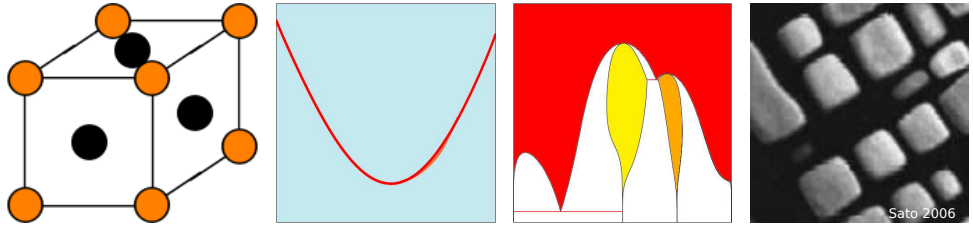
Thermodynamic modelling of the γ/γ' phases in the Calphad approach

Nathalie Dupin

Calcul Thermodynamique

Bochum, 2014 september 17th

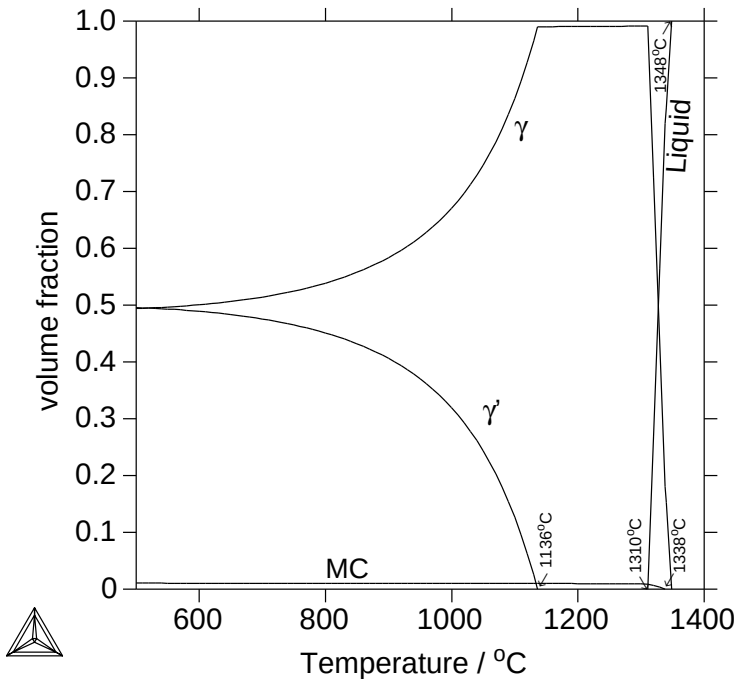


Why Calphad ?

- multicomponent calculations
- agreement with experiments

Why Calphad ?

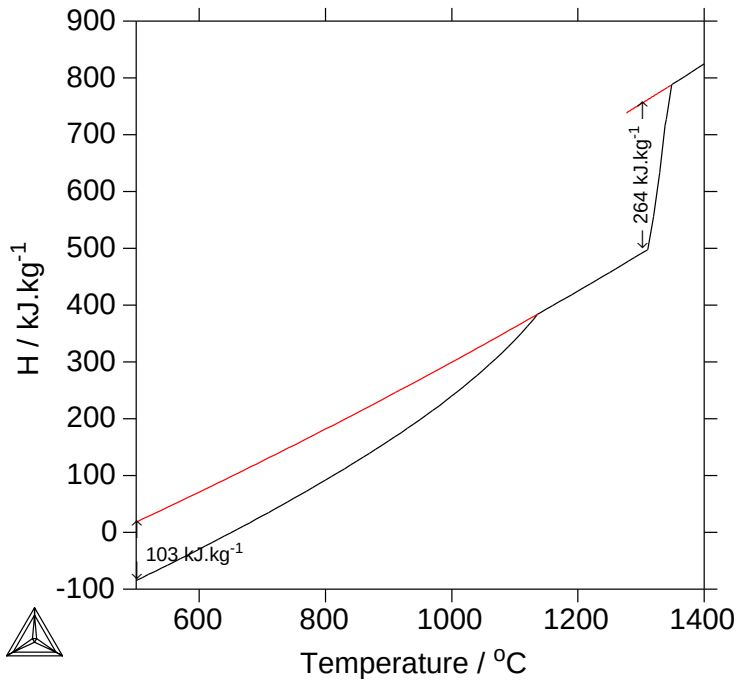
THERMO-CALC (2013.10.28:16.48) :IN738LC
DATABASE:USER
B(CR)=16.1, B(CO)=8.58, B(FE)=8E-2, B(MO)=1.74, B(W)=2.6, B(TA)=1.69,
B(AL)=3.44, B(TI)=3.44, B(NB)=0.82, B(C)=0.12, B=100, P=1E5;



F. Royer, ParisTech Thesis, 2014

Why Calphad ?

THERMO-CALC (2014.01.19:11.34) :IN738LC
DATABASE:USER
B(CR)=16.1, B(CO)=8.58, B(FE)=8E-2, B(MO)=1.74, B(W)=2.6, B(TA)=1.69,
B(AL)=3.44, B(TI)=3.44, B(NB)=0.82, B(C)=0.12, B=100, P=1E5;



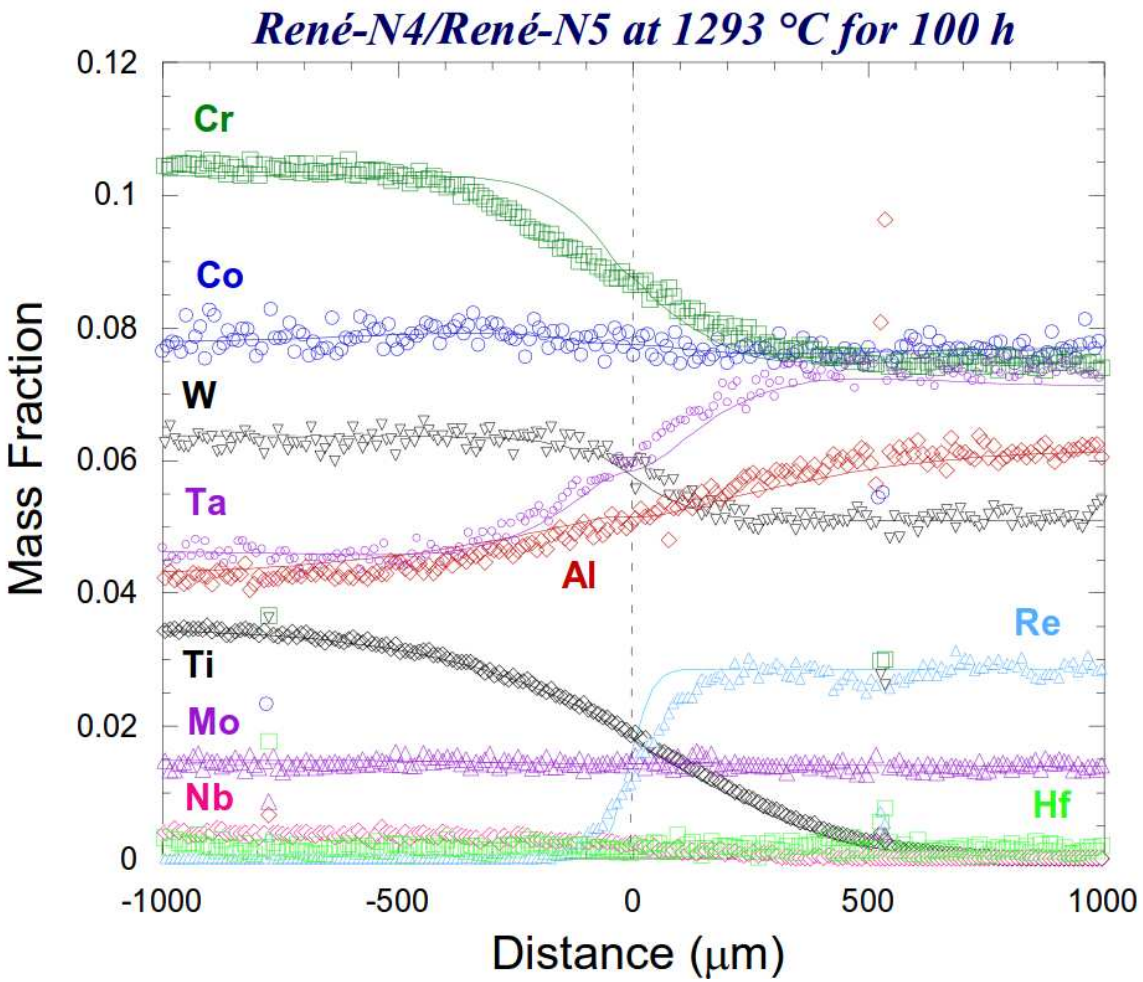
ATD on Selective Laser Melted alloy

. melting 258 kJ/kg

. γ' dissolution 60 kJ/kg
$\Rightarrow$ about 40% γ' in supersaturation

F. Royer, ParisTech Thesis, 2014

Why Calphad ?



C. Campbell, NIST

Early Al-Ni

L. Kaufman and H. Nesor, Met. Trans., 5 (1974), 1623

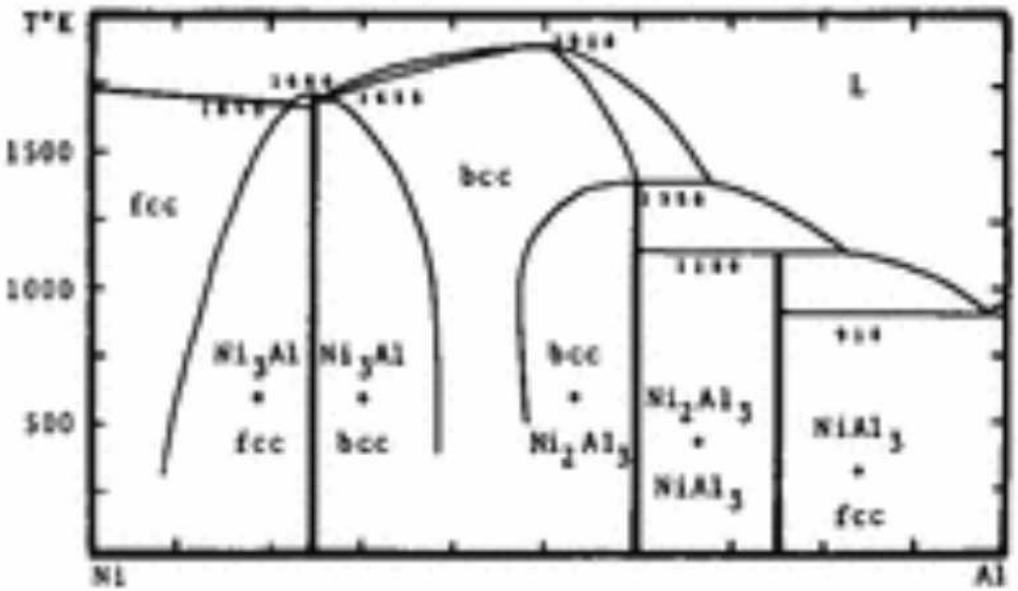
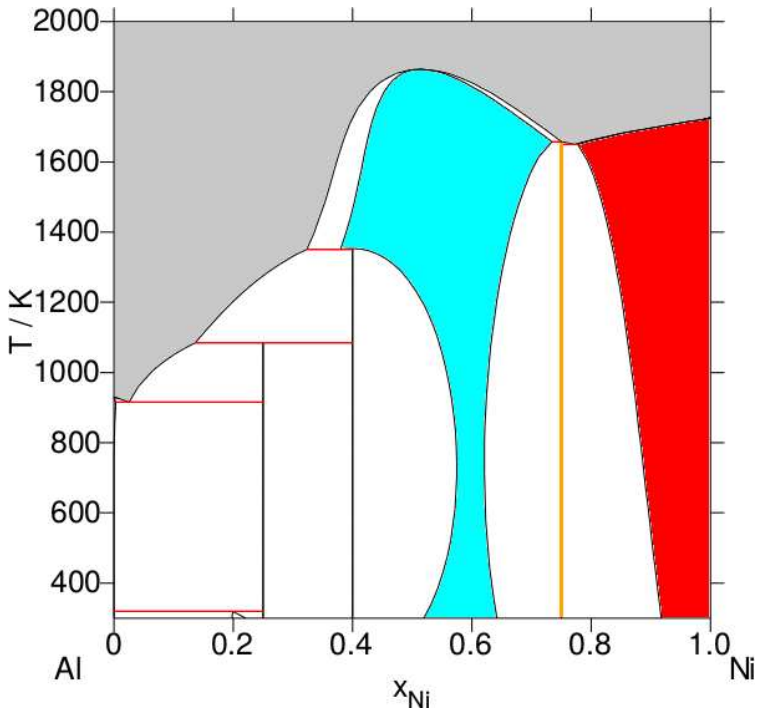


Fig. 3—Calculated Ni-Al phase diagram.

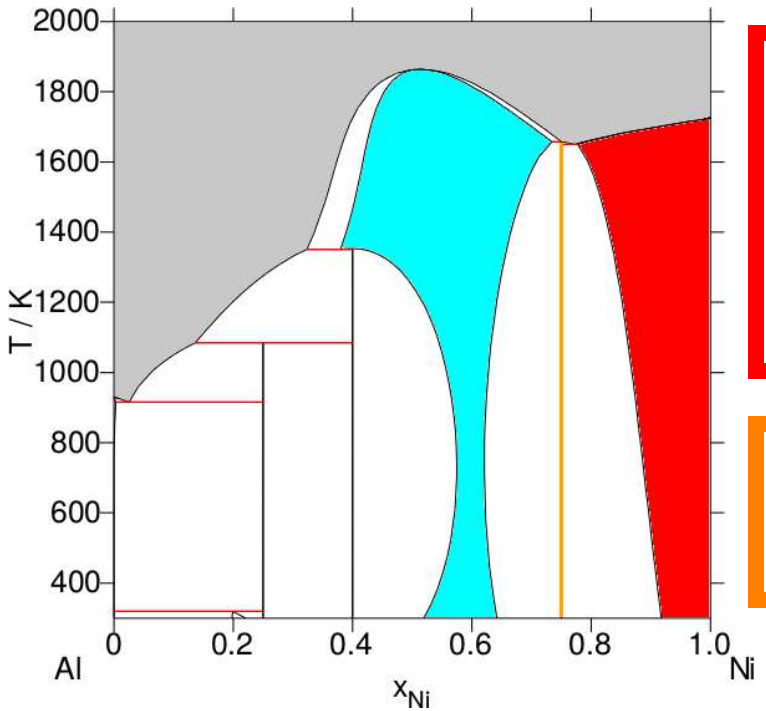
Early Al-Ni

L. Kaufman and H. Nesor, Met. Trans., 5 (1974), 1623



Early Al-Ni

L. Kaufman and H. Nesor, Met. Trans., 5 (1974), 1623



γ : fcc solution phase

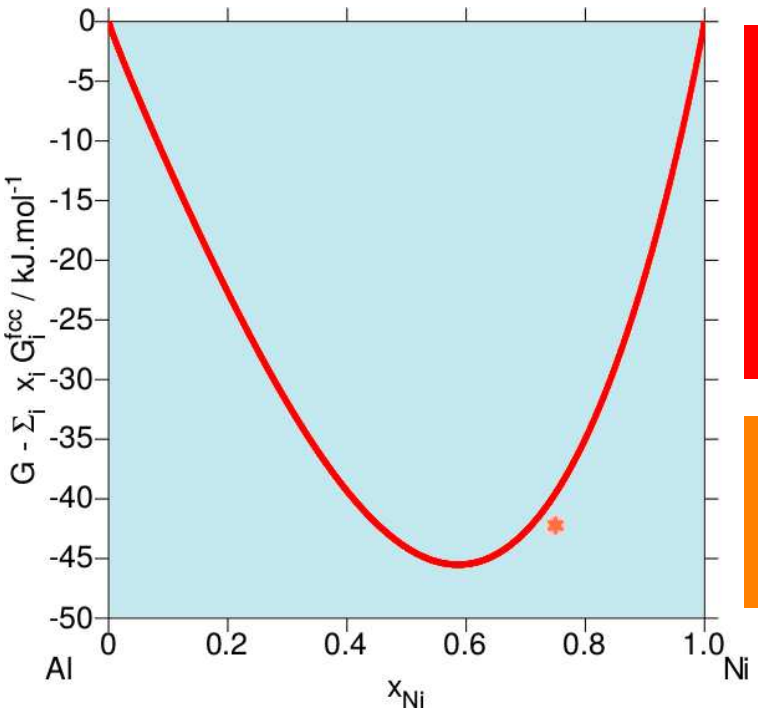
$$G^{fcc} = x_{Al} G^{fcc}_{Al} + x_{Ni} G^{fcc}_{Ni} + RT(x_{Al} \ln x_{Al} + x_{Ni} \ln x_{Ni}) + x_{Al} x_{Ni} [L0 + (x_{Al} - x_{Ni}) L1]$$

γ' : stoichiometric Ni_3Al

$$G^{Ni_3Al} = a + bT + cT^2 + dT^3$$

Early Al-Ni

L. Kaufman and H. Nesor, Met. Trans., 5 (1974), 1623



γ : fcc solution phase

$$G^{fcc} = x_{Al} G^{fcc}_{Al} + x_{Ni} G^{fcc}_{Ni} + RT(x_{Al} \ln x_{Al} + x_{Ni} \ln x_{Ni}) + x_{Al} x_{Ni} [L0 + (x_{Al} - x_{Ni}) L1]$$

γ' : stoichiometric Ni_3Al

$$G^{Ni_3Al} = a + bT + cT^2 + dT^3$$

Compound Energy Formalism

N. Saunders in "Superalloys 1996" eds. R.D. Kissinger et al. (TMS, Warrendale, 1996) 101

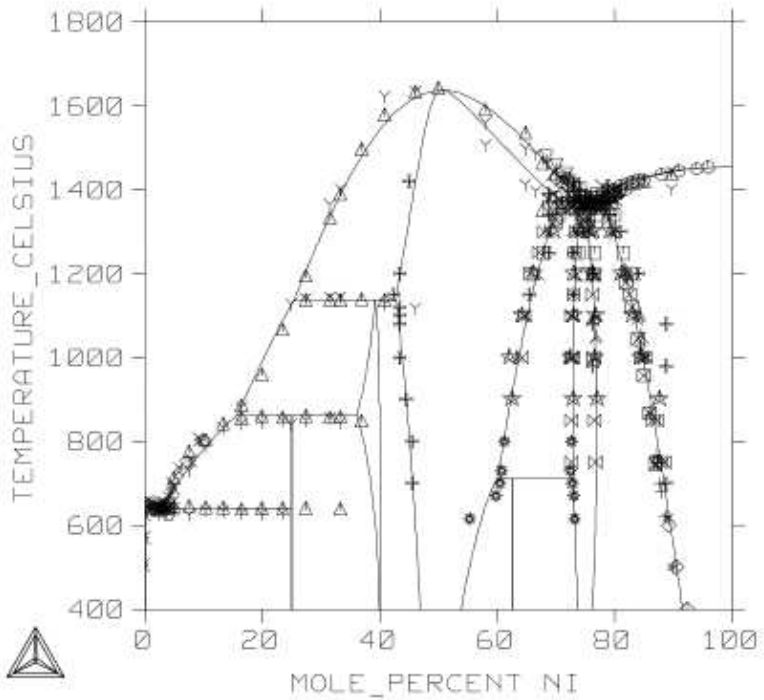
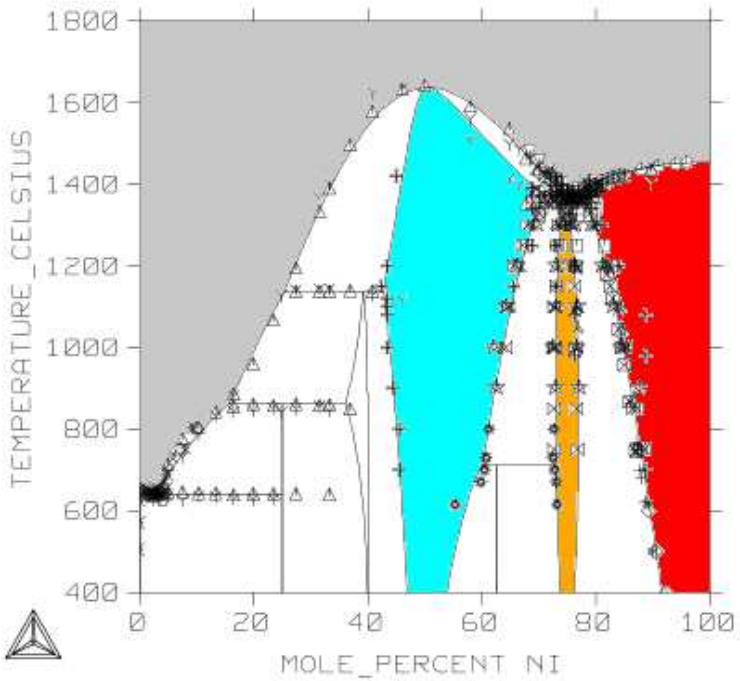


Fig. 1. Calculated Ni-Al phase diagram with experimental phase boundaries superimposed

Compound Energy Formalism

N. Saunders in "Superalloys 1996" eds. R.D. Kissinger et al. (TMS, Warrendale, 1996) 101



γ : fcc solution phase

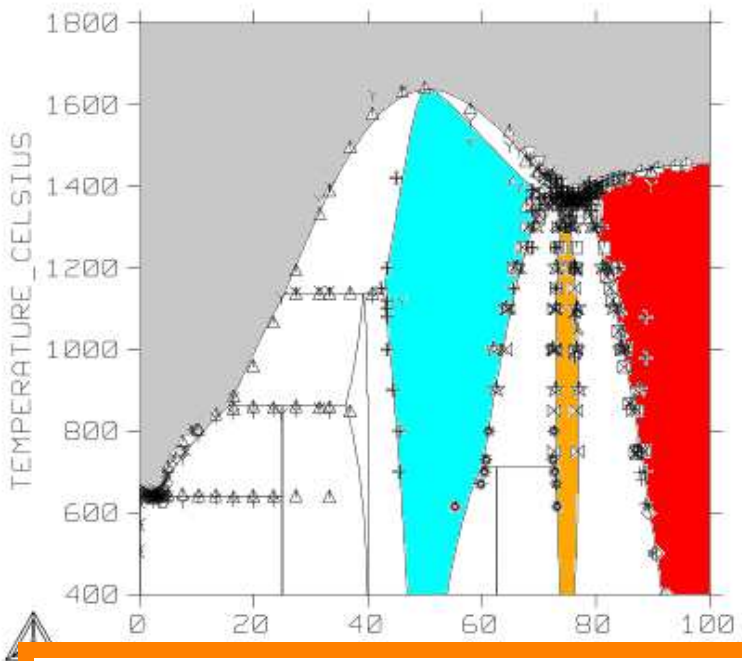
$$G^{fcc} = \sum_i x_i G_i^{fcc} + RT \sum_i x_i \ln x_i + {}^{xs}G^{fcc}$$

γ' : $(Al,Ni)_3(Al,Ni)$ CEF

$$G^{\gamma'} = \sum_i \sum_j y_i' y_j'' G_{i_3 j}^{\gamma'} + RT \left(\frac{3}{4} \sum_i y_i' \ln y_i' + \frac{1}{4} \sum_i y_i'' \ln y_i'' \right) + {}^{xs}G^{\gamma'}$$

Compound Energy Formalism

N. Saunders in "Superalloys 1996" eds. R.D. Kissinger et al. (TMS, Warrendale, 1996) 101



γ : fcc solution phase

$$G^{fcc} = \sum_i x_i G_i^{fcc} + RT \sum_i x_i \ln x_i + {}^{xs}G^{fcc}$$

γ' : $(Al,Ni)_3(Al,Ni)$ CEF

$$G^{\gamma'} = \sum_i \sum_j y_i' y_j'' G_{i_3 j}^{\gamma'}$$

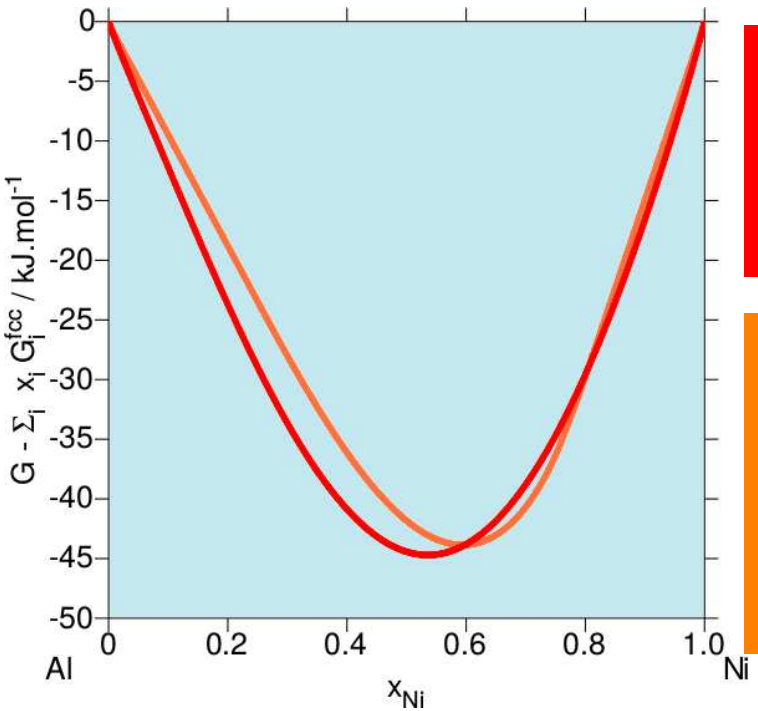
$$+ \left(3 \sum \; ' \; \; '' \right.$$

$$^{xs}G^{\gamma'} = \sum_i \sum_{j>i} \sum_k y_i' y_j' y_k'' \left(L0_{ij:k}^{\gamma'} + (y_i' - y_j') L1_{ij:k}^{\gamma'} \right)$$

$$+ \sum_i \sum_{j>i} \sum_k y_i'' y_j'' y_k' \left(L0_{k:ij}^{\gamma'} + (y_i'' - y_j'') L1_{k:ij}^{\gamma'} \right)$$

Compound Energy Formalism

N. Saunders in "Superalloys 1996" eds. R.D. Kissinger et al. (TMS, Warrendale, 1996) 101

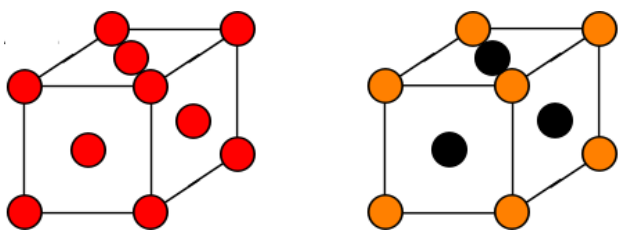


γ : fcc solution phase

$$G^{fcc} = \sum_i x_i G_i^{fcc} + {}^{id}G^{fcc} + {}^{xs}G^{fcc}$$

γ' : $(Al,Ni)_3(Al,Ni)$ CEF

$$G^{\gamma'} = \sum_i \sum_j y_i' y_j'' G_{i_3 j}^{\gamma'} + {}^{id}G^{\gamma'} + {}^{xs}G^{\gamma'}$$



$$G_{i:i}^{\gamma'} = G_i^{fcc}$$

Order-Disorder CEF

I. Ansara, B. Sundman and P. Willemin, Acta metall., 36 (1988), 977

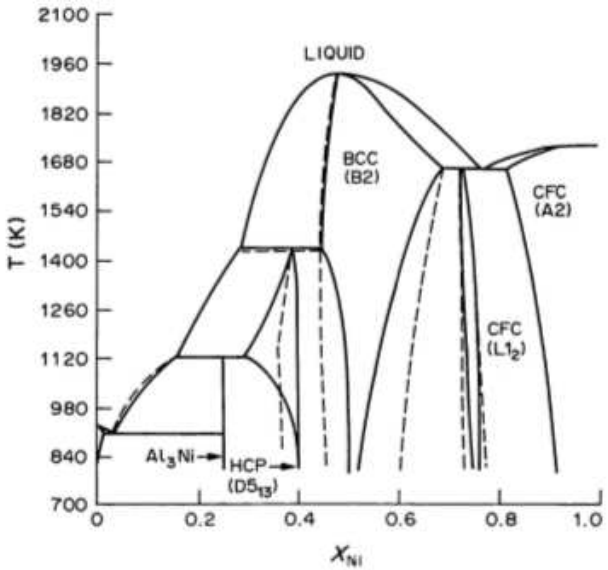


Fig. 4. Comparison between experimental [1] and calculated phas
betw

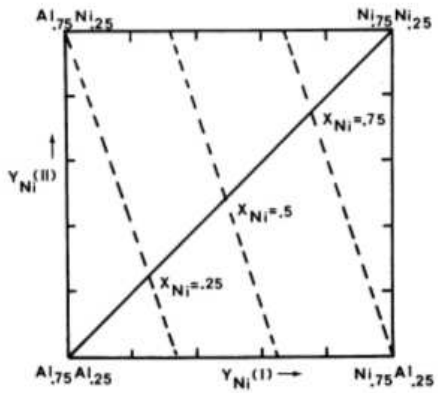


Fig. 3. Composition plane $y'_{Ni} = y''_{Ni}$ corresponding to various molar fraction of Ni in the ordered state. The diagonal represent the locus of composition in the disordered state.

$$G(\text{f.c.c., Al:Ni}) = u_1 + 3\text{L0}/16 + 6\text{L1}/64$$

$$G(\text{f.c.c., Ni:Al}) = u_2 + 3\text{L0}/16 - 6\text{L1}/64$$

$$G(\text{f.c.c., Al, Ni:Al; 0}) = 3u_1 + u_2/2 + u_3 + 9\text{L0}/16 + 27\text{L1}/64$$

$$G(\text{f.c.c., Al, Ni:Ni; 0}) = u_1/2 + 3u_2 + 3u_3 + 9\text{L0}/16 - 27\text{L1}/64$$

$$G(\text{f.c.c., Al:Al, Ni; 0}) = u_2/2 + u_3 + \text{L0}/16 + 9\text{L1}/64$$

$$G(\text{f.c.c., Ni:Al, Ni; 0}) = u_1/2 + u_3 + \text{L0}/16 - 9\text{L1}/64$$

$$G(\text{f.c.c., Al, Ni:Al; 1}) = 3u_4 + 27\text{L1}/64$$

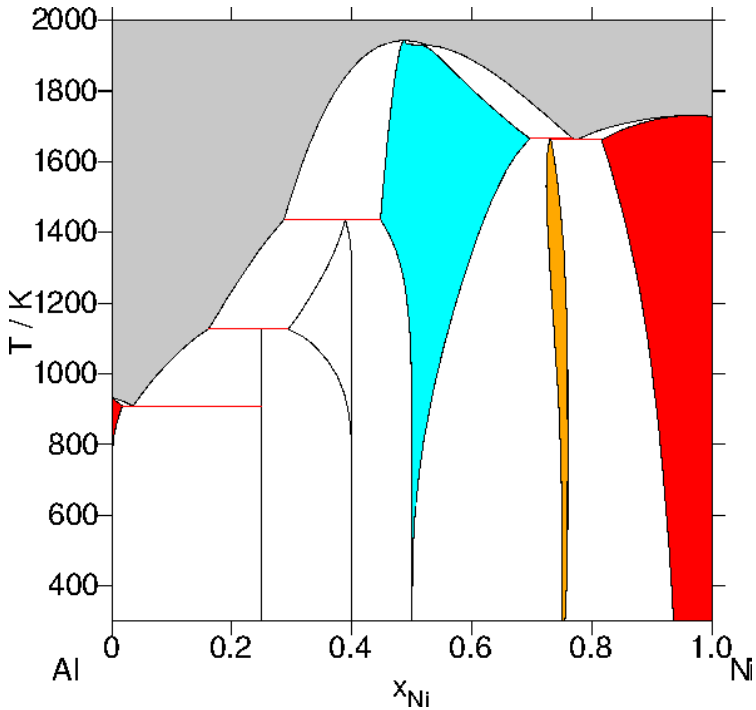
$$G(\text{f.c.c., Al, Ni:Ni; 1}) = 3u_5 + 27\text{L1}/64$$

$$G(\text{f.c.c., Al:Al, Ni; 1}) = u_4 + \text{L1}/64$$

$$G(\text{f.c.c., Ni:Al, Ni; 1}) = u_5 + \text{L1}/64$$

Order-Disorder CEF

I. Ansara, B. Sundman and P. Willemin, Acta metall., 36 (1988), 977

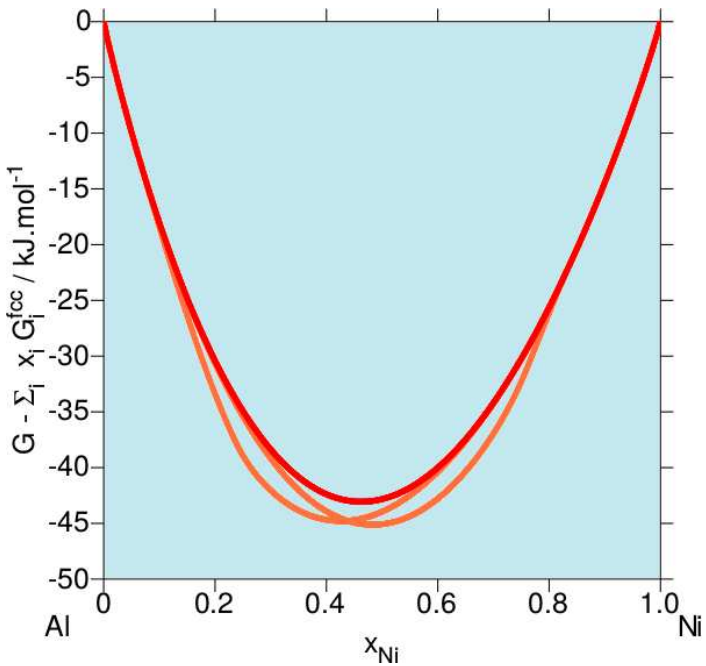


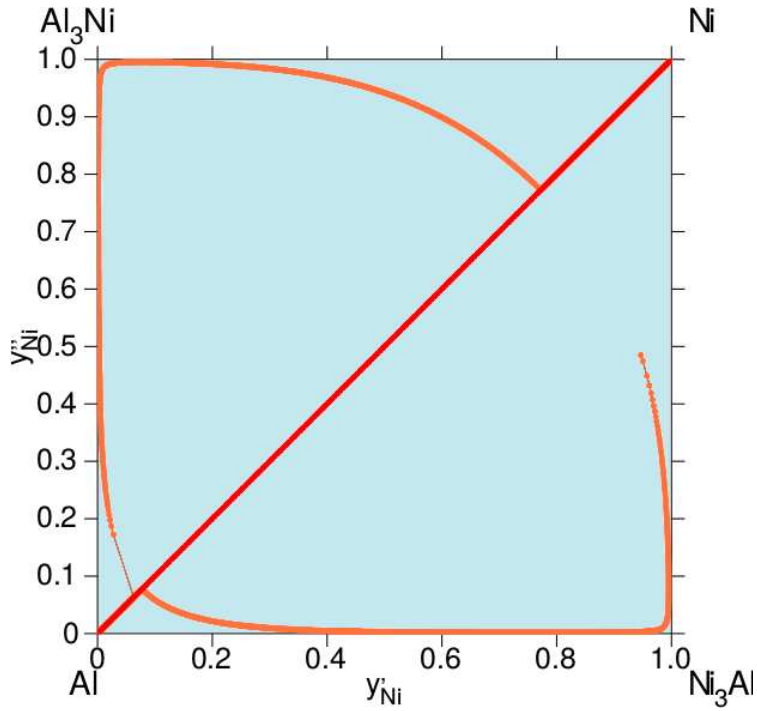
γ and γ' : a single description $(Al,Ni)_3(Al,Ni)$ CEF

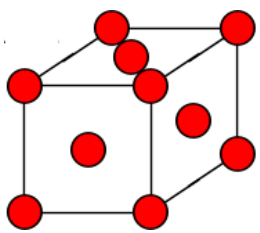
- constraints between u_i ensure $(dG = 0)_{y_i' = y_i''}$
- order independent contribution from L0 and L1

Order-Disorder CEF

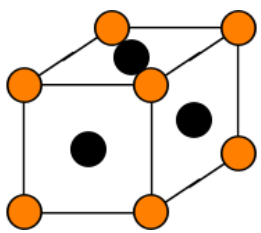
I. Ansara, B. Sundman and P. Willemin, Acta metall., 36 (1988), 977







$y_i^{'} = y_i^{''}$



$y_i^{'} \neq y_i^{''}$

Splitting Order-Disorder CEF

I. Ansara, N. Dupin, H. L. Lukas and B. Sundman, J. Alloys Compounds, 247 (1997), 20

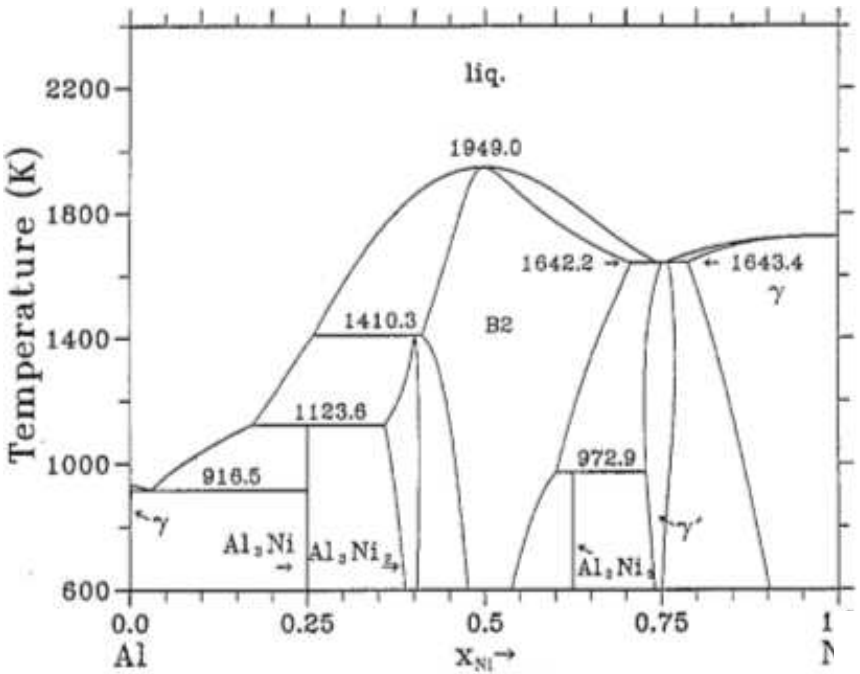


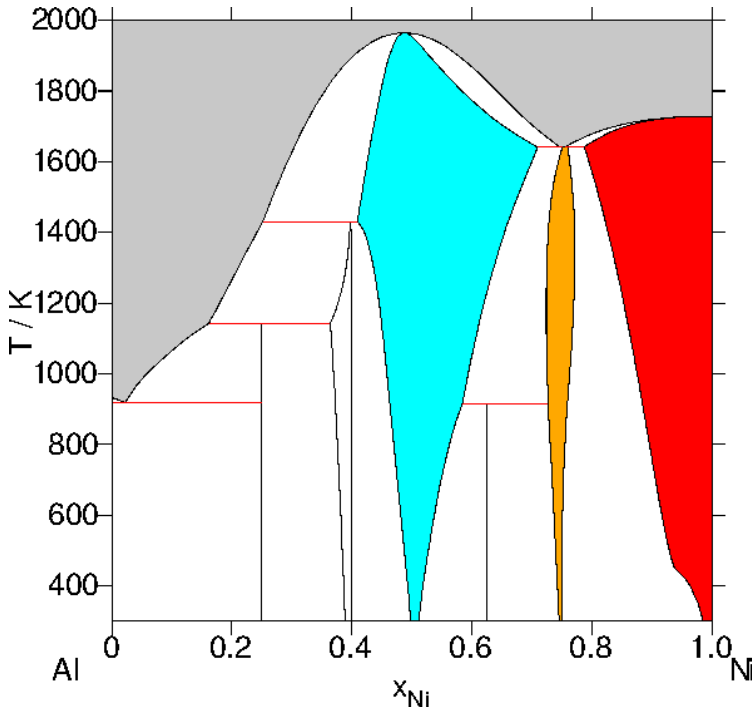
Fig. 2. Calculated phase diagram.

$$G_m = G_m^{dis}(x_i) + G_m^{ord}(y_i', y_i'') - G_m^{ord}(x_i)$$

$$G_{A:B} = G_{A:A:A:B}$$
$$G_{B:A} = G_{B:B:B:A}$$
$${}^0L_{A:A,B} = {}^0L$$
$${}^1L_{A:A,B} = {}^1L$$
$${}^0L_{B:A,B} = {}^0L$$
$${}^1L_{B:A,B} = {}^1L$$
$${}^0L_{A,B:A} = -1.5G_{A:B:B:B} + 1.5G_{A:A:B:B} + 1.5G_{A:A:A:B} + 3.0\,{}^0L$$
$${}^0L_{A,B:B} = 1.5G_{A:B:B:B} + 1.5G_{A:A:B:B} - 1.5G_{A:A:A:B} + 3.0\,{}^0L$$
$${}^1L_{A,B:A} = 0.5G_{A:B:B:B} - 1.5G_{A:A:B:B} + 1.5G_{A:A:A:B} + 3.0\,{}^1L$$
$${}^1L_{A,B:B} = -1.5G_{A:B:B:B} + 1.5G_{A:A:B:B} - 0.5G_{A:A:A:B} + 3.0\,{}^1L$$

Splitting Order-Disorder CEF

I. Ansara, N. Dupin, H. L. Lukas and B. Sundman, J. Alloys Compounds, 247 (1997), 20



γ and γ' : a single CEF

- splitting disorder description

  $$G = G^{dis}(x) + G^{ord}(y) - G^{ord}(x)$$

- disorder stability : 2SL=4SL
- $G_{Al_3Ni} = \frac{1}{3} G_{Ni_3Al}$
  $\frac{1}{4} G_{Al_2Ni_2} = \frac{1}{3} G_{Ni_3Al}$
  as Al_3Ni and Al_2Ni_2 not known experimentally

Splitting Order-Disorder

$$G = G^{dis}(x) + G^{ord}(y) - G^{ord}(x)$$

- introduced to be able to assess separately the disordered phase
- the meaning of the $G^{ord}(y)$ parameters is lost, only $G^{ord}(y) - G^{ord}(x)$ is meaningfull
- easy extrapolation in multicomponent even if many systems do not contribute to ordering

2SL = 4SL

$$G^{2SL} = \sum_i \sum_j y_i^{'} y_j^{''} G^{2SL}_{i_3 j} + RT \left(\frac{3}{4} \sum_i y_i^{'} \ln y_i^{'} + \frac{1}{4} \sum_i y_i^{''} \ln y_i^{''} \right) + {}^{xs}G^{2SL}$$

2SL = 4SL

$$G^{2SL} = \sum_i \sum_j y_i^{'} y_j^{''} G^{2SL}_{i_3 j} + RT \left(\frac{3}{4} \sum_i y_i^{'} \ln y_i^{'} + \frac{1}{4} \sum_i y_i^{''} \ln y_i^{''} \right) + {}^{xs}G^{2SL}$$

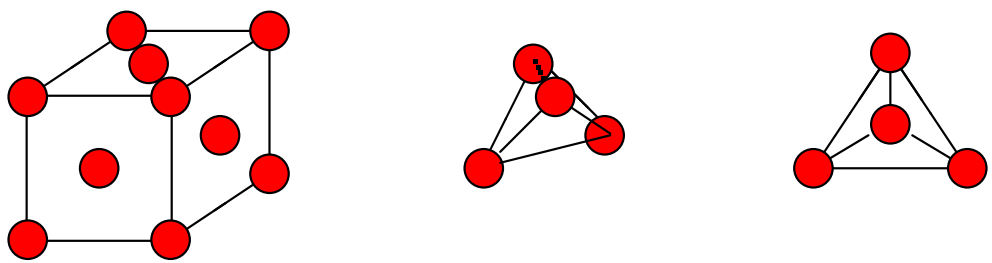
$$G^{4SL} = \sum_i \sum_j y_i^{\alpha} y_j^{\beta} y_k^{\gamma} y_l^{\delta} G^{4SL}_{ijkl} + RT \sum_s \frac{1}{4} \sum_i y_i^s \ln y_i^s + {}^{xs}G^{4SL}$$

2SL = 4SL

$$G^{2SL} = \sum_i \sum_j y_i^{'} y_j^{''} G_{i_3 j}^{2SL} + RT \left(\frac{3}{4} \sum_i y_i^{'} \ln y_i^{'} + \frac{1}{4} \sum_i y_i^{''} \ln y_i^{''} \right) + {}^{xs}G^{2SL}$$

$$G^{4SL} = \sum_i \sum_j y_i^{\alpha} y_j^{\beta} y_k^{\gamma} y_l^{\delta} G_{ijkl}^{4SL} + RT \sum_s \frac{1}{4} \sum_i y_i^s \ln y_i^s + {}^{xs}G^{4SL}$$

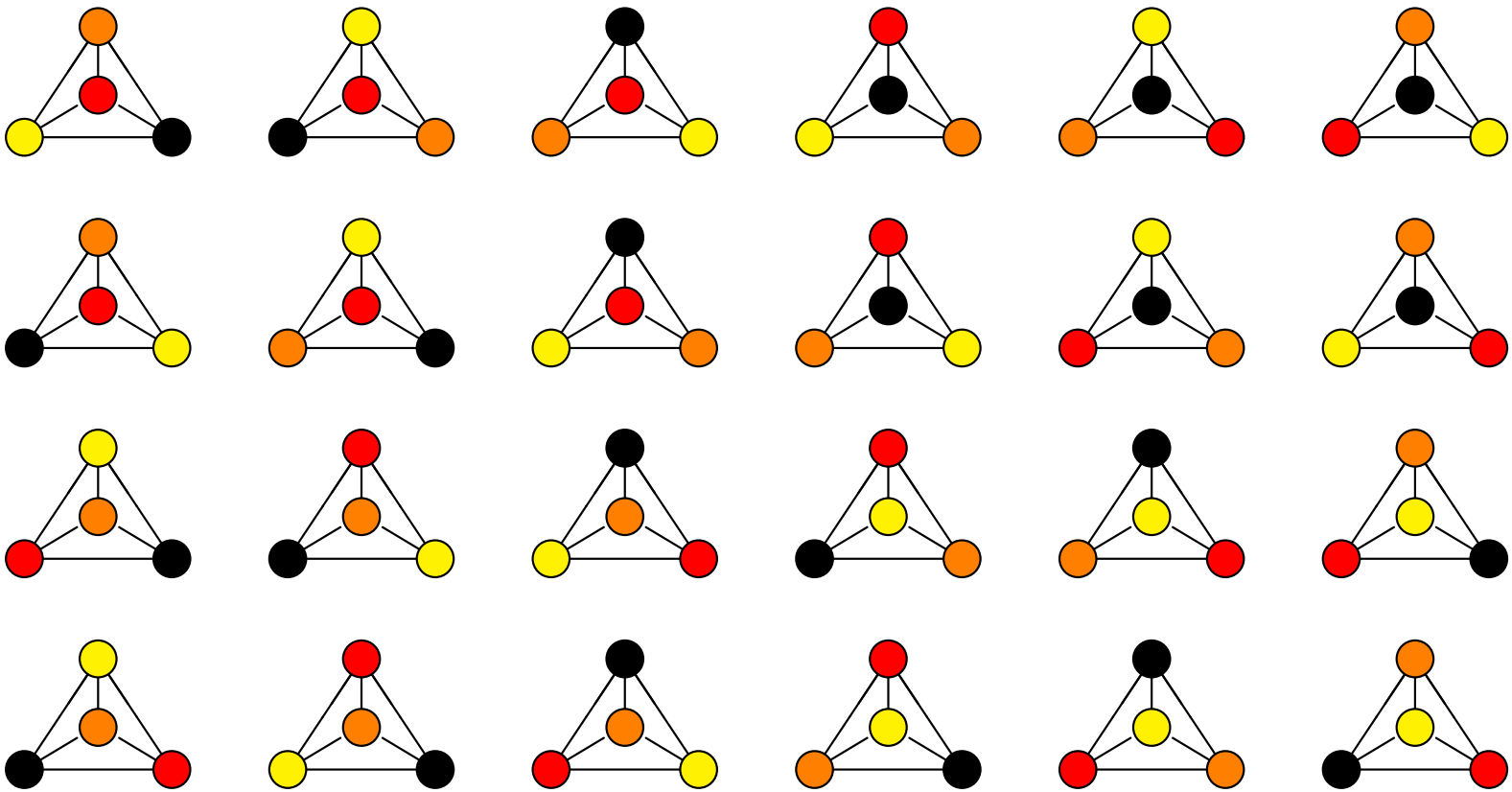
The fcc lattice is built built on regular tetrahedra.



Equivalence of the 4SL $\Rightarrow$ stability of the disorder ($A1$)

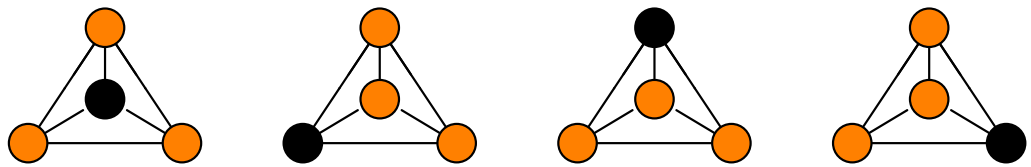
2SL = 4SL

From crystallographic symmetry,
the following configurations are equivalent.



2SL = 4SL

From crystallographic symmetry,
the following configurations are equivalent.



$L1_2$ configurations

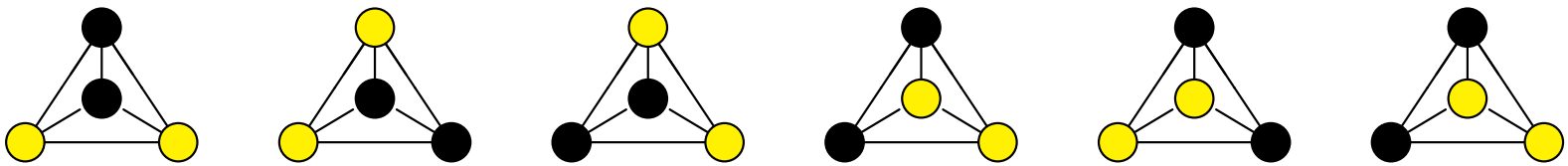
$$G^{4SL}_{AAAB} = G^{4SL}_{AABA} = G^{4SL}_{ABAA} = G^{4SL}_{BAAA}$$

Standing also for excess parameters

$$L^{4SL}_{AB:*:*:*} = L^{4SL}_{*:AB:*:*} = L^{4SL}_{*:*:AB:*} = L^{4SL}_{*:*:*:AB}$$

2SL = 4SL

From crystallographic symmetry,
the following configurations are equivalent.



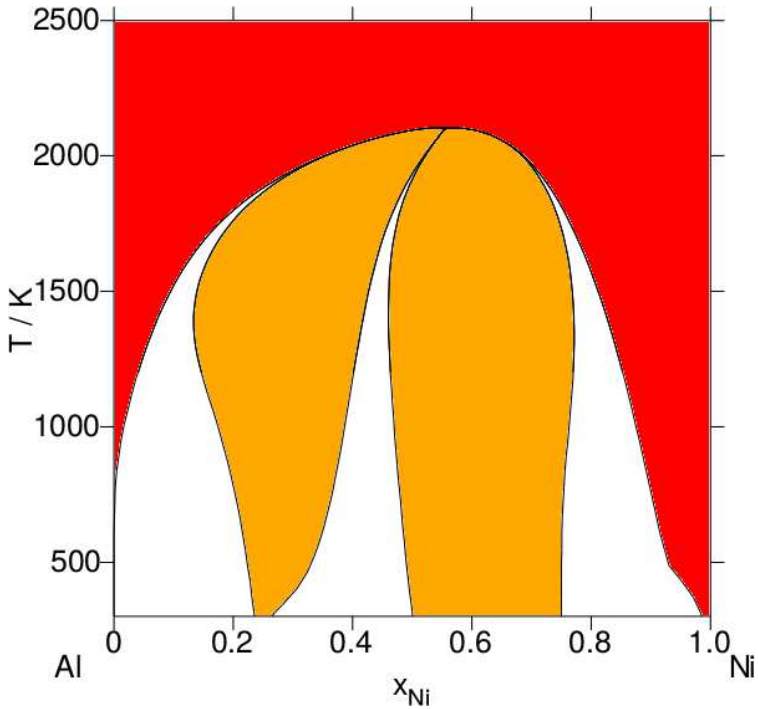
$L1_0$ configurations

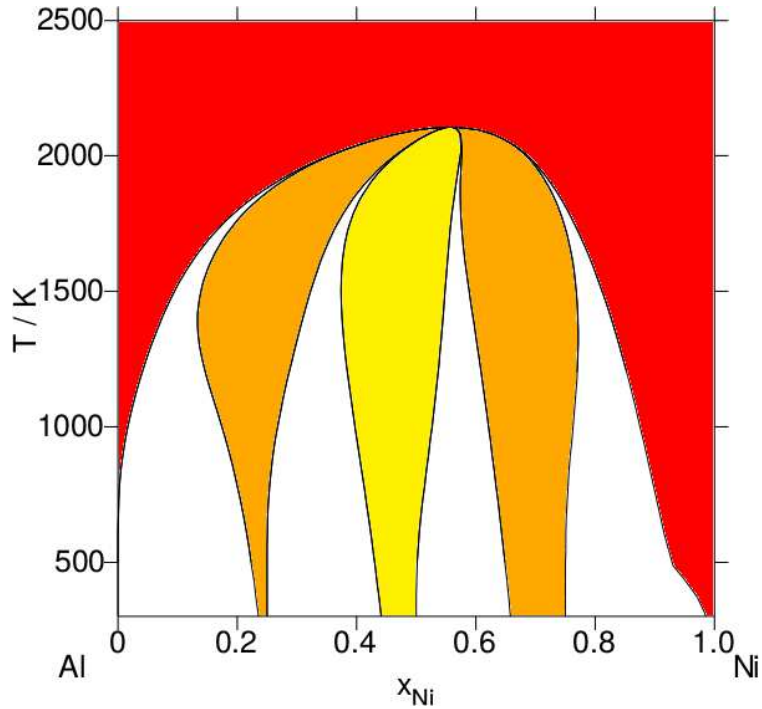
$$G^{4SL}_{AABB} = G^{4SL}_{ABAB} = G^{4SL}_{BAAB} = G^{4SL}_{ABBA} = G^{4SL}_{BABA} = G^{4SL}_{BBAA}$$

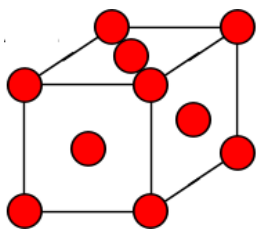
2SL = 4SL

$$
\begin{aligned}
G^{2SL}_{A_3B} &= G^{4SL}_{AAAB} \\
G^{2SL}_{AB_3} &= G^{4SL}_{ABBB} \\
L0^{2SL}_{AB:A} &= -1.5\,G^{4SL}_{ABBB} + 1.5\,G^{4SL}_{AABB} + 1.5\,G^{4SL}_{AAAB} + 3\,L0^{4SL}_{AB:*:*:*} \\
L0^{2SL}_{AB:B} &= +1.5\,G^{4SL}_{ABBB} + 1.5\,G^{4SL}_{AABB} - 1.5\,G^{4SL}_{AAAB} + 3\,L0^{4SL}_{AB:*:*:*} \\
L0^{2SL}_{A:AB} &= L0^{4SL}_{AB:*:*:*} \\
L0^{2SL}_{B:AB} &= L0^{4SL}_{AB:*:*:*} \\
L1^{2SL}_{AB:A} &= 0.5\,G^{4SL}_{ABBB} - 1.5\,G^{4SL}_{AABB} + 1.5\,G^{4SL}_{AAAB} + 3\,L1^{4SL}_{AB:*:*:*} \\
L1^{2SL}_{AB:B} &= -1.5\,G^{4SL}_{ABBB} + 1.5\,G^{4SL}_{AABB} - 0.5\,G^{4SL}_{AAAB} + 3\,L1^{4SL}_{AB:*:*:*} \\
L1^{2SL}_{A:AB} &= L1^{4SL}_{AB:*:*:*} \\
L1^{2SL}_{B:AB} &= L1^{4SL}_{AB:*:*:*}
\end{aligned}
$$

2SL = 4SL

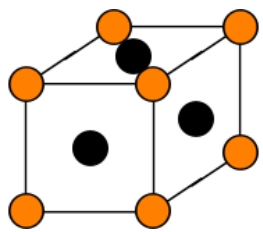






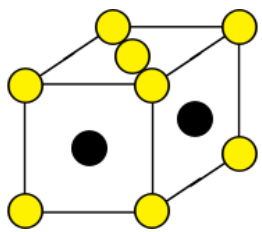
A1

$$y_i^{\alpha} = y_i^{\beta} = y_i^{\gamma} = y_i^{\delta}$$



$L1_2$

$$y_i^{\alpha} = y_i^{\beta} = y_i^{\gamma} \neq y_i^{\delta}$$



$L1_0$

$$y_i^{\alpha} = y_i^{\beta} \neq y_i^{\gamma} = y_i^{\delta}$$

2SL = 4SL

Similar to Shockley fcc prototype considering a single and constant nearest neighbours energy with BWG entropy

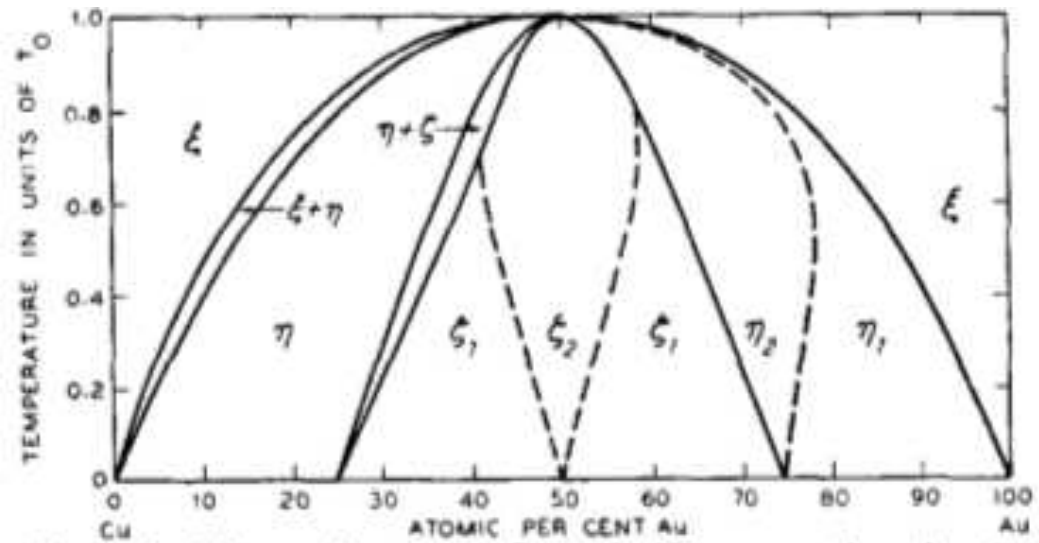
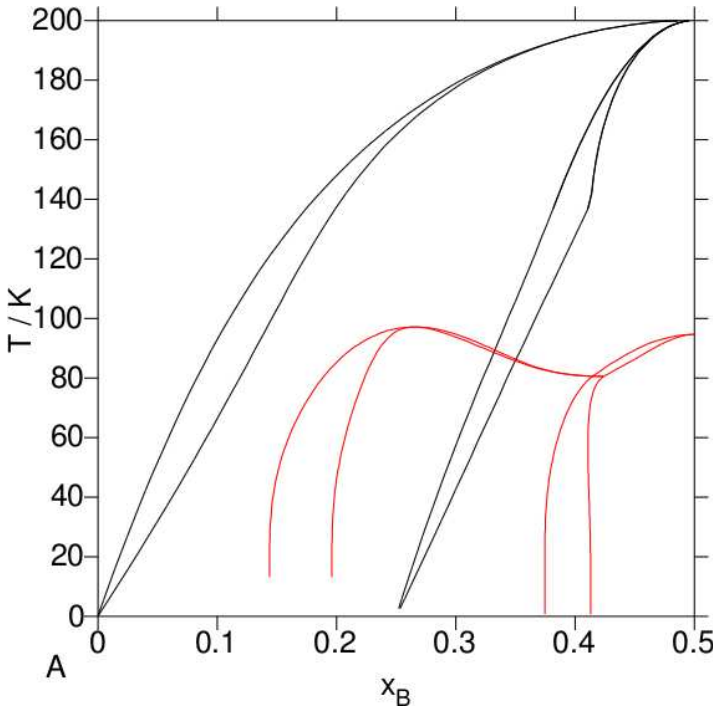


FIG. 4. Phase diagram: Left half conventional; right half alloy restrained to one phase of prescribed composition. Both diagrams when shown in full are symmetrical about 50 atomic percent.

W. Shockley, J. Chem. Phys., 6 (1938), 130

2SL = 4SL



▷ Shockley equivalent CEF

$$G = \sum_i \sum_j \sum_k \sum_l y_i^\alpha y_j^\beta y_k^\gamma y_l^\delta G_{ijkl}$$

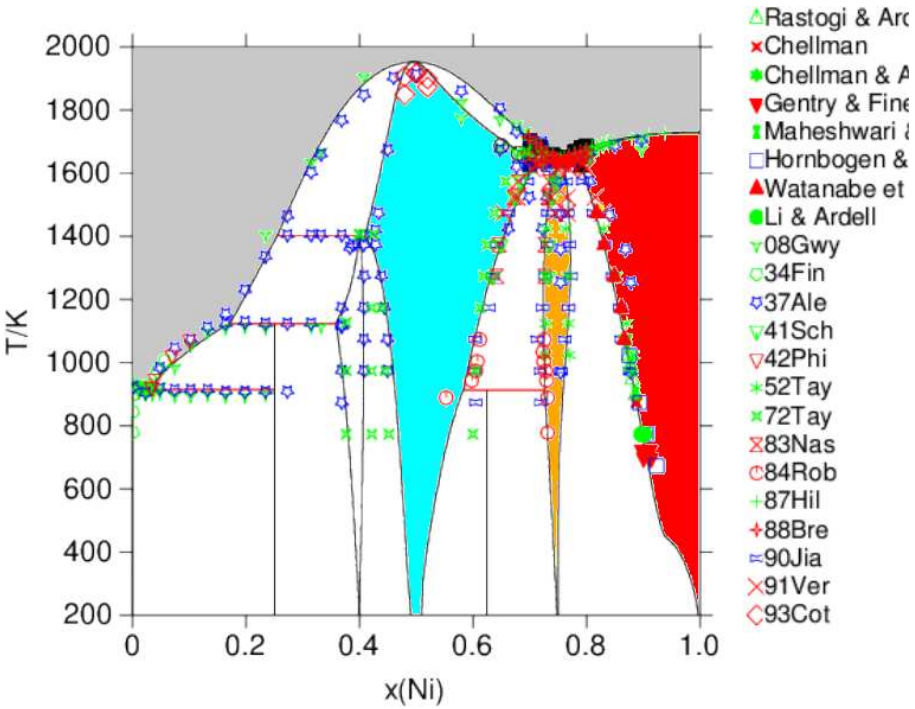
$$+RT \sum_s \sum_i \frac{1}{4} y_i^s \ln y_i^s$$

with $G_{A3B} = 3\,\epsilon_{AB}$, $G_{A2B2} = 4\,\epsilon_{AB}$

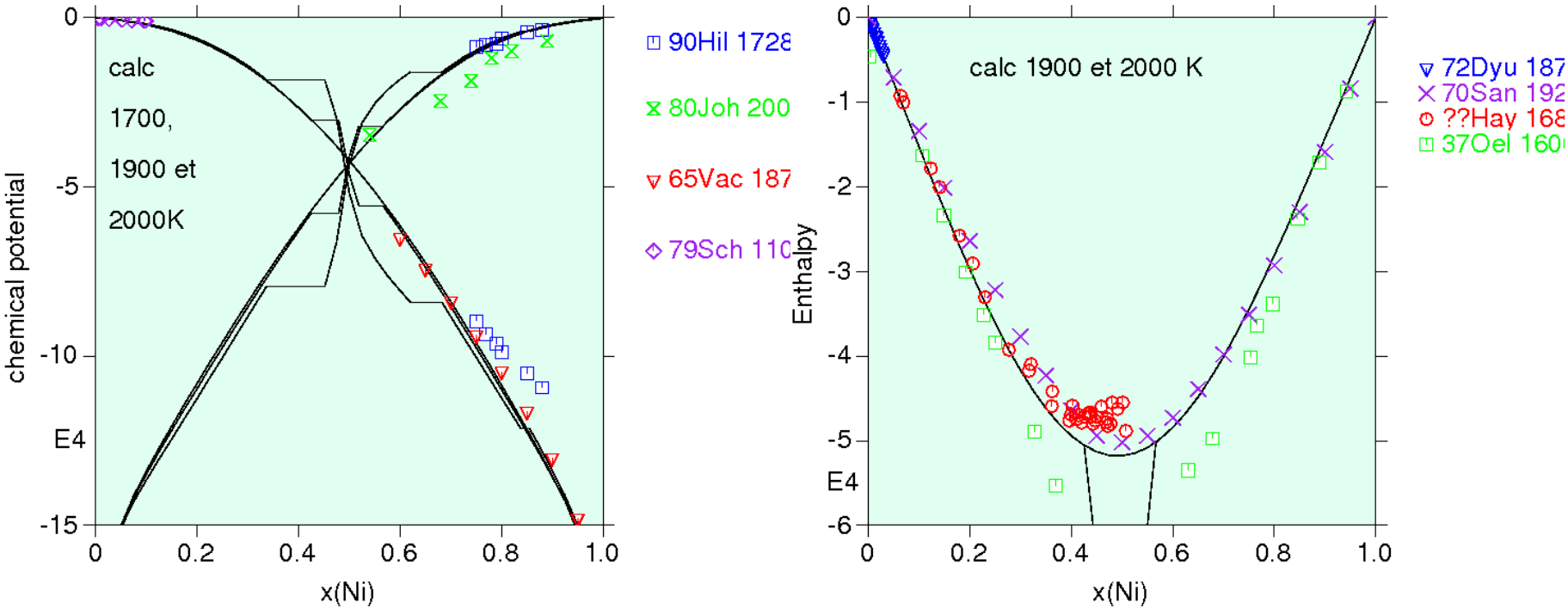
▷ Tetrahedron CVM prototype using the same pairwise energy

Bad topology, bad critical temperature

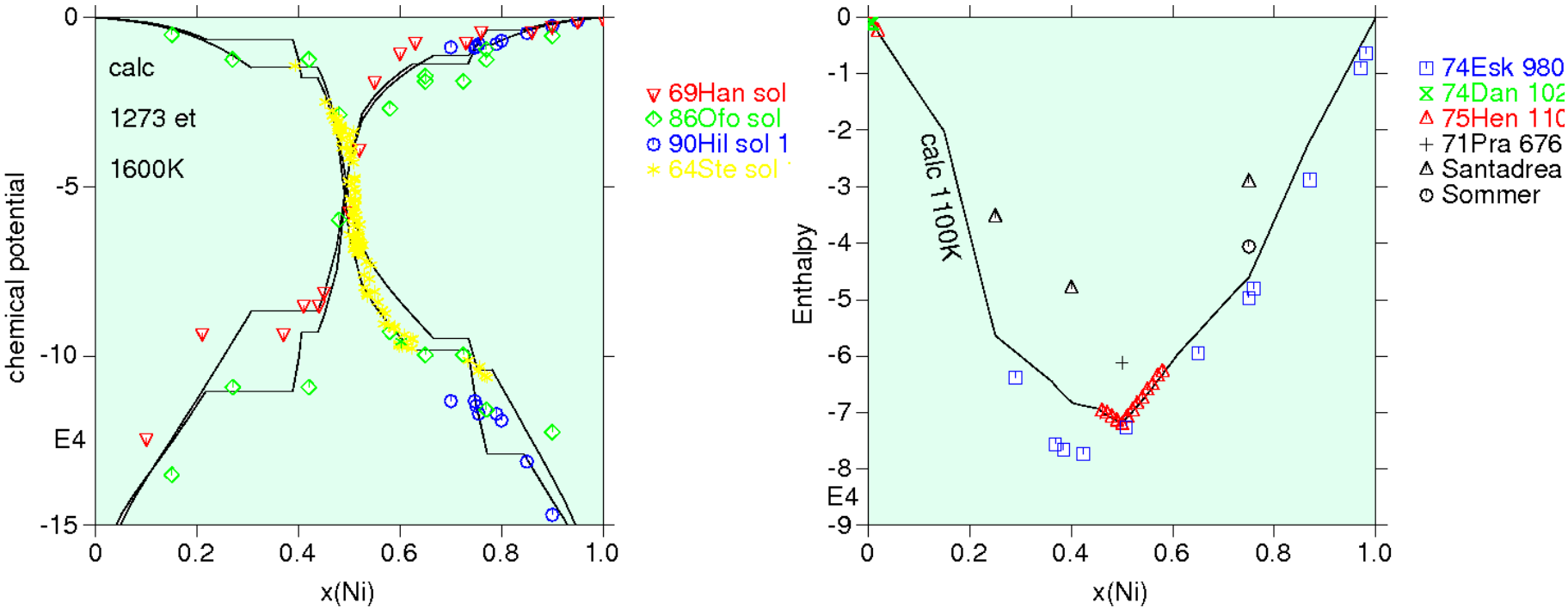
Splitting Order-Disorder CEF



Splitting Order-Disorder CEF

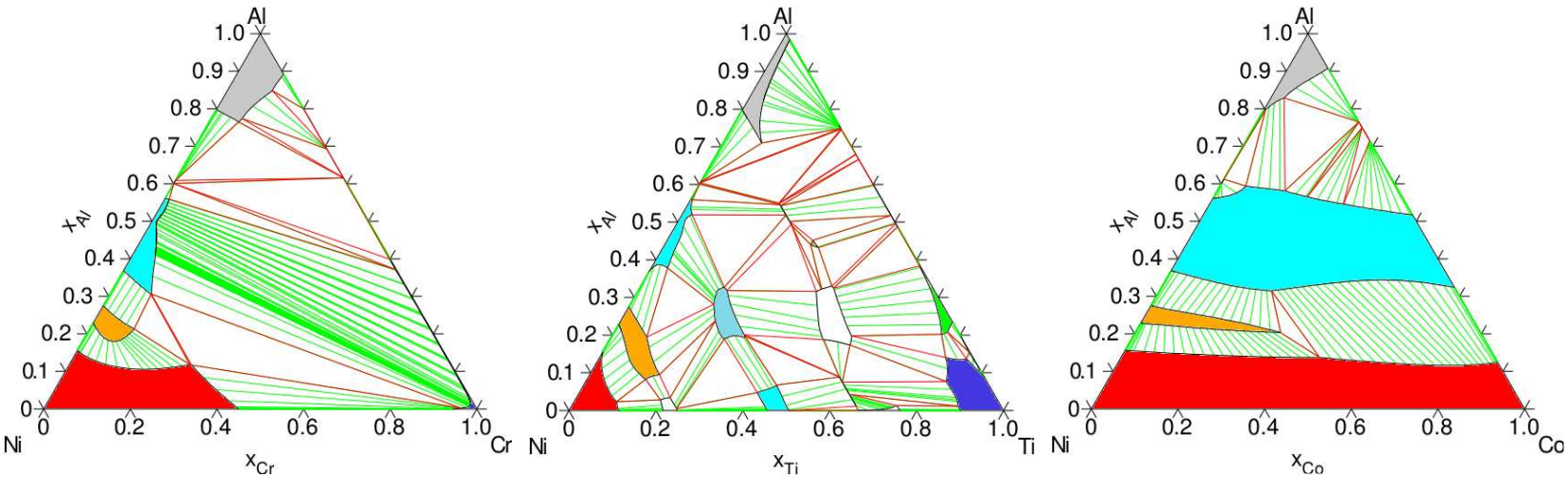


Splitting Order-Disorder CEF



Splitting Order-Disorder CEF

Despite its physical weakness, this model allowed to describe reasonably experimental data in Al-Ni as well as many ternary systems and allowed to set up a multicomponent database, today known as the commercial database TCNI6.



N. Dupin, B. Sundman, Scandinavian J. Metall., 30 (2001) 184

4SL Order-Disorder CEF

A way to get proper fcc phase diagram topology with the CEF

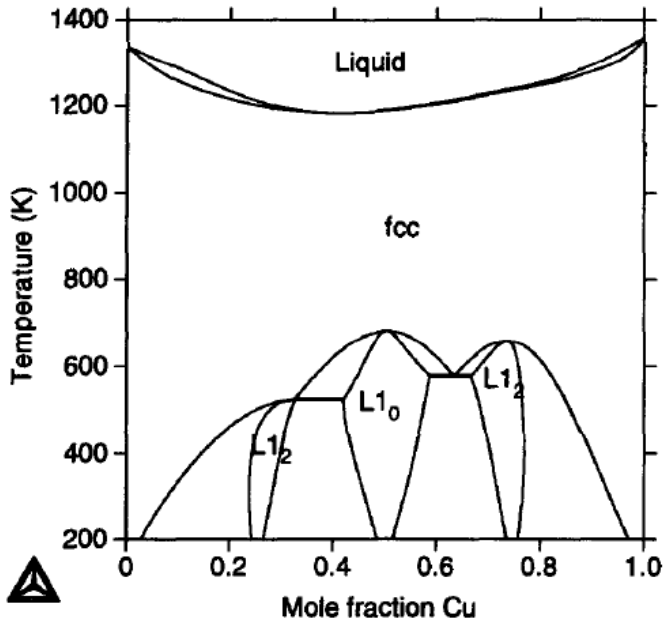
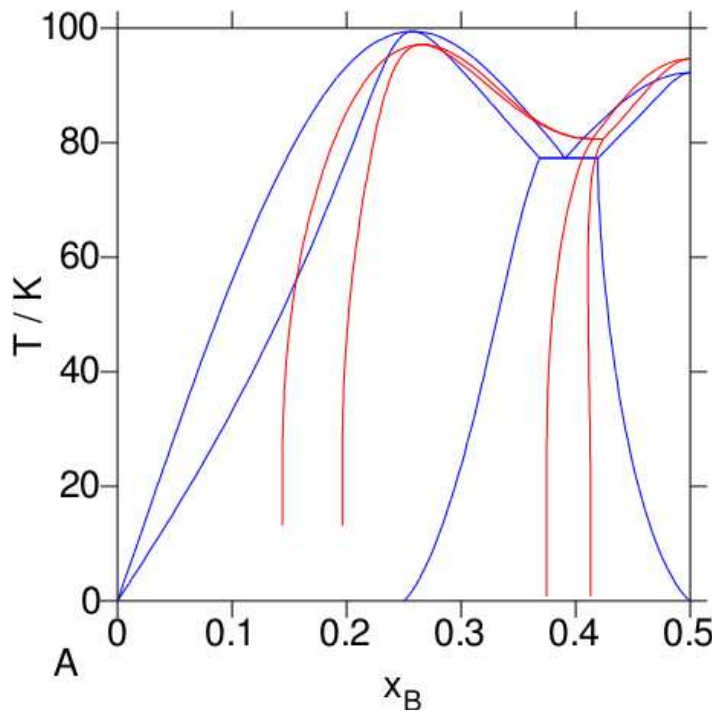


Figure 1: The assessed Au-Cu phase diagram using CEF

B. Sundman, S. G. Fries, W. A. Oates, Calphad, 22 (1998), 335

4SL Order-Disorder CEF

A way to get proper fcc phase diagram topology with the CEF



$$\triangleright\, G = \sum_i \sum_j \sum_k \sum_l y_i^\alpha y_j^\beta y_k^\gamma y_l^\delta G_{ijkl}$$

$$+RT \sum_s \sum_i \frac{1}{4} y_i^s \ln y_i^s$$

$$+ \sum_s \sum_{r>s} y_A^s y_B^s y_A^r y_B^r L_{AB:AB:*:*}$$

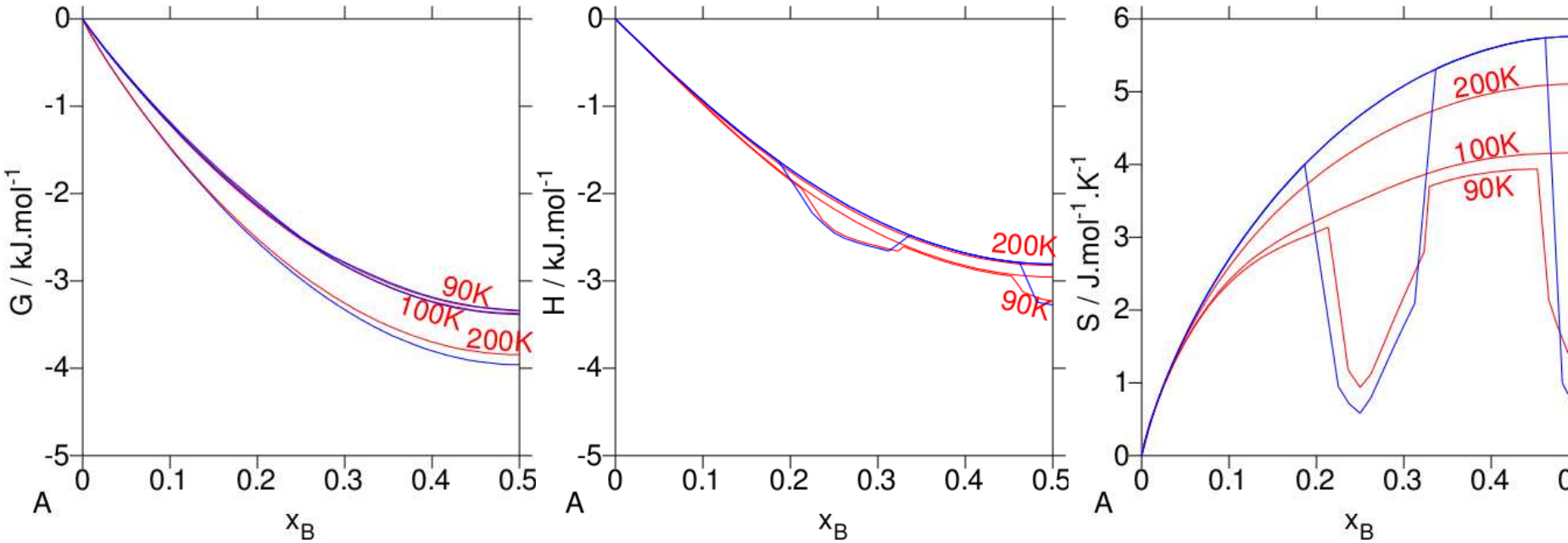
with $G_{A3B} = 3\,\epsilon_{AB}$, $G_{A2B2} = 4\,\epsilon_{AB}$,

and $L_{AB:AB:*:*} = \epsilon_{AB}$ (reciprocal)

▷ Tetrahedron CVM prototype using the same pairwise energy

4SL Order-Disorder CEF

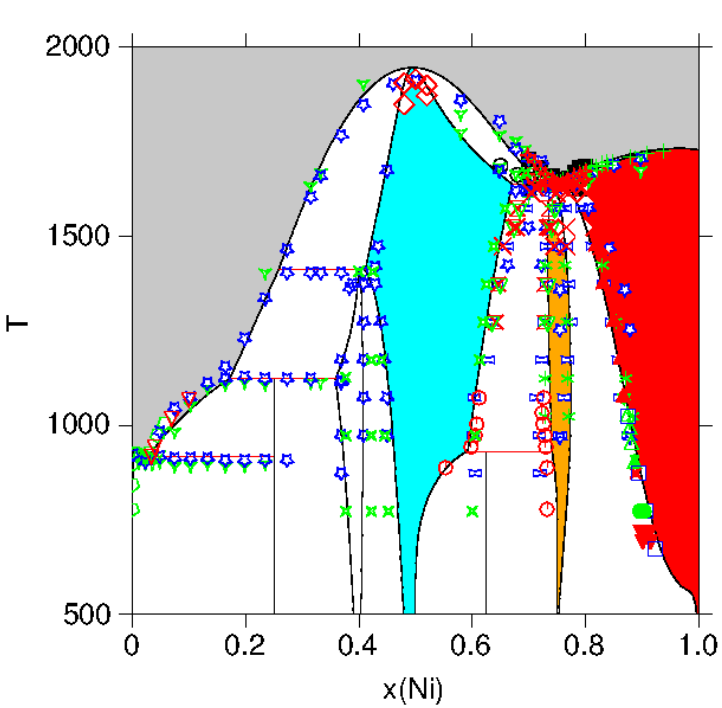
A way to get proper fcc phase diagram topology with the CEF



F. Körman et al., Phys. Status Solidi B, 251 (1), 53-80 (2014)

4SL Order-Disorder CEF

B. Sundman, N. Dupin, JEEP 2003, Lyon



γ and γ' : a single CEF

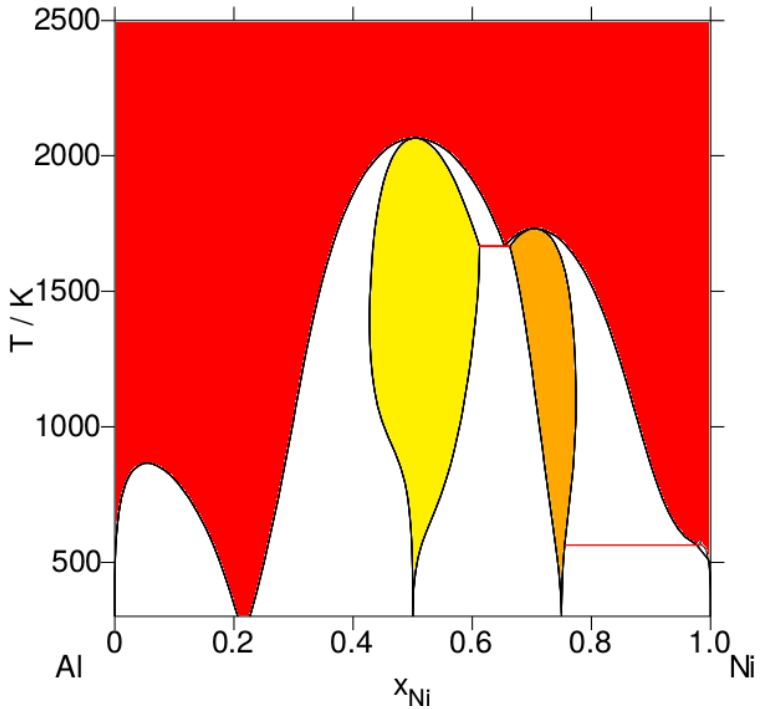
- splitting disorder description

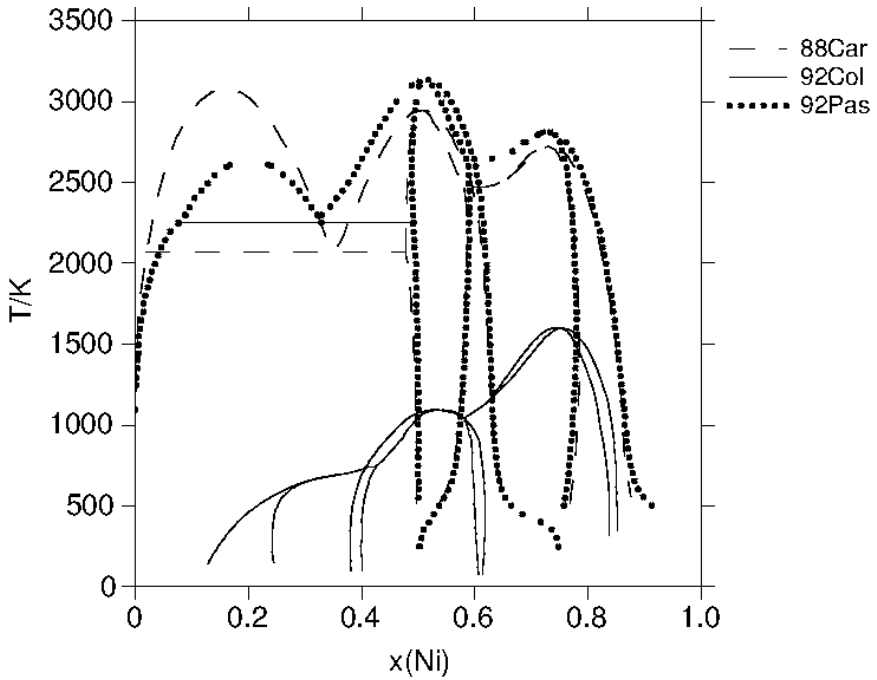
  $G = G^{dis}(x) + G^{ord}(y) - G^{ord}(x)$

- $G^{dis}(x) = G^{ord}(x)$
- G_{Al_3Ni} and $G_{Al_2Ni_2}$ assessed from FP
- Reciprocal interaction parameter allows proper fcc metastable topology

4SL Order-Disorder CEF

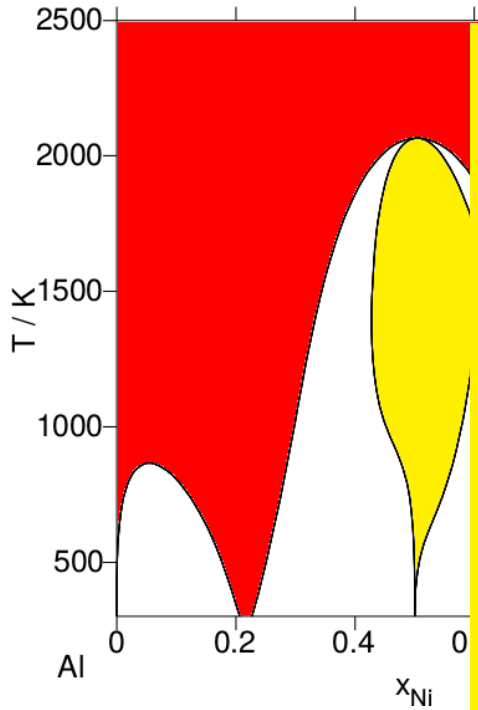
B. Sundman, N. Dupin, JEEP 2003, Lyon





4SL Order-Disorder CEF

B. Sundman, N. Dupin, JEEP 2003, Lyon



$$G^{ord}(y) =$$

$$\sum_i \sum_j \sum_k \sum_l y_i^{\alpha} y_j^{\beta} y_k^{\gamma} y_l^{\delta} G^{ord}_{ijkl}$$

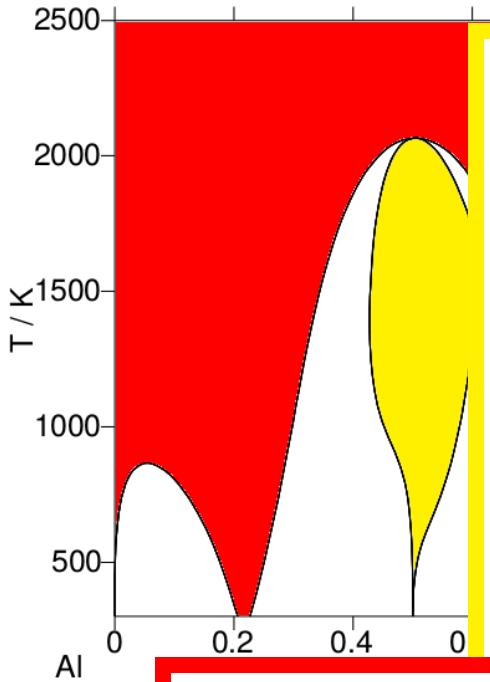
$$+\frac{1}{4} RT \sum_s \sum_i y_i^s \ln y_i^s$$

$$+\sum_s \sum_i \sum_{j>i} y_i^s y_j^s L^{ord}_{ij:*:*:*}$$

$$+\sum_s \sum_{r>s} \sum_i \sum_{j>i} y_i^s y_j^s y_i^r y_j^r L^{ord}_{ij:ij:*:*}$$

4SL Order-Disorder CEF

B. Sundman, N. Dupin, JEEP 2003, Lyon



$$G^{ord}(y) = \sum_i \sum_j \sum_k \sum_l y_i^{\alpha} y_j^{\beta} y_k^{\gamma} y_l^{\delta} G^{ord}_{ijkl} + \frac{1}{4} RT \sum_s \sum_i y_i^s \ln y_i^s + \sum_s \sum_i \sum_{j>i} y_i^s y_j^s L^{ord}_{ij:*:*:*}$$

$$G^{dis}(x) = \sum_i G_i^{dis} + RT \sum_i x_i \ln x_i + \sum_i \sum_{j>i} x_i x_j \sum_n (x_i - x_j) Ln_{ij}^{dis}$$

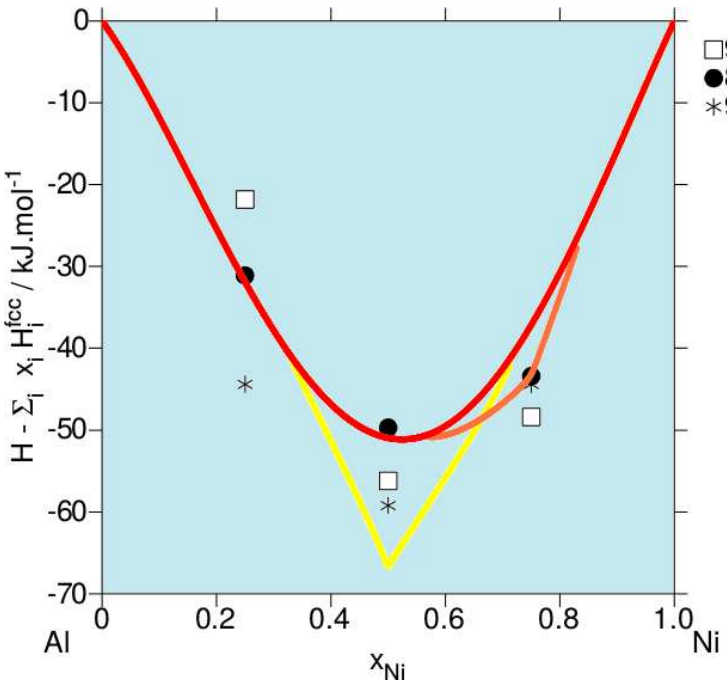
$$with\ L0_{ij}^{dis} = G^{ord}_{i_3 j} + 1.5 G^{ord}_{i_2 j_2} + G^{ord}_{ij_3} + 1.5 L^{ord}_{ij:ij:*:*} + 4 L^{ord}_{ij:*:*:*}$$

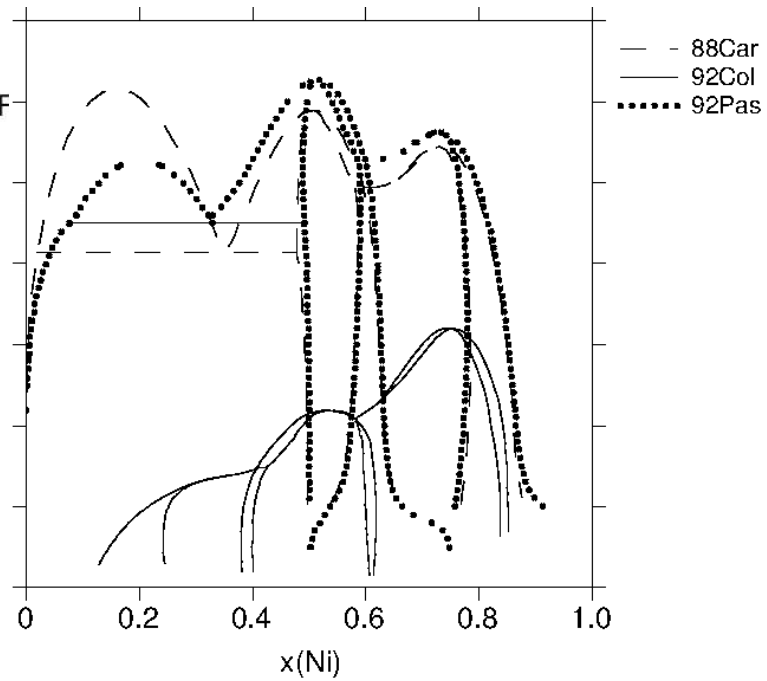
...

A. Kussoffsky et al. Calphad 25 (2001) 549

4SL Order-Disorder CEF

B. Sundman, N. Dupin, JEEP 2003, Lyon





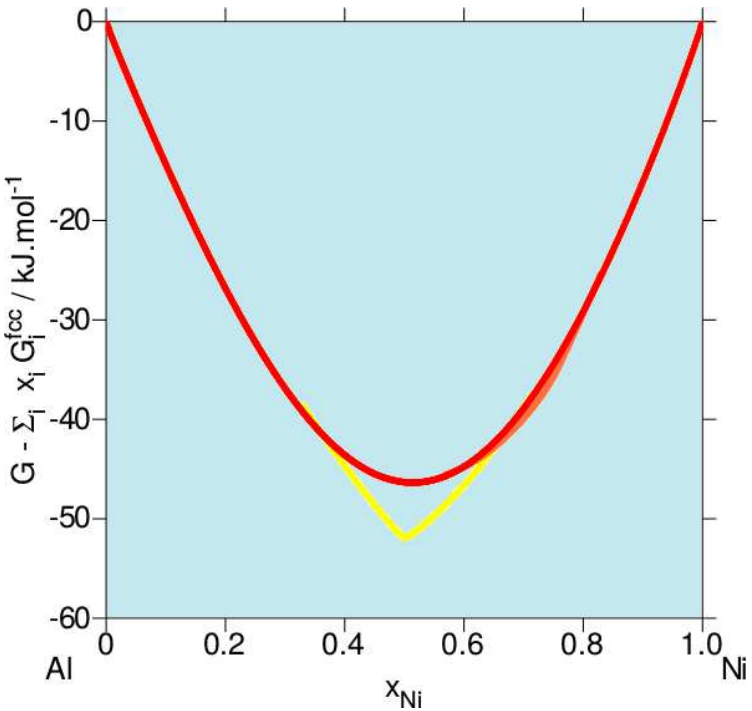
A.E. Carlsson, J.M. Sanchez, Solid State Communications, 65 (1988), 527

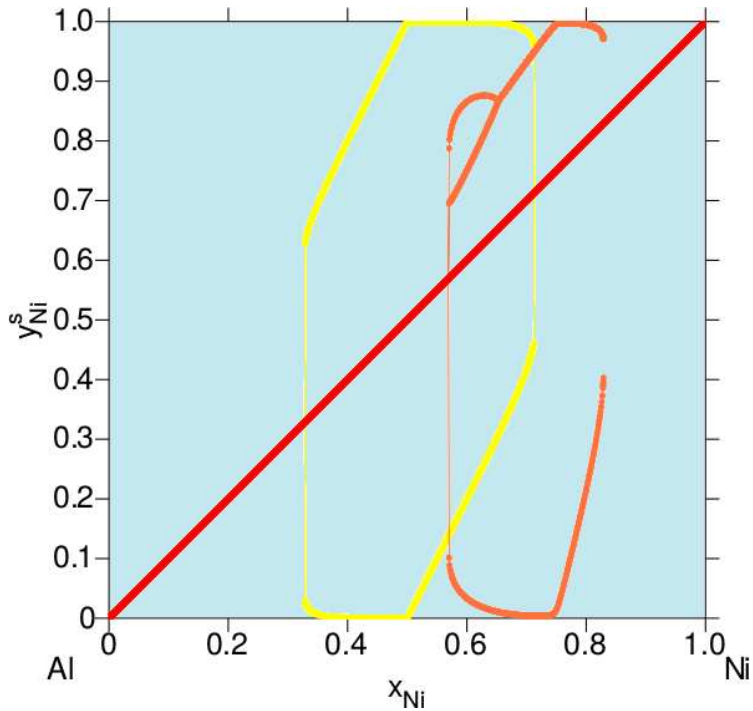
C. Colinet, P. Hicter, A. Pasturel, Phys. Rev. B, 45 (1992), 1571

A. Pasturel, C. Colinet, A.T. Paxton, M. van Schifgaarde, J. Phys.: Condens Matter, 4 (1992) 945

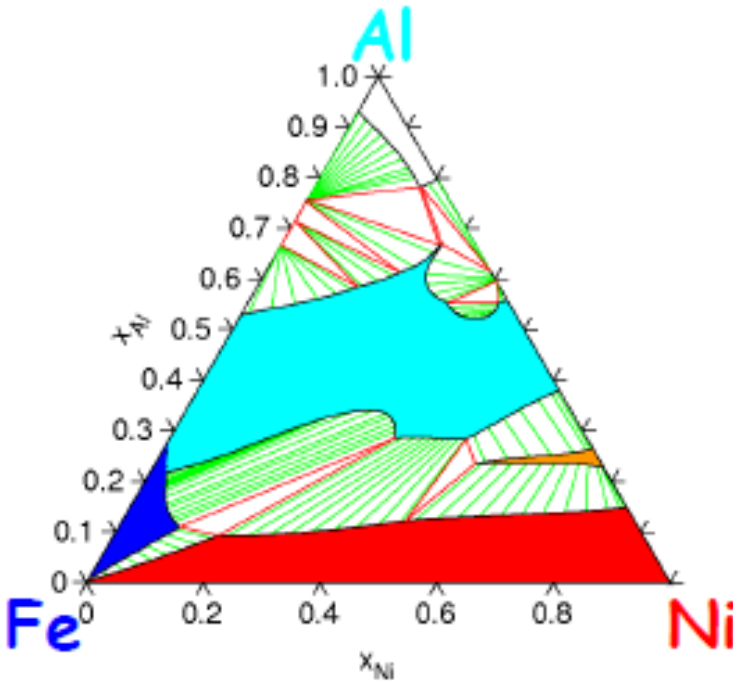
4SL Order-Disorder CEF

B. Sundman, N. Dupin, JEEP 2003, Lyon



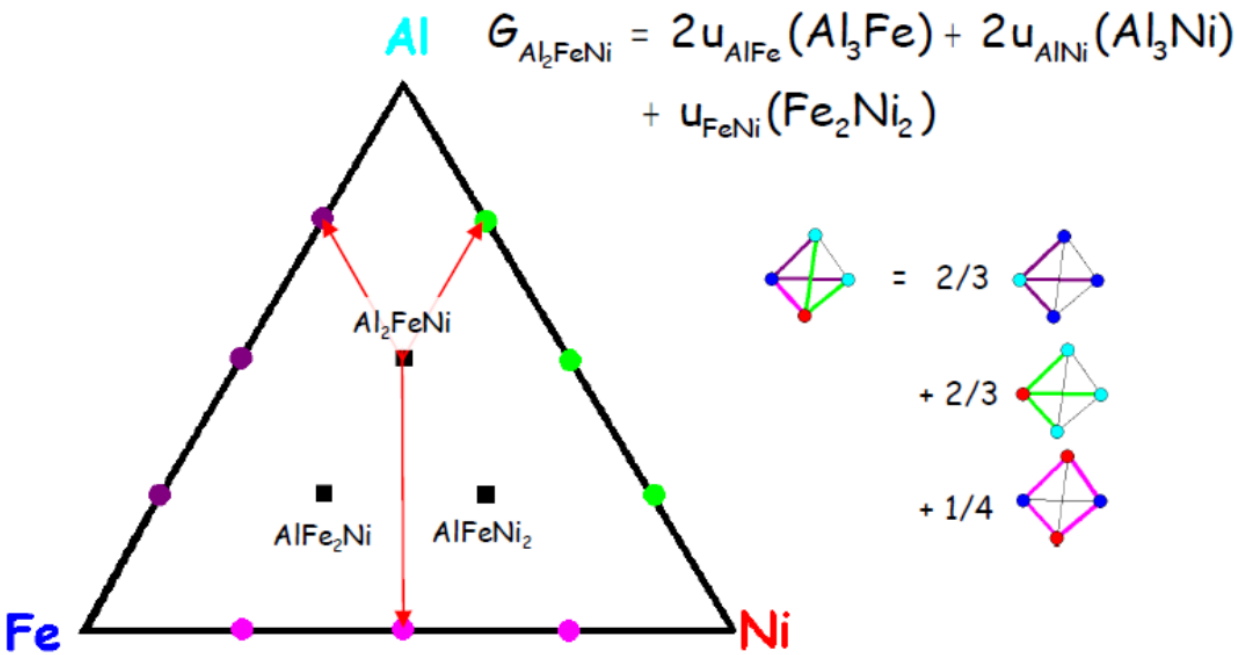


Application to ternaries



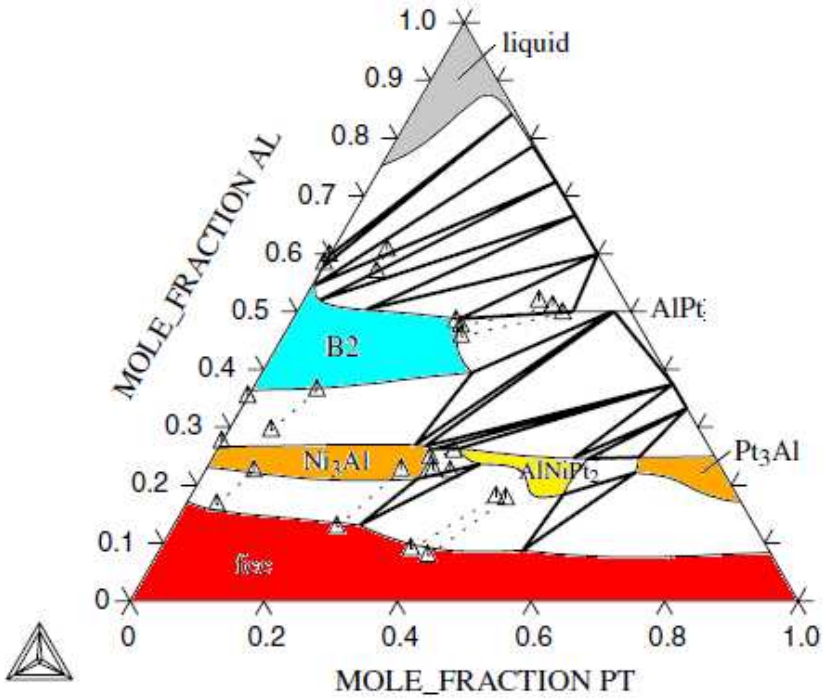
N. Dupin et al., Grenoble 2006

Application to ternaries



N. Dupin et al., Grenoble 2006

Application to ternaries



X.G. Lu et al., Calphad 33 (2009) 450.

Conclusions

- In order to derive a Calphad thermodynamic description of quality, **experimental** phase diagram, crystallographic structure, enthalpy of mixing, of formation, of transition, Cp, activities, chemical potentials, ... should be taken into account **as well as** FP enthalpies of formation, cell volume, defects, CE-CVM/MC phase diagram...

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- The current multicomponent thermodynamic database could be improved by the use of a real 4SL model.

Conclusions

- In order to derive a Calphad thermodynamic description of quality, **experimental** phase diagram, crystallographic structure, enthalpy of mixing, of formation, of transition, Cp, activities, chemical potentials, ... should be taken into account **as well as** FP enthalpies of formation, cell volume, defects, CE-CVM/MC phase diagram...
- The current multicomponent thermodynamic database could be improved by the use of a real 4SL model.
- Will another better model appear soon? When will a more *acurate* approximation describe a 10 elements system with appealing computational time, appealing agreement with experiments?