Challenges in the development of large thermodynamic databases

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Low Impact Buildings
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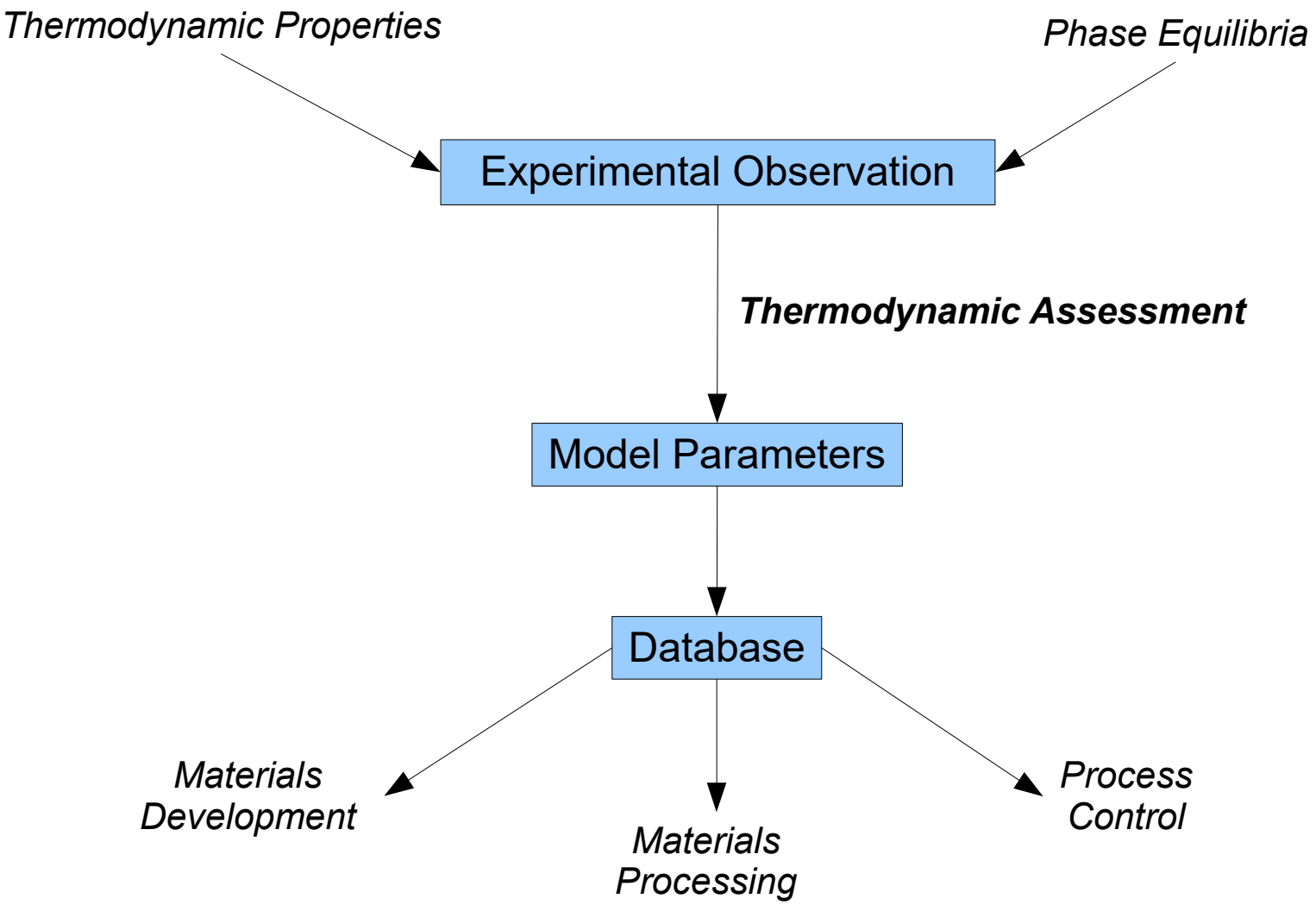
Outline

- Why the *Calphad* method?
- Datasets, databases and collections
- *So, you want a database?*
  - How to put one together
- *What do I do next?*
  - Documentation, feedback & maintenance.

Advantages of the Calphad Method



Advantages of the Calphad Method

- Bottom-up approach
  - Unary systems → binary systems → ternary systems...
- Experimentally inaccessible parts of the system can by studied by extrapolation/interpolation.
  - Reduces time and therefore costs
- Other calculation techniques (*ab initio*) are far more computationally intensive.
- *Good databases can lead to very flexible calculations*

Dataset? Collection? Database?

- *Dataset*
  - Complete set of assessed Gibbs energy descriptions of all phases within a system.
    - Generally binary or ternary system. In principle could be of higher-order.
- *Collection*
  - A collection of datasets that are not necessarily connected with one another.
    - Datasets must only be used in isolation.

Dataset? Collection? Database?

- *Database*
  - A collection of datasets that are completely consistent with one another.
    - Follows the *Kroupa rules* of database consistency
  - Allow temperature/composition(/pressure) space *between* the datasets to be investigated.

So, you want a database?

- Define the Scope
  - Database for a specific purpose – SOLDERS
    - Decide on components (elements) and modelling complexity beforehand
      - Complexity increases with the order of the system
  - General database – SGSOL
    - More difficult to manage
- Sources of data
  - Scientific literature
  - Data generated as part of the project

Kroupa Rules

- *Expression for the composition dependence of Gibbs energy should be fixed for the whole database*
  - Redlich-Kister polynomial

$$G_E^{\Phi} = x_i x_j \sum_{z=0}^{m} {}^{z}L \left(x_i - x_j \right)^z$$

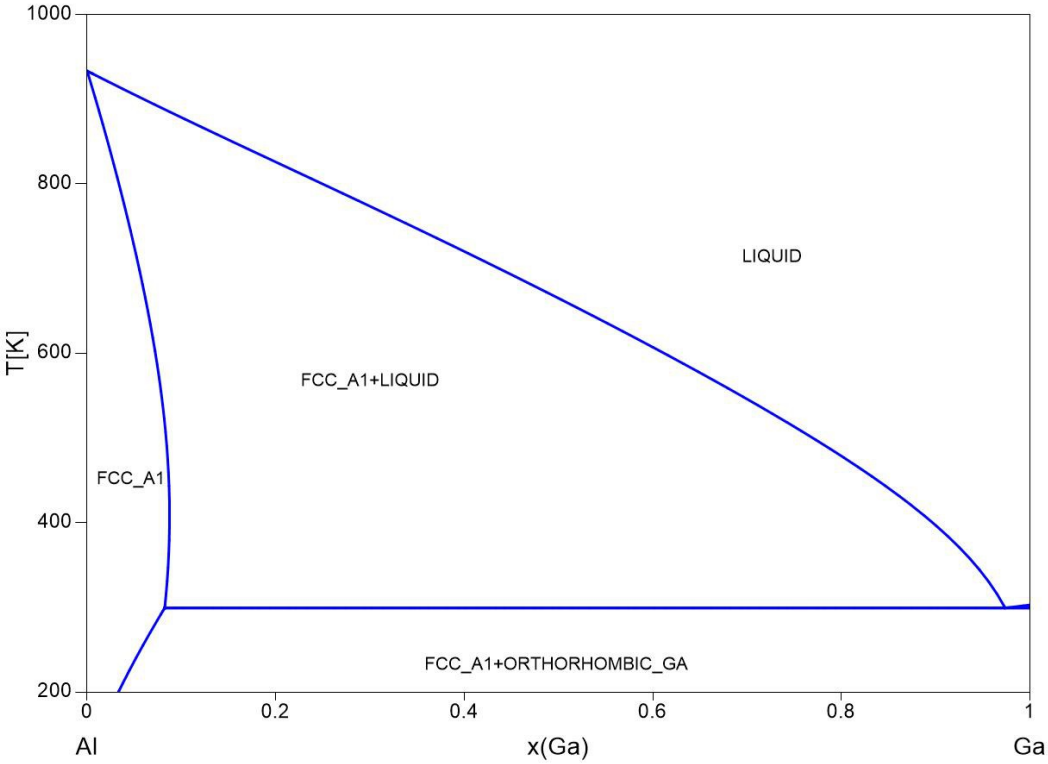
  - Muggianu for ternary extrapolation of binary excess Gibbs energies
    - Can be a problem if datasets come from multiple sources

Kroupa Rules

- Order of elements in excess terms.
  - Stick to alphabetical order – check results

$$G_E^{\Phi} = x_i x_j \sum_{z=0}^{m} {}^{z}L\left(x_i - x_j\right)^z$$

Kroupa Rules




```
$ Al-Ga system
$ A Watson Calphad 1992, 16(2), 207-217
$ "Re-assessment of  PHASE diagram and thermodynamic properties of the
$  Al-Ga system"

 PARAMETER L(LIQUID,AL,GA;0) 298.15 2613.3-2.94533*T; 6000 N AlGa !
 PARAMETER L(LIQUID,AL,GA;1) 298.15 692.4-0.09271*T; 6000 N AlGa !
 PARAMETER L(LIQUID,AL,GA;2) 298.15 319.5; 6000 N AlGa !

 PARAMETER L(FCC_A1,AL,GA:VA;0) 298.15 9195.8+8.18764*T; 6000 N
AlGa !
 PARAMETER L(FCC_A1,AL,GA:VA;1) 298.15 -7678.5; 6000 N AlGa !

$ ========================
$ For MTDATA user remove $
$ ========================
$# PARAMETER L(FCC_L12,AL,GA:VA;0) 298.15 9195.8+8.18764*T; 6000 N
AlGa !
$# PARAMETER L(FCC_L12,AL,GA:VA;1) 298.15 -7678.5; 6000 N AlGa !
$ ========================

 PARAMETER L(HCP_A3,AL,GA:VA;0) 298.15 9195.8+8.18764*T; 6000 N
AlGa !
 PARAMETER L(HCP_A3,AL,GA:VA;1) 298.15 -7678.5; 6000 N AlGa !

 PARAMETER L(BCT_A5,AL,GA;0) 298.15 80*T; 6000 N AlGa !
$ ============================
```

Kroupa Rules

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$ ========================
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AlGa !
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AlGa !
 PARAMETER L(HCP_A3,AL,GA:VA;1) 298.15 -7678.5; 6000 N AlGa !

 PARAMETER L(BCT_A5,AL,GA;0) 298.15 80*T; 6000 N AlGa !
$ ============================
```

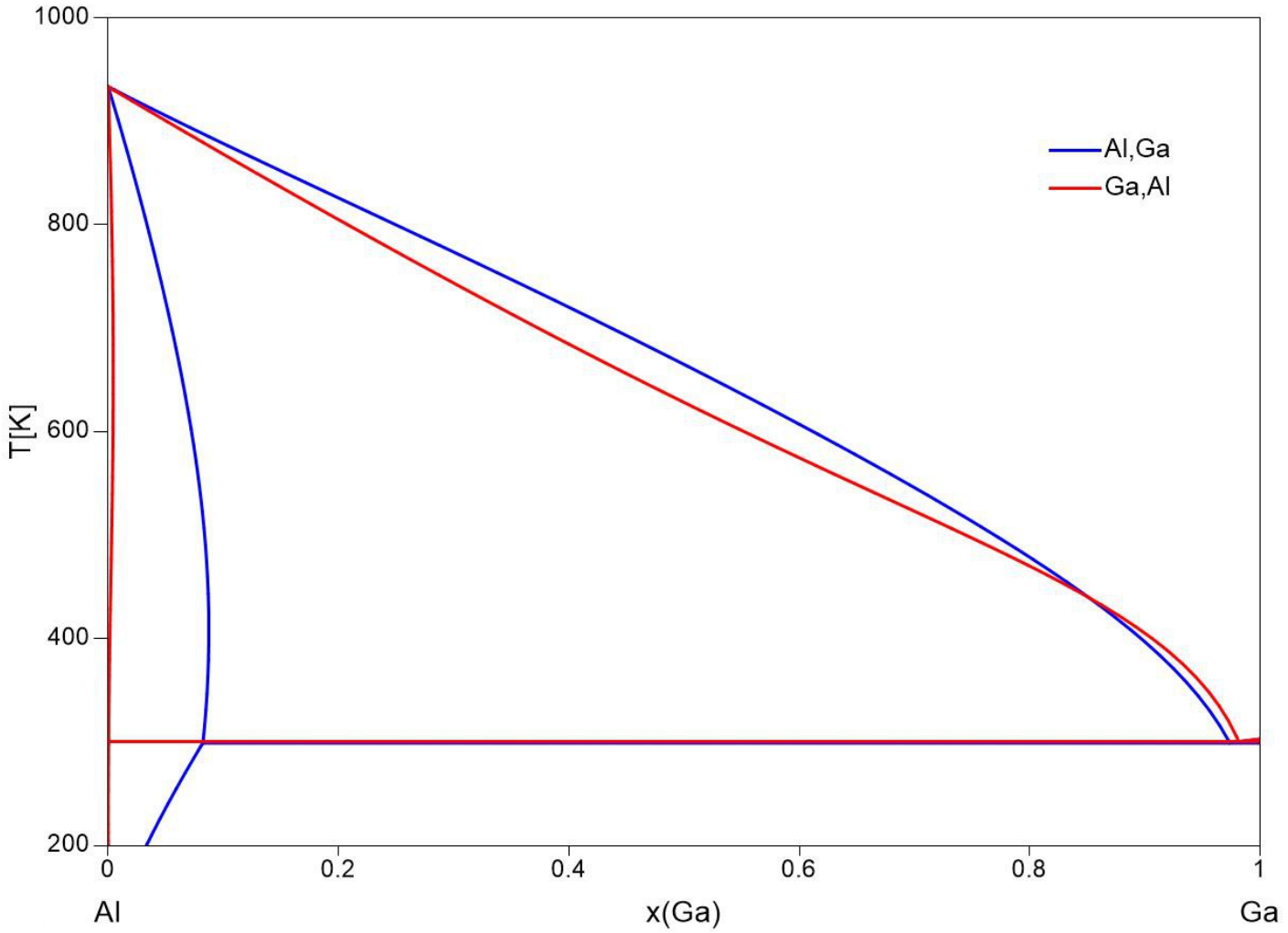
```
  PARAMETER G(LIQUID,AL;0) 298.15 +GLIQAL#; 2900 N REF0 !
  PARAMETER G(LIQUID,GA;0) 200 +GLIQGA#; 4000 N REF0 !
  PARAMETER G(LIQUID,GA,AL;0) 298.15 +2613.3-2.94533*T; 6000 N
REF73 !
  PARAMETER G(LIQUID,GA,AL;1) 298.15 +692.4-.09271*T; 6000 N REF73 !
  PARAMETER G(LIQUID,GA,AL;2) 298.15 +319.5; 6000 N REF73 !

  PARAMETER G(BCT_A5,AL;0) 298.15 +10083-4.813*T+GHSERAL#; 2900
N REF0 !
  PARAMETER G(BCT_A5,GA;0) 200 +3846-9.8*T+GHSERGA#; 4000 N
REF0 !
  PARAMETER G(BCT_A5,GA,AL;0) 298.15 +80*T; 6000 N REF73 !

  PARAMETER G(FCC_A1,AL:VA;0) 298.15 +GHSERAL#; 2900 N REF0 !
  PARAMETER G(FCC_A1,GA:VA;0) 200 +GFCCGA#; 4000 N REF0 !
  PARAMETER G(FCC_A1,GA,AL:VA;0) 298.15 +9195.8+8.18764*T; 6000 N
REF73 !
  PARAMETER G(FCC_A1,GA,AL:VA;1) 298.15 -7678.5; 6000 N REF73 !

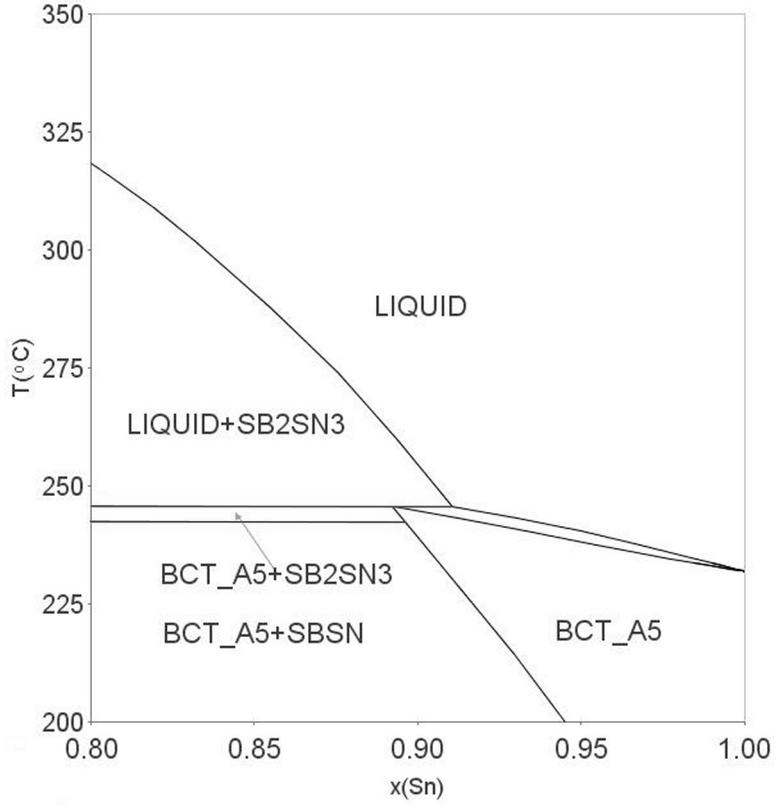
  PARAMETER G(HCP_A3,AL:VA;0) 298.15 +GHCPAL#; 2900 N REF0 !
  PARAMETER G(HCP_A3,GA:VA;0) 200 +GHCPGA#; 4000 N REF0 !
  PARAMETER G(HCP_A3,GA,AL:VA;0) 298.15 +9195.8+8.18764*T; 6000 N
REF73 !
  PARAMETER G(HCP_A3,GA,AL:VA;1) 298.15 -7678.5; 6000 N REF73 !
```

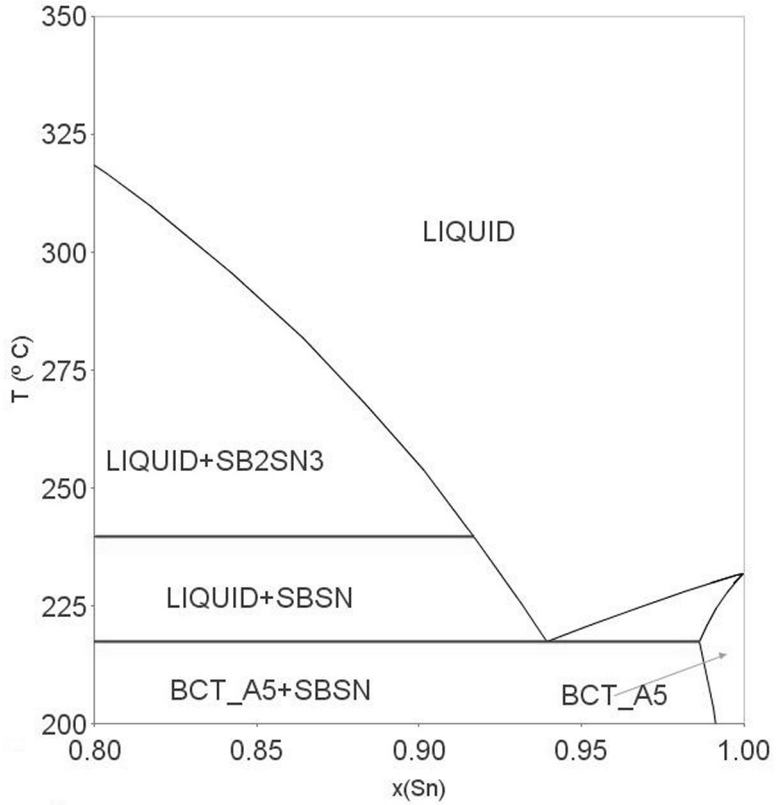
Al-Ga



Kroupa Rules

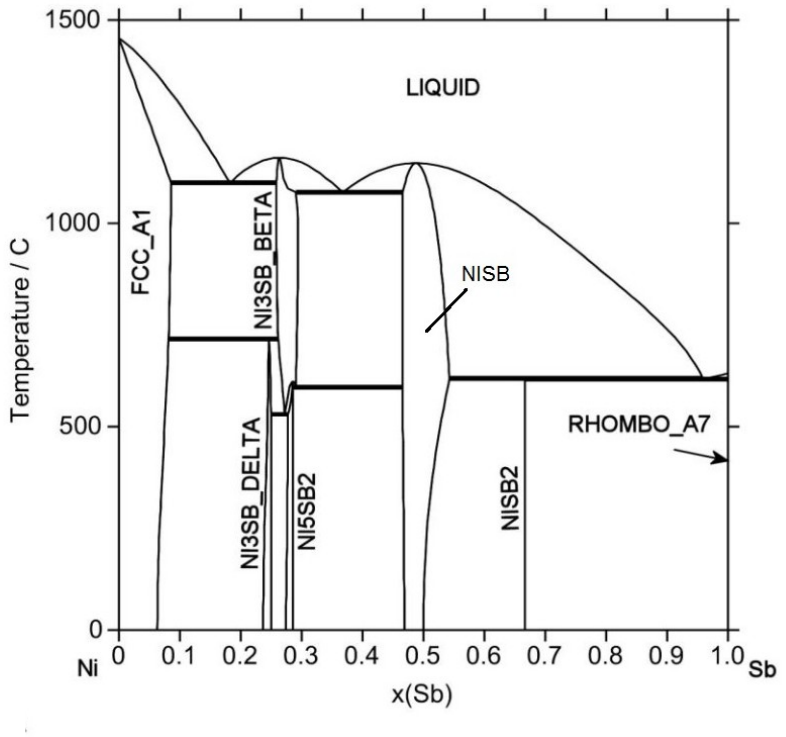
- *A single set of unary data are used for all constituents.*
  - SGTE Unary database (v4.4)

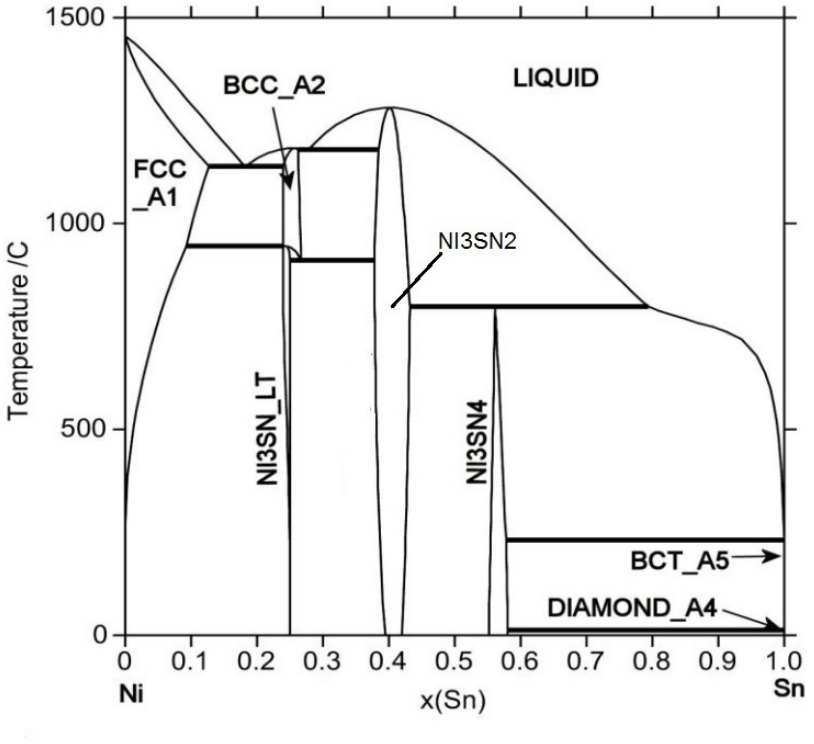


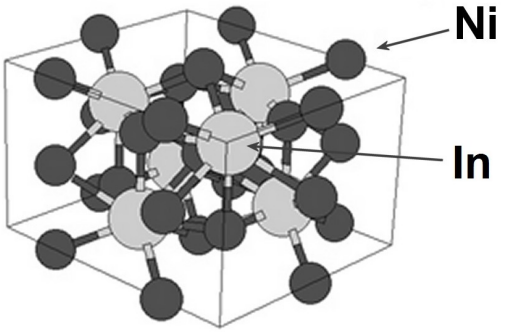


Kroupa Rules

- *Similar phases in different datasets should be modelled in the same way and the phase name used should be unique.*

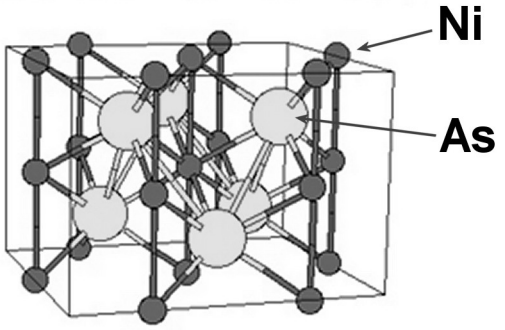


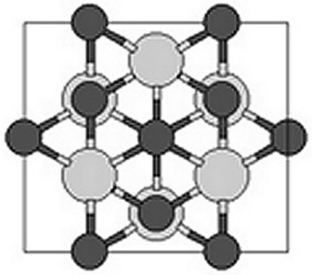




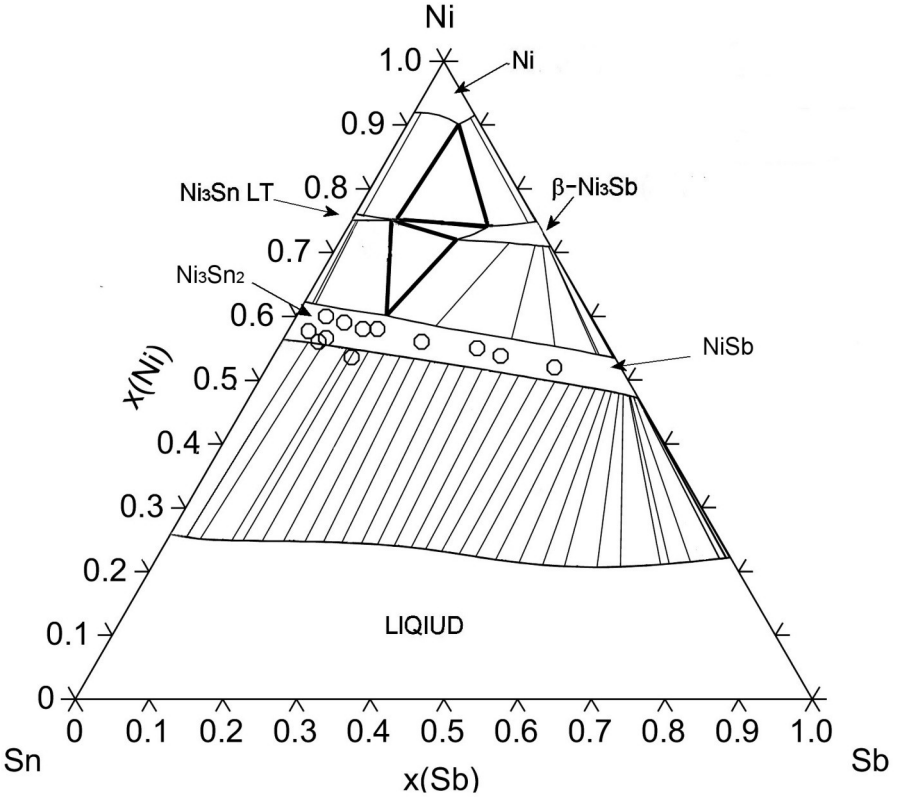
NIAS_TYPE

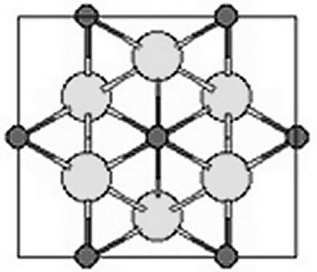
(Ni,Va) (Ni,Va) (Ni,Sb,Sn)



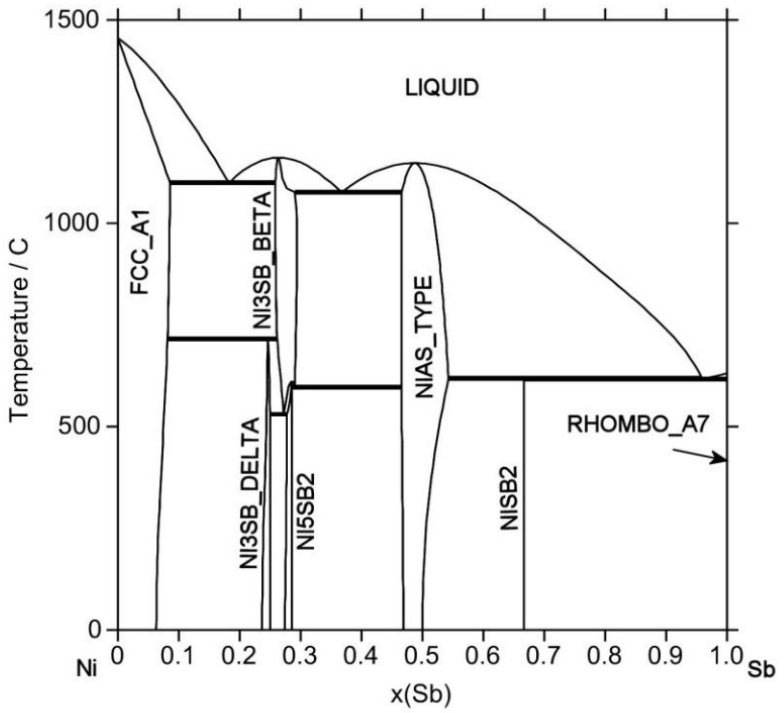


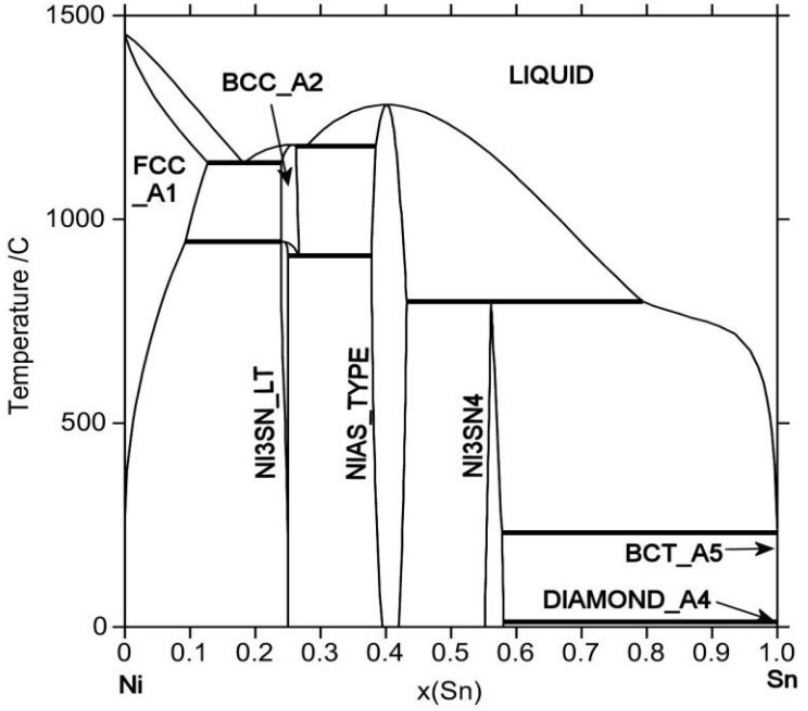
*h*P6





*h*P4


1500
1000
500
0
Temperature / C
LIQUID
FCC_A1
NI3SB_BETA
NI3SB_DELTA
NI5SB2
NIAS_TYPE
NISB2
RHOMBO_A7
Ni
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Sb
x(Sb)


1500
1000
500
0
Temperature /C
BCC_A2
LIQUID
FCC
_A1
NI3SN_LT
NIAS_TYPE
NI3SN4
BCT_A5
DIAMOND_A4
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Ni
Sn
x(Sn)

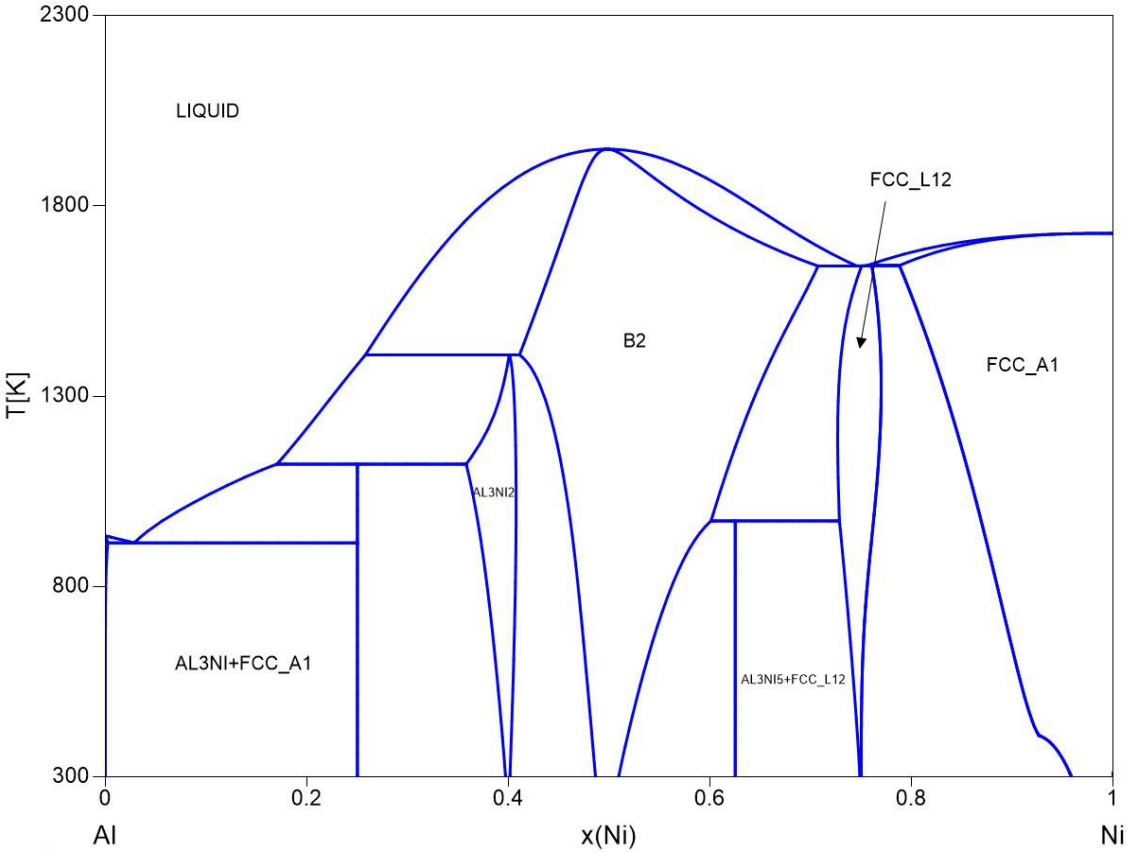
Kroupa Rules

- Fix the reference state
  - *G-HSER*
    - HSER = enthalpy of a pure component under standard conditions at 298.15K
      - H-HSER = 0

Data Challenges - Order/Disorder

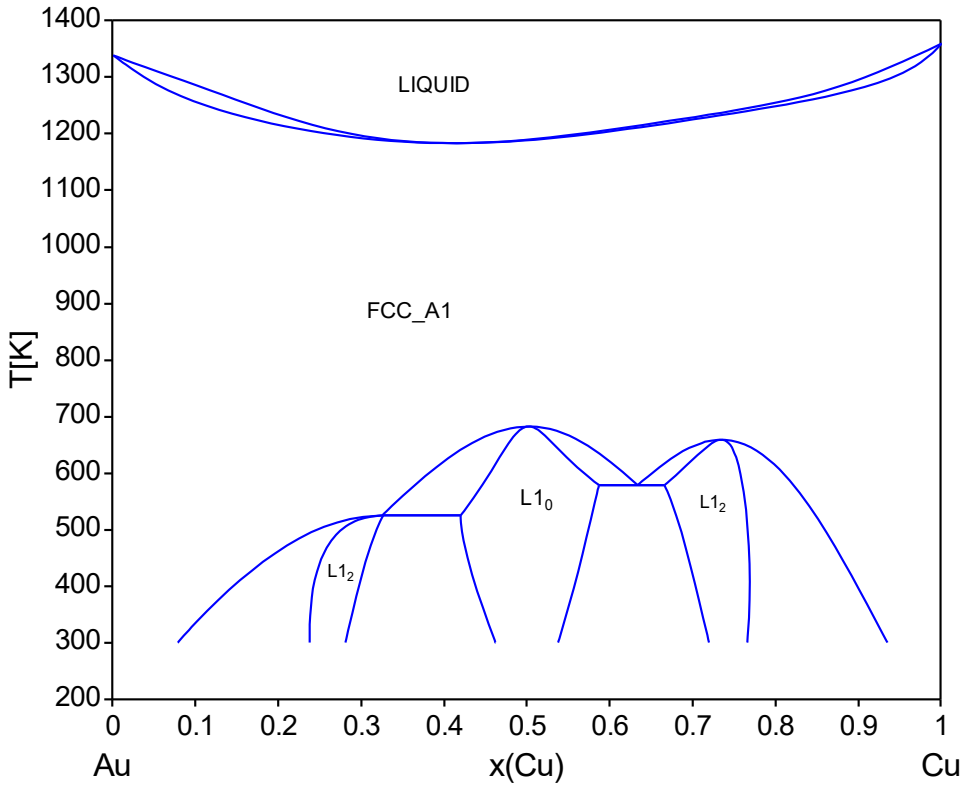
$$G_{\mathrm{m}} = G_{\mathrm{m}}^{\mathrm{dis}}(x_i) + G_{\mathrm{m}}^{\mathrm{ord}}(y_i^{'}, y_i^{''}) - G_{\mathrm{m}}^{\mathrm{ord}}(x_i)$$

- FCC_A1/L1$_2$
  - $(Al,Ni)_1\ (Va)_1$
  - $(Al,Ni)_{0.75}(Al,Ni)_{0.25}(Va)_1$
  - Data



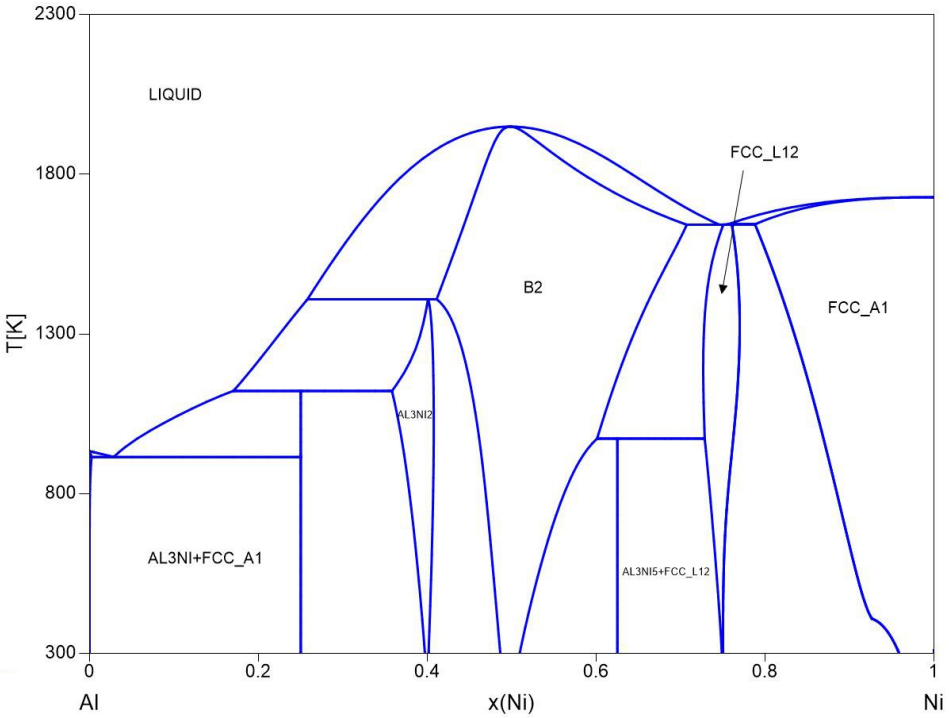
Data Challenges - Order/Disorder

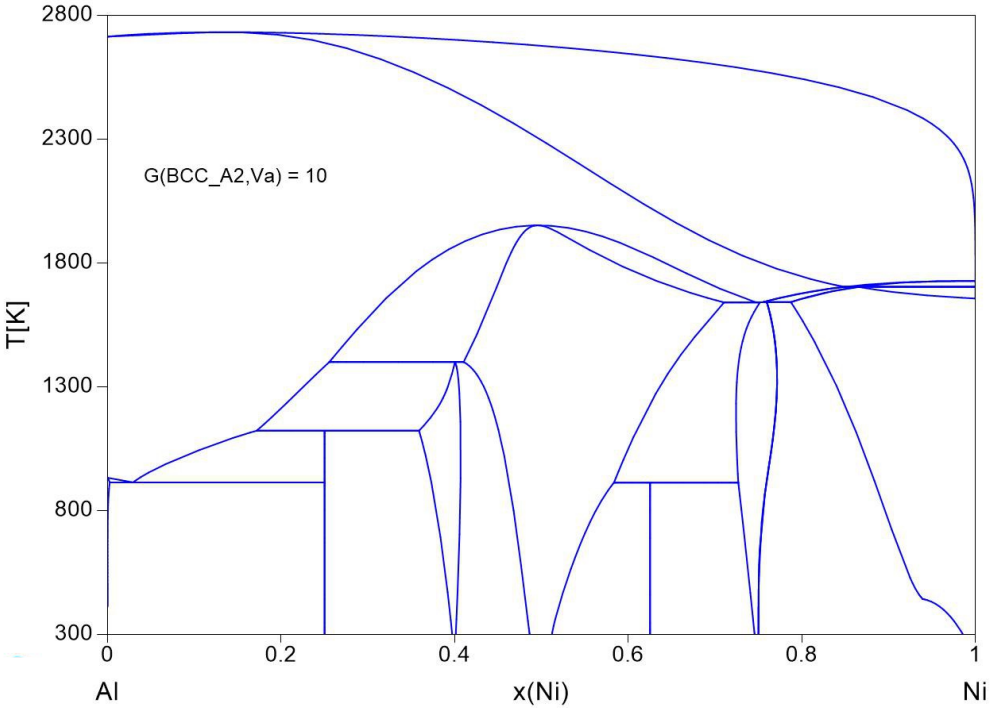
- FCC_A1/$L1_2$/$L1_0$
  - $(Au,Cu)_1\ (Va)_1$
  - $(Au,Cu)_{0.25}(Al,Cu)_{0.25}(Au,Cu)_{0.25}(Al,Cu)_{0.25}(Va)_1$
  - Data

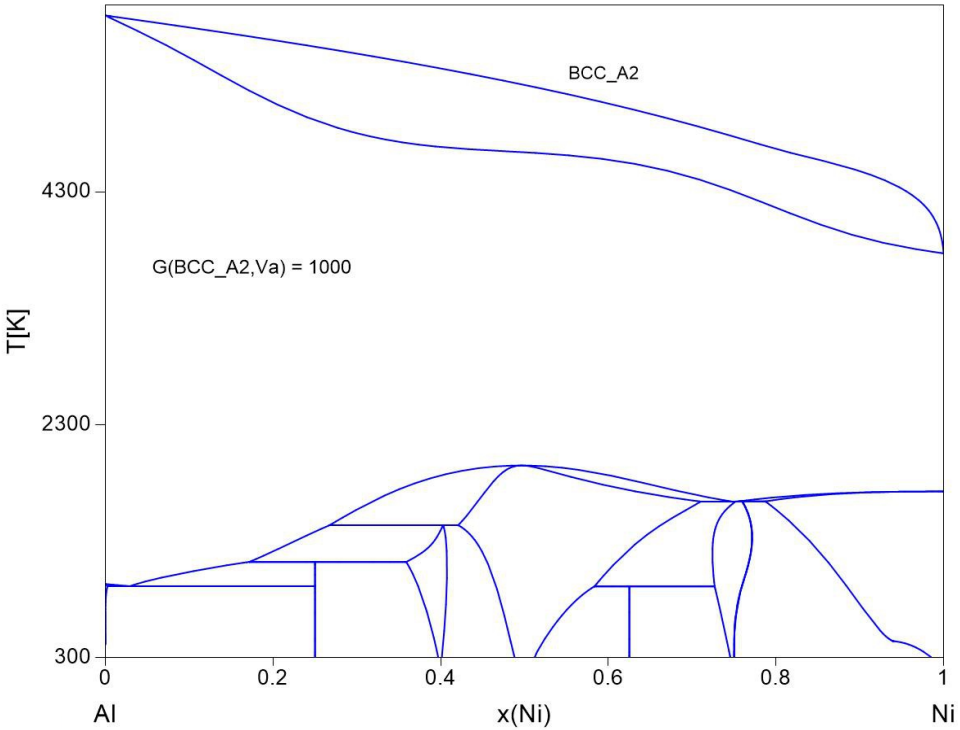


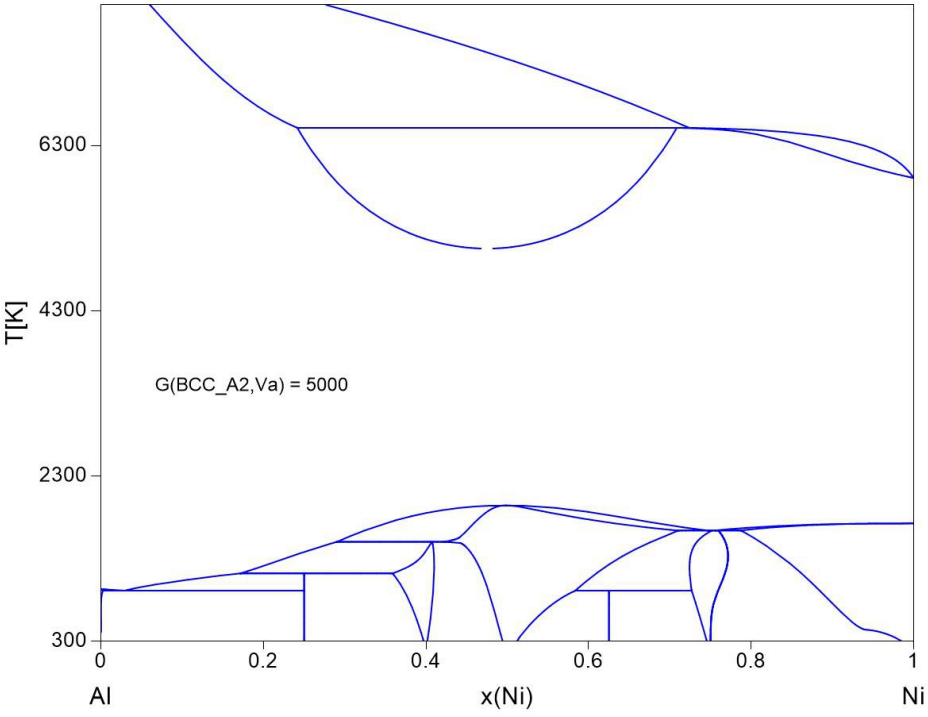
Data Challenges - Order/Disorder

- BCC_A2/BCC_B2
  - $(Al,Ni,Va)_1(Va)_3$
  - $(Al,Ni,Va)_{0.5}(Al,Ni,Va)_{0.5}(Va)_3$
- To enable the modelling of structural vacancies.
- *BUT*
  - G(BCC_A2,Va) = ?


LIQUID
FCC_L12
B2
FCC_A1
AL3NI2
AL3NI+FCC_A1
AL3NI5+FCC_L12
T[K]
2300
1800
1300
800
300
0
0.2
0.4
0.6
0.8
1
Al
x(Ni)
Ni


G(BCC_A2,Va) = 10
T[K]
2800
2300
1800
1300
800
300
0
0.2
0.4
0.6
0.8
1
Al
x(Ni)
Ni


BCC_A2
G(BCC_A2,Va) = 1000
T[K]
4300
2300
300
0
0.2
0.4
0.6
0.8
1
Al
x(Ni)
Ni


G(BCC_A2,Va) = 5000
T[K]
6300
4300
2300
300
0
0.2
0.4
0.6
0.8
1
Al
x(Ni)
Ni

B2 phases

```
 PHASE BCC_A2 %B 2 1 3 !
 CONST BCC_A2 : AG AL AM AS AU BA% BE BI CA CD CE CO CR%
    CS% CU DY ER EU FE% GA GD GE HF HO IN IR K% LA LI% MG MN MO%
    NA% NB% ND NI NP O OS P PA PB PD PR PT PU RB% RE RH RU
    S SB SC SI SM SN SR TA% TB TC TH TI% TL TM U V% W% Y YB ZN
    ZR : B C H N VA% : !

 PHASE BCC_B2 %BX 3 .5 .5 3 !
$ ****************************
$ For MTDATA implementation
$# PHASE BCC_B2 C 3 .5 .5 3 !
$# PHASE BCC_B2 C 2 1 3 !
$ ****************************
 CONST BCC_B2 : AG AL AM AS AU BA% BE BI CA CD CE CO CR%
    CS% CU DY ER EU FE% GA GD GE HF HO IN IR K% LA LI% MG MN MO%
    NA% NB% ND NI NP O OS P PA PB PD PR PT PU RB% RE RH RU
    S SB SC SI SM SN SR TA% TB TC TH TI% TL TM U V% W% Y YB ZN
    ZR : AG AL AM AS AU BA% BE BI CA CD CE CO CR%
    CS% CU DY ER EU FE% GA GD GE HF HO IN IR K% LA LI% MG MN MO%
    NA% NB% ND NI NP O OS P PA PB PD PR PT PU RB% RE RH RU
    S SB SC SI SM SN SR TA% TB TC TH TI% TL TM U V% W% Y YB ZN
    ZR : B C H N VA% : !

 PHASE B2 % 2 1 1 !
 CONST B2 : AL CO IN NI PD  : VA CO NI PD : !

$ Order/disorder where there is G(VA:VA)

 PHASE A2_BCC %B 2 1 3 !
 CONST A2_BCC : CO HF VA : VA : !

 PHASE B2_BCC %BO 3 0.5 0.5 3 !
 CONST B2_BCC : CO% HF VA : CO HF% VA : VA : !
```

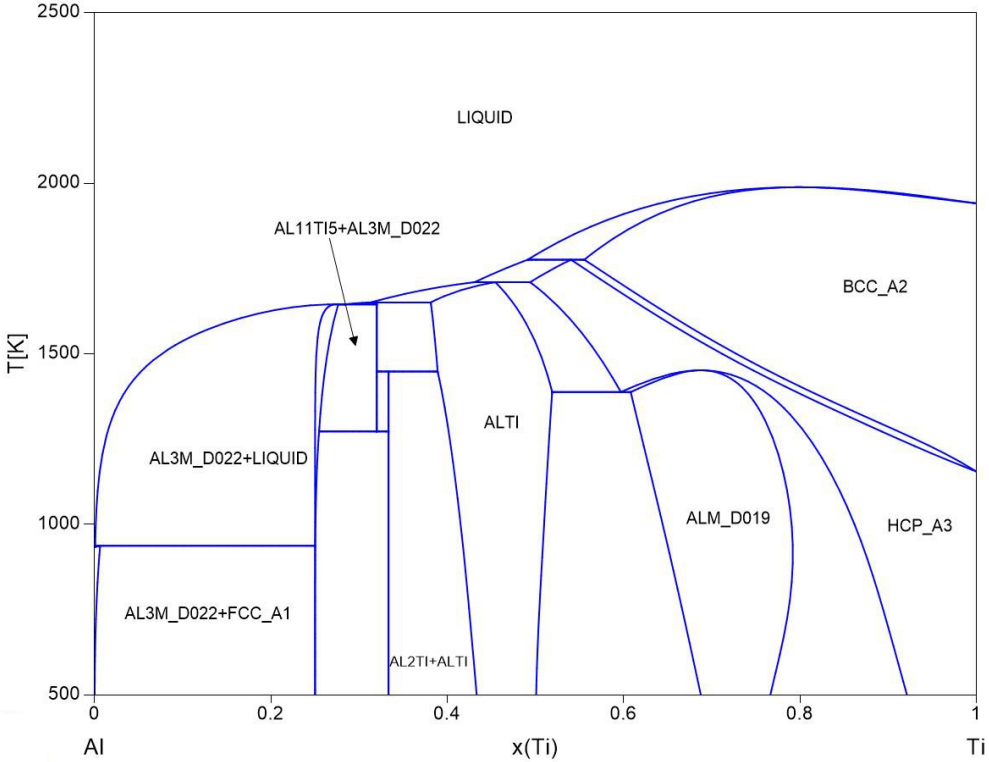
Data Challenges - Neumann-Kopp

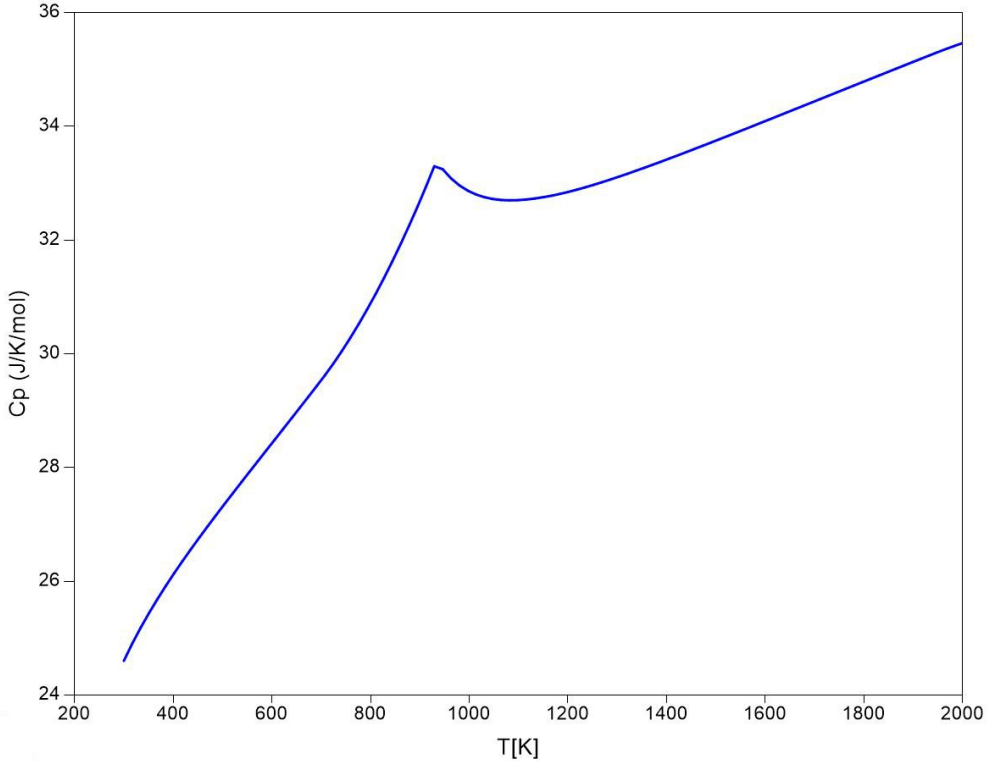
- *The molecular heat capacity of a solid compound is the sum of the atomic heat capacities of the elements composing it..*

$$^{\mathrm{o}}G^{\mathrm{A}_a\mathrm{B}_b}(T) = A + BT + a\,^{\mathrm{o}}G^{\mathrm{A}_{ref}}(T) + b\,^{\mathrm{o}}G^{\mathrm{B}_{ref}}(T)$$

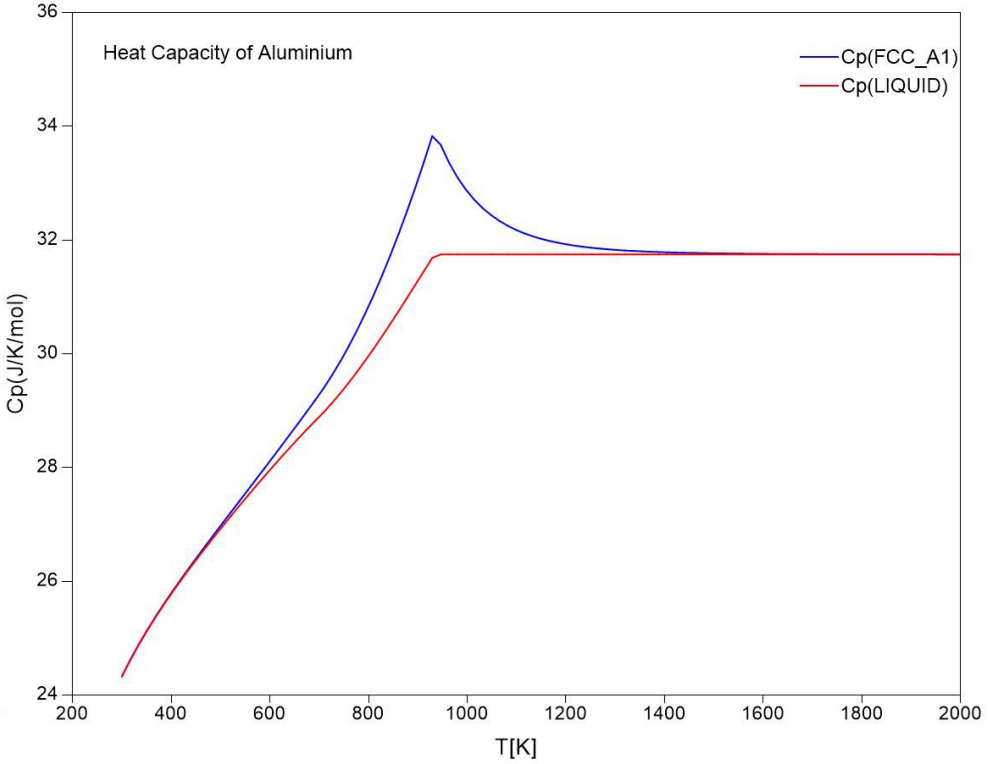
- Useful approximation
  - *BUT*

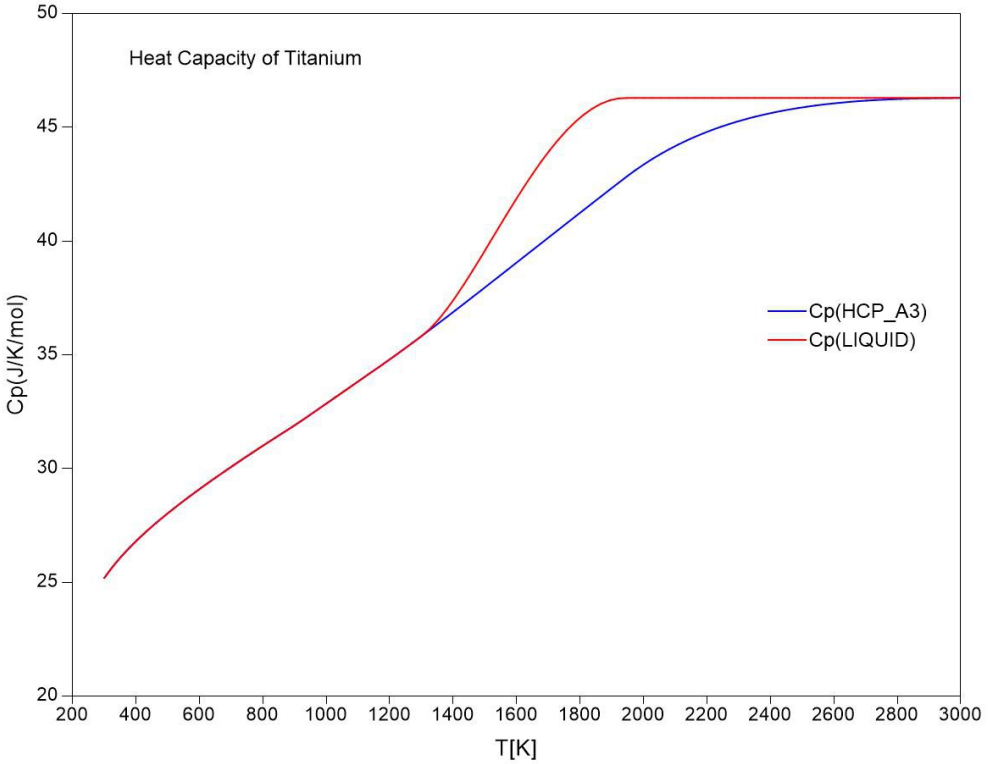
Al-Ti


LIQUID
AL11TI5+AL3M_D022
BCC_A2
ALTI
AL3M_D022+LIQUID
ALM_D019
HCP_A3
AL3M_D022+FCC_A1
AL2TI+ALTI
T[K]
2500
2000
1500
1000
500
0
0.2
0.4
0.6
0.8
1
Al
x(Ti)
Ti

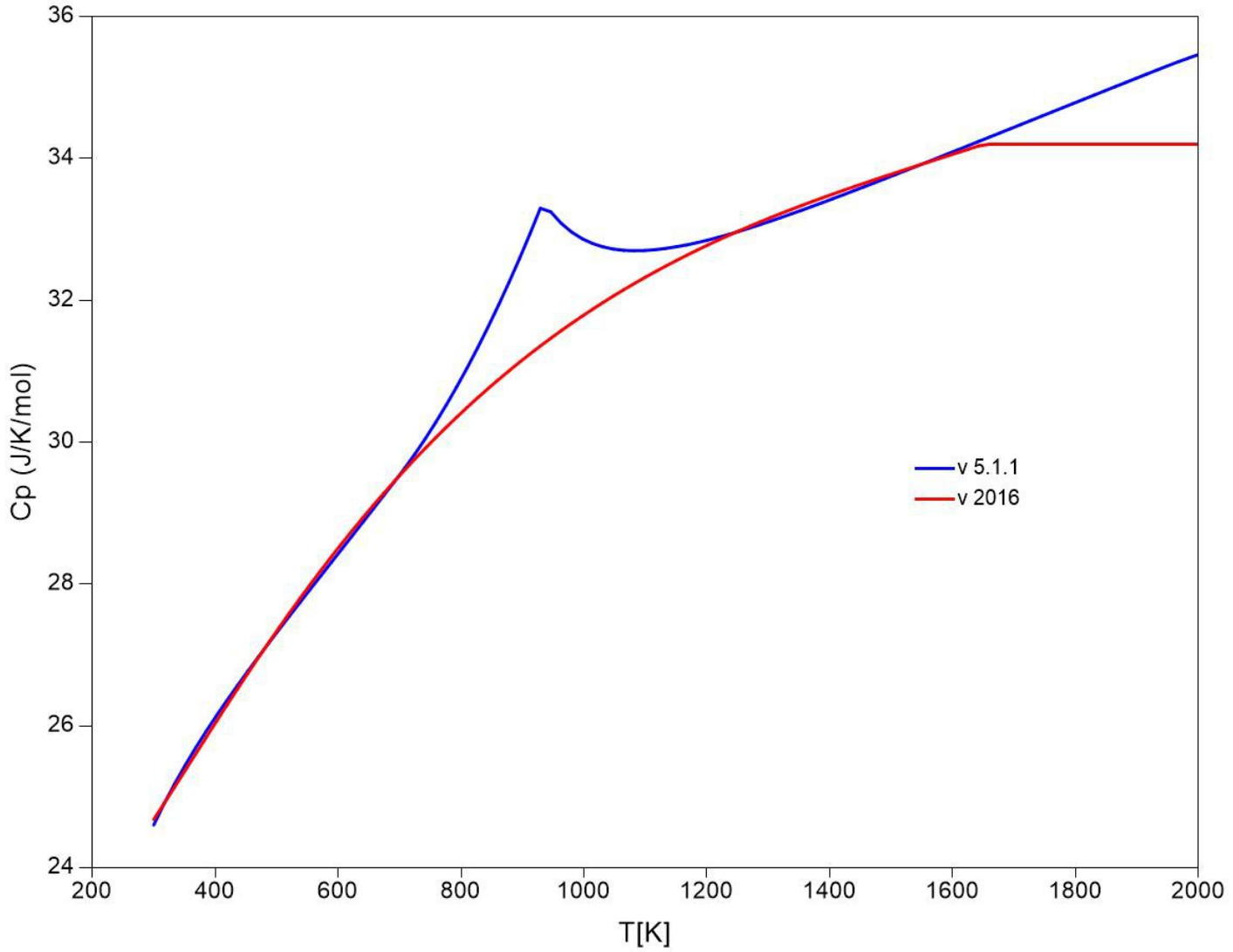

Cp (J/K/mol)
36
34
32
30
28
26
24
200
400
600
800
1000
1200
1400
1600
1800
2000
T[K]

Al-Ti – Cps of pure elements





Al-Ti – new data

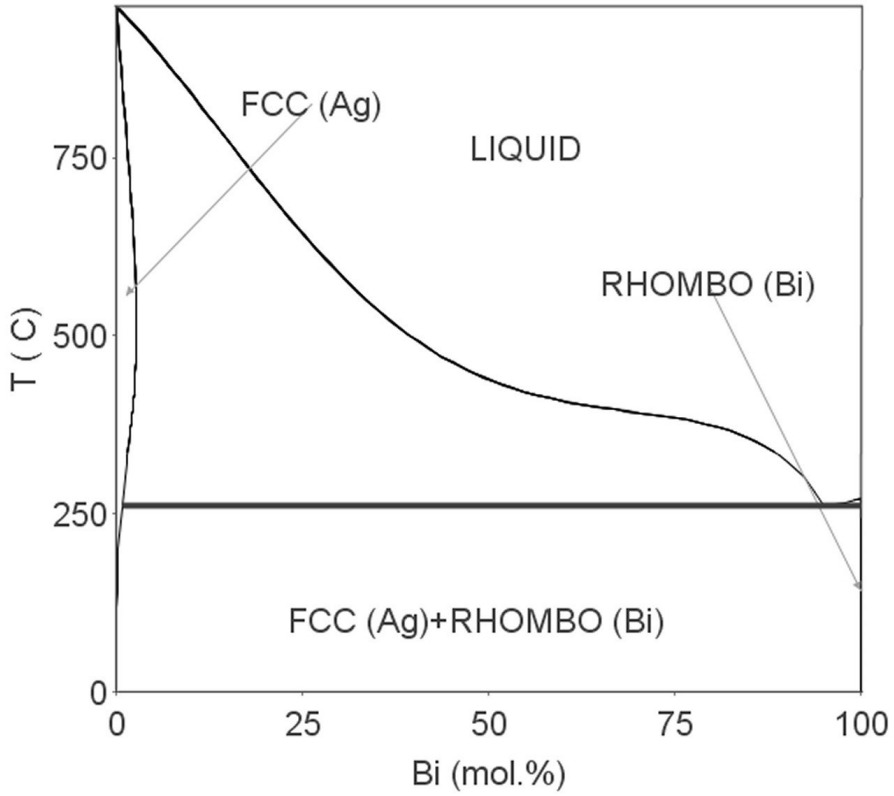


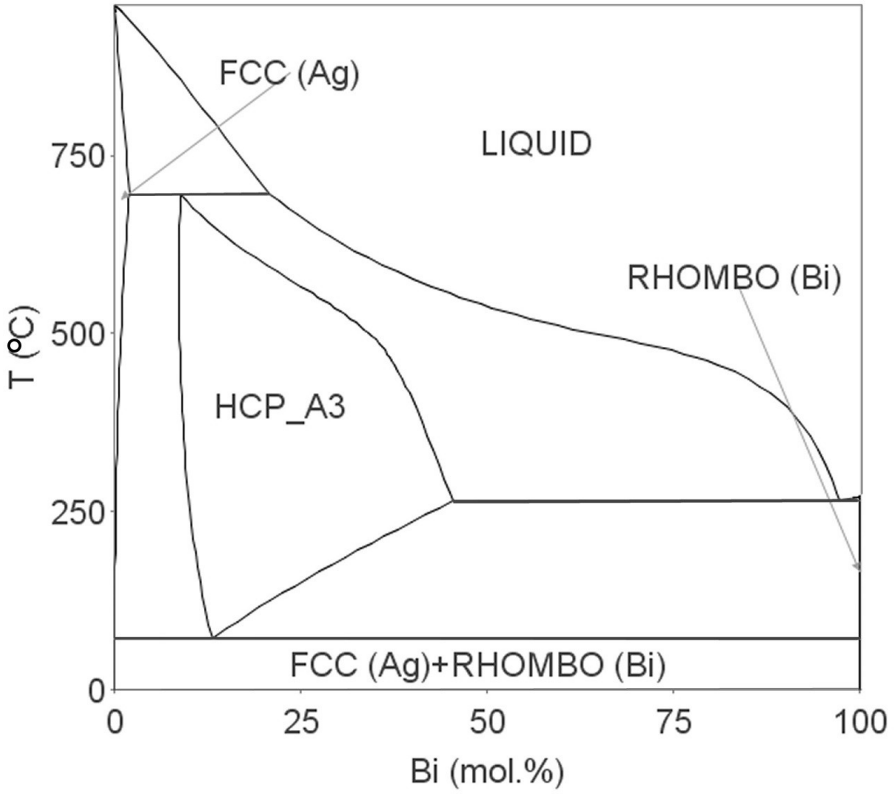
Testing

- Datasets - check with publication
  - Phase diagrams, invariants, thermodynamic properties.
- Datasets - check within databases
  - Make sure identical diagram and thermodynmaic properties are produced as when testing stand alone dataset.
    - May be changes in some unaries/lattice stabilities as these are not always transferred to the database.
- Whole database

Test with as many different software packages as possible.

Testing


FCC (Ag)
LIQUID
RHOMBO (Bi)
FCC (Ag)+RHOMBO (Bi)
T (C)
750
500
250
0
0
25
50
75
100
Bi (mol.%)


FCC (Ag)
LIQUID
RHOMBO (Bi)
HCP_A3
FCC (Ag)+RHOMBO (Bi)
T (°C)
750
500
250
0
0
25
50
75
100
Bi (mol.%)

Documentation

- List of systems
  - *What's in the database.*
- Sources of data
  - Include temperature range of applicability
- List of phases
  - Include model stoichiometry

Maintenance

- To update or not to update....
  - *What's the improvement?*
    - Modelling
    - New experimental data
      - Better phase diagram/thermodynamic properties
    - *Is there overall improvement?*
    - *What are the implications with respect to other systems in the database?*

...and finally

- *Always* encourage feedback from users
- *Always* be critical
- *Testing, testing, testing....*