Modeling of the bcc ordering using the sublattice formalism

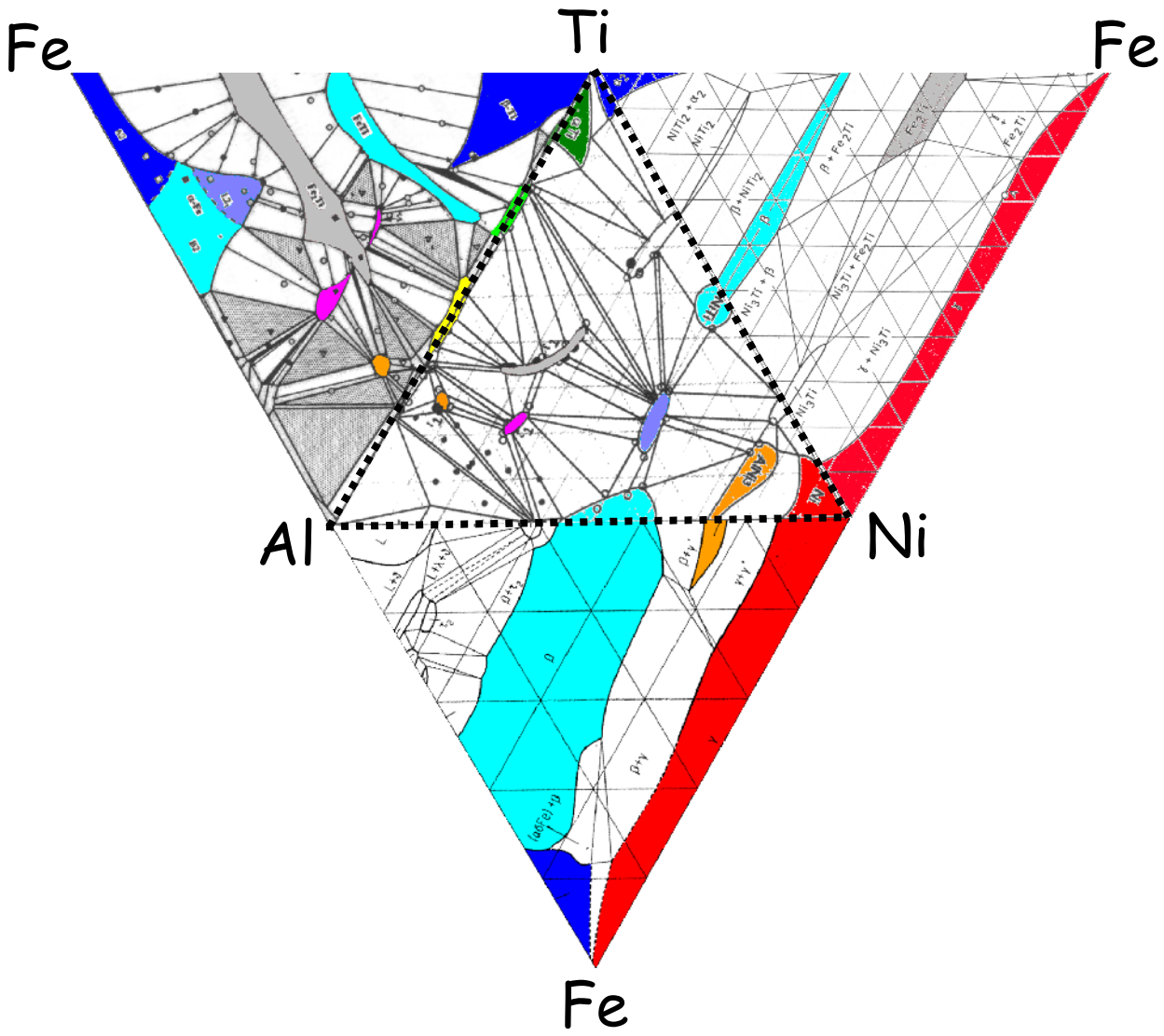
N. Dupin[a], B. Sundman[b]

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[b] Swedish Institute for Metals Research, Dorttning Kristinas v. 48, 11428 Stockholm, Sweden

Outline

- Introduction
- Crystallography
- Thermodynamic description
  - Binary cases
  - Ternary cases
  - Introducing vacancies
- Conclusion

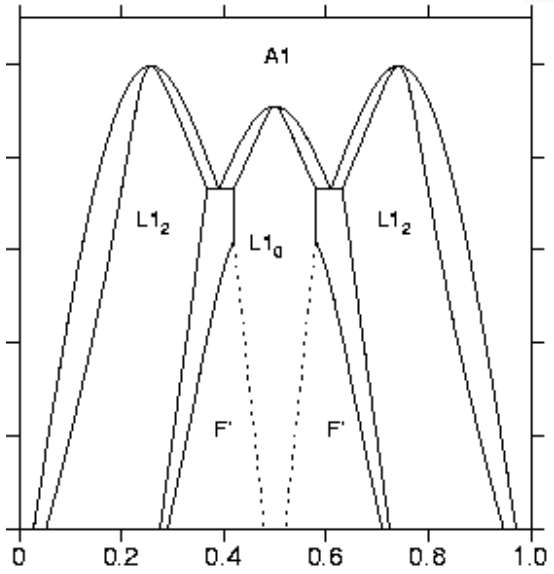
Introduction

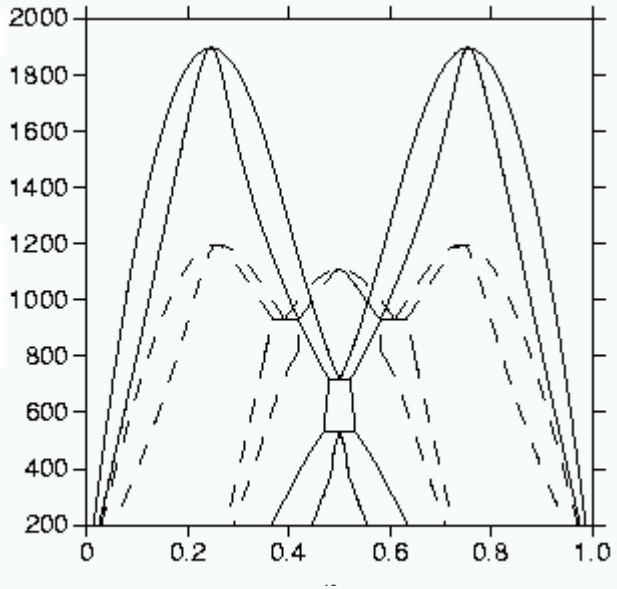


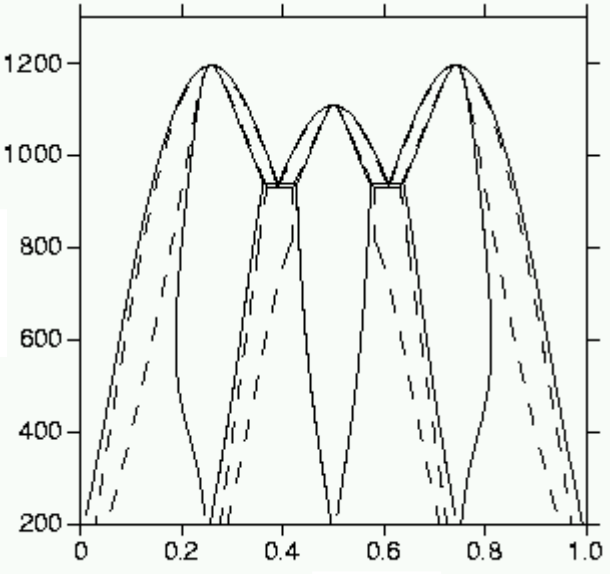
Introduction

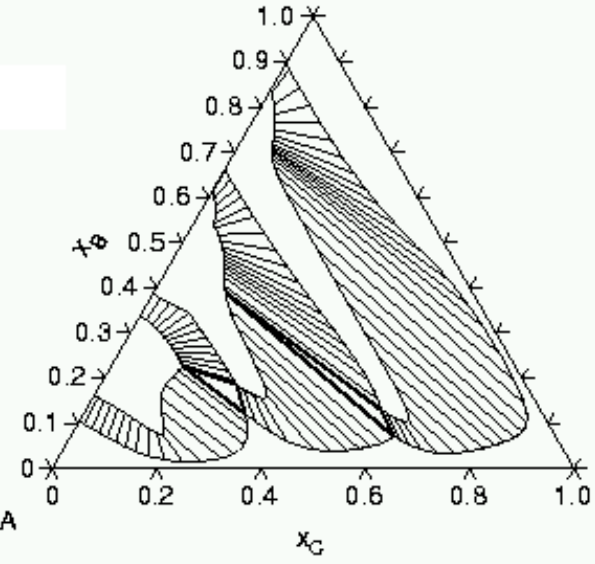
- Modeling ordering (BWG, CEF, CVM, MC)
- Why CEF?
  - rapidity
  - flexibility
- Problems with CEF?
  - too flexible (many parameters)
  - not enough if not enough sublattice
  - topology

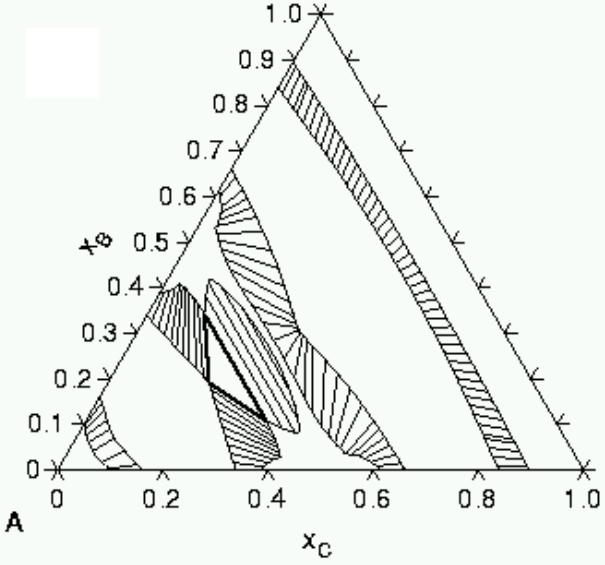
Introduction

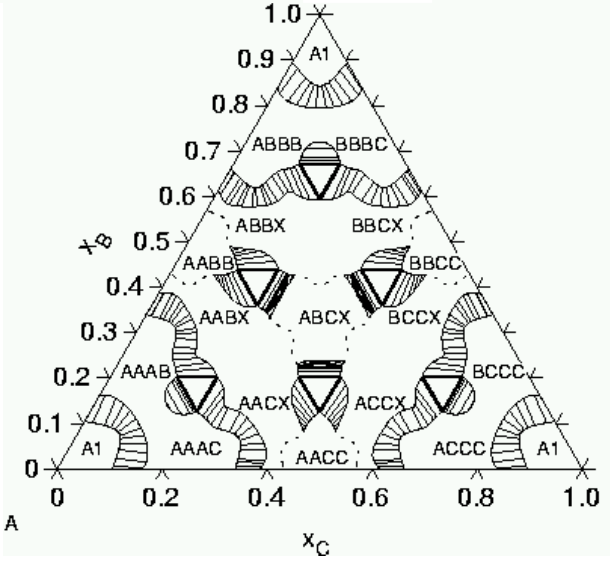










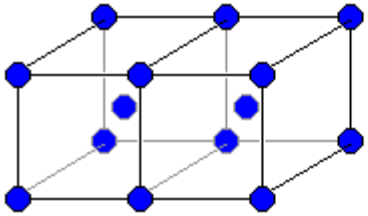


Introduction

- Goal
  - to show the ability of CEF to describe A2/B2 and $L2_1$ with a single model
  - to present some prototype calculations
    - to understand the effect of the parameters available
    - to decrease the number of parameters optimised
    - to increase the inputs from ab initio

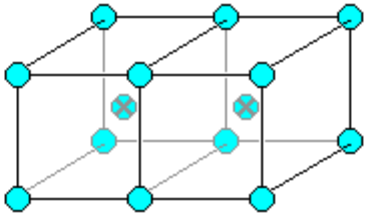
Crystallography

A2

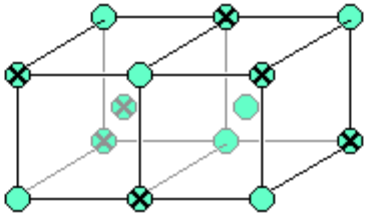


disordered bcc lattice

B2

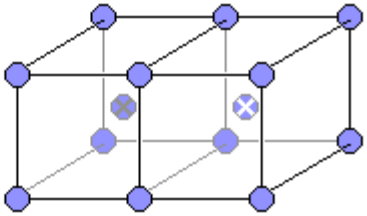


B32



AB ordering

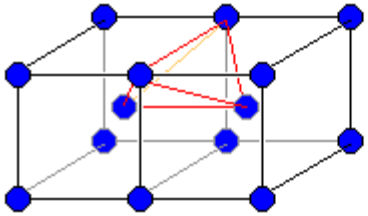
DO_3, $L2_1$



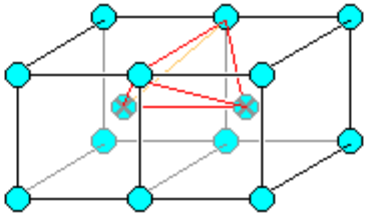
A_3B or A_2BC ordering

Crystallography

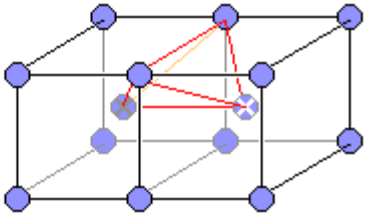
A2



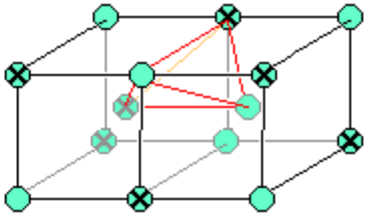
B2



DO_3, $L2_1$



B32



The minimum cluster needed to model these different orderings is an irregular tetrahedron.

Crystallography

By tetrahedron,

4 / 6

2 / 4

4 / 24 atoms

By cell,

8

6

2 atoms

12 tetrah.

By atom,

4

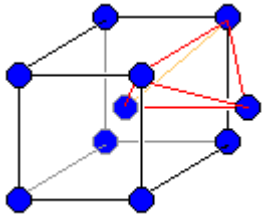
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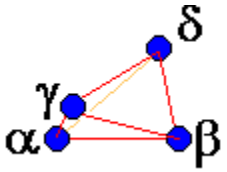
6 tetrah.

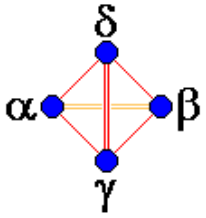
E / tetrah. :

$$1/6\ (\ e_{\alpha\delta} + e_{\alpha\gamma} + e_{\beta\delta} + e_{\beta\gamma}\ ) + 1/4\ (\ e_{\alpha\beta} + e_{\delta\gamma}\ )$$

E / atom : $(\ e_{\alpha\delta} + e_{\alpha\gamma} + e_{\beta\delta} + e_{\beta\gamma}\ ) + 3/2\ (\ e_{\alpha\beta} + e_{\delta\gamma}\ )$





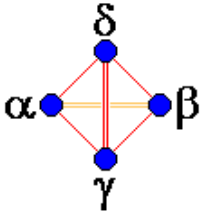


Thermodynamic description

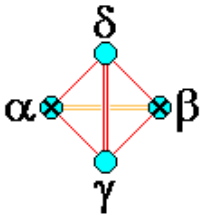
$(A,B)_{1/4}(A,B)_{1/4}(A,B)_{1/4}(A,B)_{1/4}$

s : α β γ δ

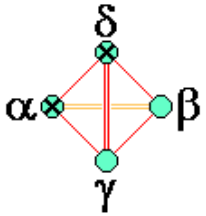
A2 $y_i^{\alpha} = y_i^{\beta} = y_i^{\gamma} = y_i^{\delta}$



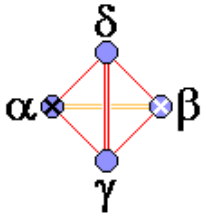
B2 $y_i^{\alpha} = y_i^{\beta} \neq y_i^{\gamma} = y_i^{\delta}$



B32 $y_i^{\alpha} = y_i^{\gamma} \neq y_i^{\beta} = y_i^{\delta}$



DO_3 or $L2_1$ $y_i^{\alpha} = y_i^{\beta} \neq y_i^{\gamma} \neq y_i^{\delta}$



Thermodynamic description

$$G = \sum_{ijkl} y_i^{\alpha} y_j^{\beta} y_k^{\gamma} y_l^{\delta} G_{ijkl}$$

$$+ RT \frac{1}{4} \sum_{s} \sum_{i} y_i^s \ln y_i^s$$

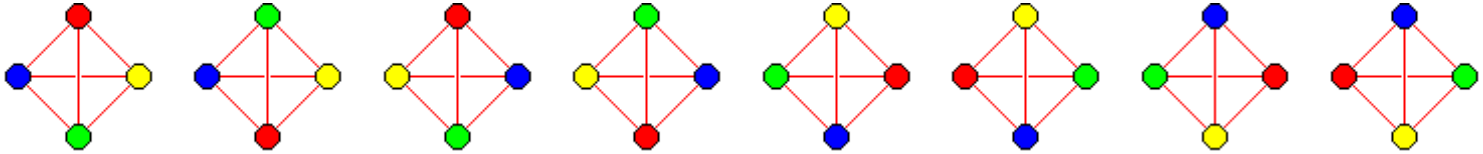
$$+ \sum_{s} \sum_{ij} y_i^s y_j^s L_{ij}^s$$

$$+ \sum_{sr} \sum_{ijkl} y_i^s y_j^s y_k^r y_l^r L_{ij:kl}^{sr}$$

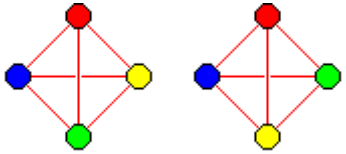
Thermodynamic description

crystallography

$$G_{ijkl} = G_{ijlk} = G_{jikl} = G_{jilk} = G_{klij} = G_{lkij} = G_{klji} = G_{lkji}$$



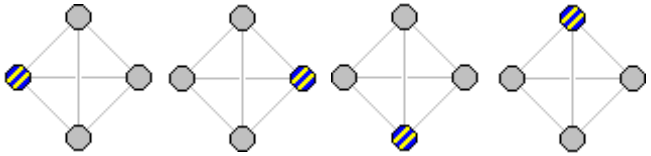
but $G_{ijkl} \neq G_{ikjl}$ (B2 ≠ B32)



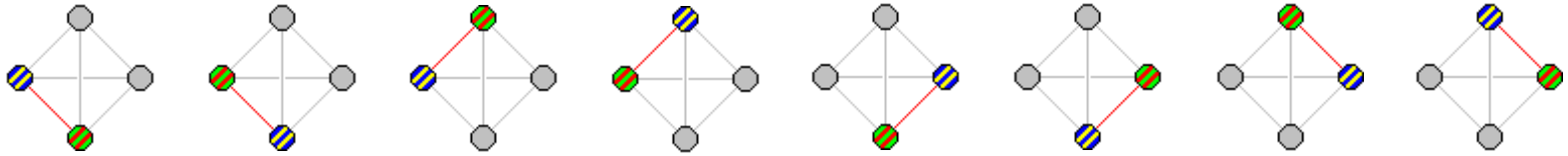
Thermodynamic description

crystallography

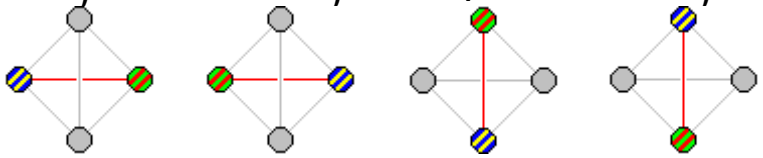
$$L_{ij}^{\alpha} = L_{ij}^{\beta} = L_{ij}^{\gamma} = L_{ij}^{\delta} = L_{ij}$$



$$L_{ij:kl}^{\alpha\gamma} = L_{kl:ij}^{\alpha\gamma} = L_{ij:kl}^{\alpha\delta} = L_{kl:ij}^{\alpha\delta} = L_{ij:kl}^{\beta\gamma} = L_{kl:ij}^{\beta\gamma} = L_{ij:kl}^{\beta\delta} = L_{kl:ij}^{\beta\delta}$$



$$L_{ij:kl}^{\alpha\beta} = L_{kl:ij}^{\alpha\beta} = L_{ii:kl}^{\gamma\delta} = L_{kl:ij}^{\gamma\delta}$$



Binary cases

1. Constant bond energies
2. Variation of the bond energies
3. Interaction parameters
4. Reciprocal interaction parameters
5. Discussion

Binary cases

1. Constant bond energies, classical BWG

u_{AB} energy of a 1st neighbour bond

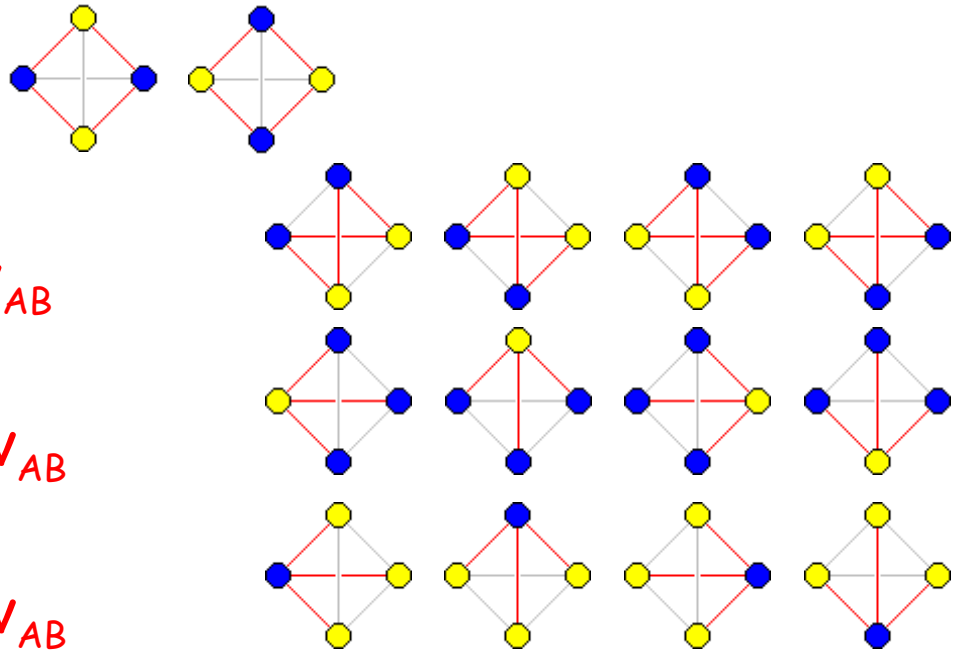
v_{AB} energy of a 2nd neighbour bond

$G_{A2B2(B2)} = 4\ u_{AB}$

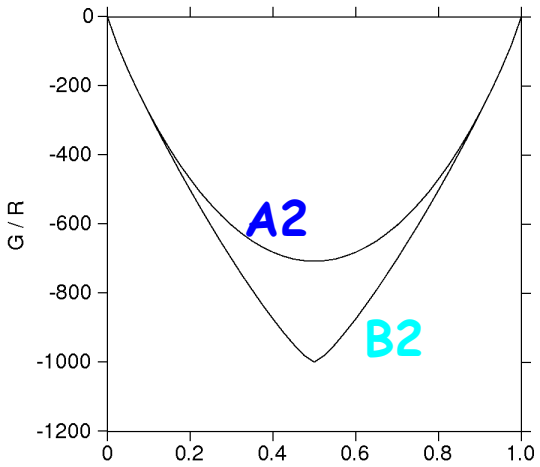
$G_{A2B2(B32)} = 2\ u_{AB} + 3\ v_{AB}$

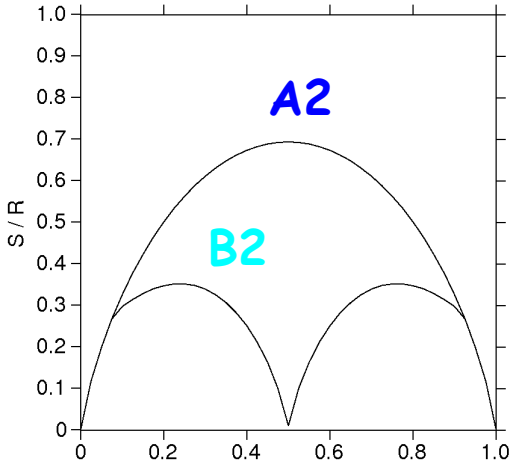
$G_{A3B(D03)} = 2\ u_{AB} + 1.5\ v_{AB}$

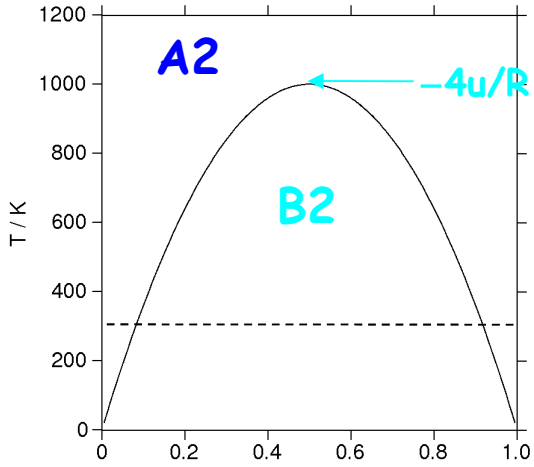
$G_{AB3(D03)} = 2\ u_{AB} + 1.5\ v_{AB}$

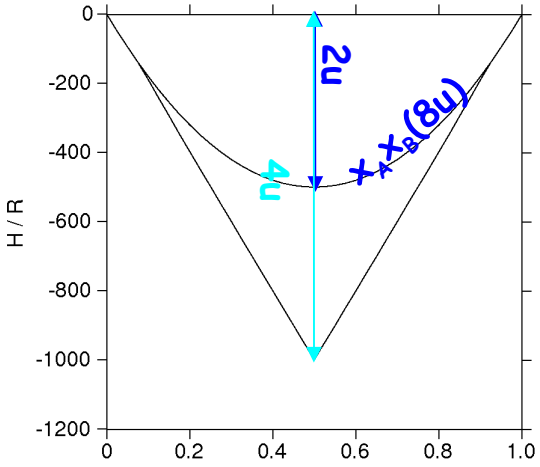


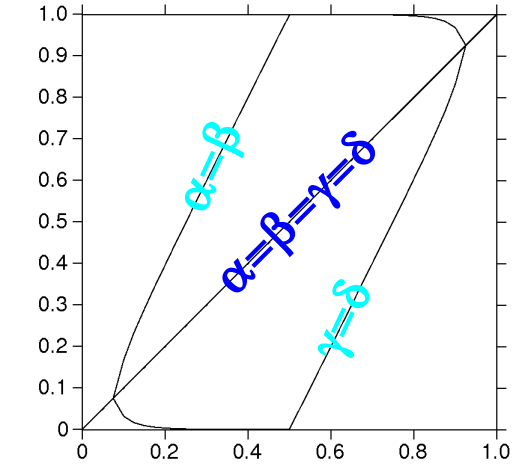
$u_{AB} = -250R$ $v_{AB} = 0$





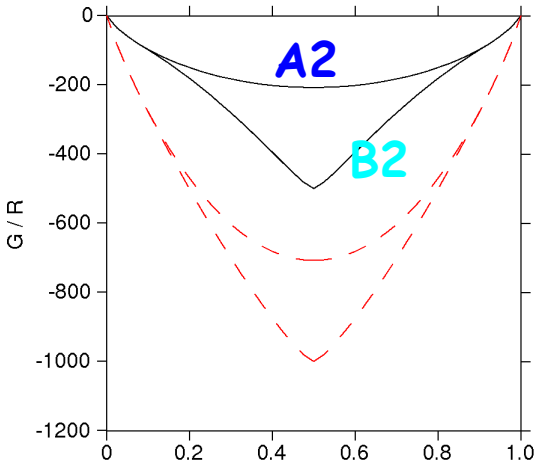


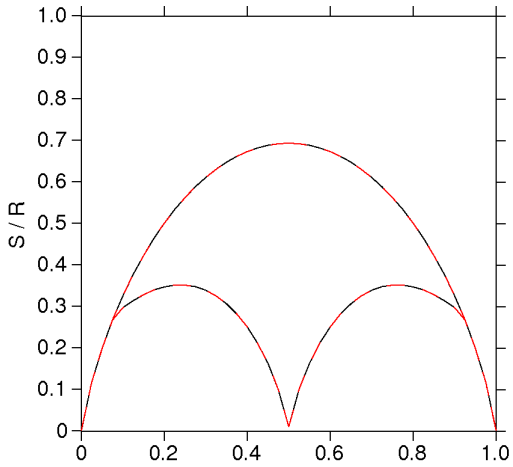


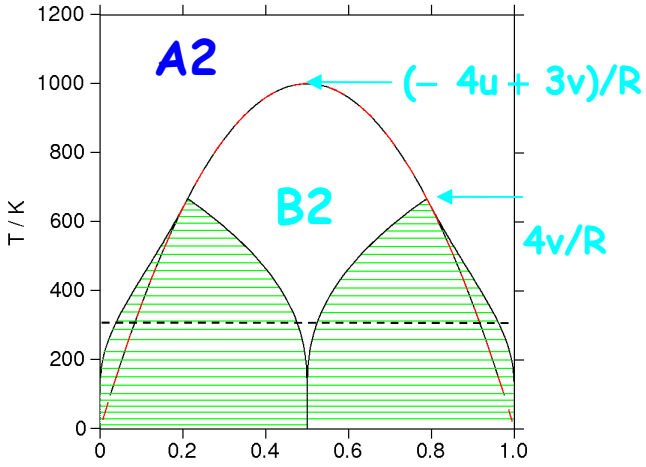


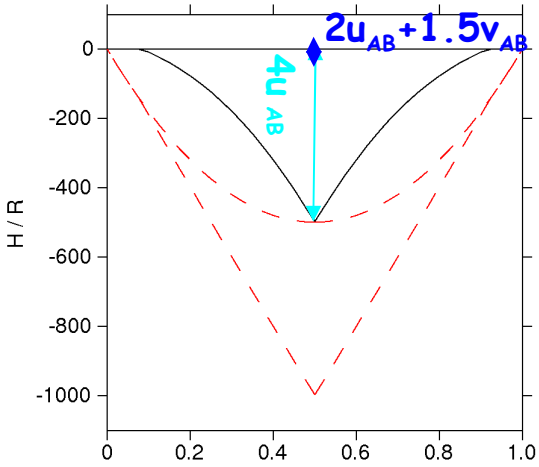
⇒ 2nd order A2/B2 transition

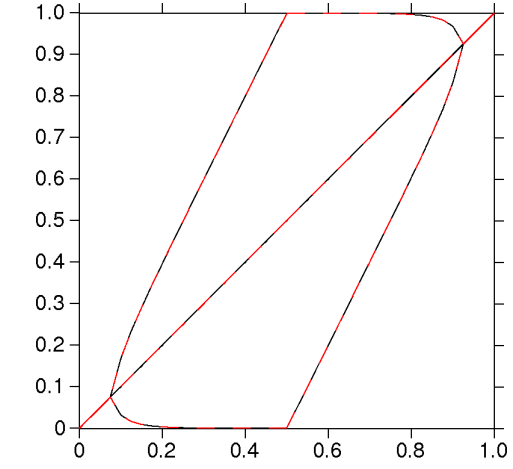
$u_{AB} = -125R$ $v_{AB} = +167R$





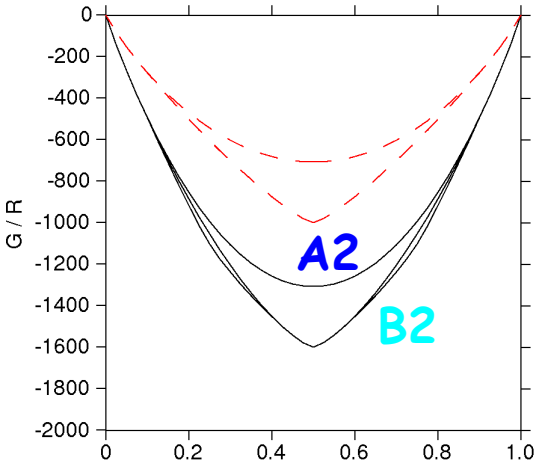


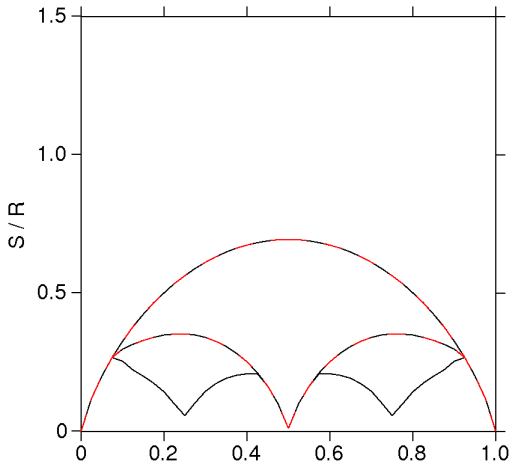


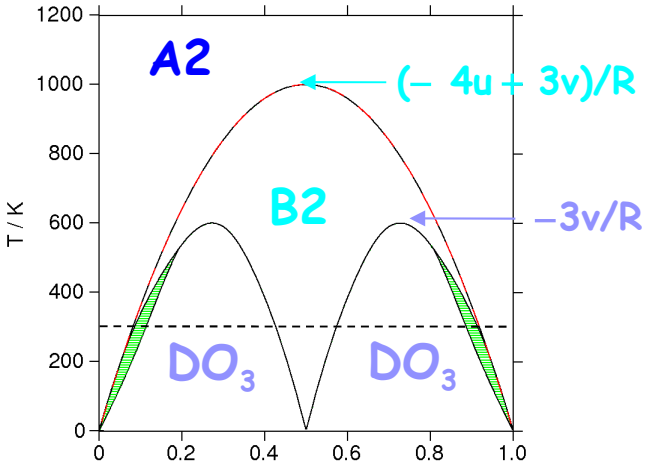


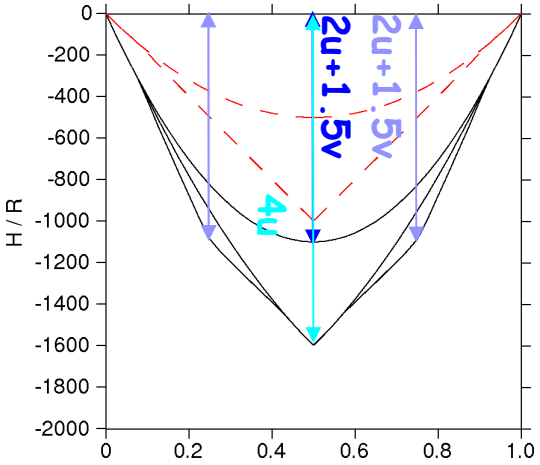
$\Rightarrow$ A2+B2 fields

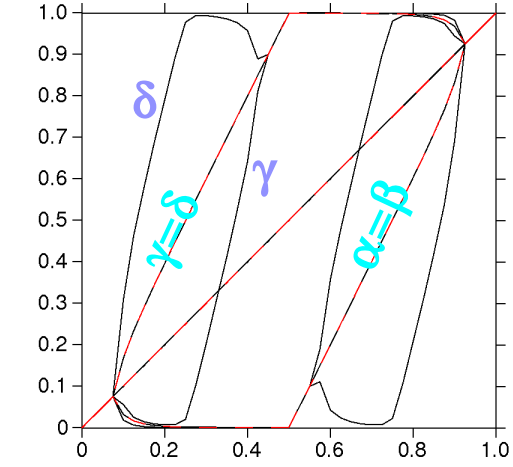
$u_{AB} = -400R$ $v_{AB} = -200R$





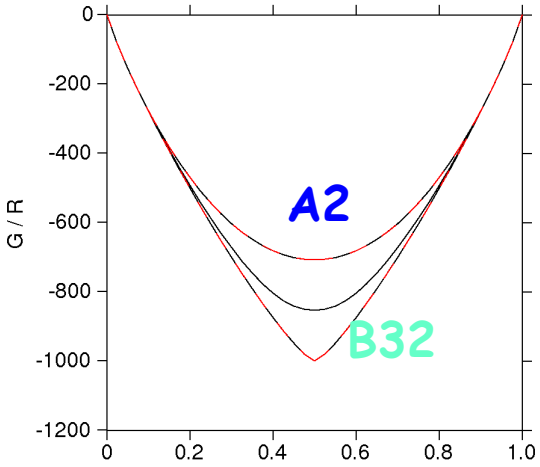


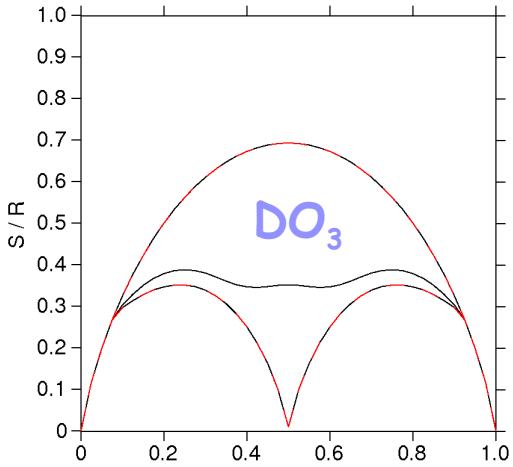


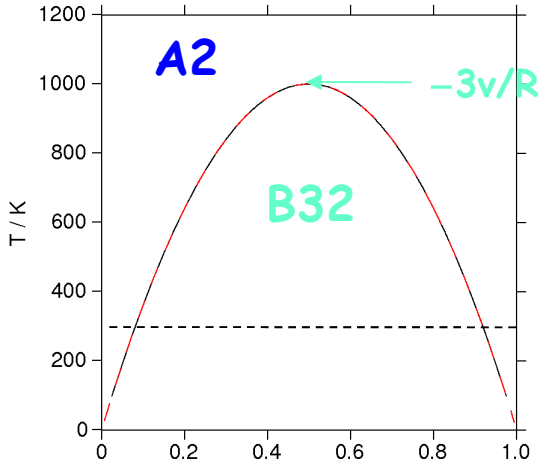


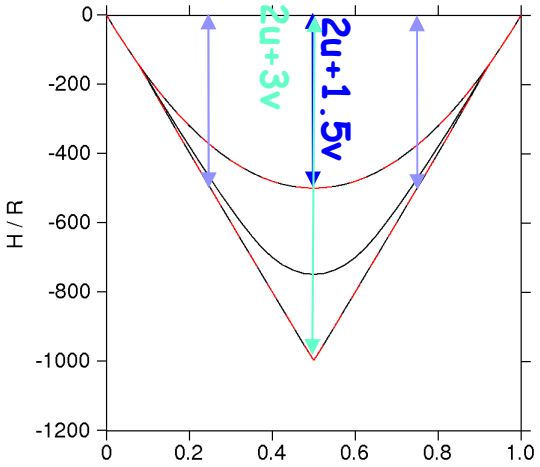
$\Rightarrow DO_3$ stabilised

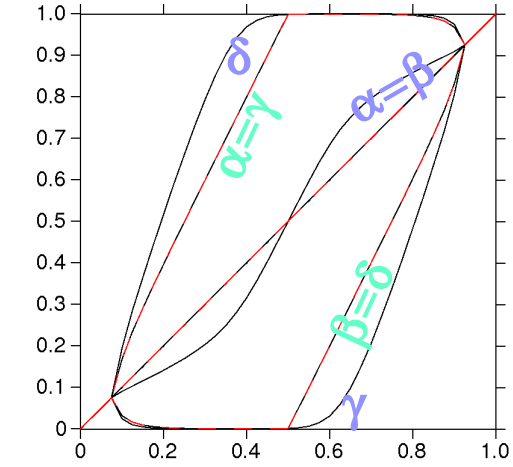
$u_{AB} = 0$ $v_{AB} = -333R$





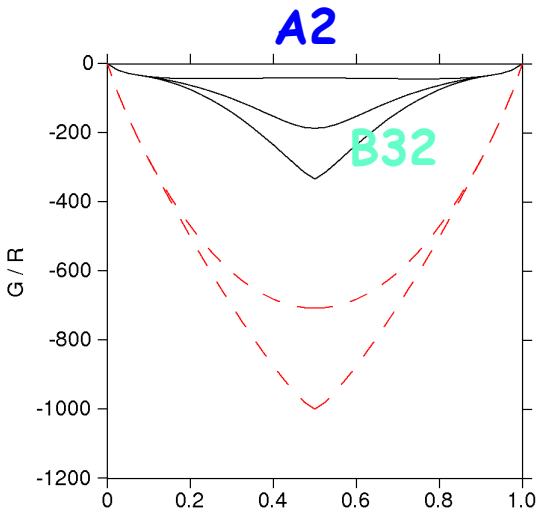


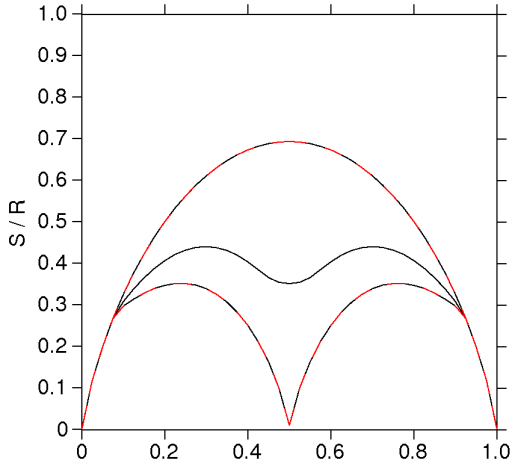


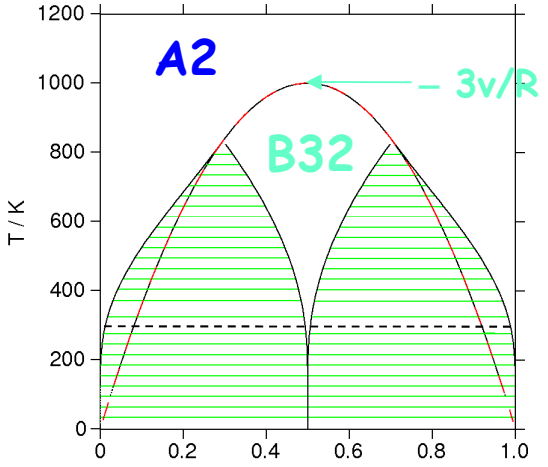


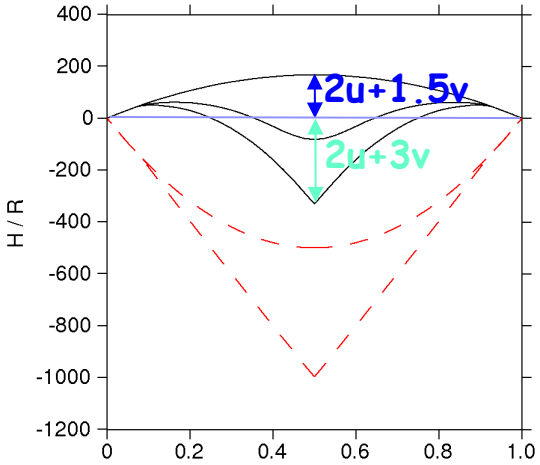
⇒ 2nd order A2/B32 transition

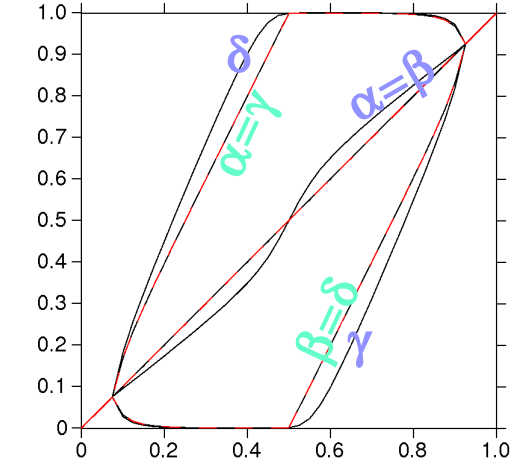
$u_{AB} = +333R$ $v_{AB} = -333R$











⇒ A2+B32 fields

Binary cases

1. Constant bond energies, classical BWG

   . describes many different cases

   . only symmetrical descriptions

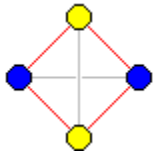
   . only two parameters available describing phase diagram and thermodynamics

   . not adapted to described most of the real systems

Binary cases

- Variation of the bond energies

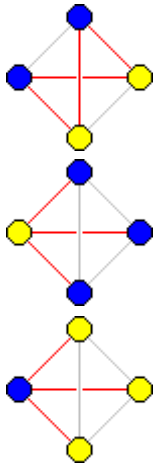
$G_{A2B2(B2)} = 4\ u_{AB} + \alpha_{B2}$



$G_{A2B2(B32)} = 2\ u_{AB} + 3\ v_{AB} + \alpha_{B32}$

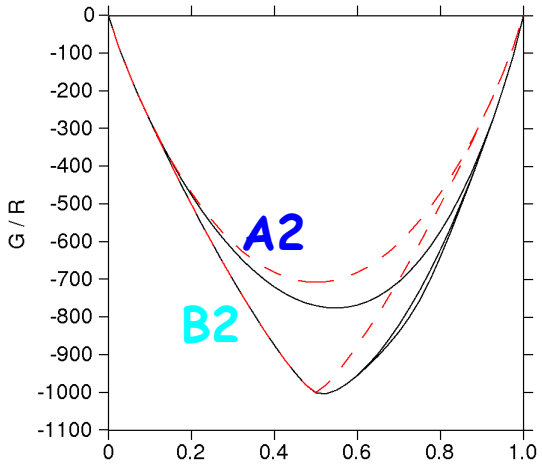
$G_{A3B(D03)} = 2\ u_{AB} + 1.5\ v_{AB} + \alpha_{A3B}$

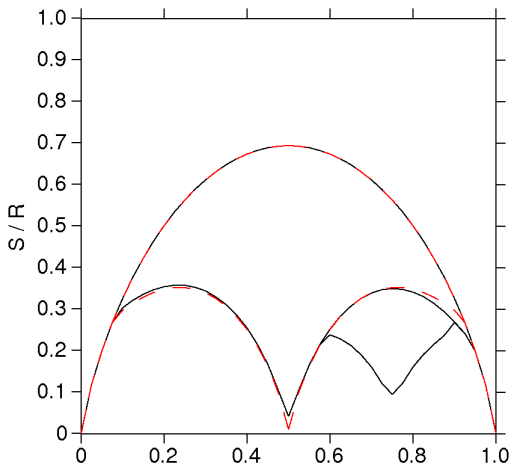
$G_{AB3(D03)} = 2\ u_{AB} + 1.5\ v_{AB} + \alpha_{AB3}$

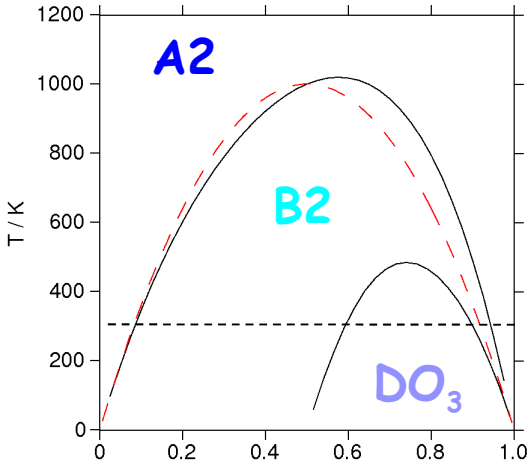


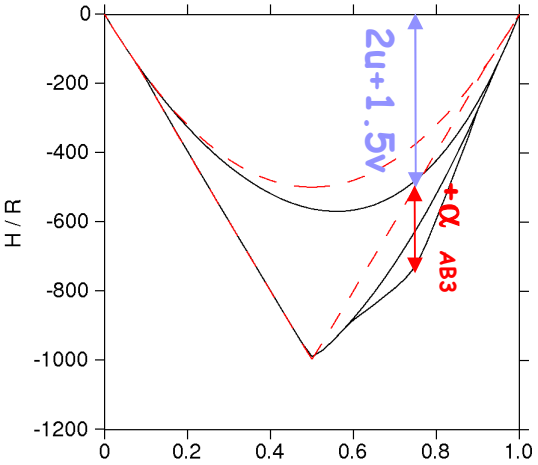
examples with $u_{AB} = -250R$, $v_{AB} = 0$

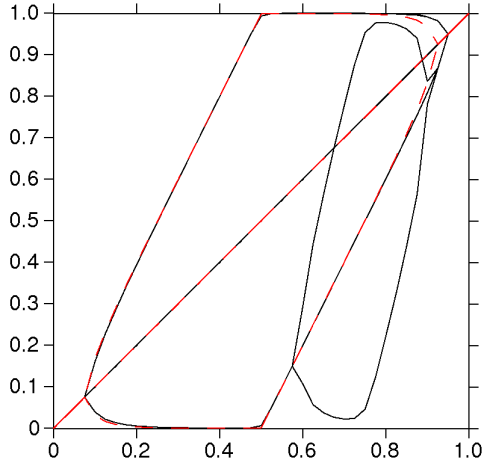
$\alpha_{AB3} = -250R$







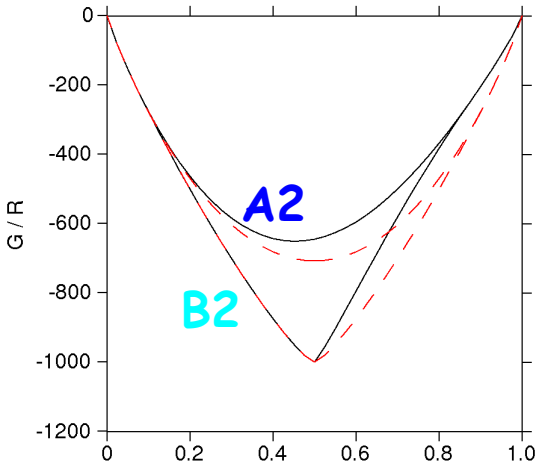


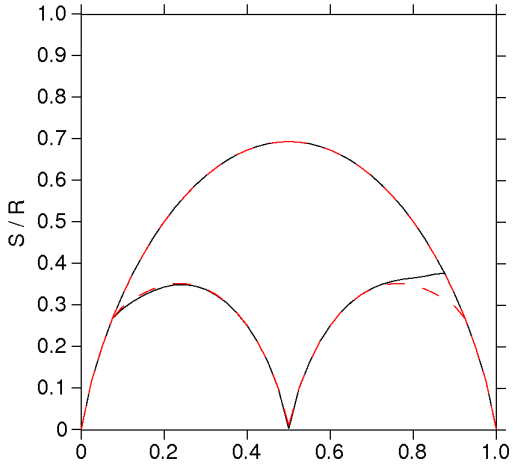


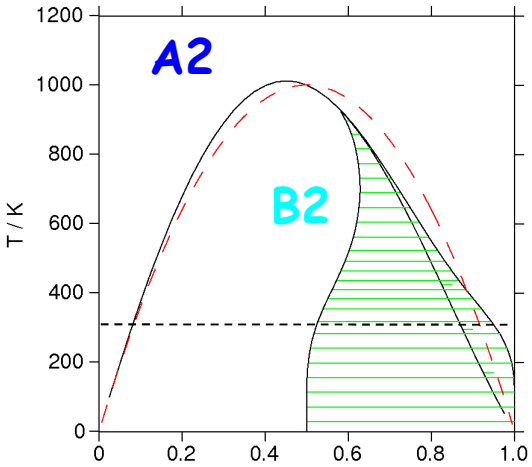
⇒ DO_3 stabilised

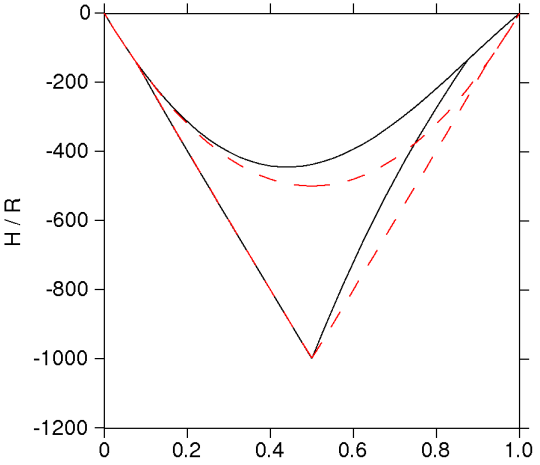
⇒ but also A2 and B2, mostly on B side

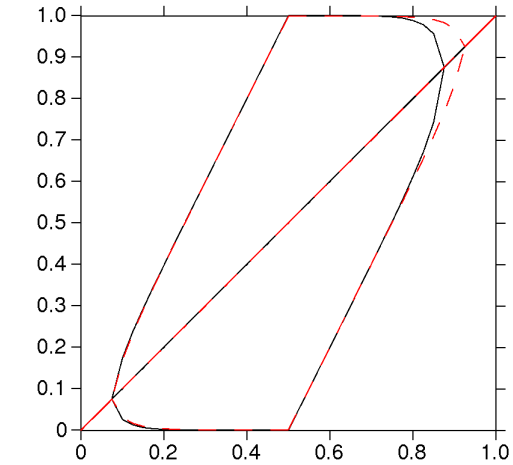
$\alpha_{AB3} = +250R$







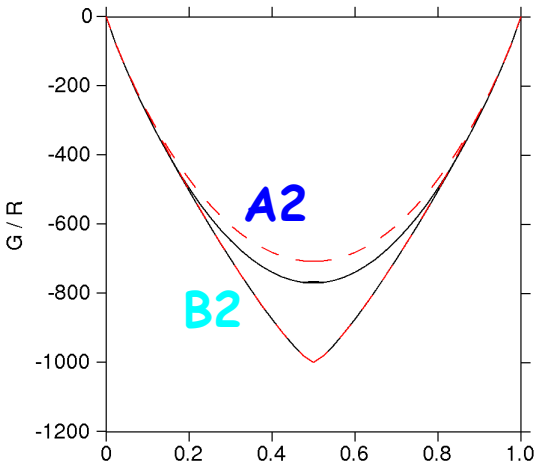


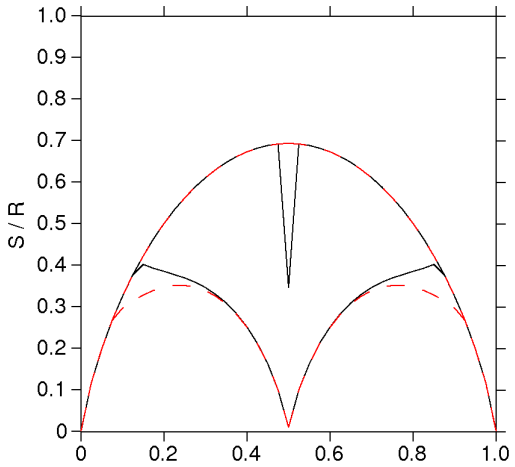


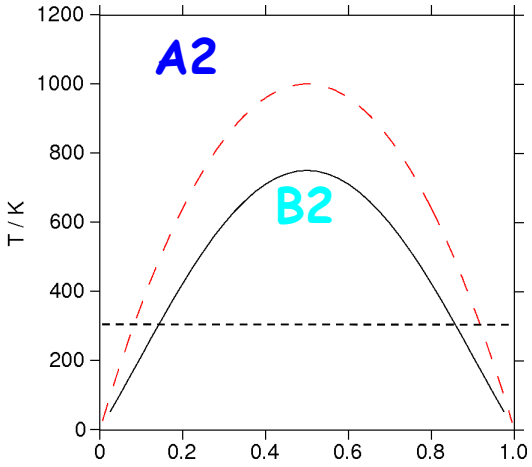
⇒ destabilisation of A2, and B2phases, mostly on B side

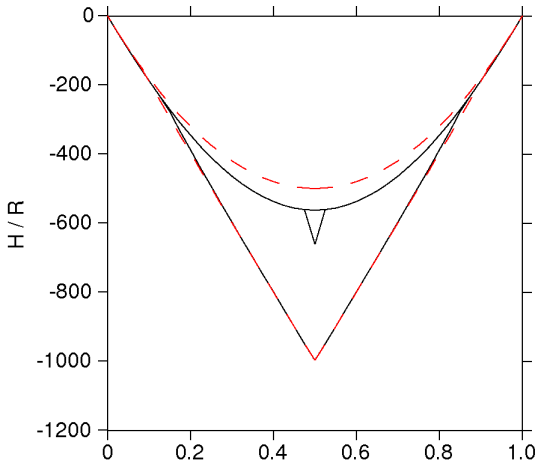
⇒ A2+B2

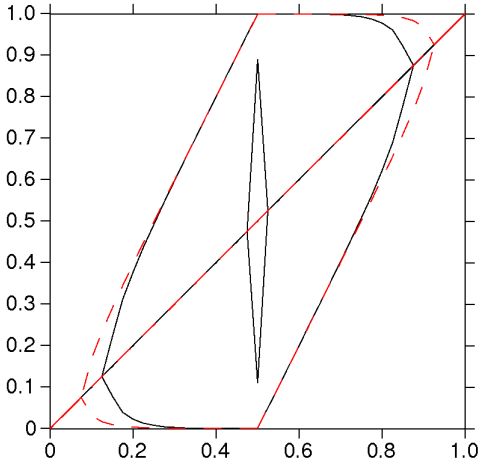
$\alpha_{B32} = -250R$





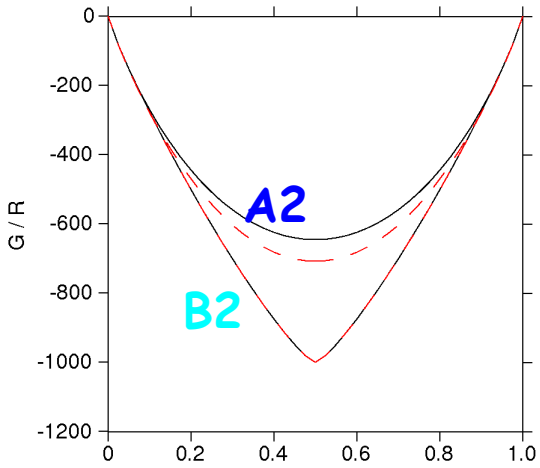


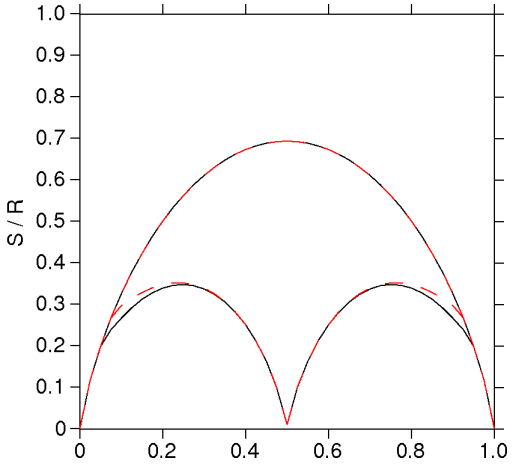


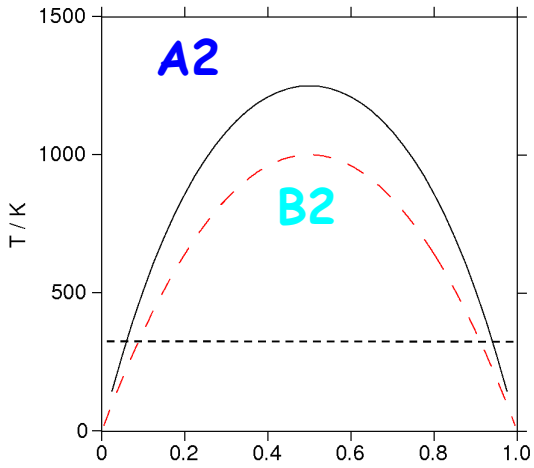


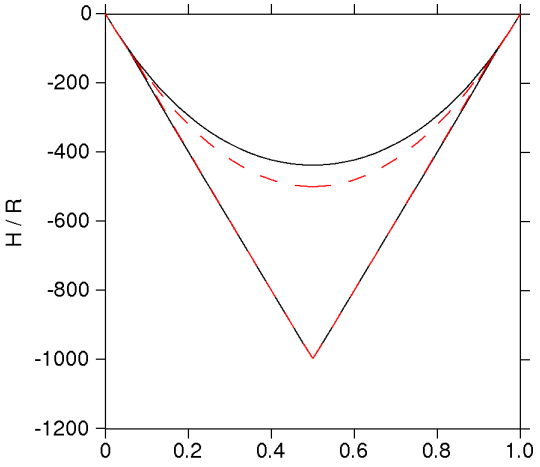
$\Rightarrow$ A2 stabilised

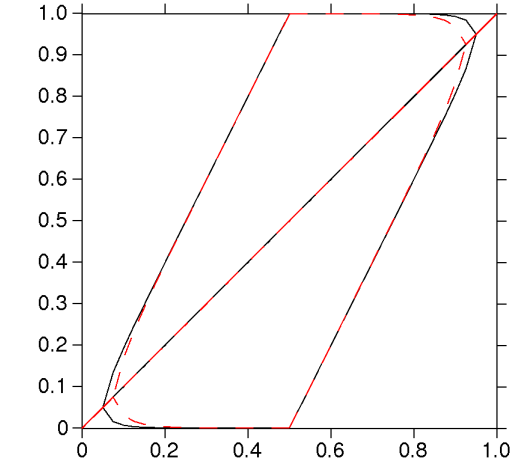
$\alpha_{B32} = +250R$





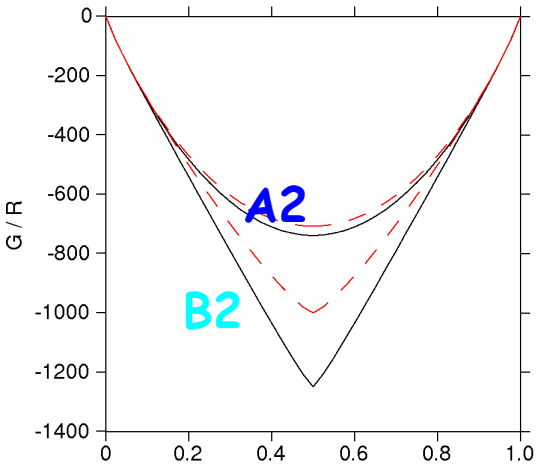


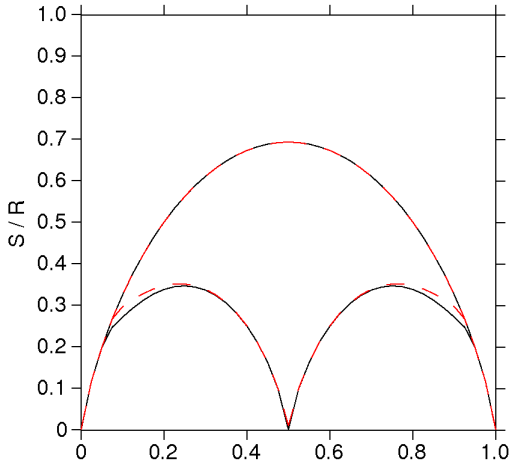


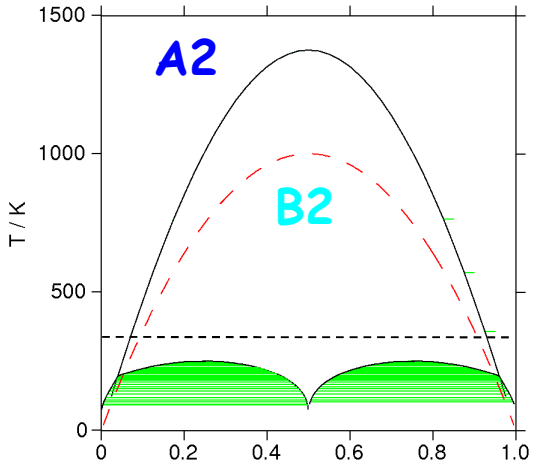


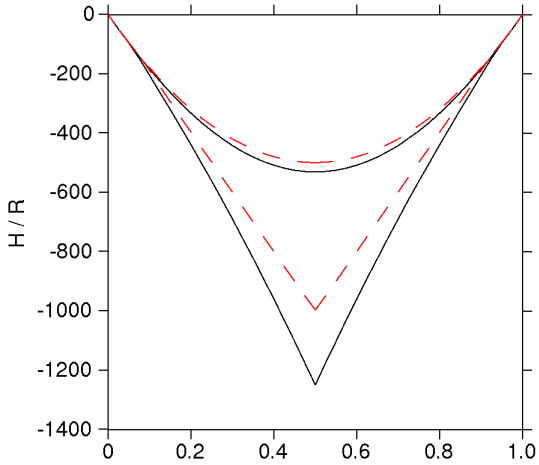
$\Rightarrow$ A2 destabilised

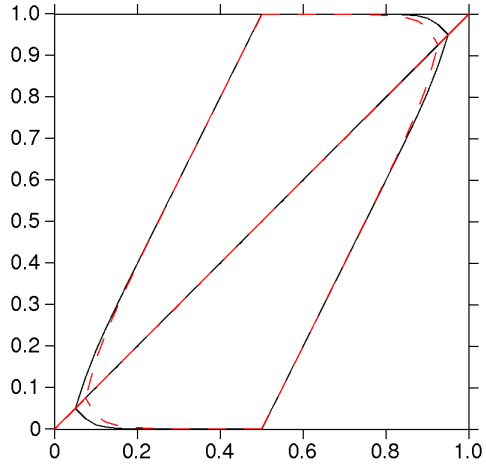
$\alpha_{B2} = -250R$









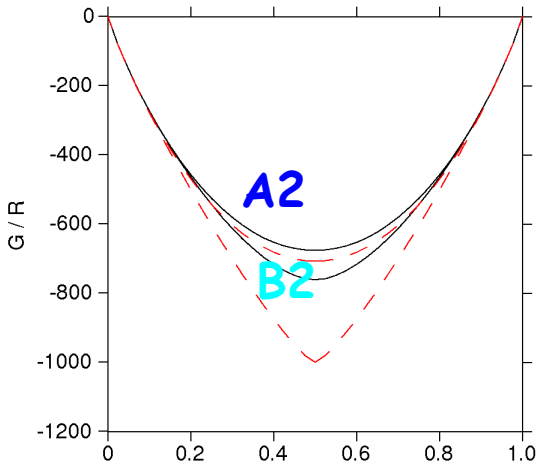


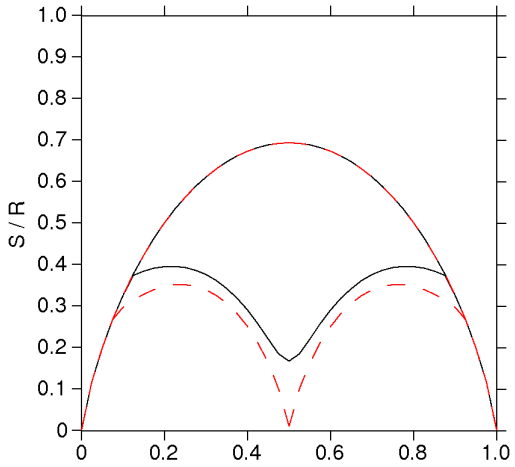
⇒ B2 stabilised

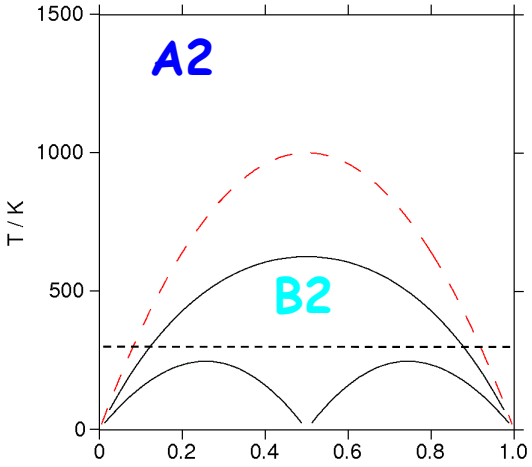
⇒ A2 slightly stabilised

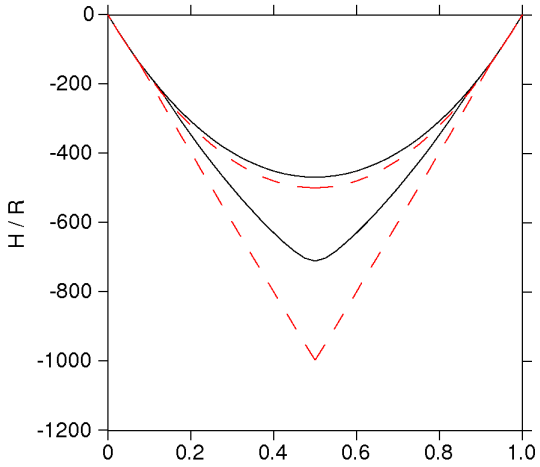
⇒ A2+B2, B2+B2

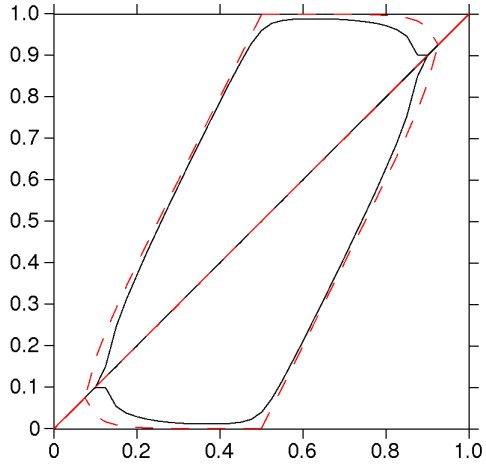
$\alpha_{B2} = +250R$











⇒ B2 destabilised

⇒ A2 slightly destabilised

⇒ DO_3 stabilised

Binary cases

1. Variation of the bond energies

   . of one compound affects its stability but also the one of other orders and of the A2

   . allows asymmetrical descriptions

   . increases freedom to describe real systems

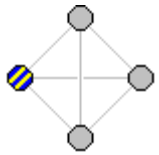
   . can be difficult to estimate in metastable area

   . can be estimated thanks to first principle calculations for each stoichiometric compound

Binary cases

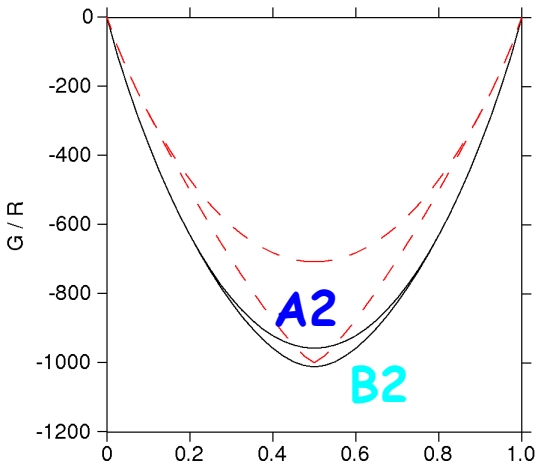
- Interaction parameters

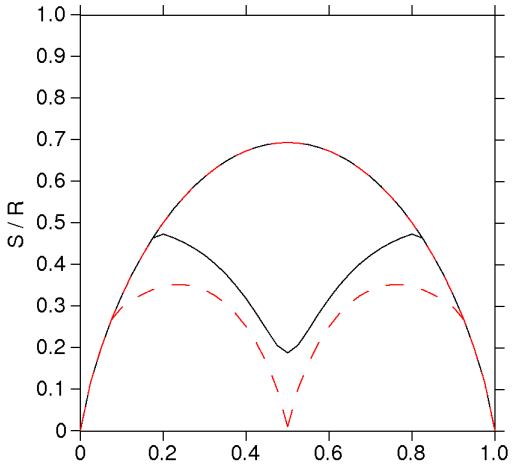
$$L_{AB} = \mathrm{L0} + (y_A^s - y_B^s)\ \mathrm{L1}$$

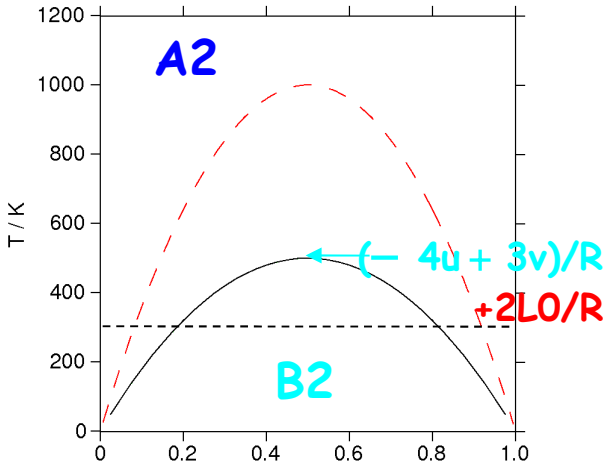


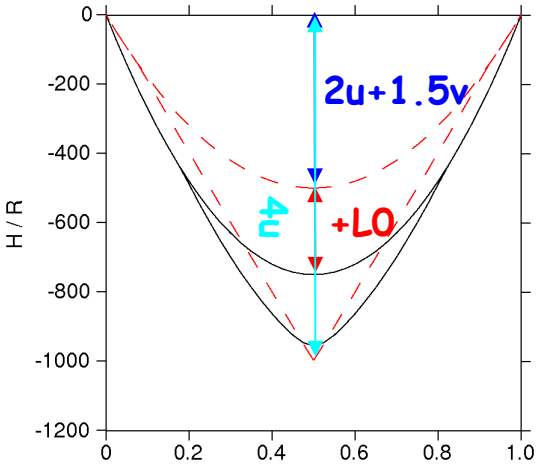
examples with $u_{AB} = -250R$, $v_{AB} = 0$

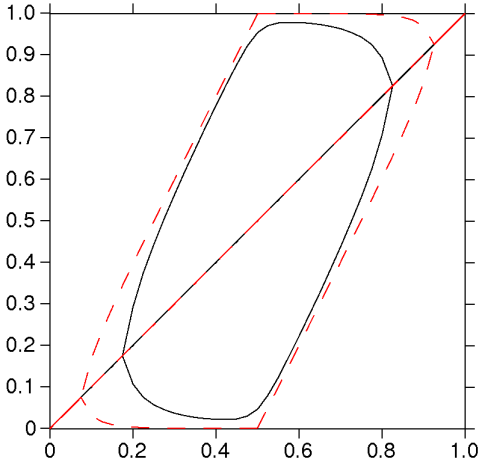
L0 = – 250R







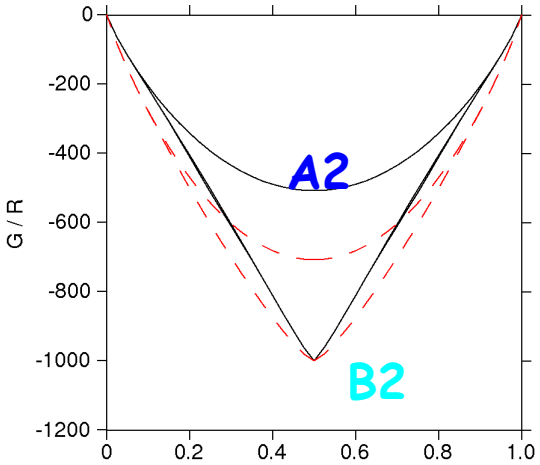


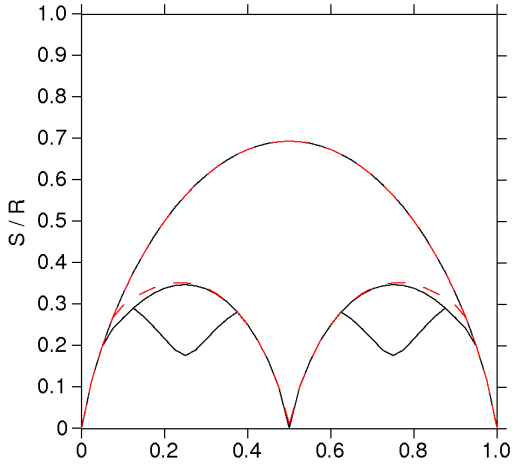


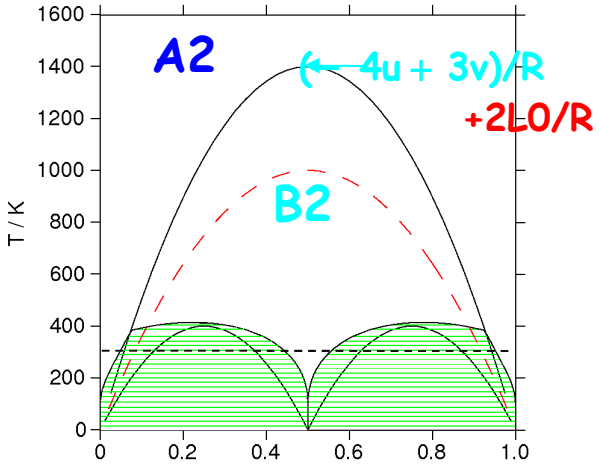
⇒ A2 stabilised

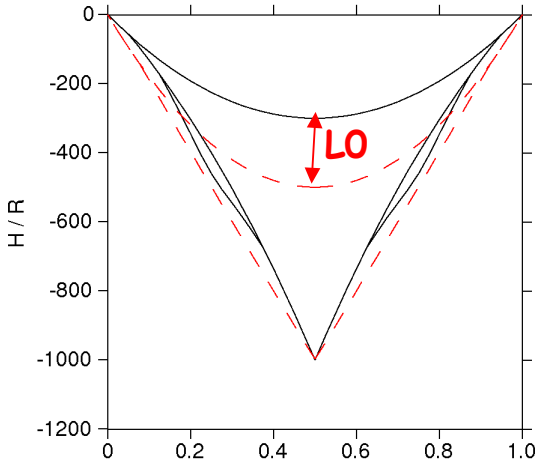
⇒ B2 less ordered

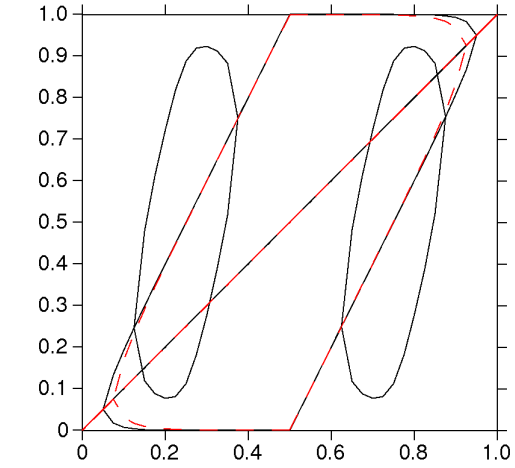
L0 = + 200R









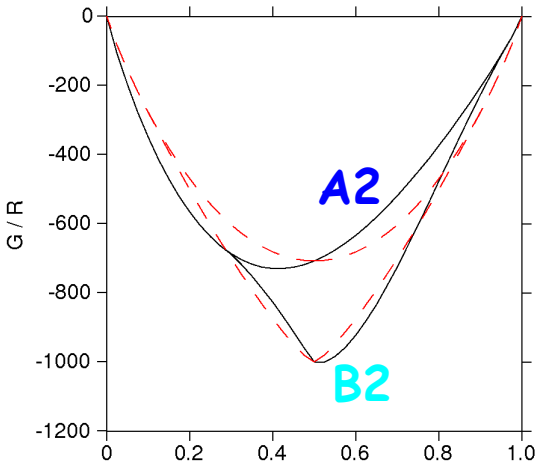


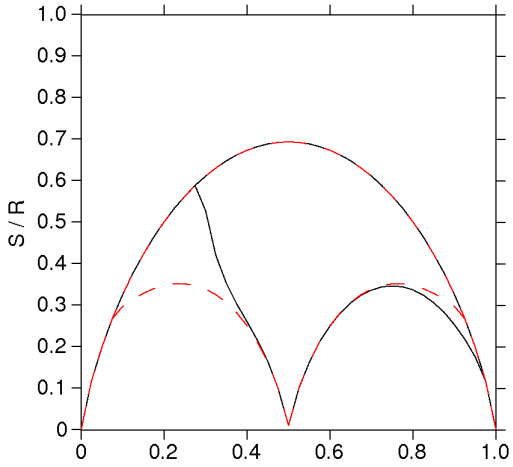
⇒ A2 destabilised

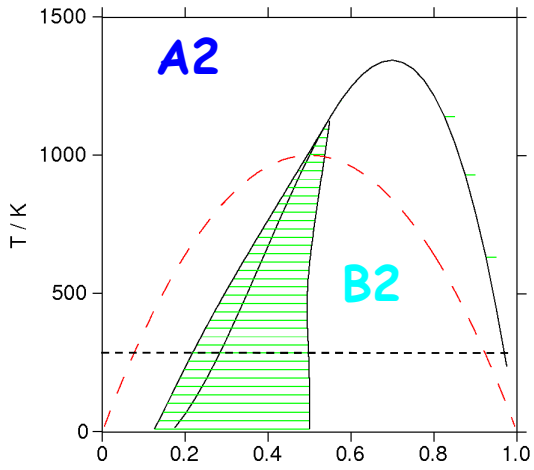
⇒ A2+B2

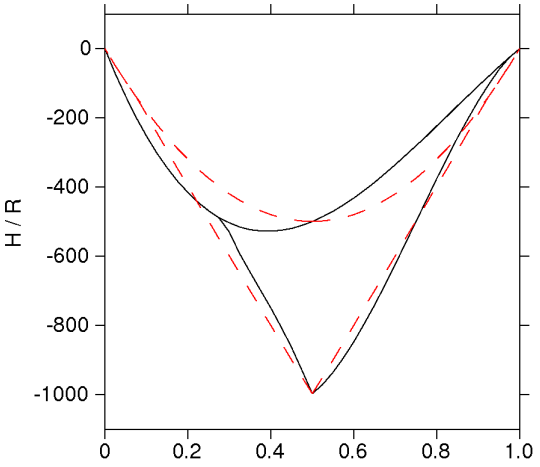
⇒ B2+B2

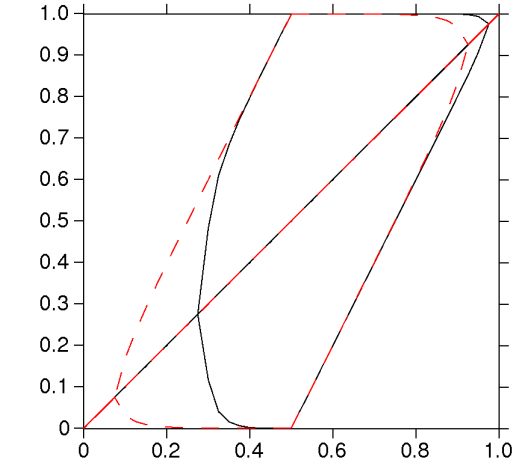
L1 = – 250R











⇒ asymmetry

⇒ A2 and B2 affected

⇒ A2+B2

Binary cases

1. Interaction parameters

   . may affect all the phases on the whole range of composition but A2 in larger extent

   . allow asymmetrical descriptions

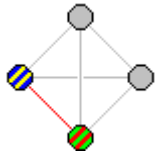
   . increase freedom to describe real systems

   . need experiments in order to be assessed reasonably

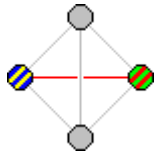
Binary cases

- Reciprocal parameters
  - shown to improve the description of the topology for fcc alloys simulating the SRO,
  - two different ones in the bcc alloys

$$L^{\alpha\gamma}_{AB:AB} = \mathrm{LR1}$$

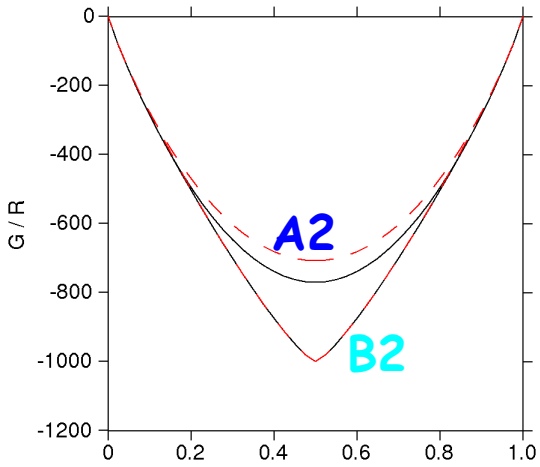


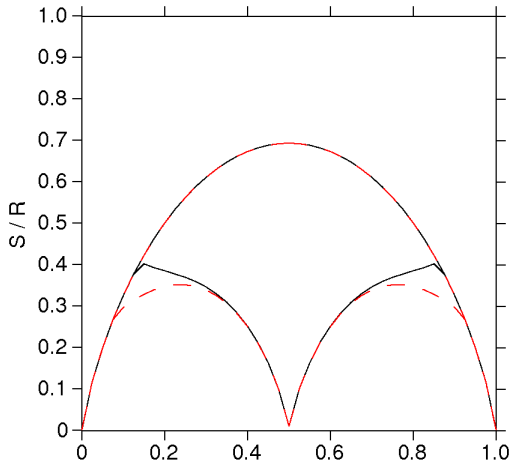
$$L^{\alpha\beta}_{AB:AB} = \mathrm{LR2}$$

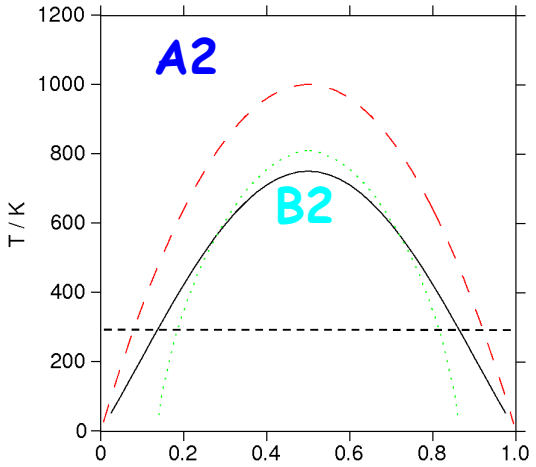


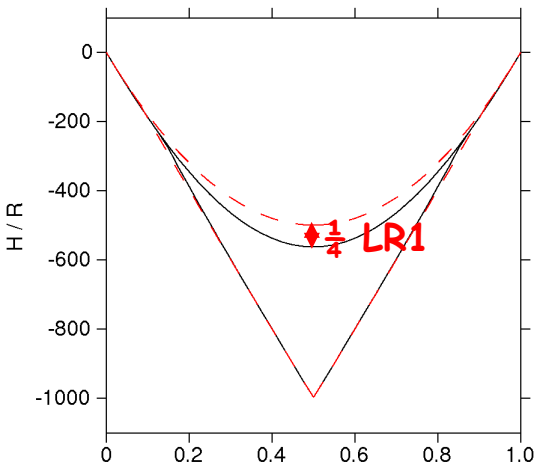
examples with $u_{AB} = -250R$, $v_{AB} = 0$

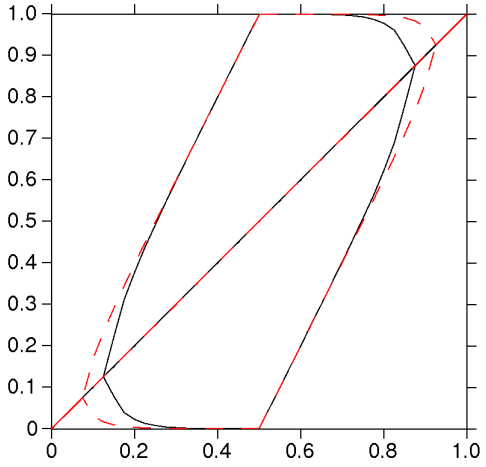
LR1 = – 250R







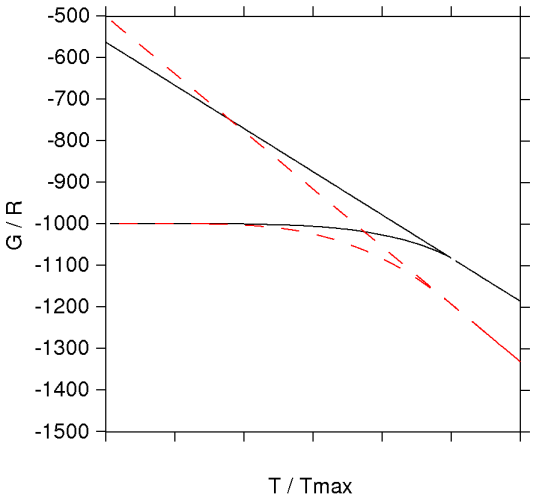


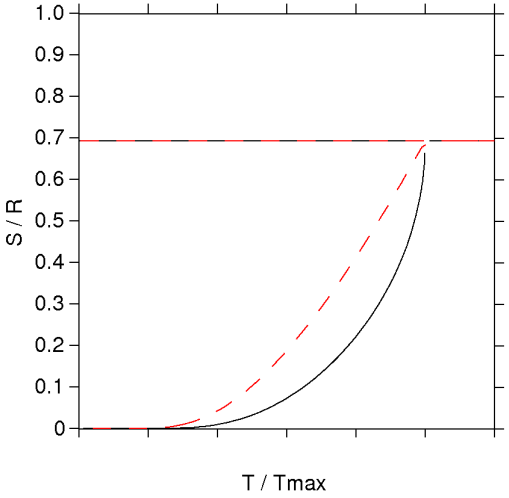


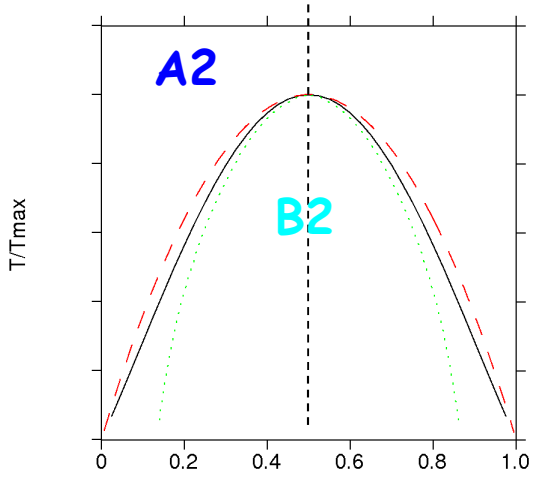
⇒ A2 stabilised

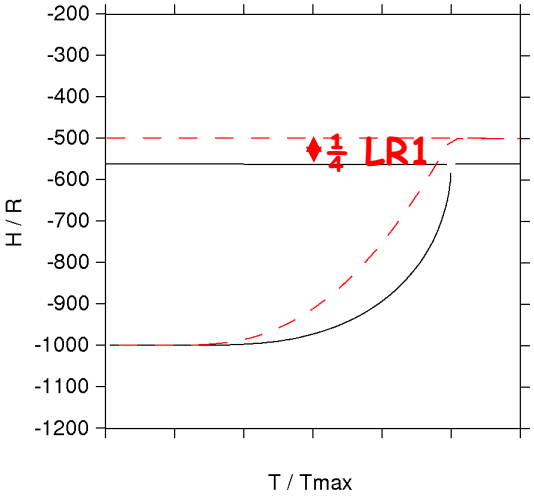
⇒ Tmax closer to CVM

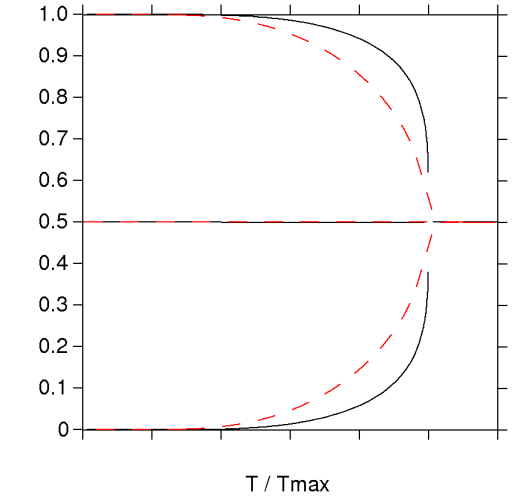
LR1 = – 250R







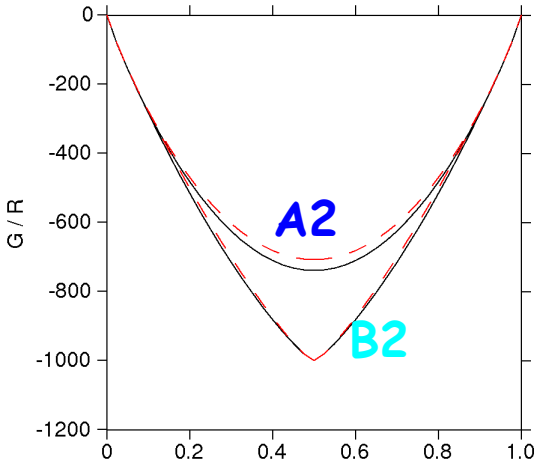


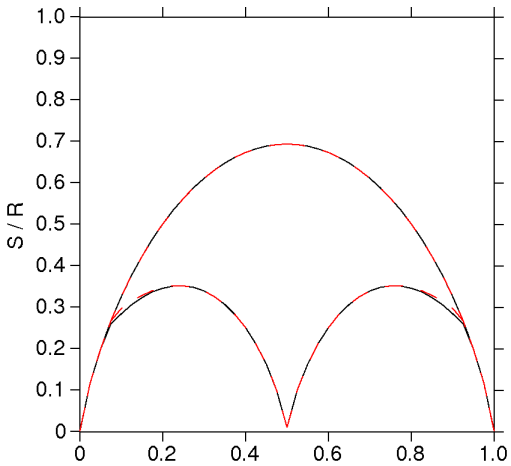


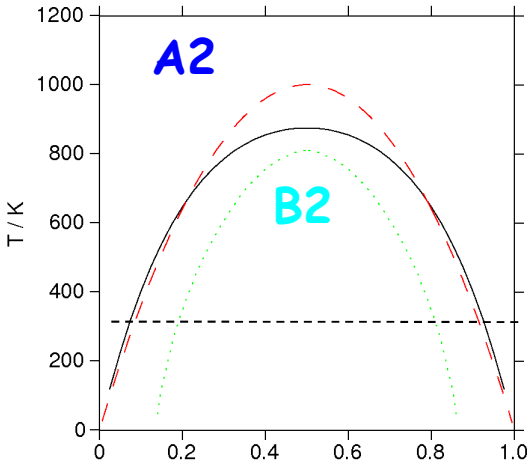
⇒ A2 stabilised

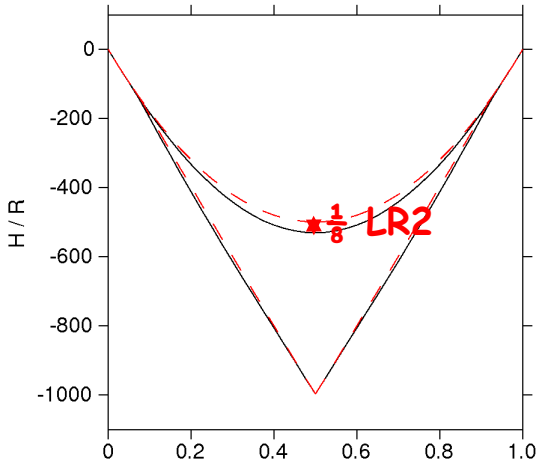
⇒ Tmax closer to CVM

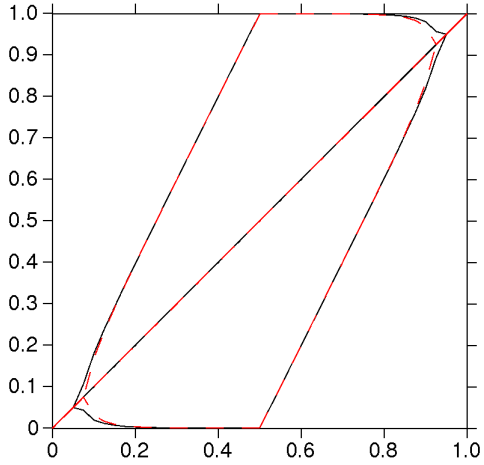
LR2 = – 250R







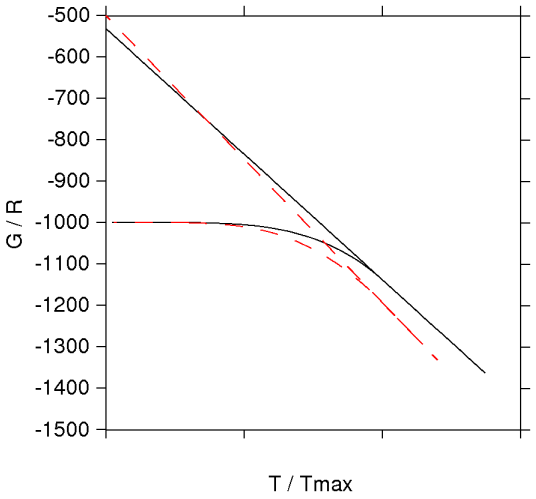


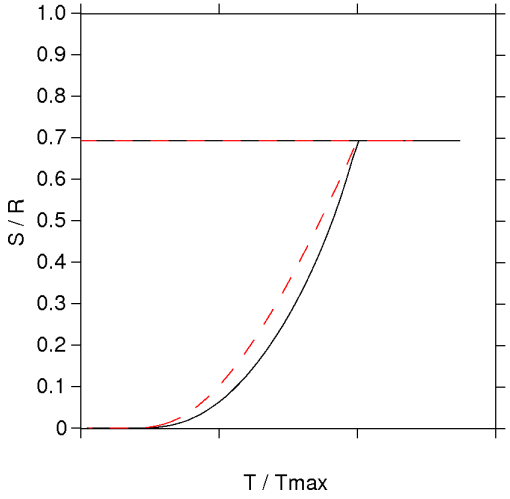


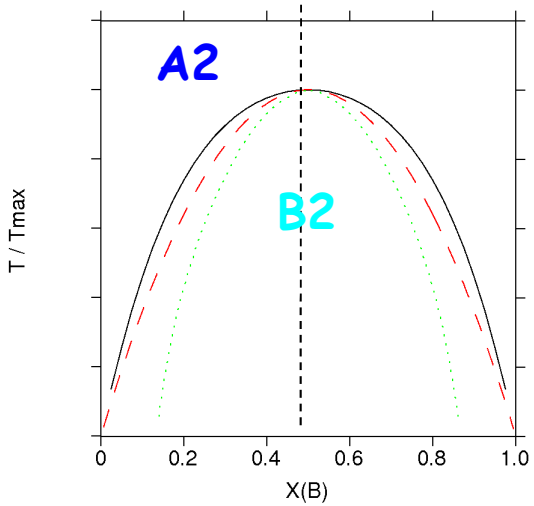
⇒ A2 stabilised

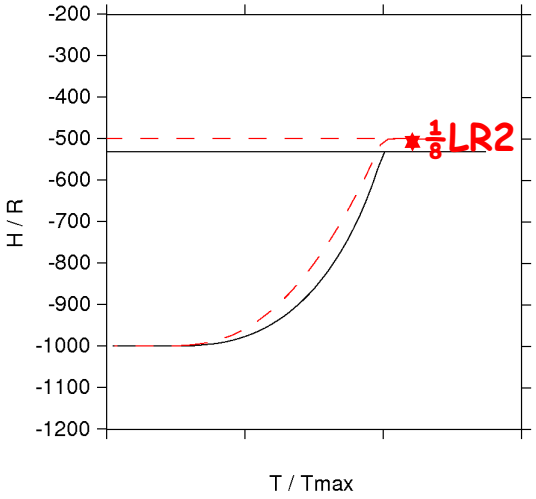
⇒ Tmax closer to CVM

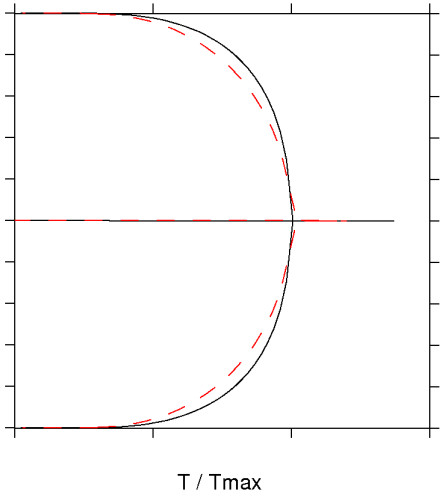
LR2 = – 250R











⇒ A2 stabilised

Binary cases

1. Reciprocal parameters
   - allow Tmax closer to CVM calculations
   - affect mostly the A2 phase
   - simulate SRO

Binary cases

1. Discussion

   - The different parameters available should allow a close description of any real systems.
   - Similar high temperature A2/B2 phase diagram can be obtained with many different descriptions, low temperature equilibria can difficult to study or hiden by other phases; the knowledge on the thermodynamic behaviours by experiments or theoretical calculations is the basis of a reliable description.

Ternary cases

Extrapolation of binary bond energies

$G_{i2j2(B2)} = 4\ u_{ij}$

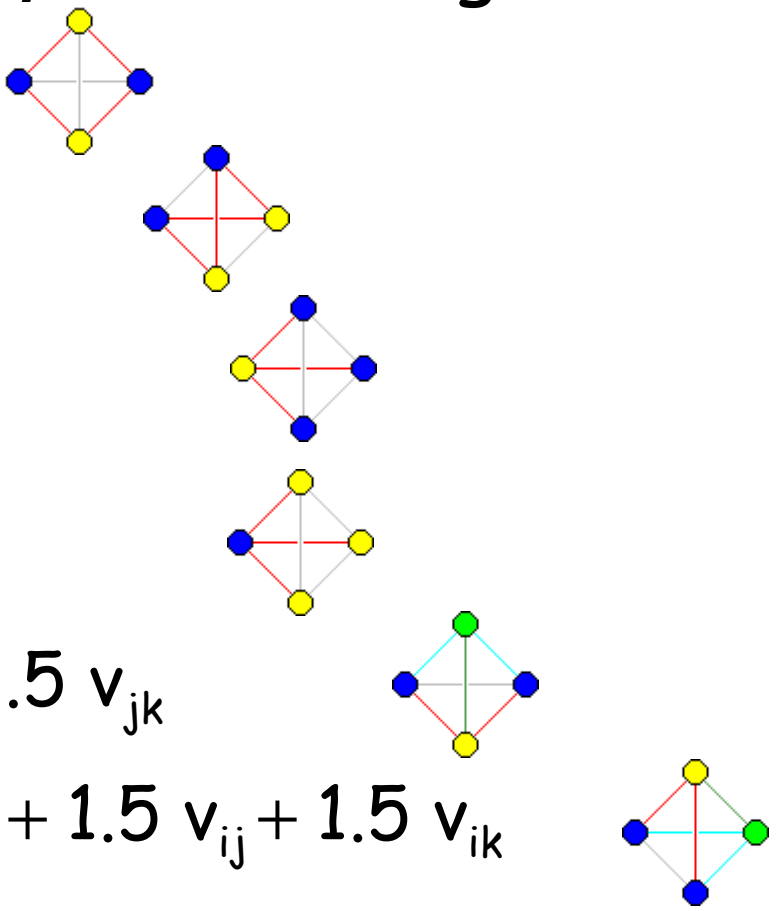
$G_{i2j2(B32)} = 2\ u_{ij} + 3\ v_{ij}$

$G_{i3j(D03)} = 2\ u_{ij} + 1.5\ v_{ij}$

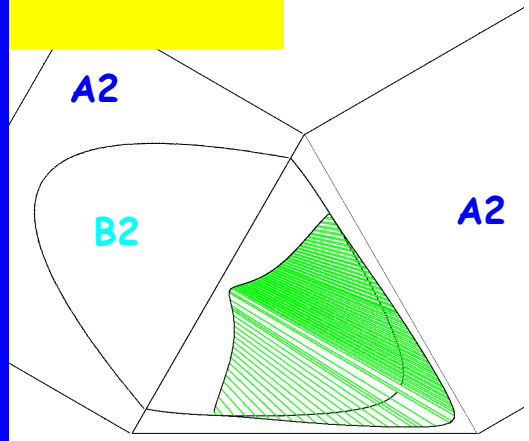
$G_{ij3(D03)} = 2\ u_{ij} + 1.5\ v_{ij}$

$G_{iijk(L21)} = 2\ u_{ij} + 2\ u_{ik} + 1.5\ v_{jk}$

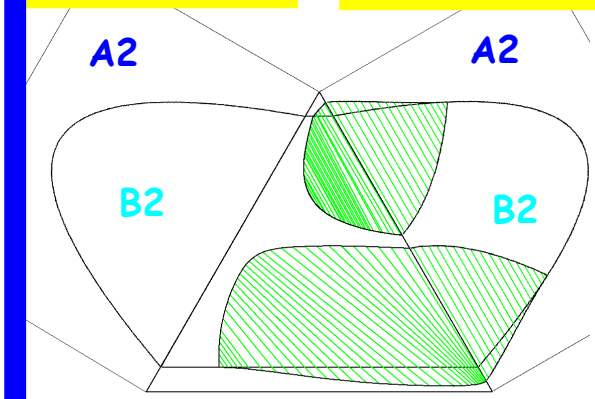
$G_{ikij(F4\text{-}3m)} = u_{ij} + u_{ik} + u_{jk} + 1.5\ v_{ij} + 1.5\ v_{ik}$



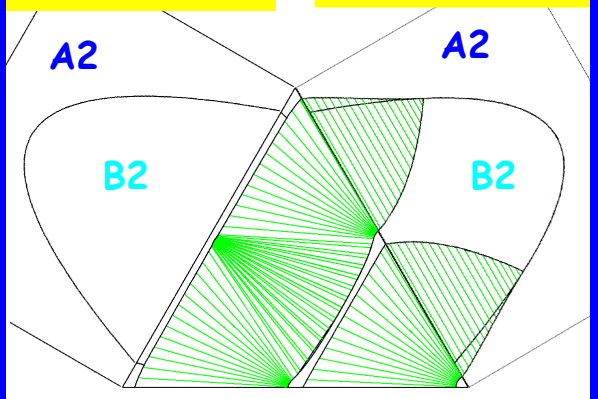
$u_{AB} = -250R$



$u_{AB} = -250R$ $u_{BC} = -125R$ $v_{BC} = +167R$

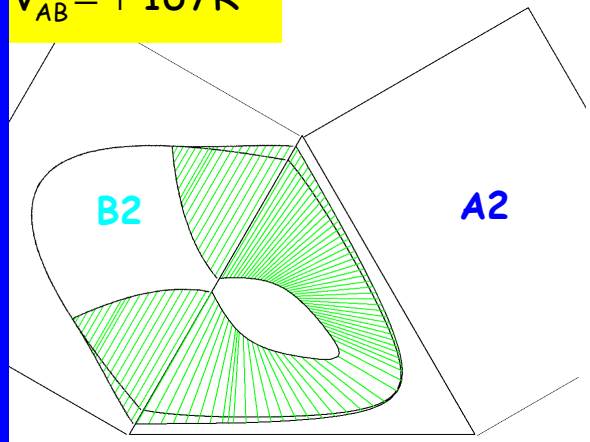


$u_{AB} = -250R$ $u_{BC} = -125R$ $v_{BC} = +167R$

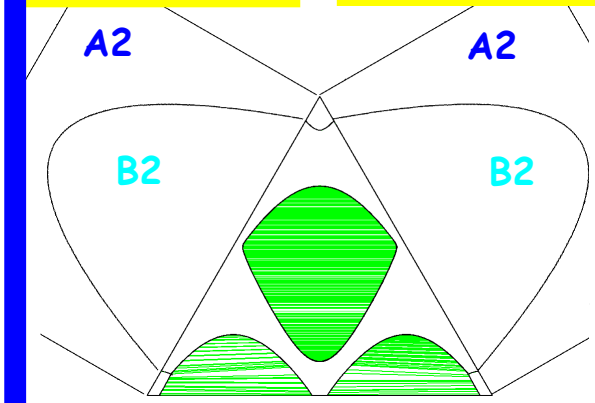


$u_{AC} = -125R$ $v_{AC} = +167R$

$u_{AB} = -125R$ $v_{AB} = +167R$

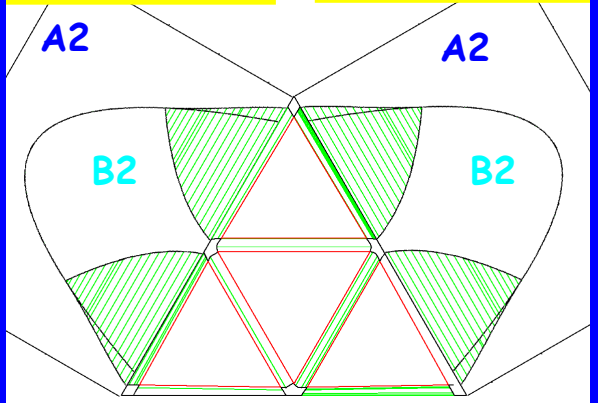


$u_{AB} = -250R$ $u_{BC} = -250R$



$u_{AC} = -125R$ $v_{AC} = +167R$

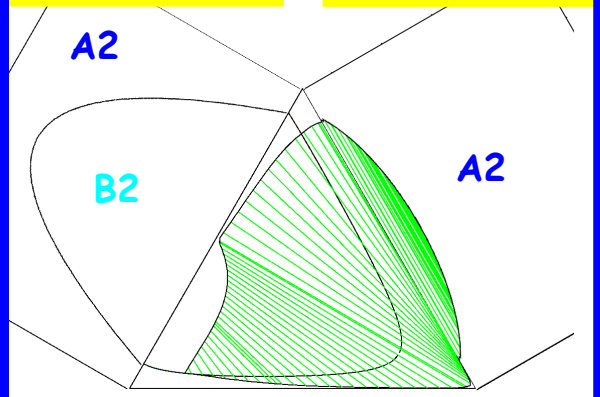
$u_{AB} = -125R$ $v_{AB} = +167R$ $u_{BC} = -125R$ $v_{BC} = +167R$



$u_{AC} = -125R$ $v_{AC} = +167R$

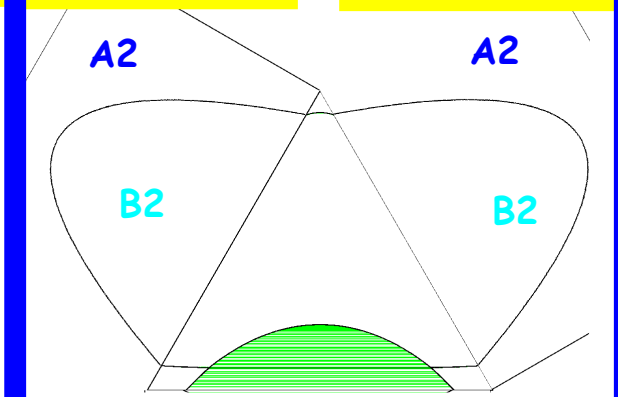
$u_{AB} = -250R$

$u_{BC} = +100R$



$u_{AB} = -250R$

$u_{BC} = -250R$

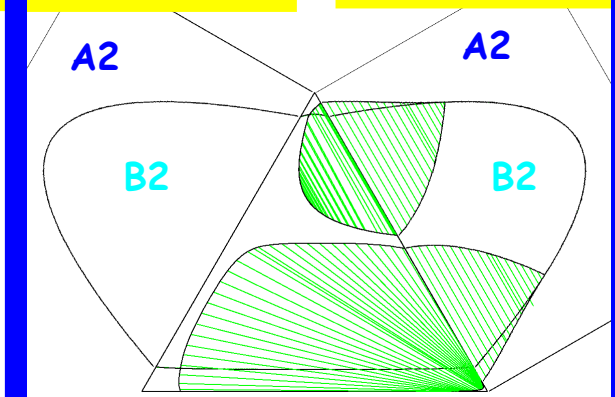


$u_{AC} = +100R$

$u_{AB} = -250R$

$u_{BC} = -125R$

$v_{BC} = +167R$

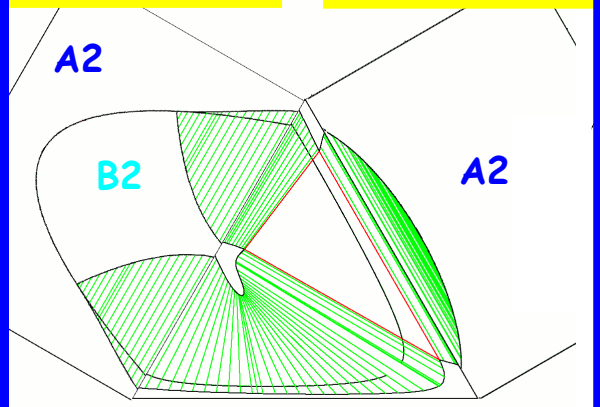


$u_{AC} = +100R$

$u_{AB} = -125R$

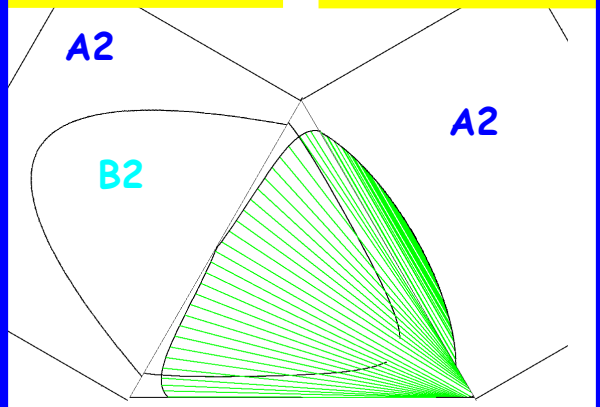
$v_{AB} = +167R$

$u_{BC} = +100R$



$u_{AB} = -250R$

$u_{BC} = +100R$



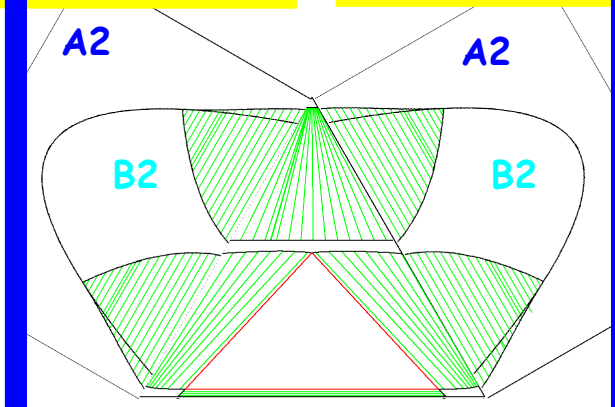
$u_{AC} = +100R$

$u_{AB} = -125R$

$v_{AB} = +167R$

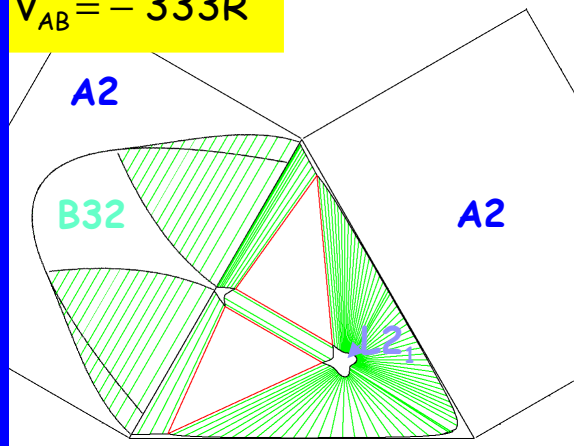
$u_{BC} = -125R$

$v_{BC} = +167R$

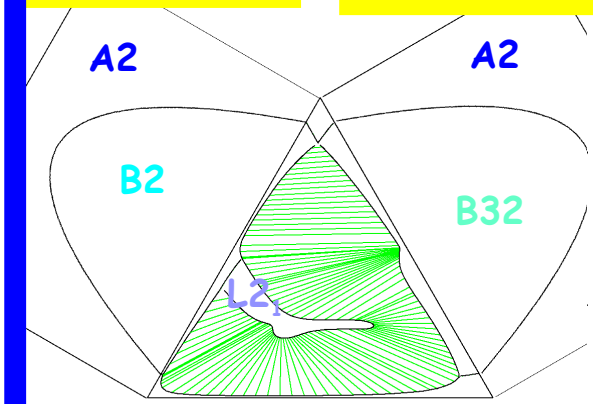


$u_{AC} = +100R$

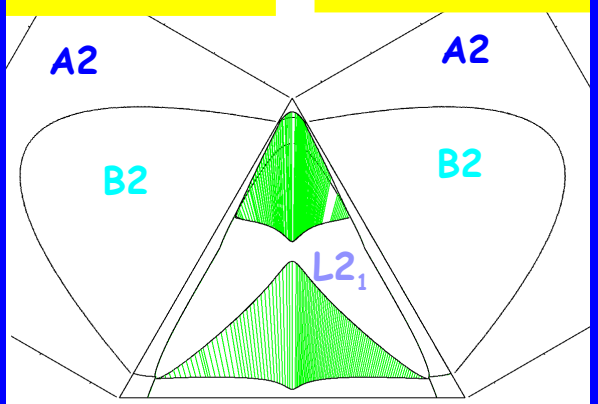
$u_{AB} = +333R$
$v_{AB} = -333R$



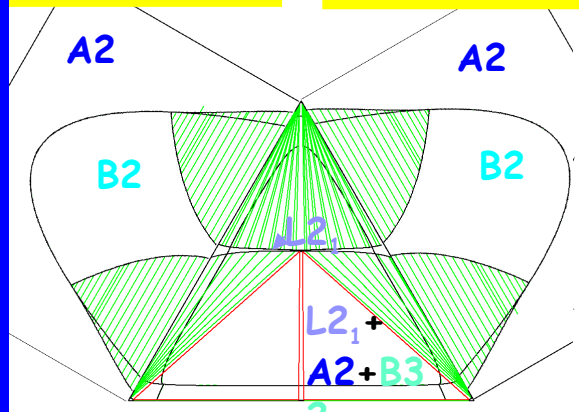
$u_{AB} = -250R$
$v_{BC} = -333R$



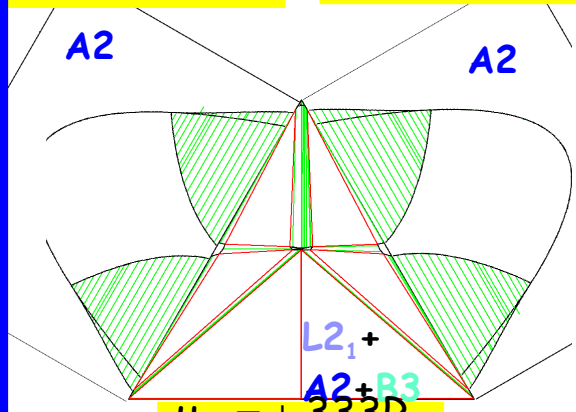
$u_{AB} = -250R$
$u_{BC} = -250R$
$v_{AC} = -333R$



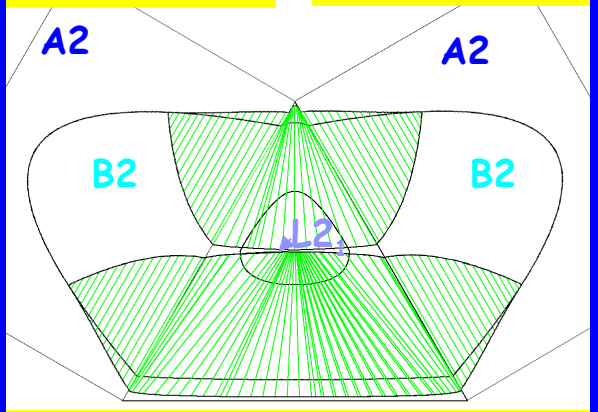
$u_{AB} = -125R$
$v_{AB} = +167R$
$u_{BC} = -125R$
$v_{BC} = +167R$
$u_{AC} = +333R$
$v_{AC} = -333R$



$u_{AB} = -125R$
$v_{AB} = +167R$
$u_{BC} = -125R$
$v_{BC} = +167R$
$u_{AC} = +333R$
$v_{AC} = -333R$
$LO_{AC} = 200R$



$u_{AB} = -125R$
$v_{AB} = +167R$
$u_{BC} = -125R$
$v_{BC} = +167R$
$G_{AB2C(L21)} = 2\,u_{AB} + 2\,u_{BC} + 1.5$
$v_{AC} - 250\ R$



Ternary cases

- Many different phase equilibria obtained just extrapolating very simple binary systems.
- Ternary descriptions have to be based on careful binary modeling.
- Ternary parameters are available to describe more precisely real ternary systems.
- First principle calculations can also help to estimate the energies of ternary compounds, in particular when metastable.

Introducing vacancies

Vacancies (□) are known as point defects in B2

$\Rightarrow \quad (A,B,\square)_{1/4}(A,B,\square)_{1/4}(A,B,\square)_{1/4}(A,B,\square)_{1/4}$

For A2, it is equivalent to (A,B,□)
where □ are "thermal vacancies"

Simplest model for "thermal vacancies": (A,□)

Introducing vacancies

CEF, for one mole of site (A,$\square$)

$$G - y_A H_A = y_A(G_A - H_A) + y_\square G_\square + G^{id} + y_A y_\square L_{A\square}$$

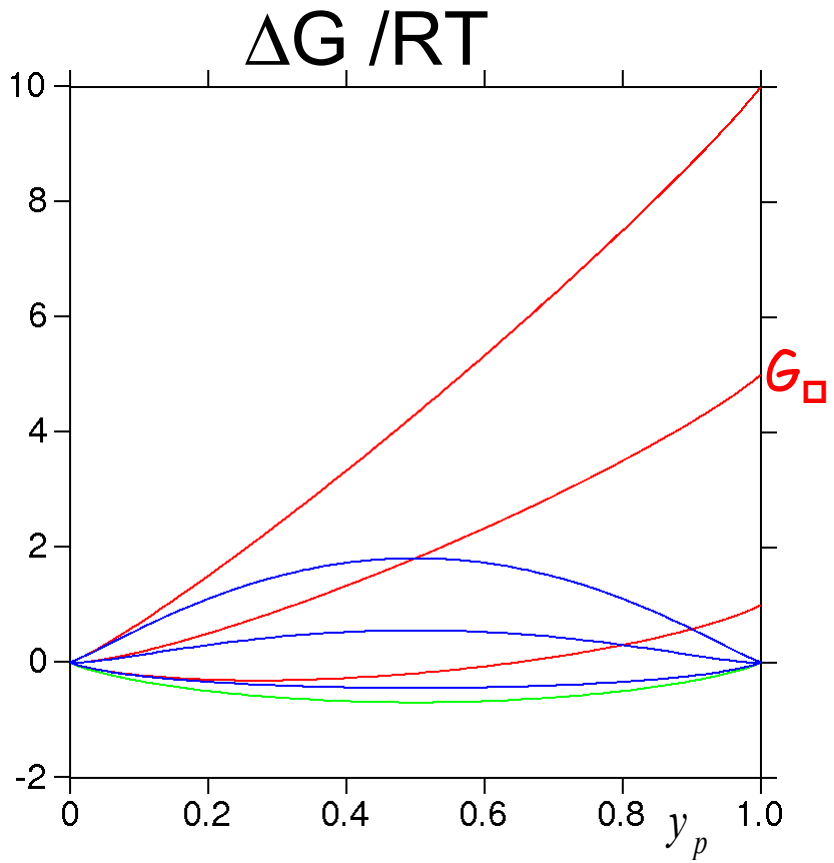
$$\text{with } G^{id} = RT(y_A \ln y_A + y_\square \ln y_\square)$$

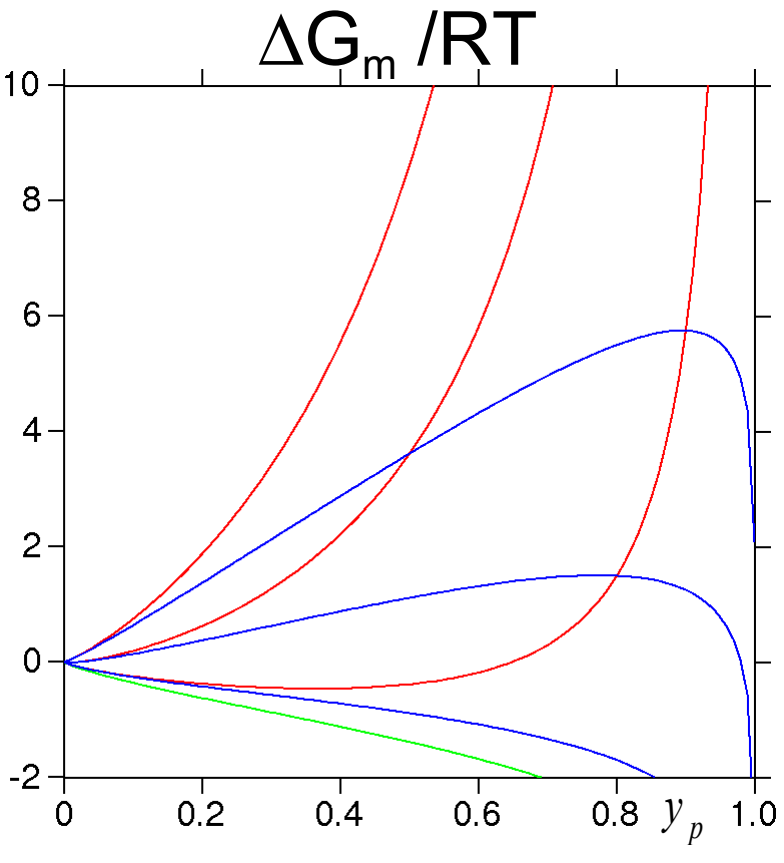
$G_A - H_A$ Gibbs energy of one mole totally full of A refered to its enthalpy in the reference state

$G_\square$ Gibbs energy of one mole totally empty, should be identical whatever A, =0 or >>0?

$L_{A\square}$ Interaction parameter of A and $\square$

$$\Delta G = G - y_A G_A = y_\square G_\square + G^{id} + y_A y_\square L_{A\square}$$





For one mole of site:

- a single minimum for $y_A \simeq 1$
- two minima $y_A \simeq 1$ and $y_\square \simeq 1$

For one mole of *A*

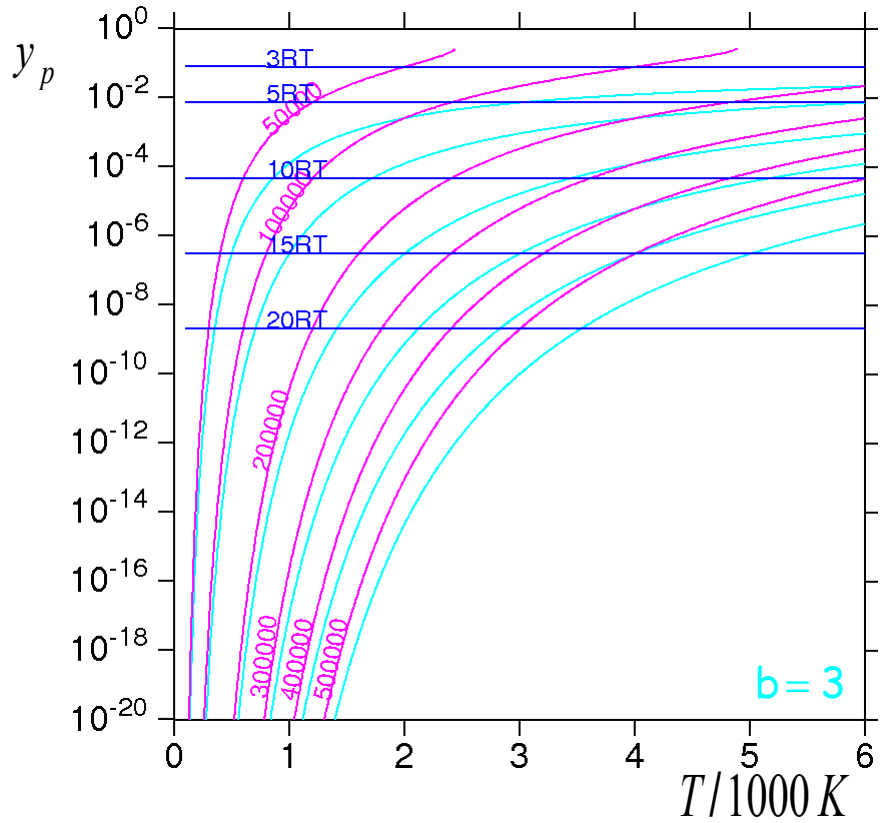
- minima for $y_A \simeq 1$
- divergency for $y_\square \simeq 1$

Introducing vacancies

For theoritical reasons,

$G_{\square} = 0$ favoured and used bellow

And what expression for $L_{A\square}$?



$L_{A\square} = bRT$ unreasonnable

$L_{A\square} = a$ problems at high T for lower a

roughly $y_{\square} \approx 10^{-5}$–$10^{-6}$ at $T_{fus} \Rightarrow L_{A\square} \approx 100 T_{fus}$

$L_{A\square} = a+bRT$ can allow a better fit if experiments

Introducing vacancies

$(A,\square)$ with $L_{A\square}$

is mathematically equivalent to

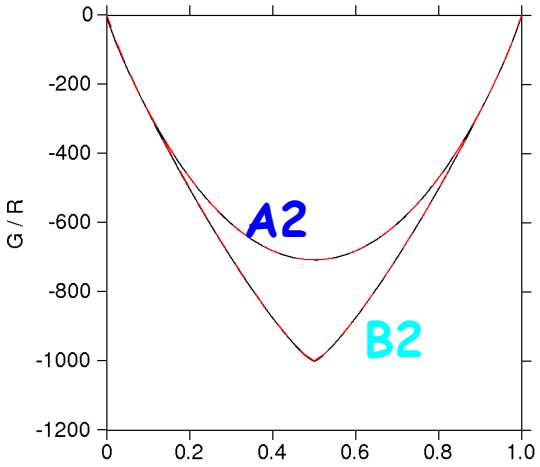
$(A,\square)_{\frac{1}{2}}$ $(A,\square)_{\frac{1}{2}}$ with $G_{A:\square} = G_{\square:A} = \frac{1}{2} L_{A\square}$

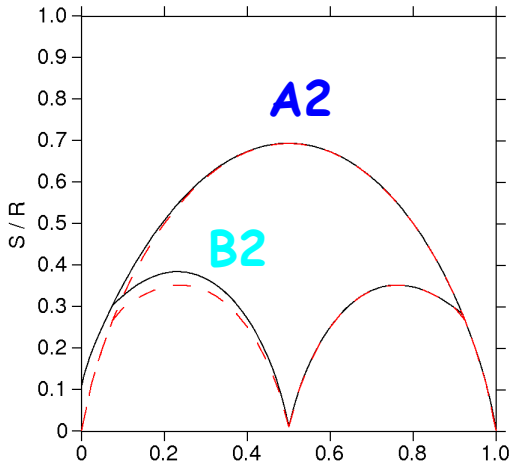
or to

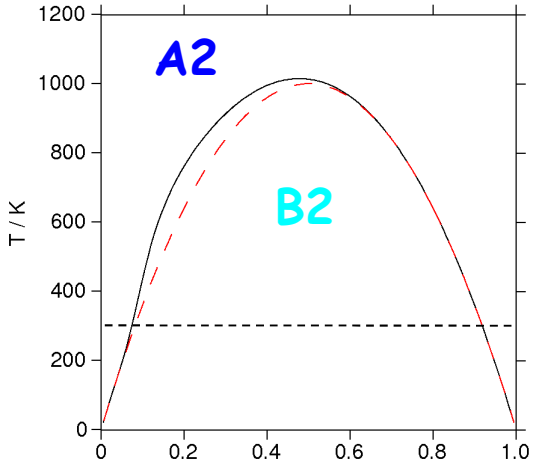
$(A,\square)_{\frac{1}{4}}$ $(A,\square)_{\frac{1}{4}}$ $(A,\square)_{\frac{1}{4}}$ $(A,\square)_{\frac{1}{4}}$ with $u_{A\square} = \frac{1}{8} L_{A\square}$

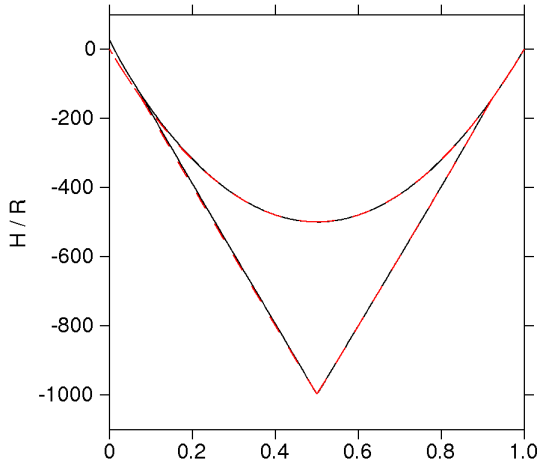
$L_{A\square} \neq L_{B\square} \Rightarrow$ triple defects $(A,B)(B,\square)$

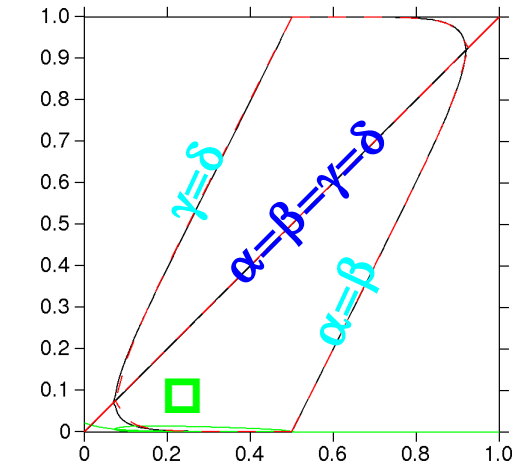
$u_{AB} = -250R$ $u_{A\square} = +150R$ $u_{B\square} = +500R$









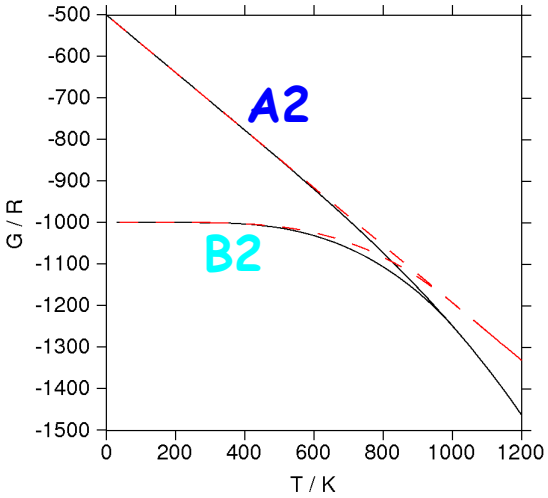


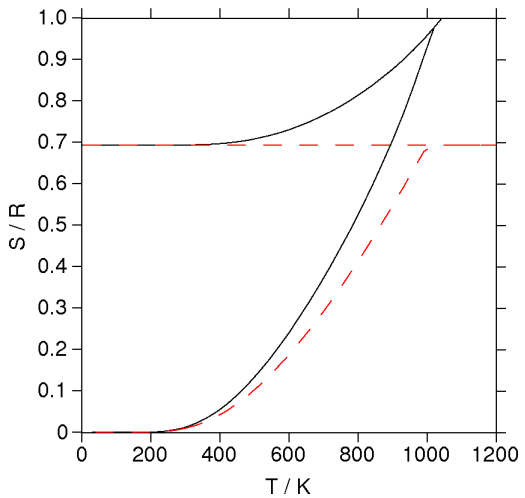
⇒ On A side, B2:
(A) (A) (B, □) (B, □)

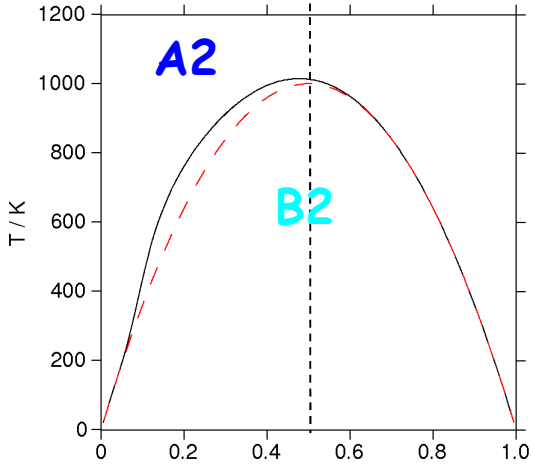
⇒ On B side, B2:
(A,B) (A,B) (B) (B)

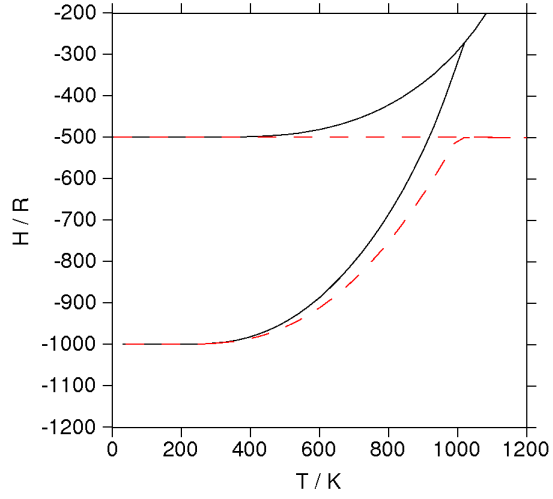
⇒ B2 stabilised asymmetrically

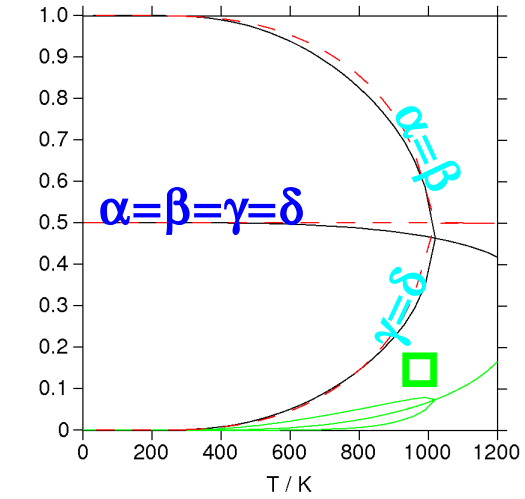
$u_{AB} = -250R$ $u_{A\square} = +150R$ $u_{B\square} = +500R$











⇒ A2 and B2 stabilised by entropy effect

Introducing vacancies

- The introduction of vacancies allows to easily describe triple defects.

- The introduction of vacancies may stabilise asymmetrically the B2 phase.

Thermodynamic description

- The formalism $G = G(A2,x) + G(ord,y) - G(ord,y=x)$ can be used equivalently.
- The relations imposed by the crystallography remain.
- Once A2 fixed, some freedom is removed to describe the different ordered phases.
- The parameters of G(ord,y) are not defined uniquely; there is an infinity of values giving the same overall description with G(ord,y=x) between G(A2,x) and 0.

Conclusion

- It is important to know the crystallography of a phase and its defects in order to model it satisfactorily.
- It is important to know the effect of the different parameters of the thermodynamic model used.
- The experimental knowledge of a system allows to get into the real world.
- The use of first principle results helps to avoid unrealistic metastable extrapolation.

Acknowlegments

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- to Suzana Fries for simulating discussions on ordering.