$(A)_8(B)_4(B)_{12}$

$(A)_8(B)_{10}(B)_6$

Configurational Entropy Test for C14

Phase $AB_2 = (A,B)_4(A,B)_6(A,B)_2$

Combination of sublattices vs. no substitution on some, i.e.,

$(A,B)_4(A,B)_8 \Leftrightarrow (A,B)_4(A,B)_6(B)_2$

	$\Sigma a_s \Sigma y_i \ln y_i$	
$(A,B)_4(0.33A,0.67B)_6(0.2A,0.8B)_2$	-0.602	1.5 %
$(A,B)_4(0.3A,0.7B)_8$	-0.611	16.1 %
$(A,B)_4(0.4A,0.6B)_6(B)_2$	-0.505	

➔ Choice of model must reflect the mechanisms that occur on deviation from stoichiometry as realistically as possible!

Modeling of C14 and C36: A Substitution on B sites

- The similarity of the coordination polyhedra makes it unlikely that preferred substitution will occur on one of the B sublattices
- No experimental evidence for preferred substitution could be found
  - ICSD data for quaternary C14:

	$Mn_{1.22}V_{0.64}Ti_{1.01}Zr_{0.13}$	$Mn_{1.487}V_{0.288}Ti_{1.095}Zr_{0.13}$	$Ni_{1.7}V_{0.3}Ti_{0.43}Hf_{0.57}$
	$A_{1.14}B_{1.86}$	$A_{1.225}B_{1.775}$	A_2B
4f	0.87Ti + 0.13Zr	0.88Ti + 0.12Zr	0.25Ti + 0.575Hf + 0.175V
2a	0.73Ti + 0.27V	0.39 Mn + 0.61 V	0.359Ti + 0.39Ni + 0.251V
6h	0.81Mn + 0.19V	0.85Mn + 0.15Ti	0.008Ti + 0.987Ni+0.005V
	Rietveld, neutron, powder	Rietveld, X-ray, powder	Rietveld, X-ray, powder

➔ Two sublattice model more accurately reflects site occupations on deviation from stoichiometry than a three sublattice that does not consider the occurence of A atoms on one of the sublattices.

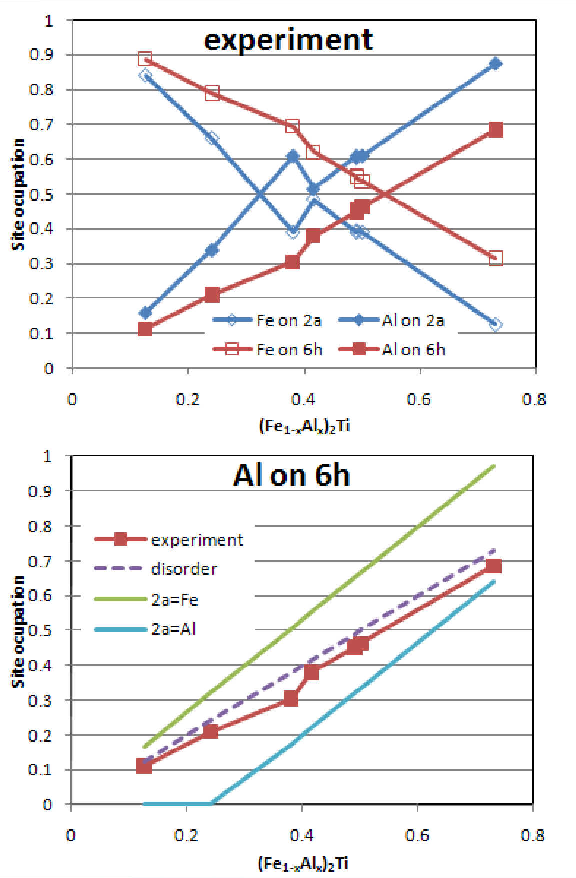
Crystallographic Data for C14 and C36

- C14: 226 entries in ICSD-2009.1
  - 108 entries with more than 2 metallic components
    - Only 5 have substitution on 4f site
    - Only 3 with A element occurring on 2a and/or 6h site
    - 56 are “disordered”, equal distribution on 6h and 2a sites
      - Only 8 have order parameter $\eta > 0.3$ ($\eta = y^1_{B'} - y^2_{B'} = y^2_{B''} - y^1_{B''}$)

- C36: 22 entries in ICSD-2009.1
  - 12 entries with more than 2 metallic components
    - 2 are “disordered”, equal distribution on 6h, 6g and 4f sites
    - Only 1 has order parameter $\eta > 0.3$

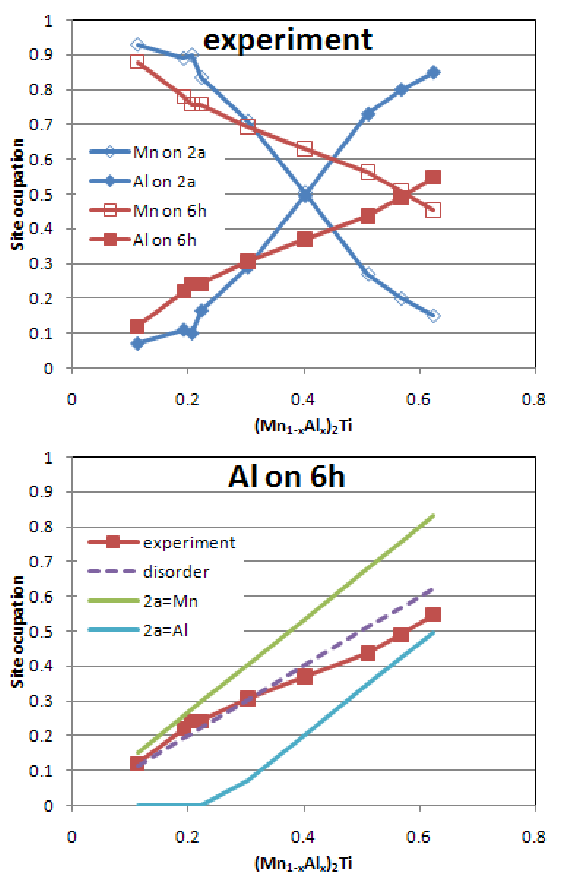
B Element Distribution on 2a and 6h Sites in Ternary C14

$(Fe_{1-x}Al_x)_2Ti$



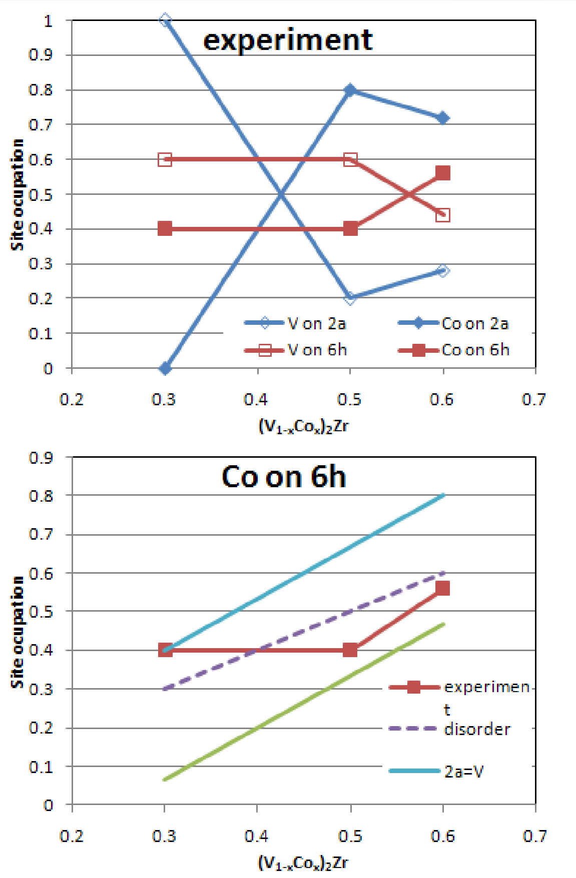
Yan et al., Z. Metallkd. 97 (2006) 450

$(Mn_{1-x}Al_x)_2Ti$



Yan et al., Intermetallics 16 (2008) 16

$(V_{1-x}Co_x)_2Zr$



Faller and Skolnick, Trans. Met. Soc. AIME 227 (1963) 687

$(Ni_{1-x}Al_x)_2Nb$: no ordering on 2a and 6h observed, Yan et al. CALPHAD 33 (2009) 11

Summary C14 Modeling

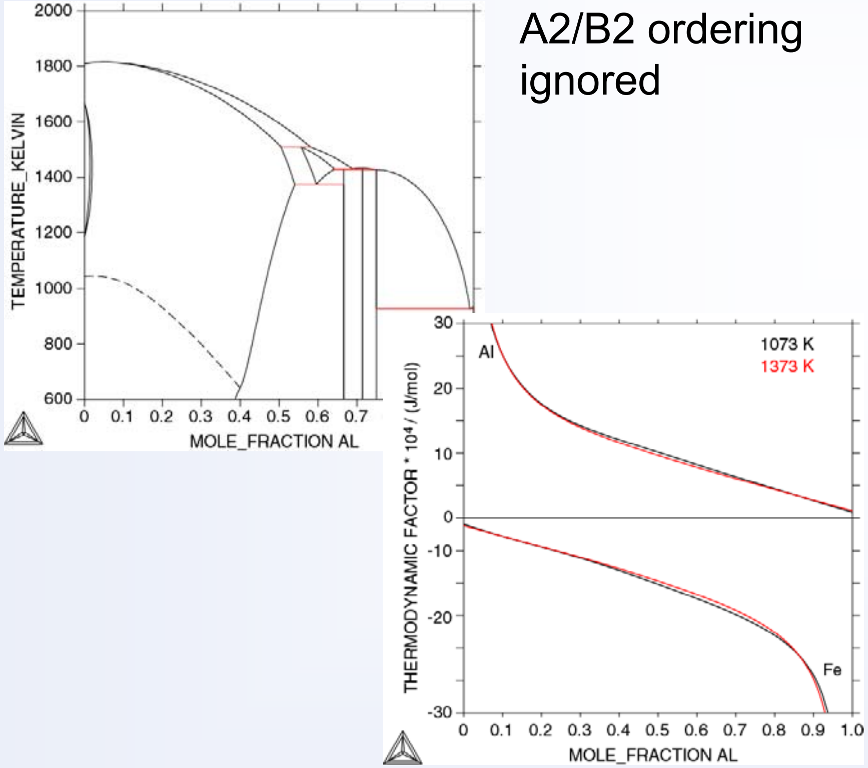
- The two sublattice model is suitable for the majority of C14 and C36 Laves phases.
- However, for a few systems the order in the C14 and C36 phases should be considered.
- Constraints for the three sublattice model description for C14 and C36 phases with a low degree of order offer a compromise.
- However, the numerical stability of calculations decreases with increasing number of variables.

Further Reading: Ansara et al., CALPHAD 21 (1997) 171; Ferro and Cacciamani, CALPHAD 26 (2002) 439

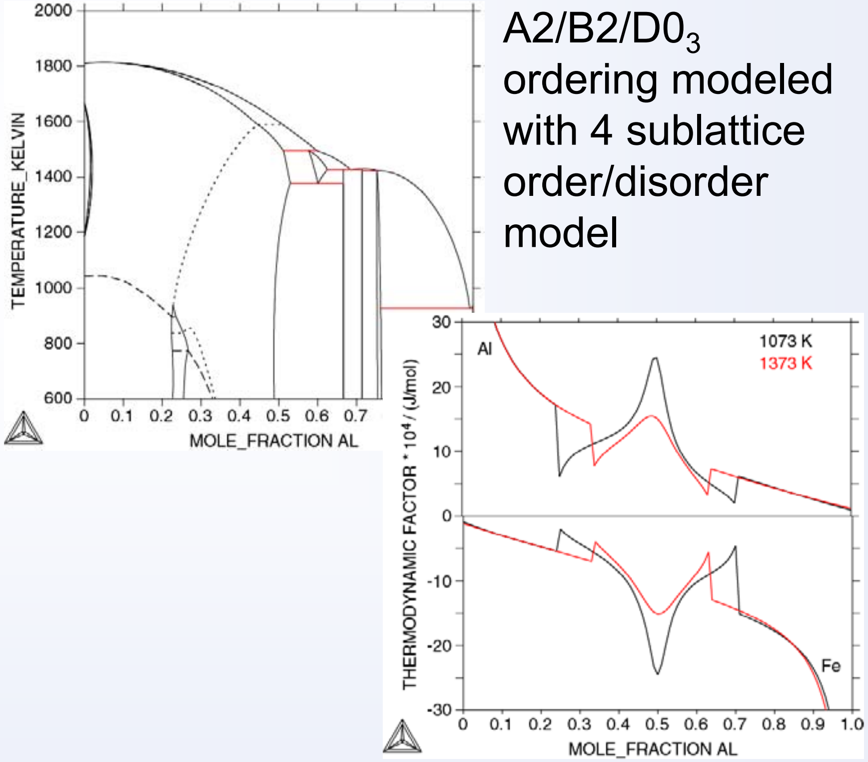
Importance of Proper Models for Diffusion Simulations

Intrinsic diffusivity: $${}^{L}D_{kj} = \sum_{i=1}^{n} \delta_{ik} x_i M_i \boxed{\frac{\partial \mu_i}{\partial x_j}}$$ and $$\sum_{k=1}^{n} {}^{L}J_k = -{}^{L}J_{Vacancy}$$

thermodynamic factor



A2/B2 ordering ignored



A2/B2/D0_3 ordering modeled with 4 sublattice order/disorder model

Kattner and Burton, “Phase Diagrams of Binary Fe Alloys”, 1993

Sundman et al., Acta Mater., 2009

Experimental Data

- Phase diagram data
  - Thermal analysis (TA), differential thermal analysis (DTA), differential scanning calorimetry (DSC)
  - Phase analysis: Microstructure, diffraction and spectroscopy methods
  - Diffusion couples and multiples: electron probe microanalysis (EPMA)
  - Thermogravimetry, dilatometry, …
- Thermochemical data
  - Calorimetry: solution, drop, reaction, …
  - Electromotive force measurements (emf)
  - Vapor pressure measurements

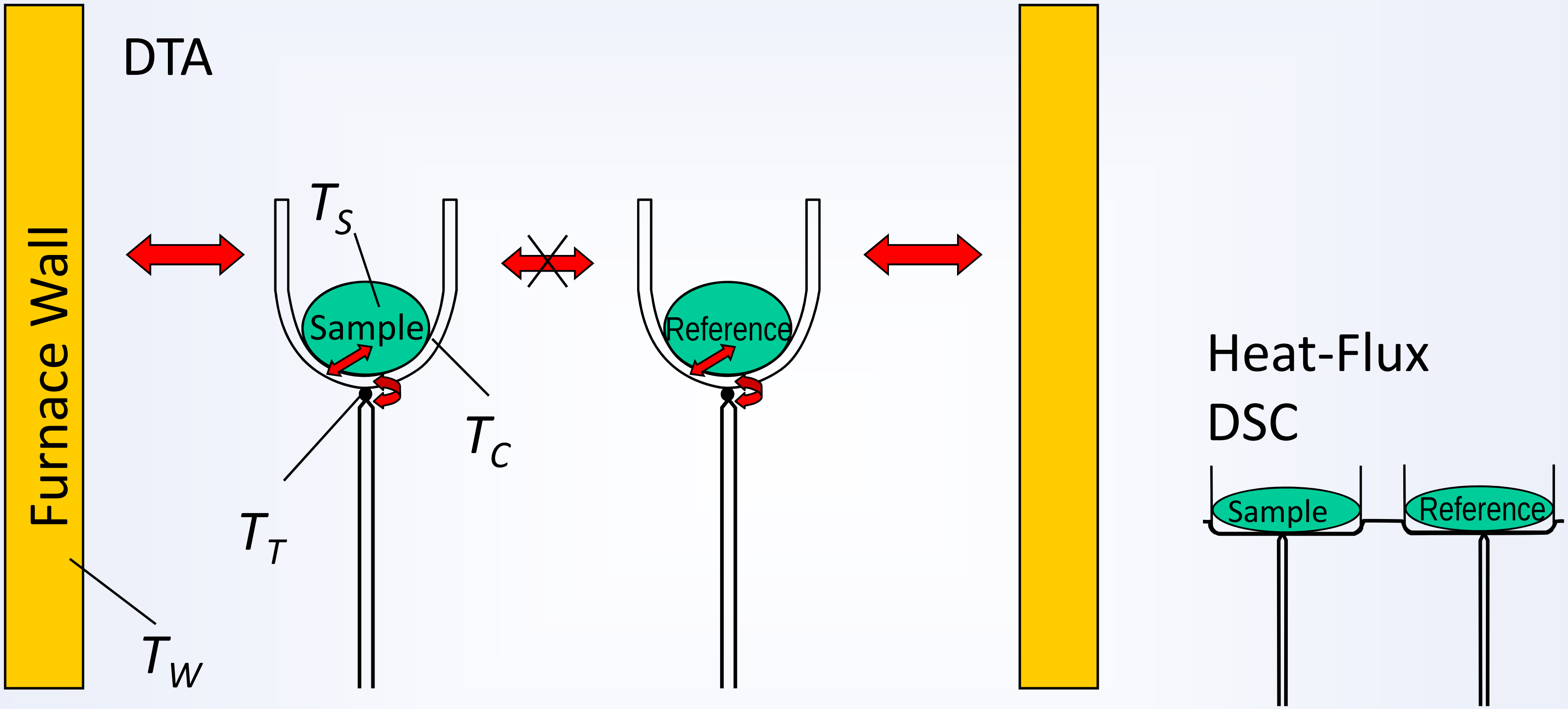
Further Reading: "Methods for Phase Diagram Determination," Zhao (ed.), Elsevier, 2007

All Experimental Data

- Purity of starting materials
  - For many metals the amount of impurities stated does not include interstitial elements
    - 99.99 % (metal basis) Cr may contain 0.5 % (atomic) oxygen resulting in about 1 % (volume) Cr_2O_3 in the microstructure
- Reactions with the environment
  - Evaporation
  - Reaction with crucible and/or encapsulation material
  - Reaction with impurities in protective gas atmosphere
- Calibration of the instrument
- Newer does not mean better !
- Ask what could have gone wrong

Further Reading: APDIC selected papers from JPED
http://www.springer.com/materials/journal/11669?detailsPage=press

DTA Geometry & Heat Flow

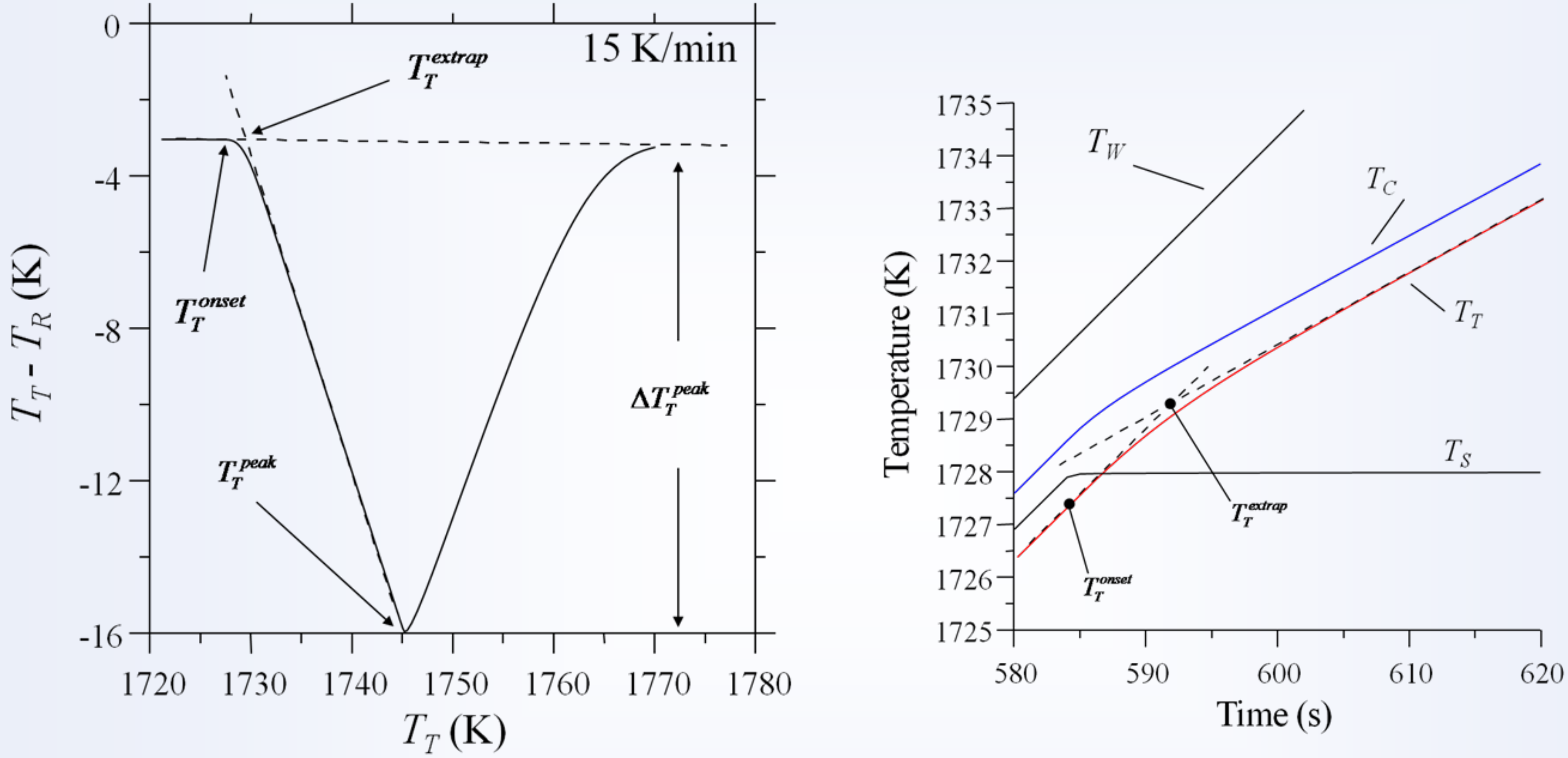


NIST Recommended Practice Guide:

DTA and Heat-flux DSC Measurements of Alloy Melting and Freezing

http://www.nist.gov/manuscript-publication-search.cfm?pub_id=901091

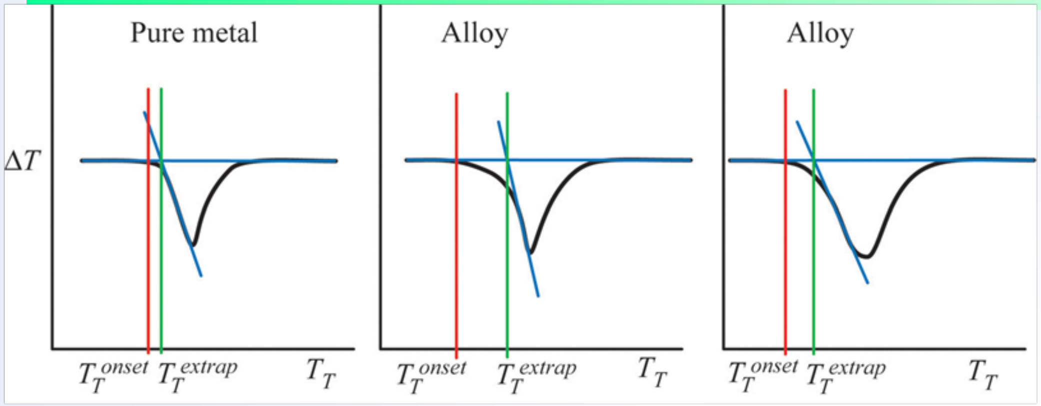
Calculated Melting: Pure Metal

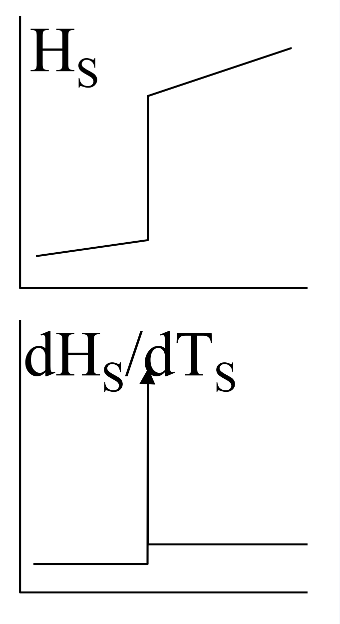


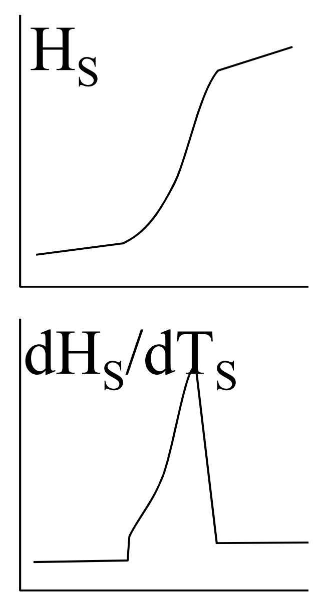
As result of thermal conductivity, the temperature of the sample thermocouples lags behind the actual sample temperature

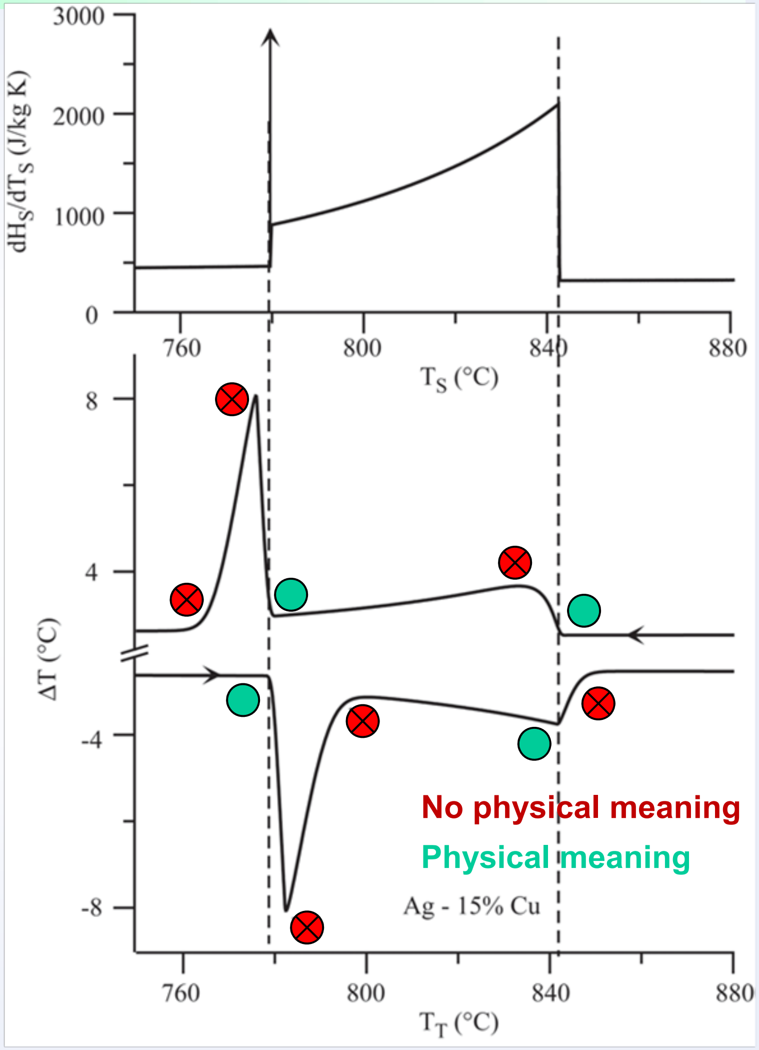
Determination of onset of the event is not straightforward

General Aspects of DTA Curve Analysis for Alloys



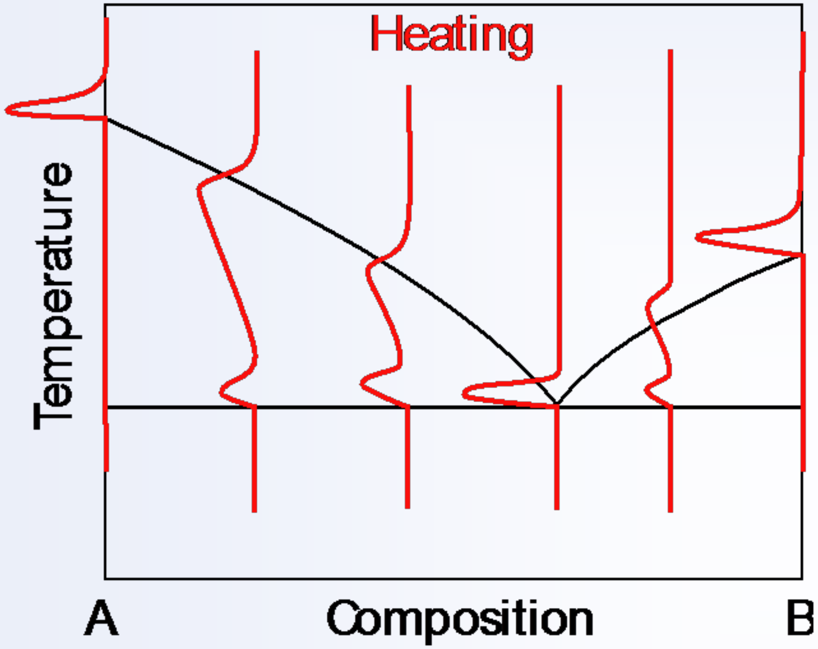


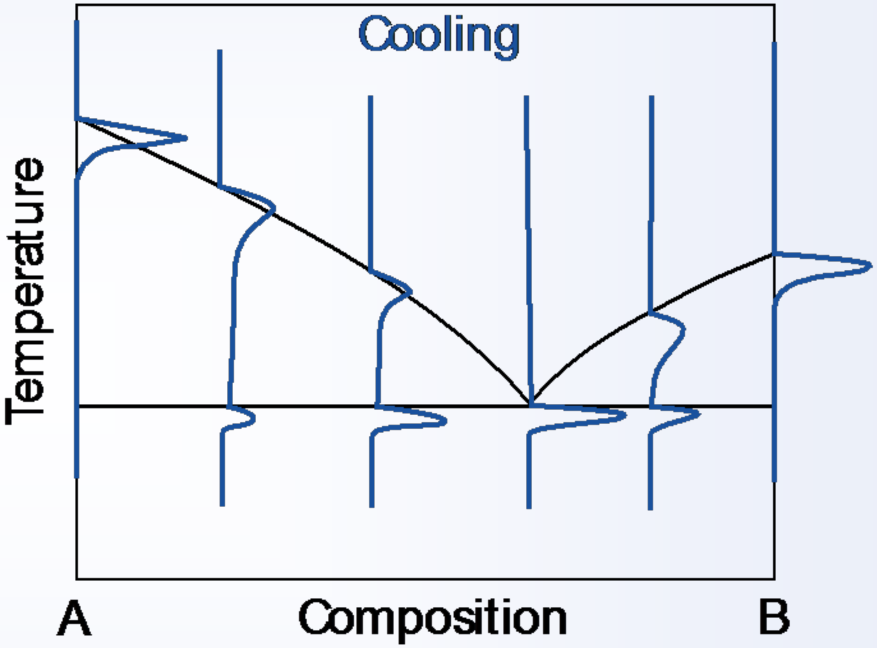




Unless dH_S/dT_S shows a delta function, there is **NO** physical basis for linear extrapolation of the DTA curve!

Binary Alloys: Schematic DTA Response





DTA response superimposed on phase diagram of a simple eutectic system with no solid solubilities (equilibrium heating and cooling)

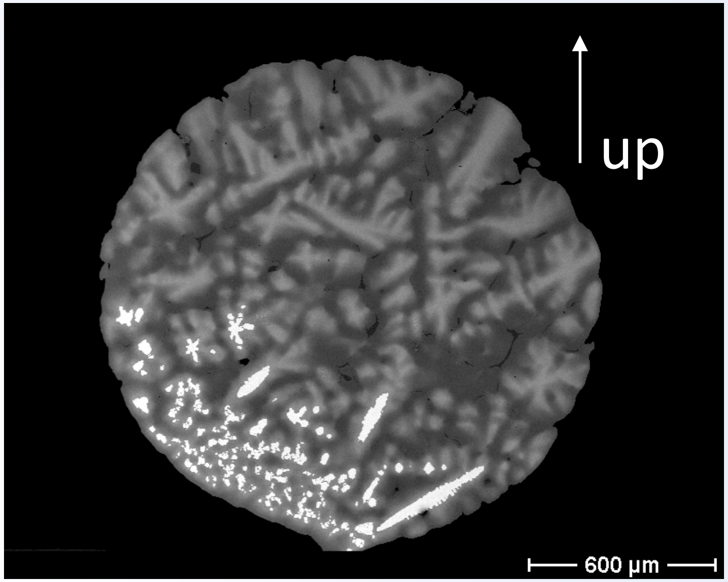
Note the different signal shapes on heating and cooling!

Phase Analysis

- Microstructure
  - Optical microscope, > 1 μm
  - Scanning electron microscope (SEM), 10 nm to 1μm
  - Transmission electron microscope (TEM), < 10 nm
- Diffraction
  - X-ray
  - Electron
  - Neutron
- Spectroscopy
  - Electron probe micro analysis (EPMA, instrument SEM)
  - Electron energy loss spectroscopy (EELS, instrument TEM)
  - Raman, infrared, …

Microstructures

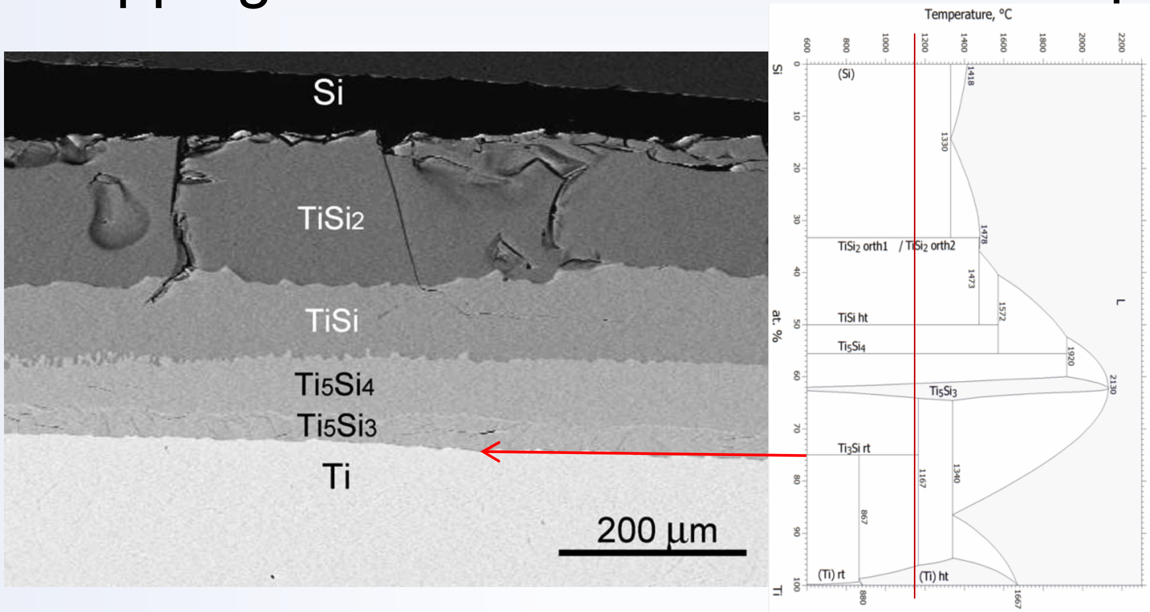
- Microsegregation: slower diffusion in solid may result in concentration gradient in solid phase during solidification
  - Scheil solidification: worst case, no diffusion in solid
  - Lever rule solidication: all phases are in equilibrium
- Macrosegregation: significant differences in atomic masses of the elements may result in settling of the heavier components at bottom of sample



Micro- and macrosegregation in DTA sample of Ni-36%Re (mass)

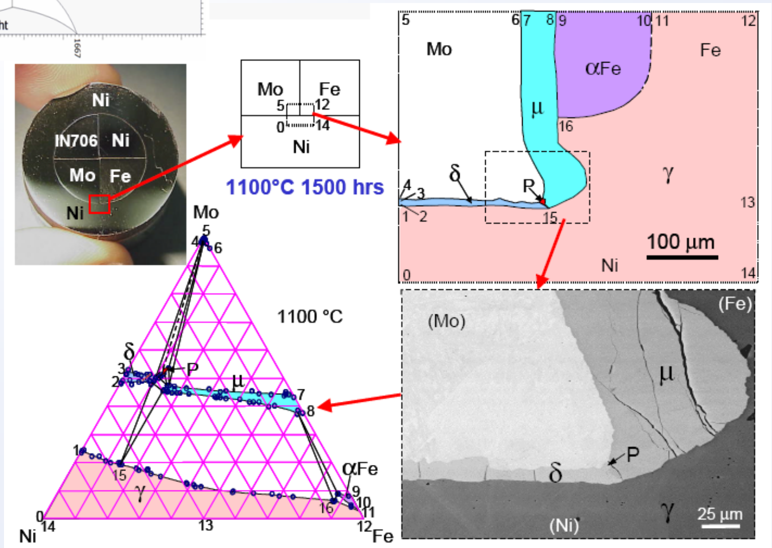
Diffusion Couples and Multiples

- Mapping of an isothermal section of a phase diagram

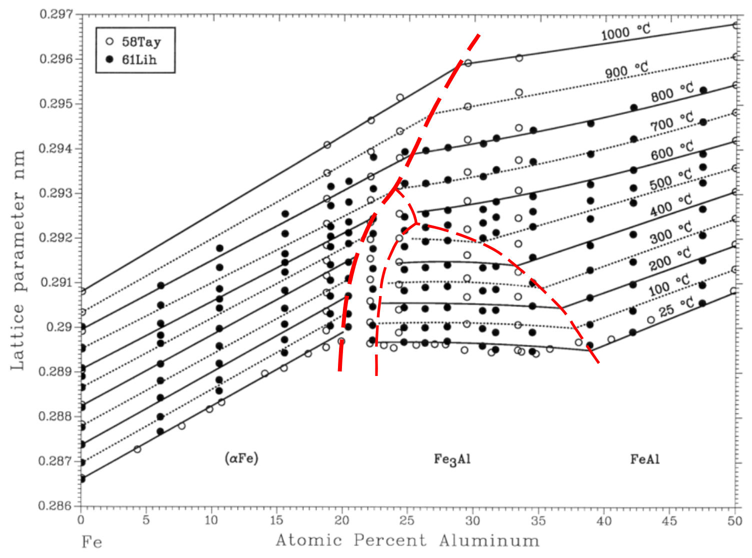


Ti–Si binary area of a diffusion-multiple annealed at 1150 °C for 2000 h showing the formation of the Ti silicides (Zhao et al., Mater. Sci. Eng. A, 2004)

- Diffusion multiples allow simultaneous investigation of several systems (Zhao, Annu. Rev. Mater. Res., 2005)



Diffraction and Spectrometry



- Lattice parameters can be used to determine phase boundaries
- Not every method is suited for every material
- Sensitivity depends on radiation and elements
  - Light elements are “invisible” to X-rays but not necessarily to neutrons
  - Increased background signal from fluorescence
- Measurement accuracy depends on radiation penetration depth and grain size
  - Signal originating under measured grain
- Texture effects may affect accuracy

Why Phases Fail to Form

- Nucleation difficulties
- Coherency effects may hinder phase precipitation
  - Suppression of miscibility gap formation
    - Ti–V (Murray, 1987):

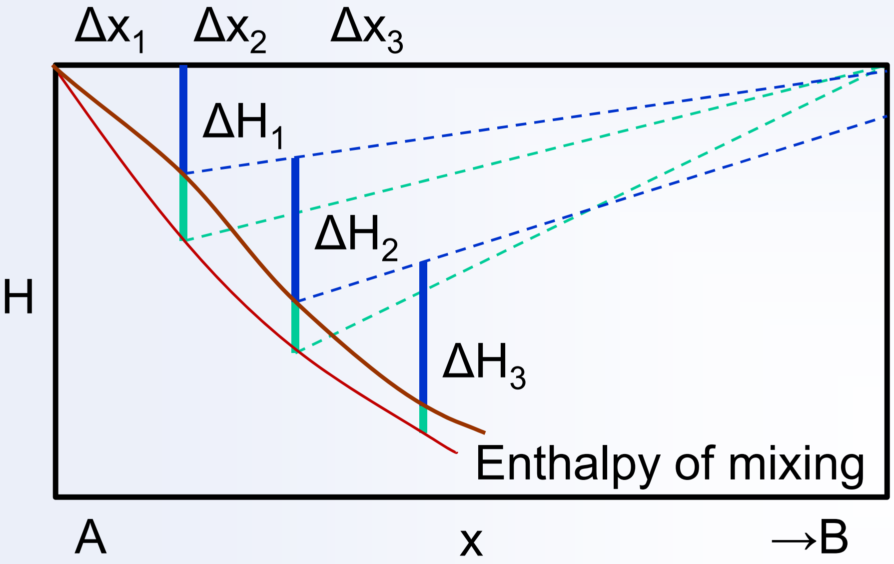
$$\Delta G^{ex}_{incoherent} = +18581\,x(1-x)\text{ J/mol} \quad \Leftrightarrow \quad \Delta G^{ex}_{coherent} \approx -19000\,x(1-x)\text{ J/mol}$$

- Bond breaking energies
  - Diamond → graphite: ΔG_{298} = -3 kJ/mol
  - Graphite → CO_2: ΔG_{298} = -394 kJ/mol
- Macro strain energies
  - ZrO_2 tetragonal → monoclinic with ≈ 3 % volume increase may result in significant undercooling of transformation (basis for transformation toughened ceramics)

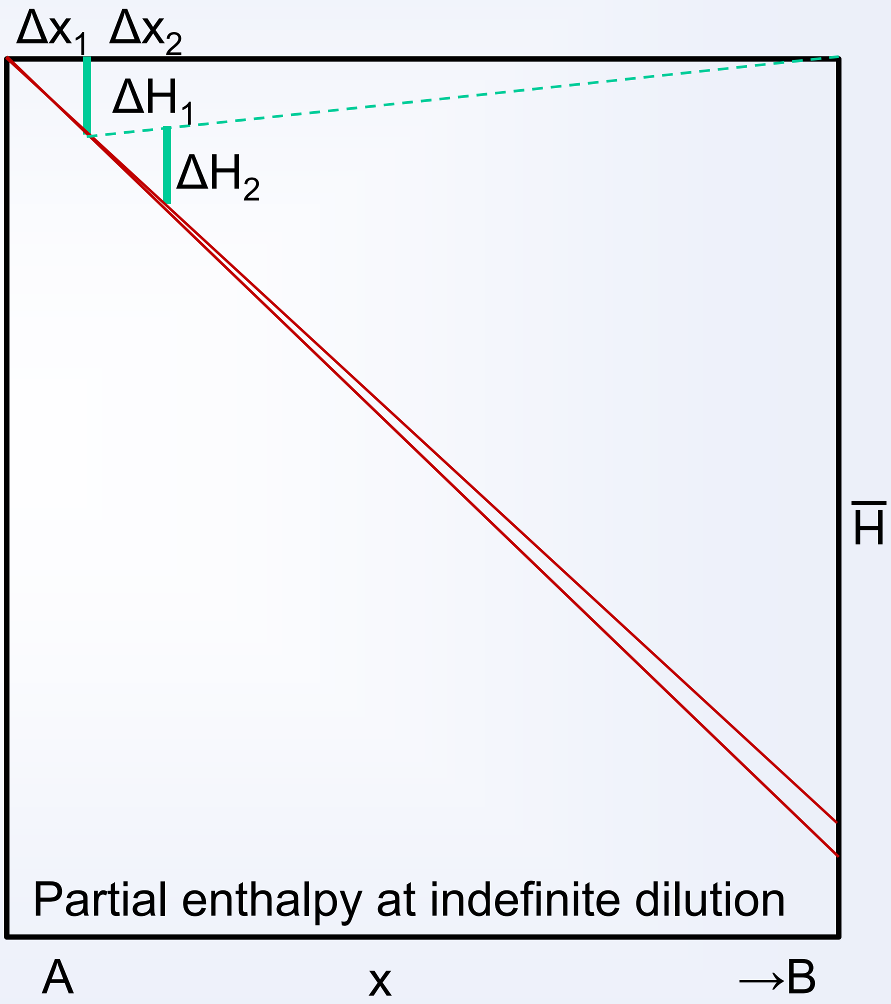
Calorimetry

- Solution calorimetry
  - Partial enthalpies of mixing
  - Integral enthalpies of mixing
  - Enthalpies of formation
- Drop calorimetry
  - Enthalpy content
- Reaction calorimetry
  - Enthalpies of formation
- Differential Scanning Calorimetry (DSC)
  - Heat capacity
- Combustion calorimetry
  - Enthalpies of formation *– Not well suited for alloys*
- …

Solution Calorimetry



- Second components added in steps
- Addition may have different temperature from measurement
- Errors from individual measurement are propagated through entire series



Other Calorimetry Methods

- Drop calorimetry
  - Sample at T_S is dropped into calorimeter block at initial T_I , the resulting temperature change is a measure for the sample heat content
- Reaction calorimetry
  - Thoroughly mixed components are reacted in the calorimeter, integral temperature change is a measure of the enthalpy of formation.
- Differential Scanning Calorimetry (DSC)
  - Sample and reference are heated in two identical furnaces, the difference in energy input to keep the two furnaces at the same temperature is a measure of the heat capacity

Further Reading: Colinet, J. Alloys Comp. 220 (1995) 76

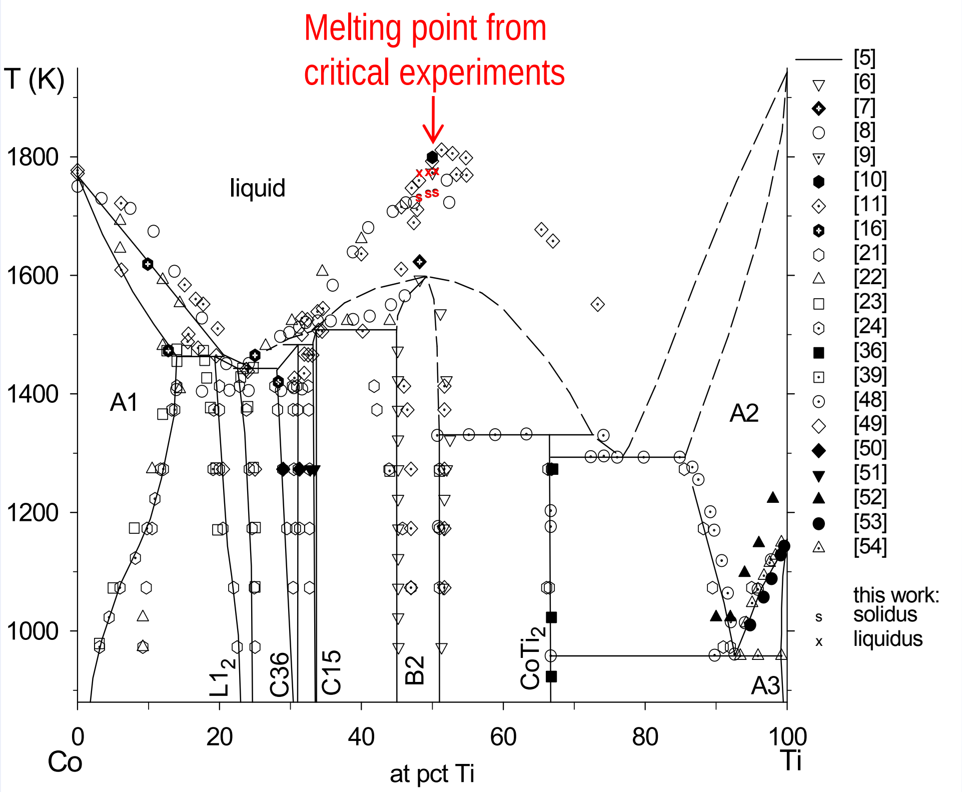
EMF and Vapor Pressure Data

- Electromotive force measurements (emf)
  A(s,l) | ionic electrolyte, A^{z+} *(or* A^{z-}*) |* $A_xB_{1-x}(s,l)$
  - Potential measurement
  - Coulombmetric titration
- Vapor pressure measurements
  - Knudsen cell methods
  - Mass spectrometry
- Use only data that were measured and not derived
  - Use $\Delta\overline{G_A} = -z_A FE; \quad \Delta\overline{G_A} = RT\ln\frac{P_A}{P_A^\circ}$
  - And not Gibbs Duhem integration (evaluation of $\Delta\overline{G_B}$ and ${}^{ex}G$)

Further Reading: Ipser et al., CALPHAD 34 (2010) 271 (emf); Ipser, Ber. Bunsenges. Phys. Chem. 102 (1998) 1217 (vapor)

Evaluation of Data from Different Sources

- Differences larger than individual experimental error

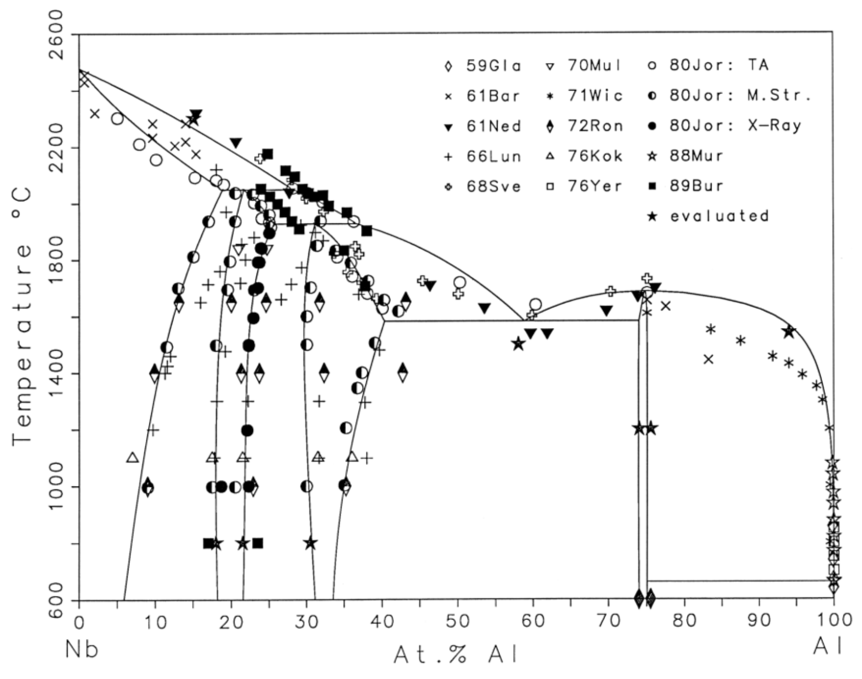


Experimental data and diagram evaluated by Murray (BAPD, 1982)

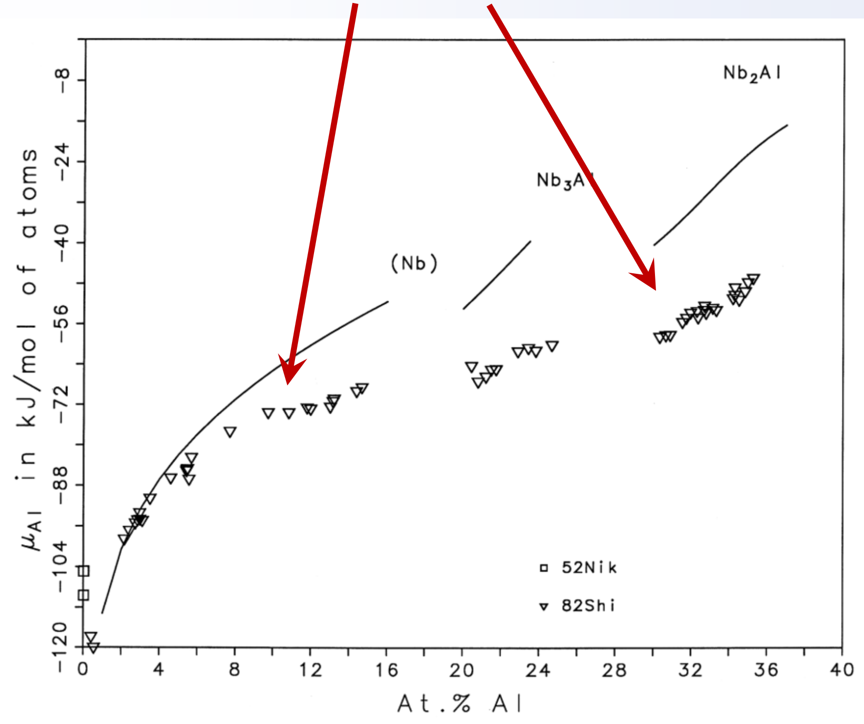
- Selection of a reliable dataset
- Critical experiments desirable

Evaluation of Data of Different Kind

- Data inconsistencies may not be obvious



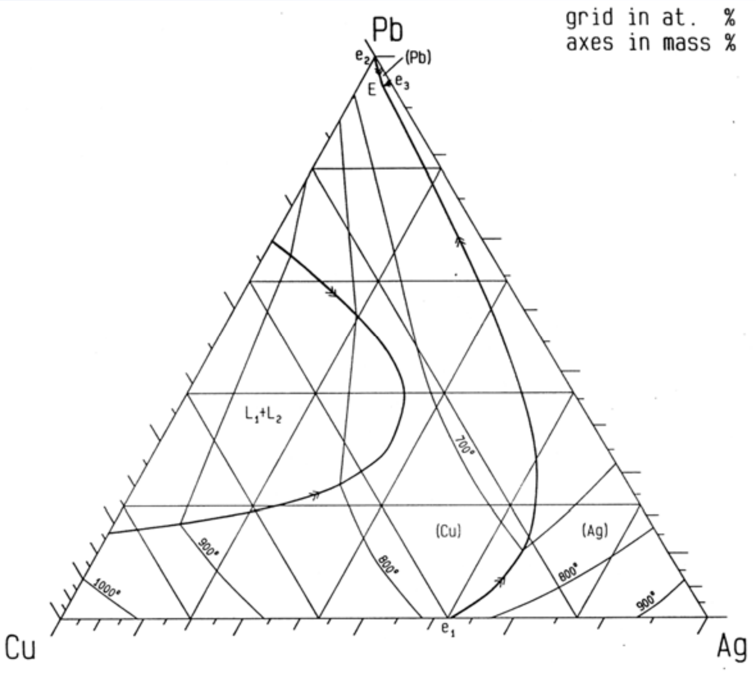
observed P_{Al} from Knudsen cell experiments lower than calculated by a factor of 2 to 6



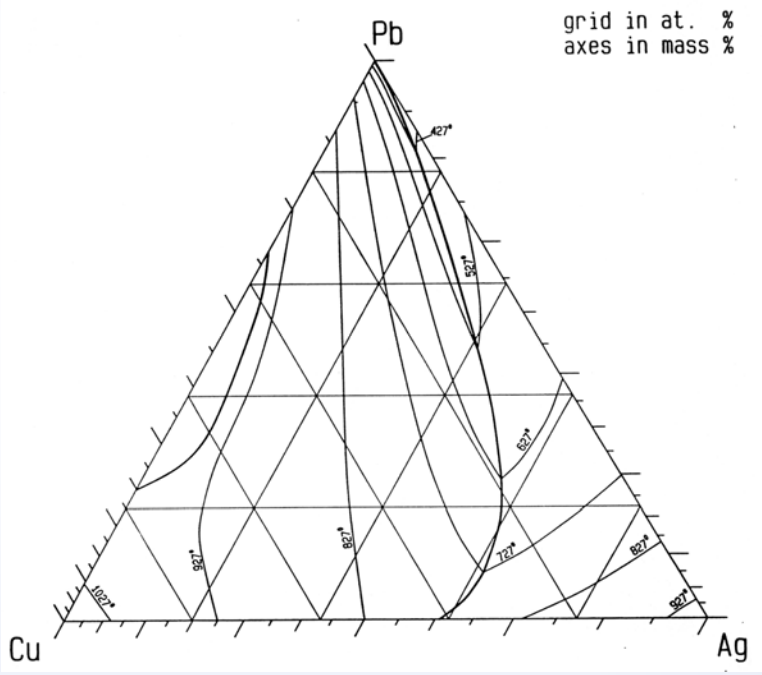
- Inconsistency can only be found during assessment

Data from Evaluated Diagrams

- Provide good basis for main features of phase diagram
- Are valuable source for references
- Provide initial guidance in evaluation of data
- **BUT ARE NOT ABSOLUTES!**

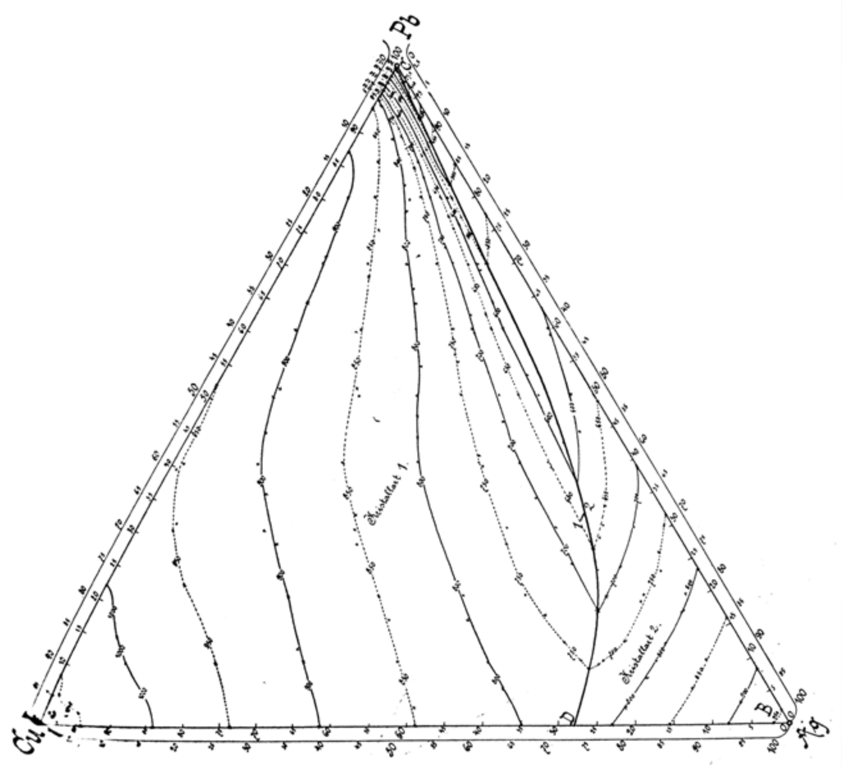


Evaluated: Petzow and Effenberg (1988) adopted from Chang et al. (1979) adopted from Jänecke (1937) based on data from Friedrich and Leroux (1907)

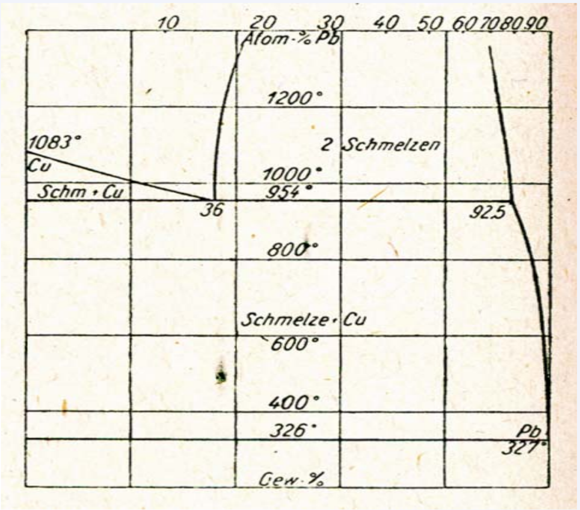


Calculated: Hayes et al. (Z. Metallkd., 1986) based on data from Friedrich and Leroux (Metallurgie,1907)

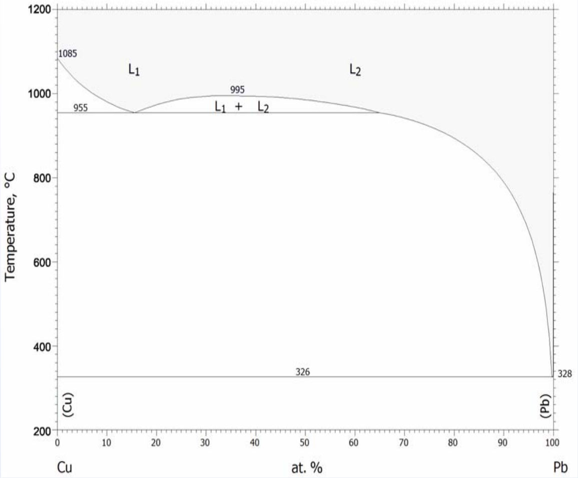
Original Data and Origin for the Two Liquidus Projections



Friedrich and Leroux
(Metallurgie,1907)



Jänecke,
("Kurzgefaßtes
Handbuch aller
Legierungen,"
1937)



Chakrabarti
and Laughlin,
BAPD, 1984

Calculated Data

- Miedema model
    - Semi-empirical method for calculating enthalpies of formation
    - Does not distinguish different crystal structures
- Density Functional Theory (DFT)
    - Based on quantum chemistry
    - 0 K energies, but also for higher temperature
    - Generally limited to ordered stoichiometric compounds
- Classic atomistic simulations (Molecular Dynamics (MD) and Monte Carlo (MC))
    - DFT based semi-empirical interatomic potentials
    - Generally limited to two or three elements
- Cluster Variation (CVM) Methods and Monte Carlo (MC)
    - Statistical methods to obtain order/disorder solution phase relations
    - Effective cluster interaction energies usually obtained from DFT

Further Reading: Turchi et al., CALPHAD 31 (2007) 4

Calculated and Experimental Data

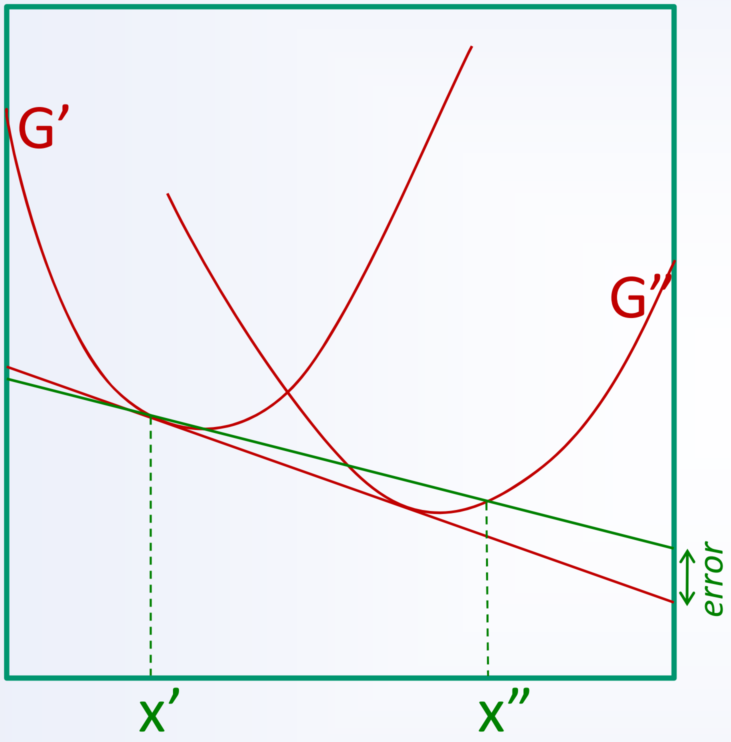
- Calculated data are **NO** substitute for experimental data
- Calculated data supplement available experimental data
  - Especially if experimental data of a particular kind are not available
    - Enthalpies of formation
    - Provide guidance on topology of order/disorder phase diagram in case where most of these equilibria are metastable
    - Supplemental data
      - Volume, bulk modulus, …
- Calculated data are not perfect
  - Depend on parameters chosen for calculation
  - Scatter between data from different calculations is **NOT** an equivalent to an experimental error
- Experimental data are not perfect

Assignment of “Error” and Weight

- Magnitude of error(s) assigned to a data point creates an implicit weight
- Relative magnitude of errors assigned to different quantities of a data point may influence optimization process and results
- Optimizers may provide different equations of error for the same kind of data
- Weight of data points needs to be reevaluated during optimization process

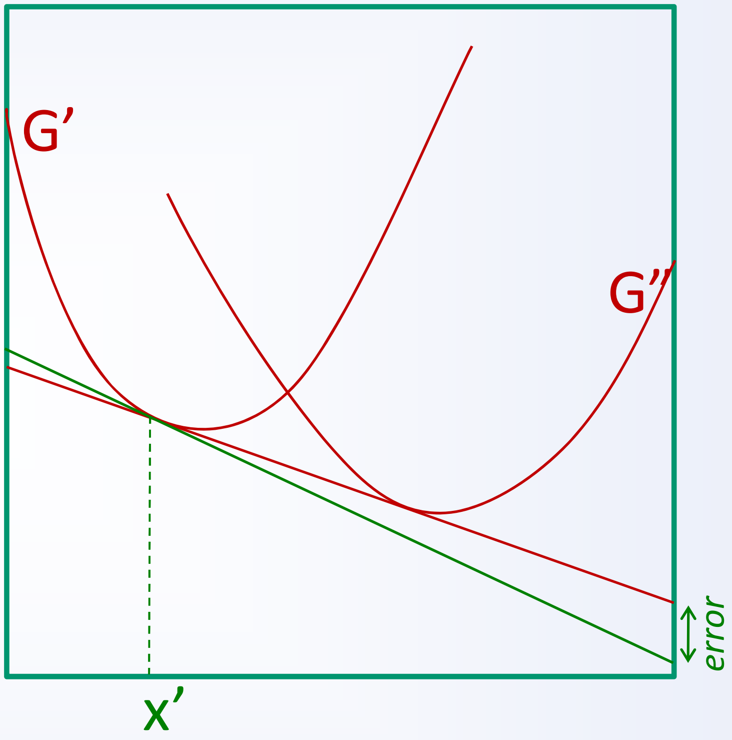
Further Reading: Lukas et al., “Computational Thermodynamics – The Calphad Method”, Cambridge, 2007

Partial Gibbs Energy of a Two Phase Equilibrium



$\mathrm{IVERS} = 1:$

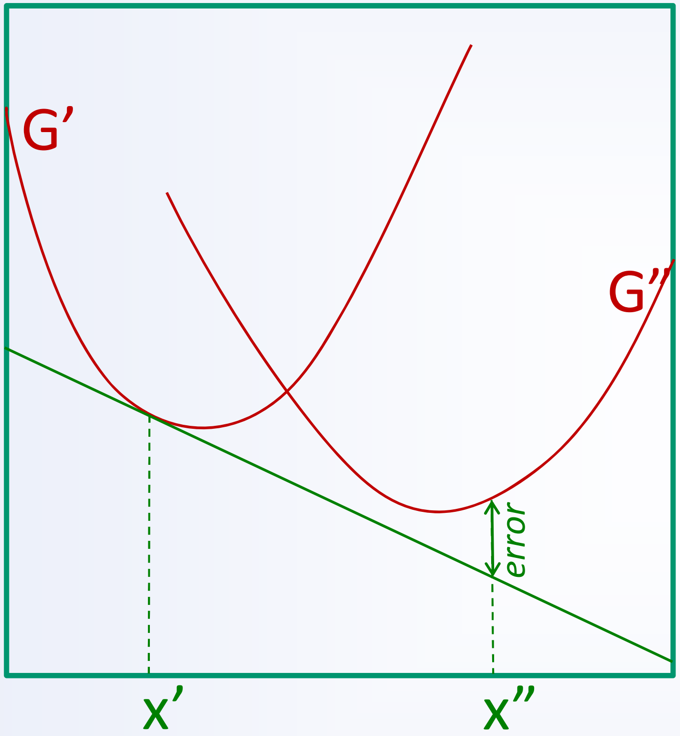
$$G'\frac{(\mathrm{x}''-1)}{(\mathrm{x}''-\mathrm{x}')}+G''\frac{(\mathrm{x}'-1)}{(\mathrm{x}'-\mathrm{x}'')}-{}^{\circ}G^{ref}-W=error$$

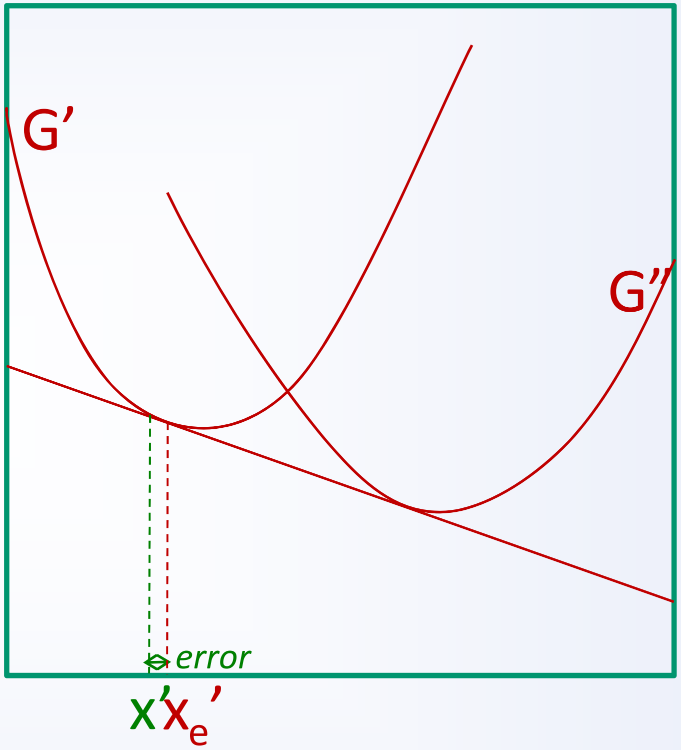


$\mathrm{IVERS} = 2:$

$$\mu-{}^{\circ}G^{ref}-W=error$$

Compositions of a Two Phase Equilibrium





IVERS = 1:

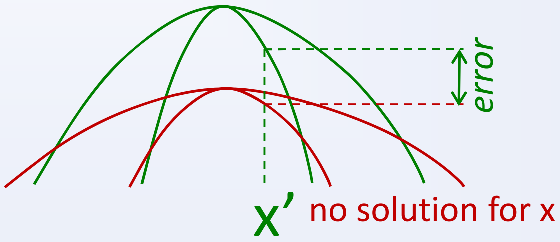
$$G' + (x' - x'')\frac{\partial G'}{\partial x} - G'' = error$$

IVERS = 2:

$$x'_e - x' = error$$

or

$$T_e - T = error$$

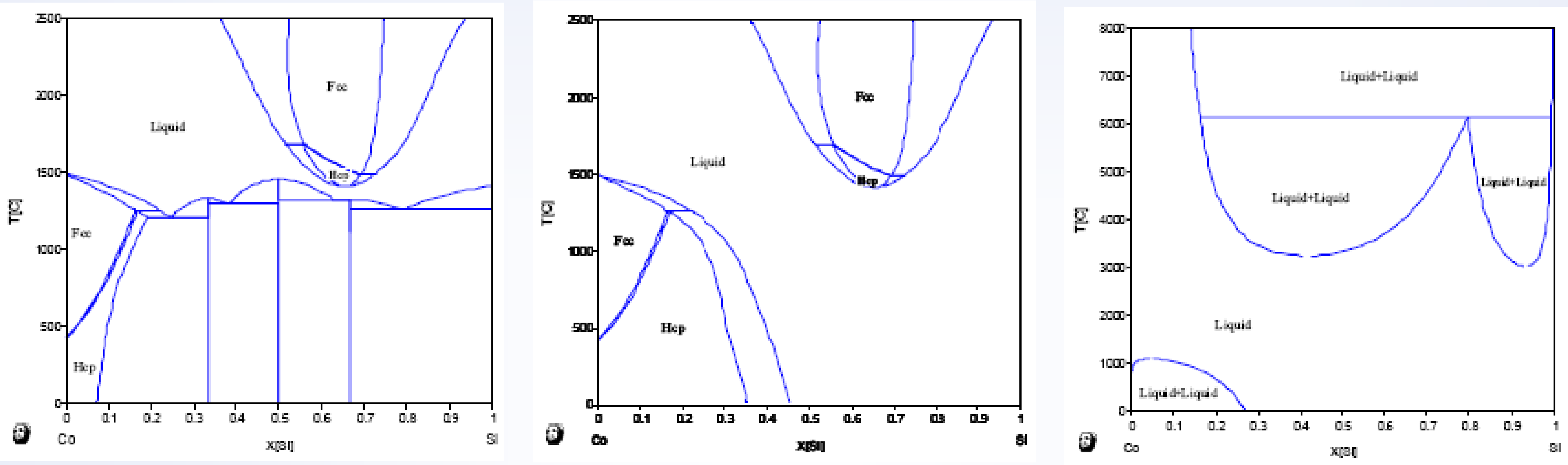


Evaluation of the Description

- Physically realistic parameters
  - Too large entropies may result in restabilization of phases at higher temperatures
- Proper extrapolation of phase boundaries to metastable regimes
- Realistic order/disorder transformation diagrams in metastable regimes

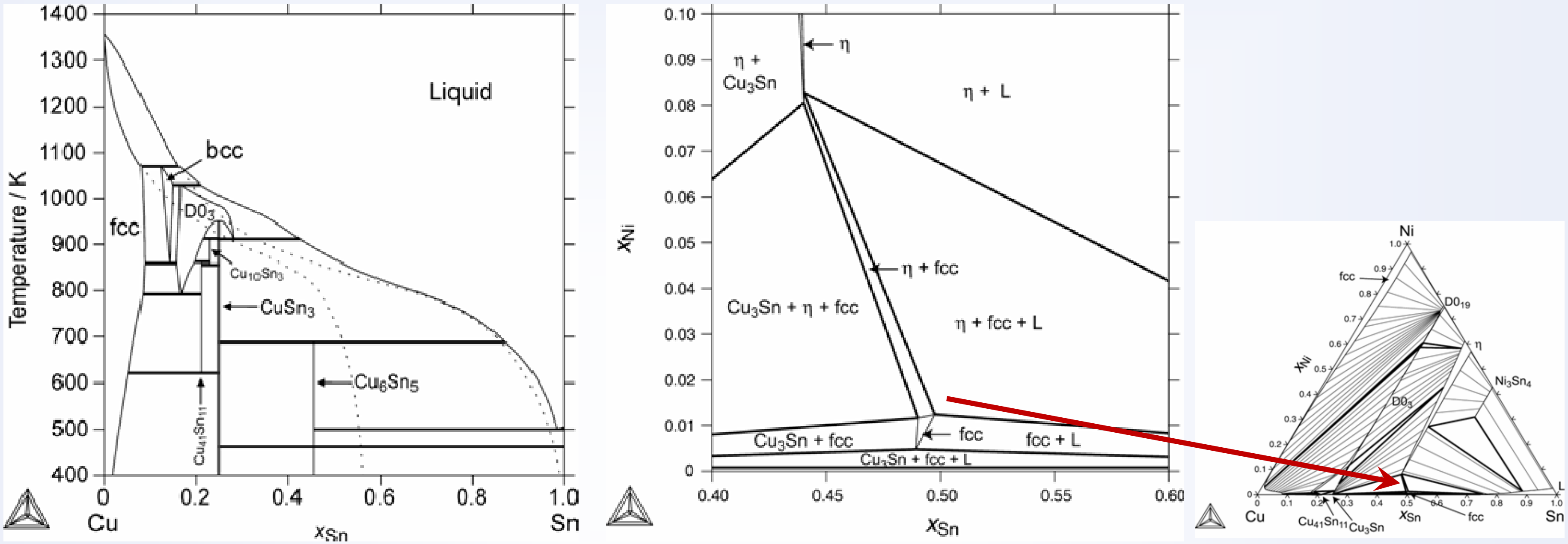
Further Reading: Schmid-Fetzer et al., CALPHAD 31 (2007) 38

Restabilization of Phases



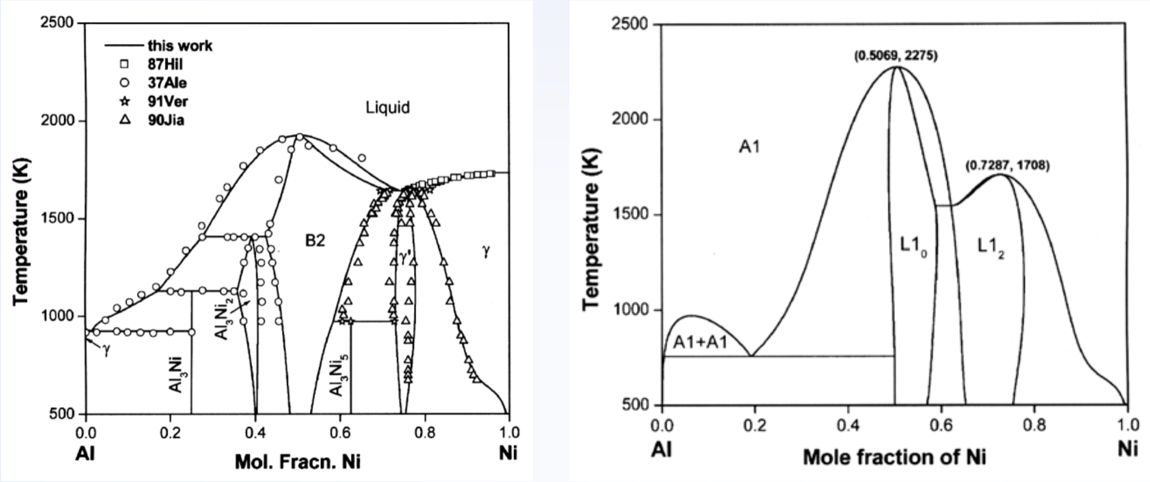
- Co –Si phase diagram (Choi, CALPAHD, 1992):
  - Inadvertent re-stabilization of solid phases at high temperature
  - Only the low temperature part of the liquidus lines corresponds to experimental data
  - Metastable diagrams
    - Hcp, fcc and liquid only
    - Liquid phase only: two inverted miscibility gaps at temperatures > 3000K

Metastable Phase Boundaries

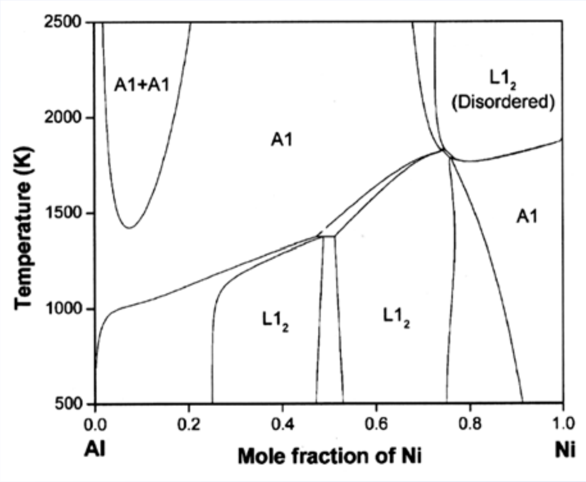


- Cu-Sn phase diagram (Shim et al., Z. Metallkd., 1996)
  - Metastable fcc liquidus merely below equilibrium liquidus
  - Artificial appearance of the fcc phase in Sn-rich alloys near the Cu–Sn binary in the 773 K section of Cu-Ni-Sn

Topology of Metastable Order/Disorder Phase Diagrams

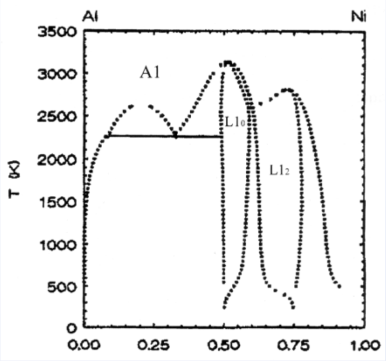


Zhang et al., Acta Mater., 2003

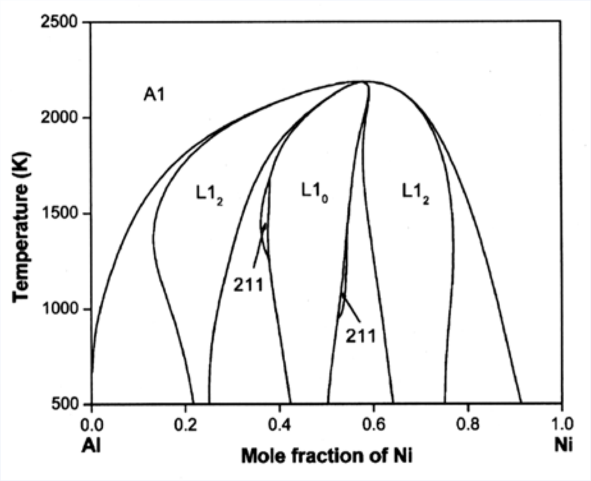


Huang and Chang, Intermetallics, 1998

- Correct topology crucial for extrapolation to multicomponent systems
- Topology from first principles calculations needed



Pasturel et al., J. Phys. Condens. Matter, 1992



Ansara et al., J. Alloys Comp., 1997

From Assessment of Individual Systems to Database Development

General Strategy for the Development of Thermodynamic Databases

- Survey literature, critically evaluate available assessments of binary and ternary systems
    - Re-evaluate model selections if necessary
    - Models should be physically reasonable
- Compile list of intermediate phases and their crystal structures
    - Identify structure families
    - Select model descriptions for phases
    - Assign phase names
- Full thermodynamic description of ternary systems
    - Data only available for few systems
    - Development of complete thermodynamic descriptions for all systems time consuming - even for the few for which data are available
        - Emphasis on systems that include base element
        - Qualitative test of other systems - adjust parameters to give a “reasonable” phase diagram
- Prioritize addition of elements

Development of a Thermodynamic Database for Ni-based Superalloys

Available thermodynamic descriptions for the 10-component system Ni-Al-Co-Cr-Hf-Mo-Re-Ta-Ti-W

Constituent systems	Total number of systems	Available assessments **1996**	Available assessments **2000**
binary	45	28	42
ternary	120	11	20
Ni-base ternary	36	9	14
Ni-Al base ternary	8	4	8

Solid Phases in Binary Systems with

Al-Co-Cr-Fe-Hf-Mo-Nb-Ni-Re-Ta-Ti-W

- Terminal solid solutions:
  - fcc-A1: Al, Co, Fe, Ni
  - bcc-A2: Cr, Fe, Hf, Mo, Nb, Ta, Ti, W
  - hcp-A3: Co, Hf, Re, Ti
- Close-packed structures:
  - fcc-based: $L1_0$, $L1_2$, $D0_{22}$, $D0_{23}$
  - bcc-based: B2, $D0_3$
  - hcp-based: $D0_{19}$, $D0_{24}$
- Topologically close-packed structures:
  - Laves: C14, C15, C36
  - Others: μ, σ, χ
- Other intermediate phases

Intermediate Phases	**Systems**
None	19
CP	2
TCP	19
OI	4
CP&TCP	3
CP&OI	6
TCP&OI	8
CP&TCP&OI	5
Total	66

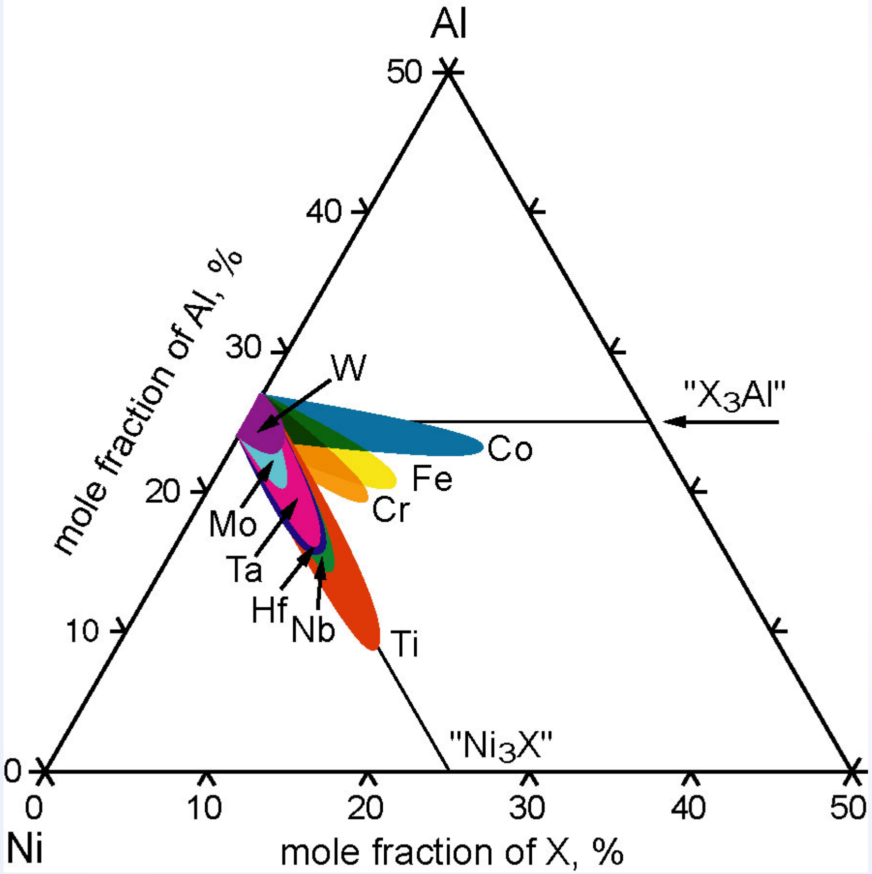
Homogeneity Ranges of “Important” Intermetallics

Phase	**Str. B.**	**Homogeneity Range**
β	B2	(Al,Co,Fe,Ni,Ti,Hf,Zr,Va)(Al,Co,Fe,Ni,Ti,Hf,Zr,Va)
γ'	$L1_2$	(Al,Co,Cr,Fe,Mo,Ni,Nb,Ta,Ti,W,Hf,Re?,Zr) $(\mathrm{Al,Co,Cr,Fe,Mo,Ni,Nb,Ta,Ti,W,Hf,Re?,Zr})_3$
γ''	$D0_{22}$	$\mathrm{Ni_3(Cr?,Nb,Ta)}$, $\mathrm{Al_3(Co,Mo,Ni,Nb,Ta,Ti,Hf,Zr)}$
Laves	C14	$(\mathrm{Al,Co,Cr,Fe,Ni})_2(\mathrm{Mo,Nb,Ta,Ti,W,Hf,Zr})$
μ	$D8_5$	$(\mathrm{Al,Co,Fe,Ni})_7(\mathrm{Cr?,Mo,Nb,Ta,W,Hf,Re})_6$
σ	$D8_b$	$(\mathrm{Al,Co,Cr,Fe,Mo,Nb,Ni,Ta,Ti,W,Re})_x(\mathrm{Al,Co,Cr,Fe,Mo,Nb,Ni,Ta,Ti,W,Re})_y$ or $(\mathrm{Co,Cr,Fe,Mo,Nb,Ni,Ta,Ti,W,Re})_x(\mathrm{Co,Cr,Fe,Mo,Nb,Ni,Ta,Ti,W,Re})_y$ & $(\mathrm{Al,Nb,Ta})_3(\mathrm{Al,Nb,Ta})$
$\mathrm{Ni_3Nb}$	$D0_a$	$(\mathrm{Co,Ni})_3(\mathrm{Mo,Nb,Ta,Ti})$
$\mathrm{Ni_3Ti}$	$D0_{24}$	$\mathrm{Ni_3(Al,Nb,Ta,Ti)}$

The β and γ' phases are likely candidates for order/disorder modeling.

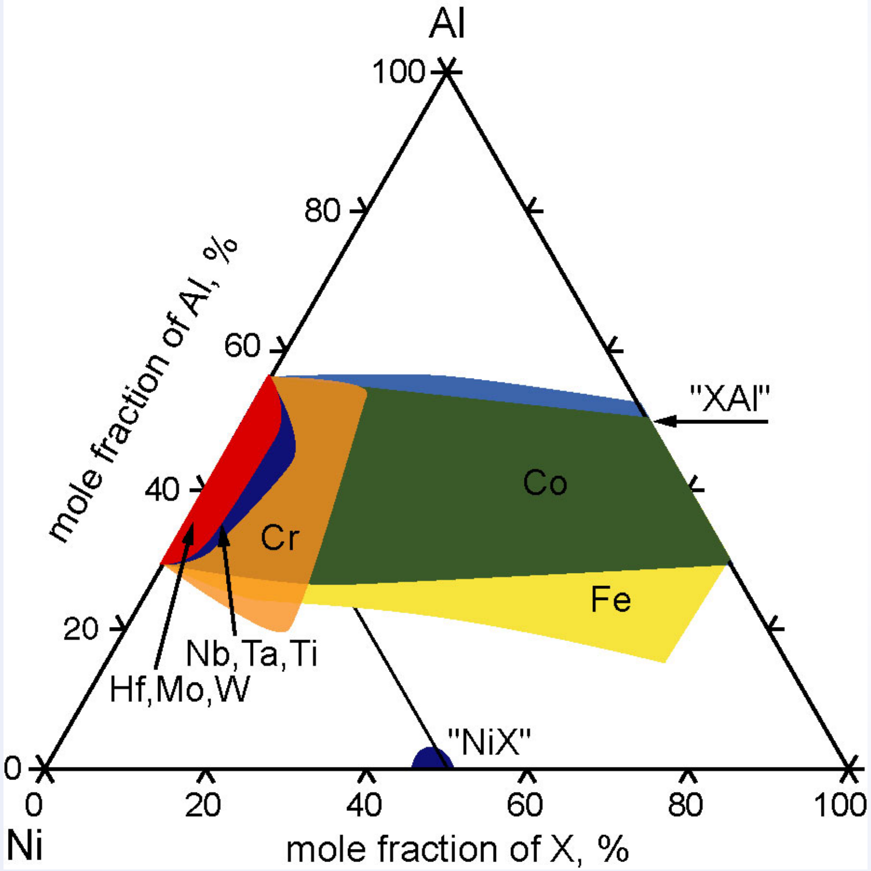
⇒ The same elements must occur in the description of the ordered and disordered phase

Schematic Ternary Homogeneity Ranges of γ' ($L1_2$)



Site preference of the elements		
Site	**"Ni"**	**"Al"**
Ordered	**Ni, Co**	**Al, Hf, Mo, Nb, Ta, Ti, W**
Dis-ordered	**Cr, Fe, Re?**	

Schematic Ternary Homogeneity Ranges of β (B2)

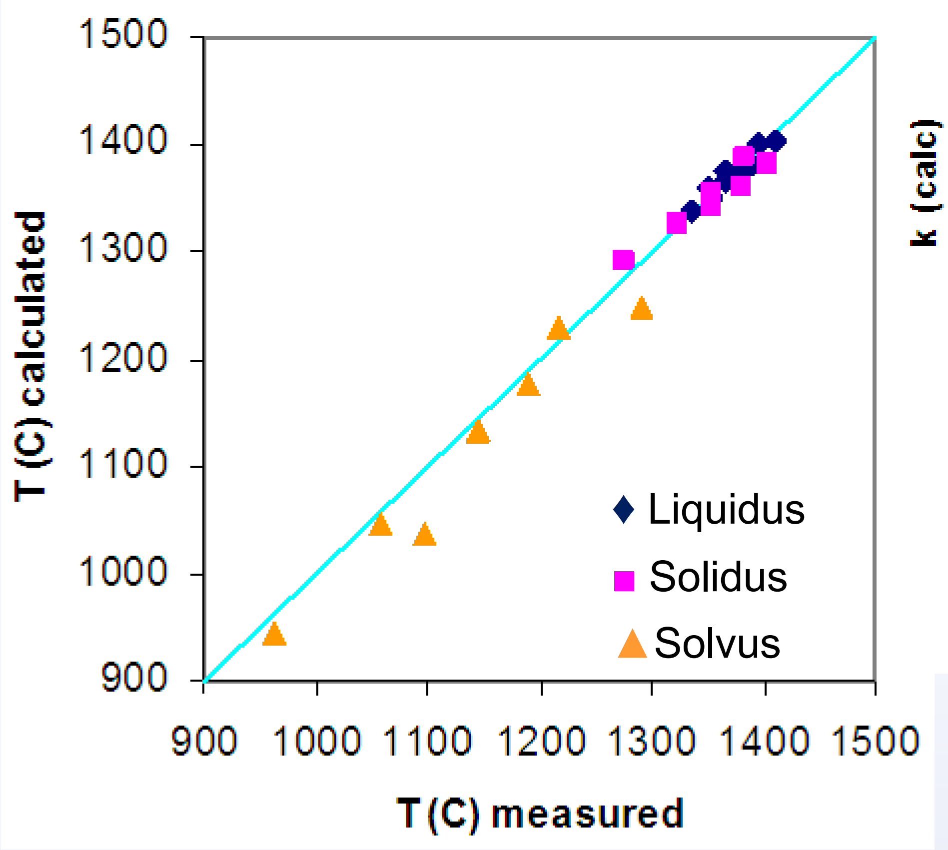


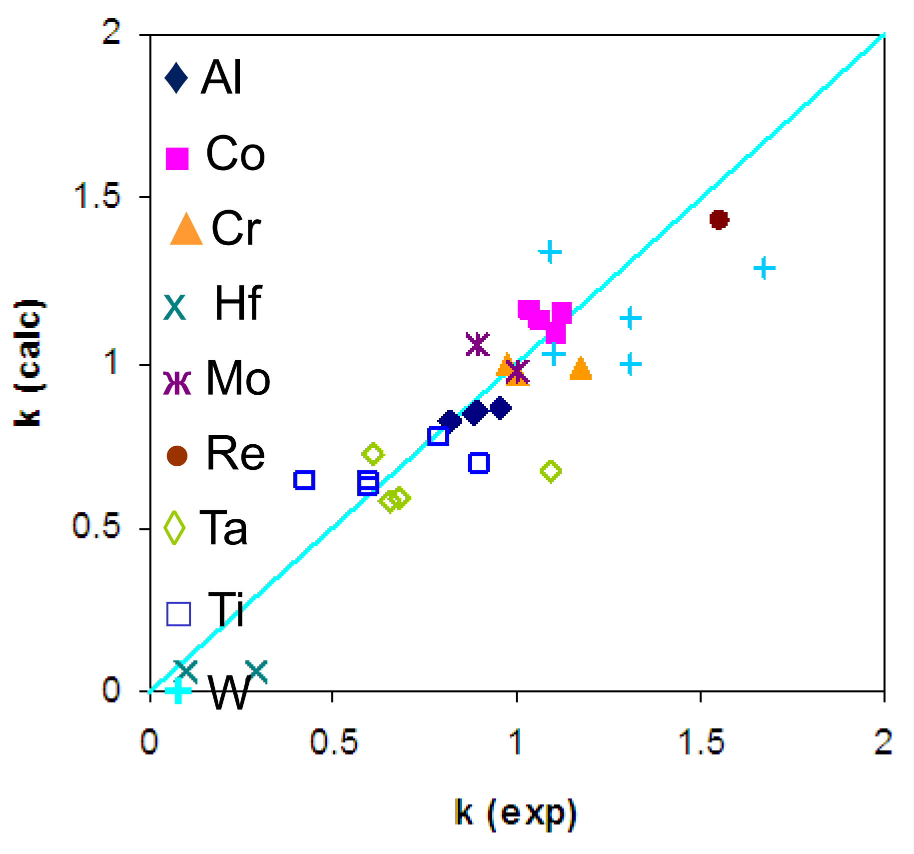
Site preference of the elements		
Site	**"Ni"**	**"Al"**
Ordered	**Ni, Co, Fe**	**Al, Hf?, Mo? , Ti?, W?**
Dis-ordered	**Cr, Nb?, Re?, Ta?**	

Note: **CoFe, CoHf, CoTi, FeTi, NiTi** have also B2 structure !

Comparison of Experiment and Calculation

Liquidus, solidus and solvus temperatures

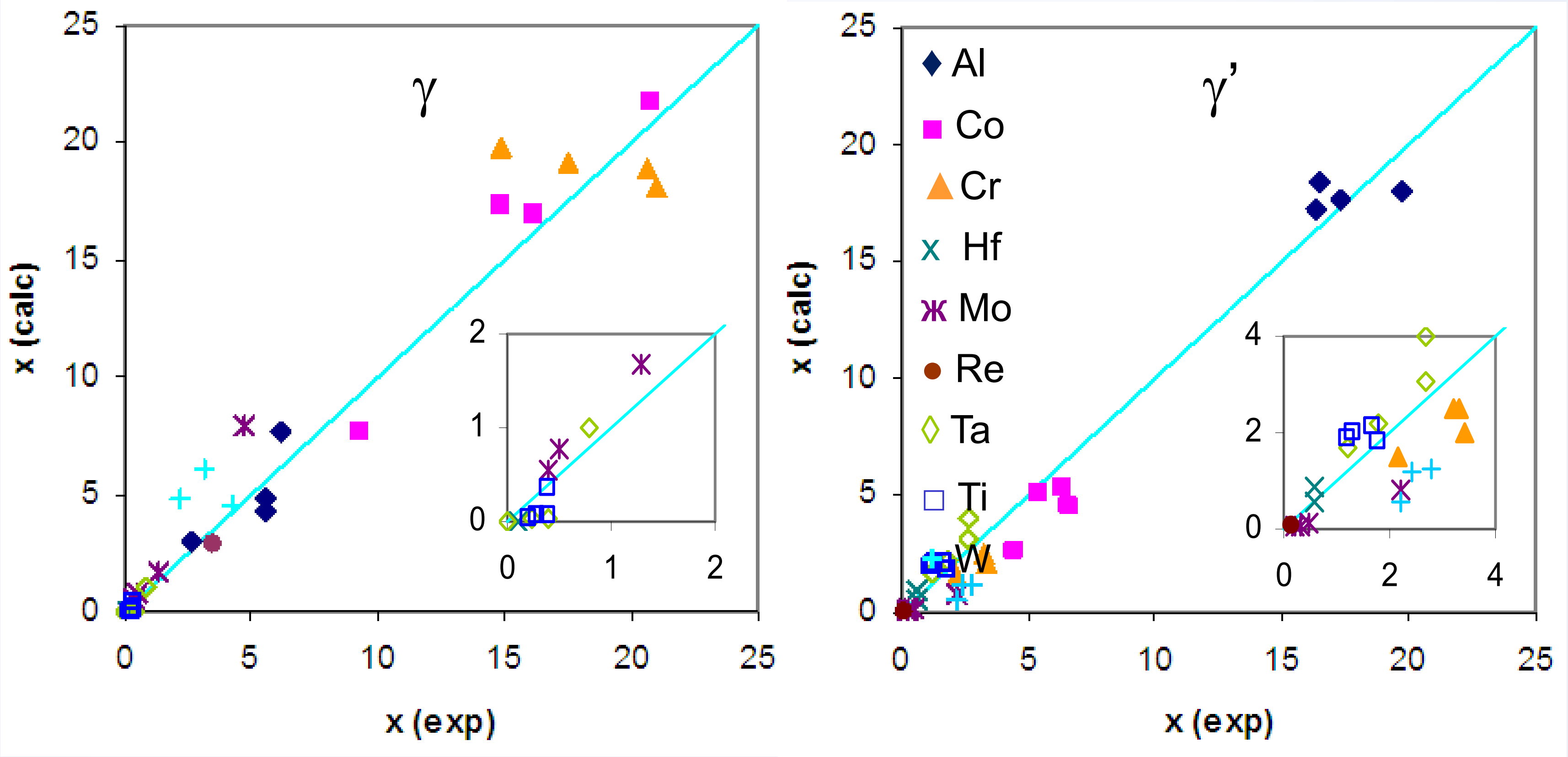




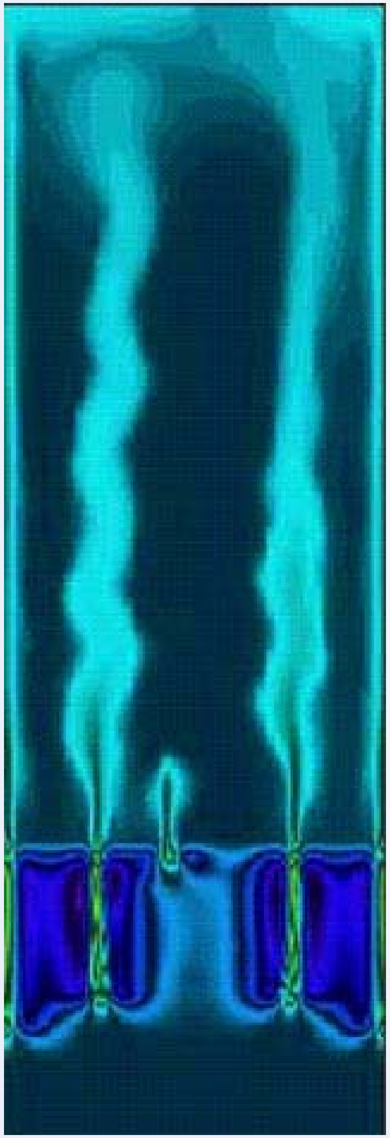
Partition ratios

Comparison of Experiment and Calculation

γ / γ’ tie lines in superalloys

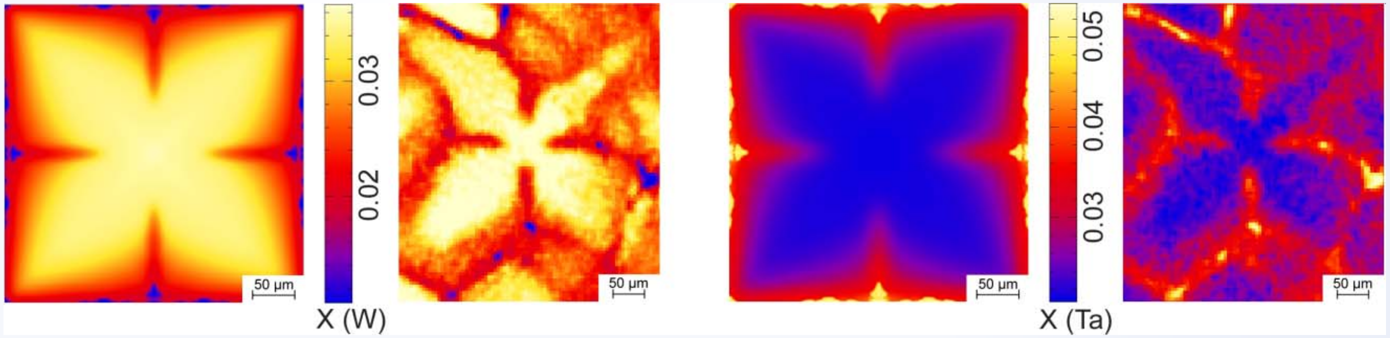


After all this Work:
Application of Databases in Simulations



Example: Casting Simulations

Mushy zone fluid flow calculations (C. Beckermann, U. Iowa):
Concentration profile of the liquid phase in the mushy zone is used to compute buoyancy terms. Density inversion causes localized plume flow and “freckles” in mushy zone.
(Calculations interfaced with PMLFKT)



Warnken et al., MCWASP 2003:
Distribution of alloy elements in a dendritically solidified 5 component superalloy. MICRESS results for tungsten compared to experimental EDX element mapping.
(Calculations interfaced with Thermo-Calc)

End