Alloy Phase diagrams from first-principles

by

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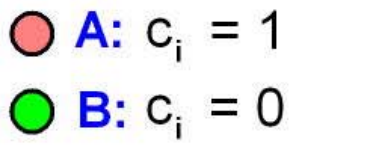
narrated by

Hans L. Skriver

Monte Carlo for alloys

Lattice gas Hamiltonian:

$$H = \frac{1}{2}\sum_{ij}{}' V_{ij} c_i c_j - \mu \sum_i c_i$$



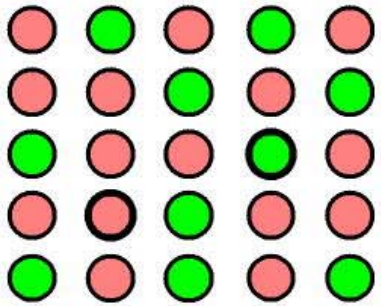
Metropolis algorithm:

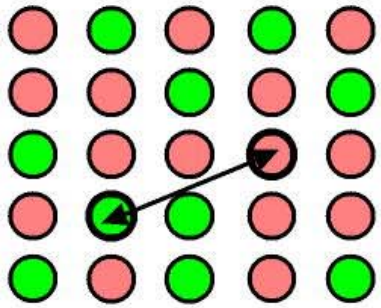
1) Exchange atoms for fixed lattice, concentration, and temperature

2) Keep configuration in sample if

$$r < \exp(-\Delta E/k_B T)$$

- r: Random number between 0 and 1
- ΔE: Configurational energy difference





Landau and Binder: *A guide to Monte Carlo Simulations in statistical physics*

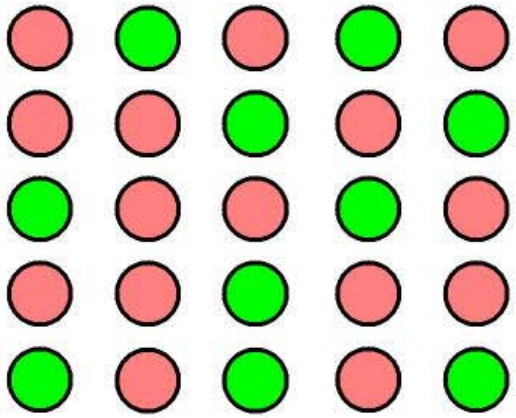
Cluster expansion i terms of effective interactions

Configurational energy:

$$E = \sum_i{}' V_i^{(1)} \langle c_i \rangle + \sum_{ij}{}' V_{ij}^{(2)} \langle c_i c_j \rangle + \sum_{ijk}{}' V_{ijk}^{(3)} \langle c_i c_j c_k \rangle$$

Occupation number:

$$c_i = \begin{cases} 1 & \text{if i occupied by A} \\ 0 & \text{if i occupied by B} \end{cases}$$



Spin variable:

$$\sigma_i = 2c_i - 1$$

Correlation function:

$$\xi_p^{(n)} = \langle \sigma_i \sigma_j \ldots \sigma_k \rangle - \sigma^n$$

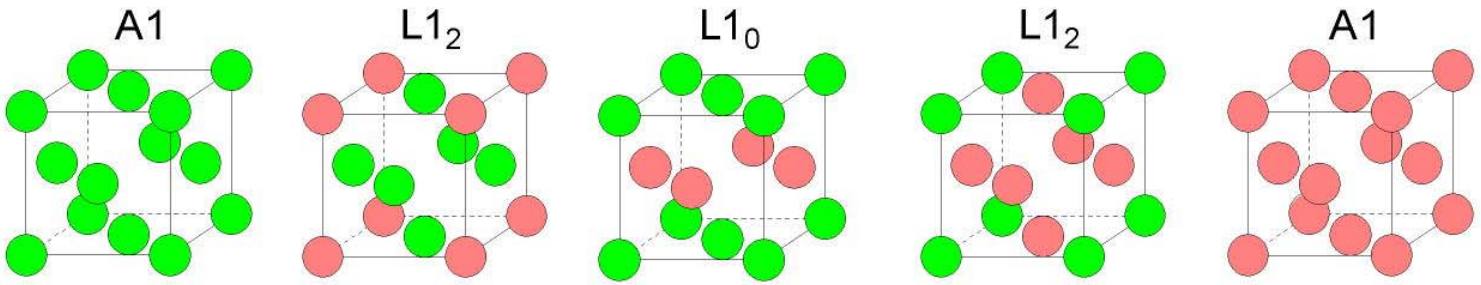
Random alloy:

$\xi_p^{(n)} = 0 \quad \forall$ n, p

p: shell, triangle, etc.

Structure inversion method

$$E_{tot} = V^{(0)} + V^{(1)}\xi^{(1)} + V^{(2)}\xi^{(2)} + V^{(3)}\xi^{(3)} + V^{(4)}\xi^{(4)} + \ldots$$



$\xi^{(i)}$

i	A1	$L1_2$	$L1_0$	$L1_2$	A1
1	**1**	**1/2**	**0**	**-1/2**	**-1**
2	**1**	**0**	**-1/3**	**0**	**1**
3	**1**	**-1/2**	**0**	**1/2**	**-1**
4	**1**	**-1**	**1**	**-1**	**1**

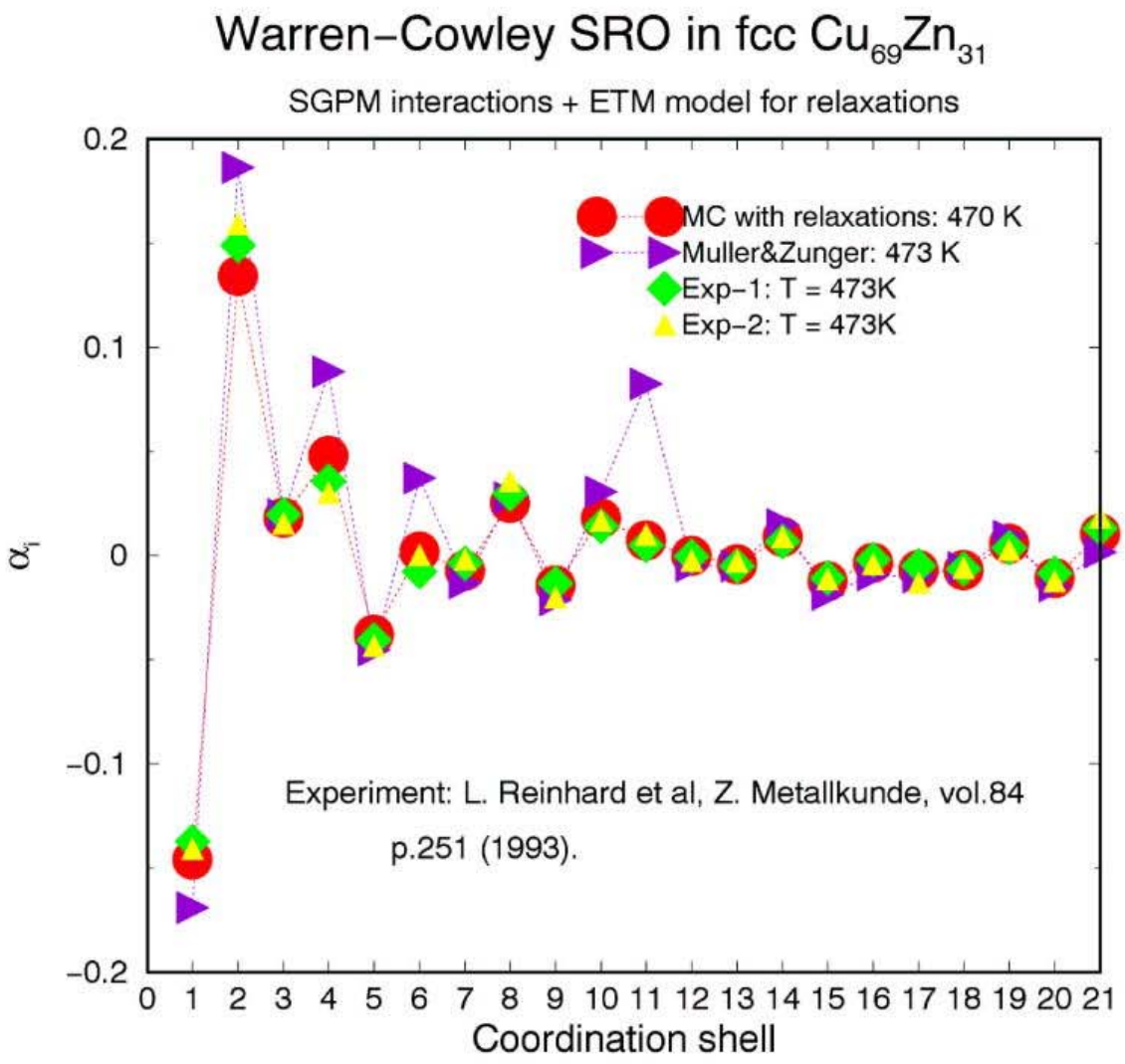
Short-range order in α-brass

Diffuse neutron scattering:

$$I_{SRO}(Q) = I \sum_{R} \alpha_R \, e^{i\,Q\cdot R}$$

Monte-carlo simulations:

$$\alpha_R = 1 - \frac{\langle c_i(1 - c_j)\rangle}{c(1-c)}$$



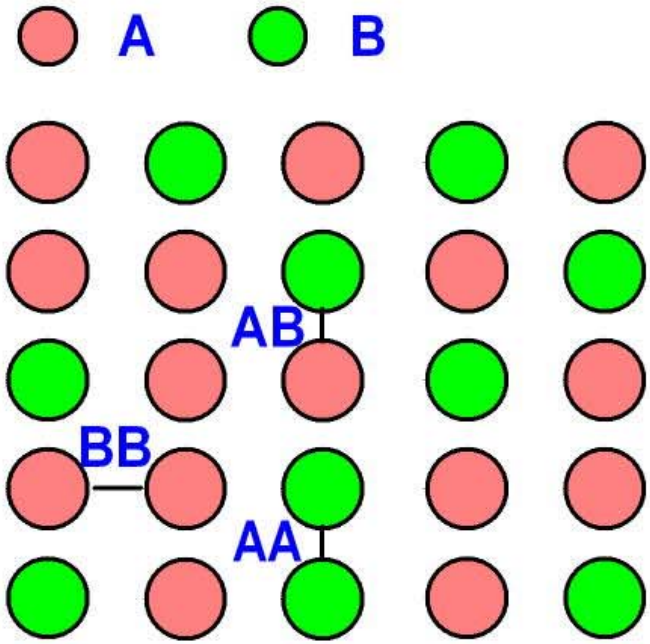
A_cB_{1-c} alloy

Configurational energy:

$$E_{conf} = \frac{1}{2} \sum_{ij}{}' V_{ij} c_i c_j$$

Effective pair potential:

$$V_{ij}^{(2)} = V_{ij}^{AA} - 2V_{ij}^{AB} + V_{ij}^{BB}$$



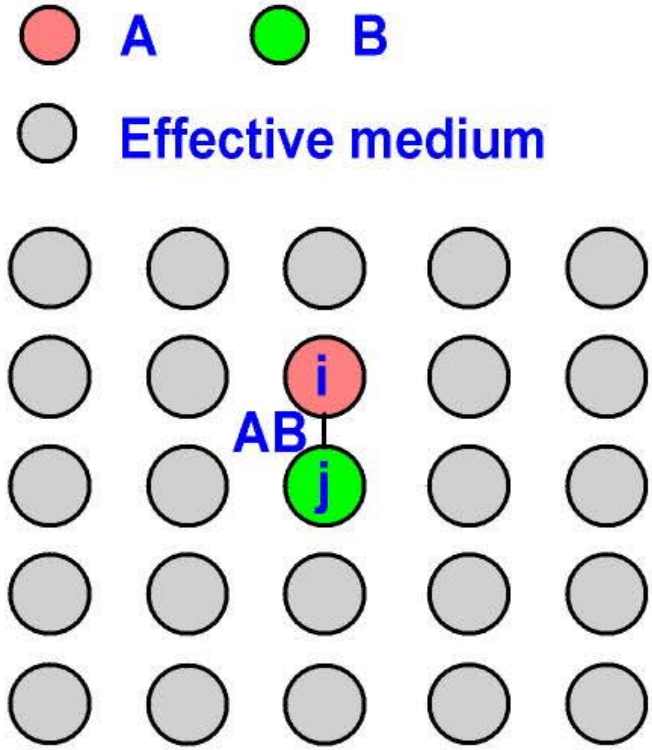
General perturbation method (GPM)

$$V_{ij}^{AB} \propto \int dE\, f(E)\, t_i^A \overline{G}_{ij}\, t_j^B\, \overline{G}_{ji}$$

V_{ij}^{AB} : Pair potential

$\overline{G}_{ij}$: Coherent potential Green function

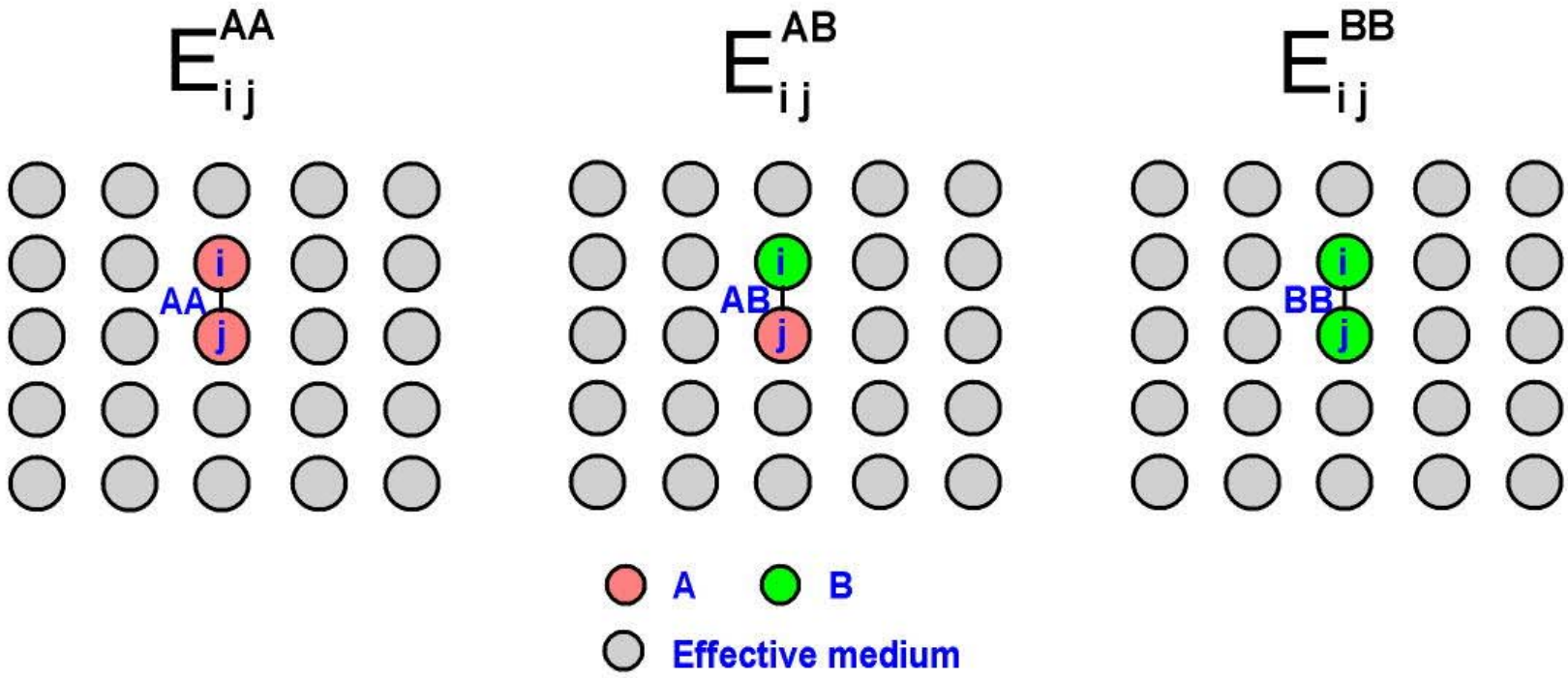
t_i^A : Single-site t-matrix



Ducastelle and Gautier, J. Phys. **F 6,** 2039 (1976)

GPM one-electron contribution

$$V_{ij}^{(2)} = E_{ij}^{AA} - 2E_{ij}^{AB} + E_{ij}^{BB}$$



GPM potentials

One-electron contribution:

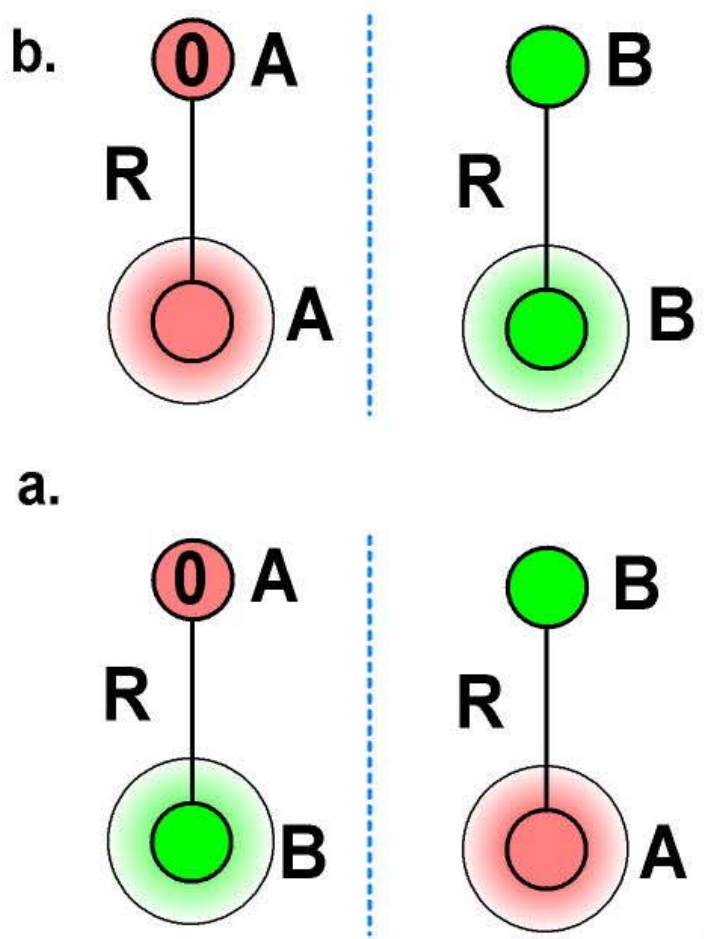
$$V^{(2)}_{GPM}(R) = \frac{1}{2}\,[E_b(R) - E_a(R)]$$

Screening contribution:*)

$$V_{scr}(R) = Q^2_{AB}\, I^{sc}(R)$$

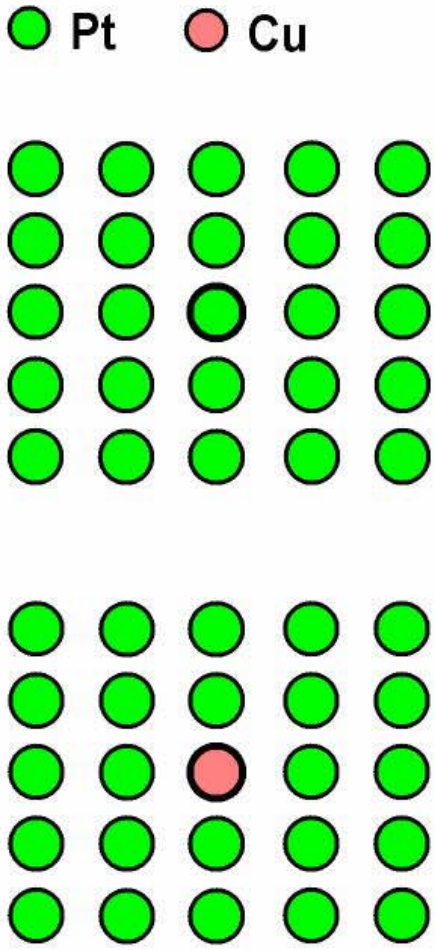
GPM pair-potential:

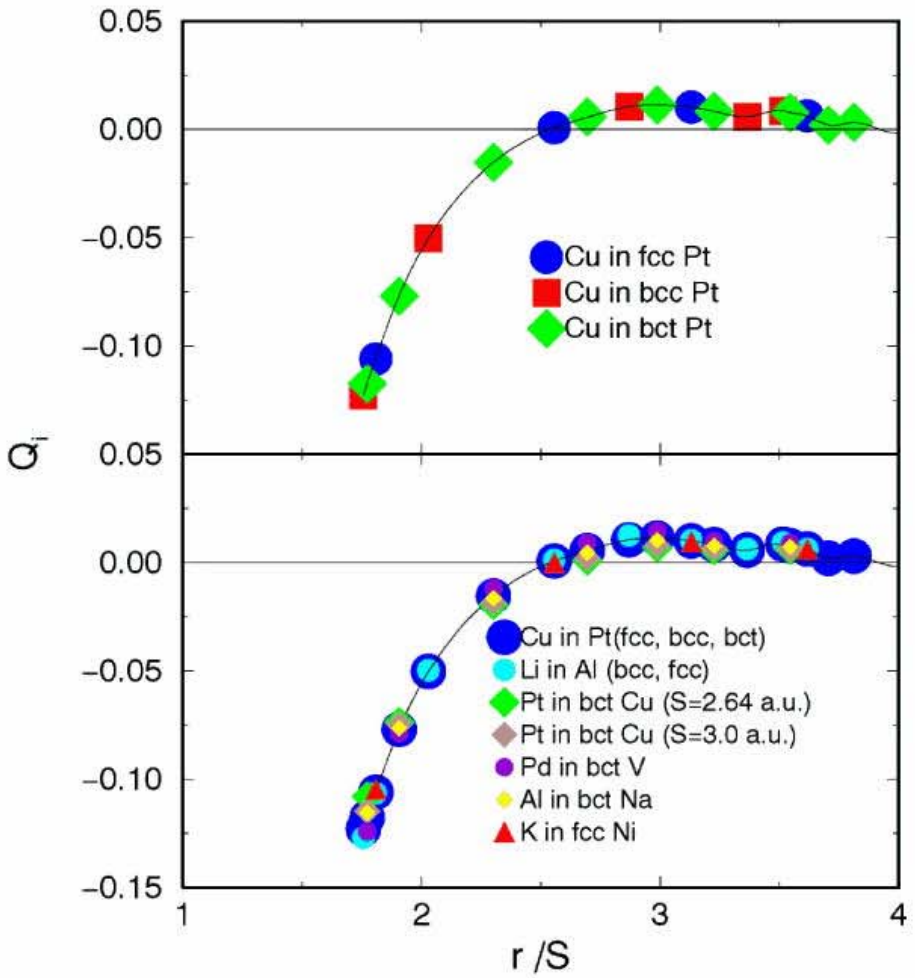
$$V^{(2)}(R) = V^{(2)}_{GPM}(R) + V_{scr}(R)$$



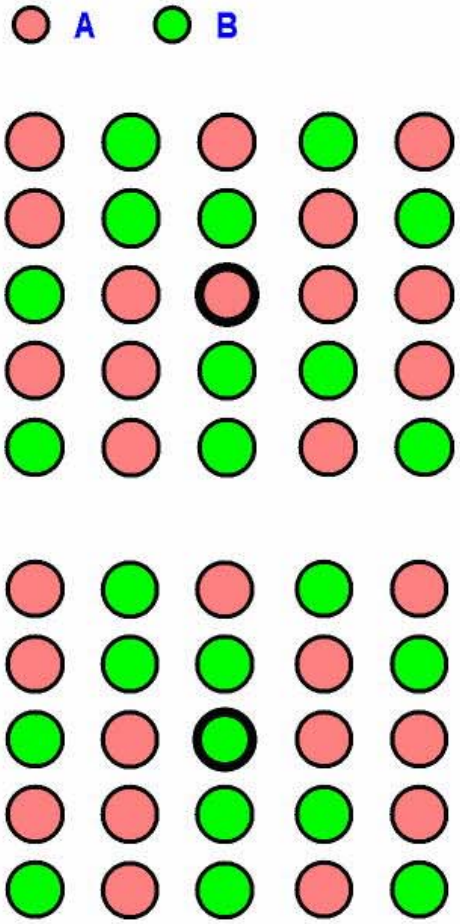
*) Ducastelle: *Order and Phase Stability in alloys*, 1991, pg. 468

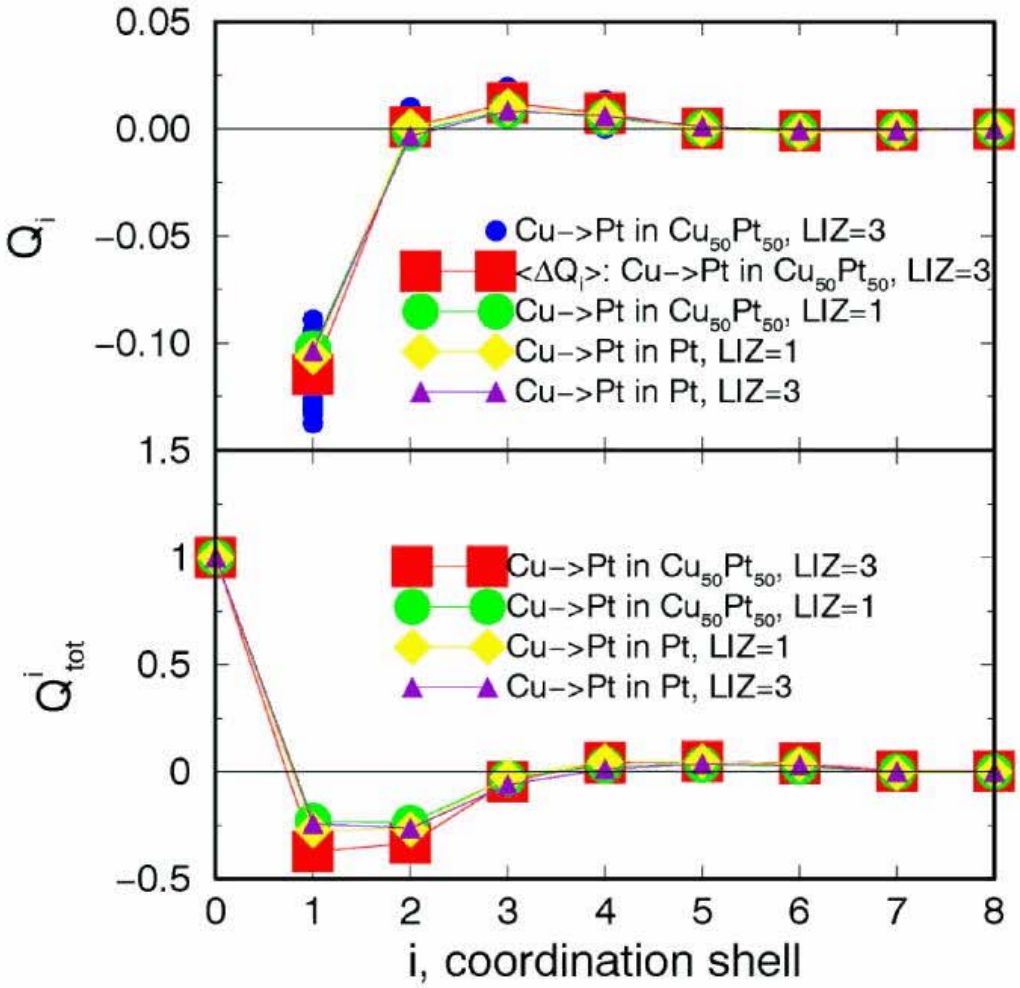
Screening of an impurity





Screening in random alloys

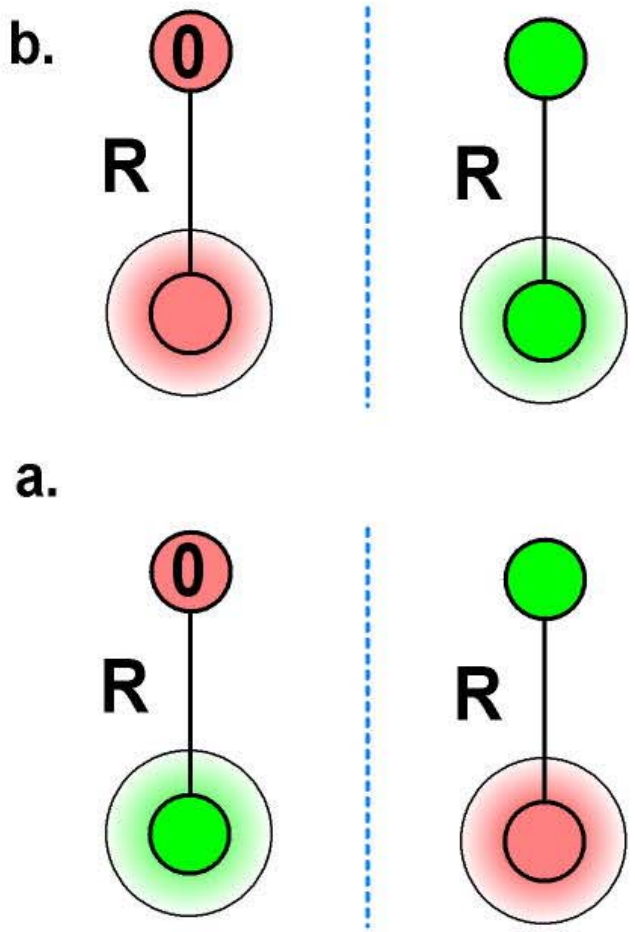




GPM screened Coulomb contribution

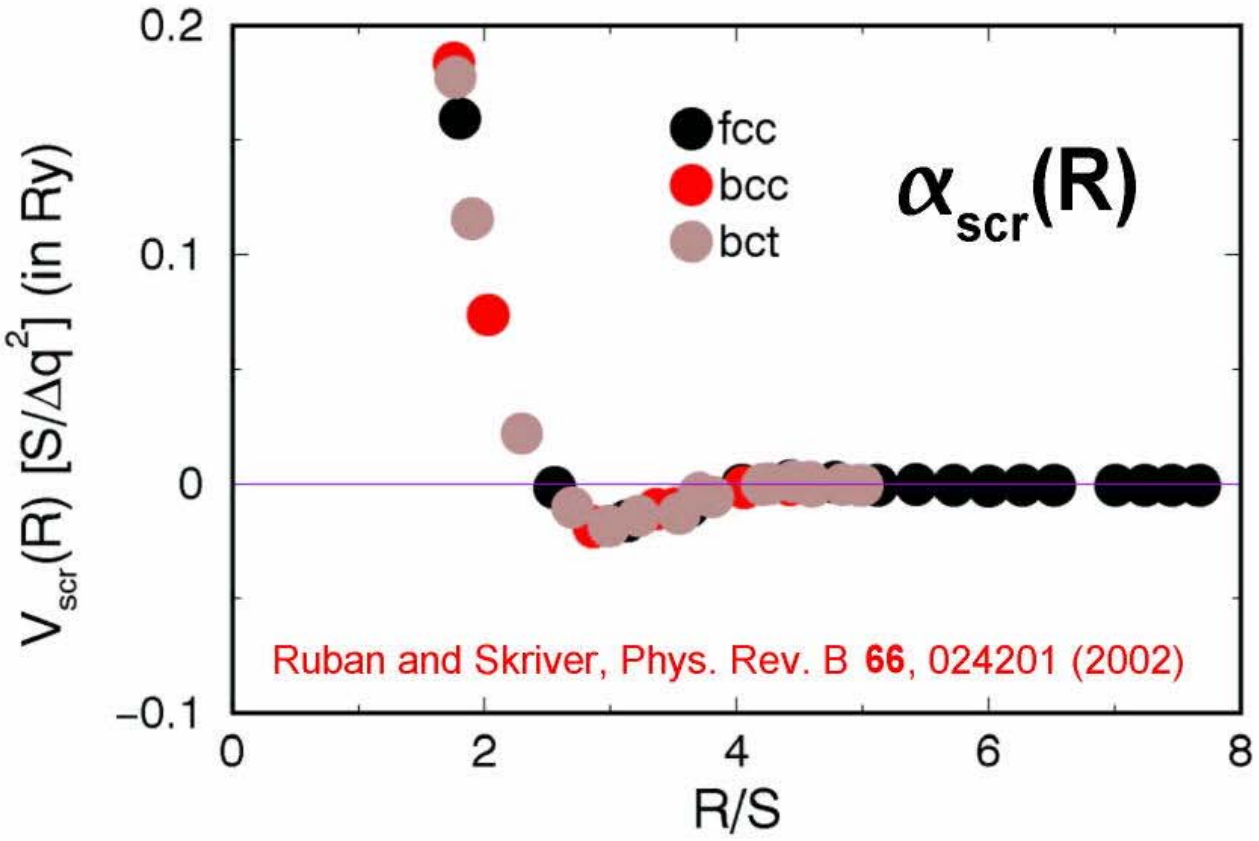
Change in electrostatic energy upon exchange of A and B atoms on site 1 projected onto site 0:

$$V_{scr}(R) = \frac{1}{2}\left[E_b^{el}(R) - E_a^{el}(R)\right]$$



Screened Coulomb interaction

$$V_{scr}(R) = e^2 Q_{AB}^2 \frac{\alpha_{scr}(R)}{2\,S}$$



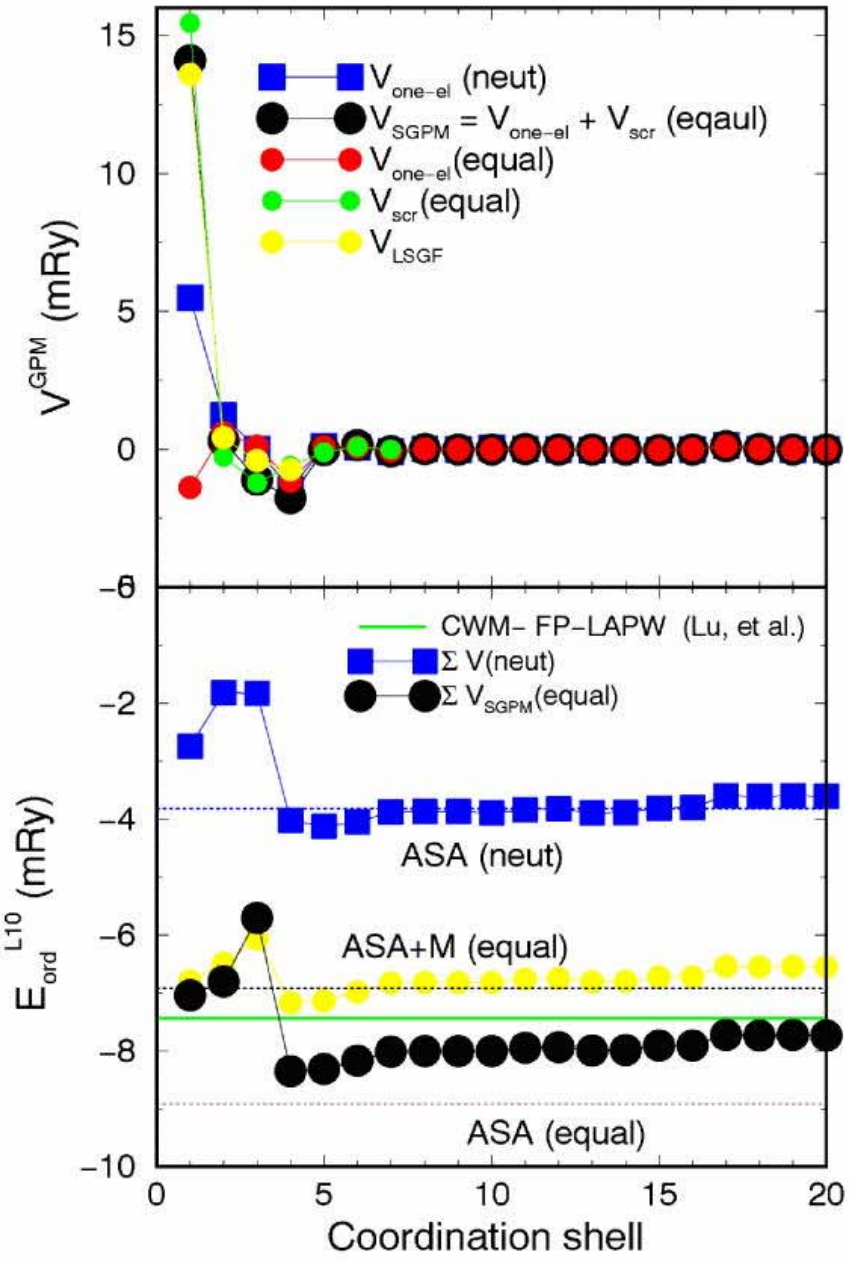
SGPM potentials and ordering in NiPt

Ordering energy:

$$E_{ord}^{L1_0} = \tfrac{1}{2} c(1-c) \sum_R \alpha_R^{L1_0} V_R$$

Short-range order parameter:

$$\alpha_R^{L1_0} = (-\tfrac{1}{3}, 1, -\tfrac{1}{3}, 1, \ldots)$$



Ordering energy in fcc $Cu_{75}Zn_{25}$

Ordering energy:

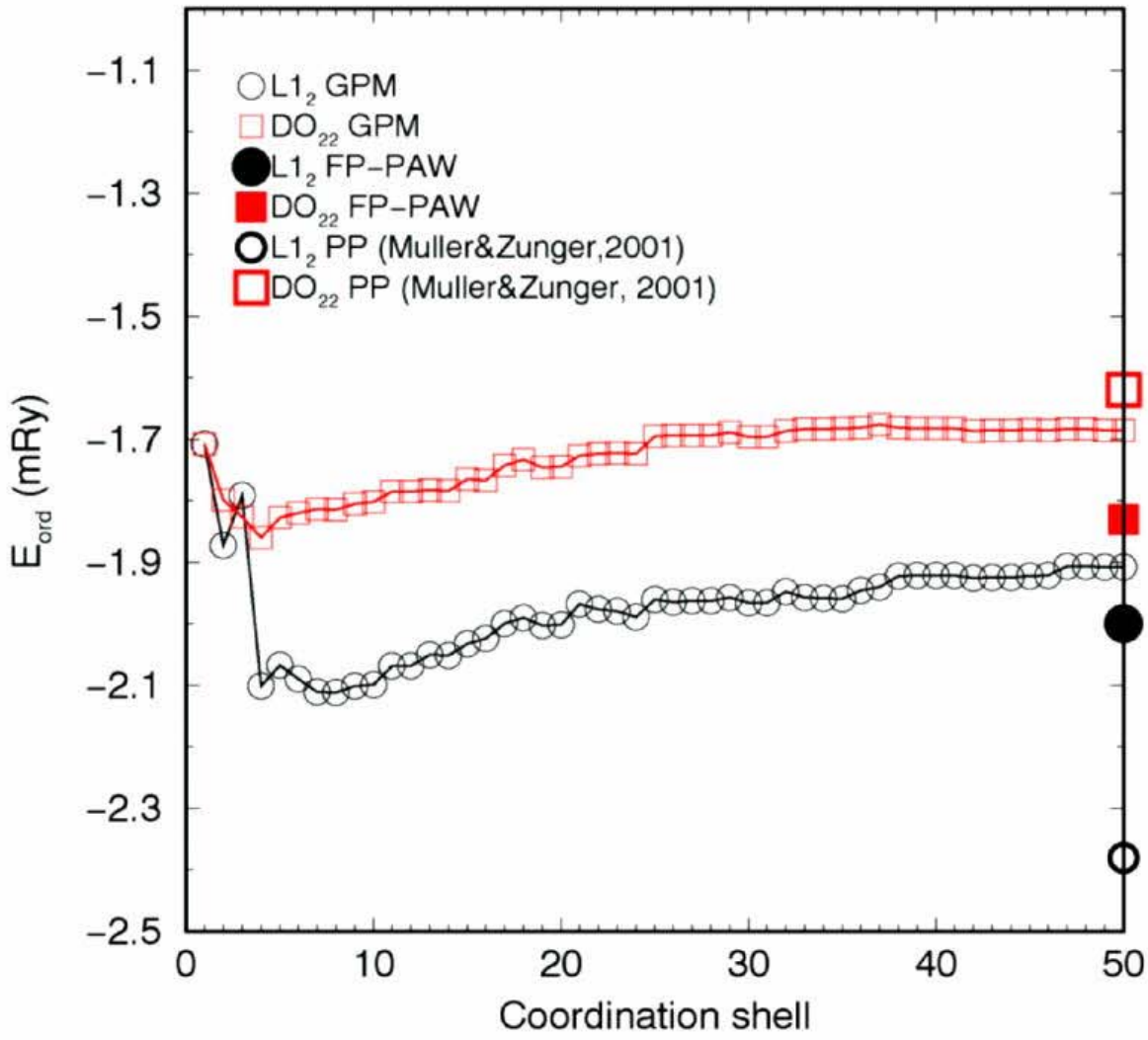
$$E_{ord} = \tfrac{1}{2} c(1-c) \sum_R \alpha_R V_R$$

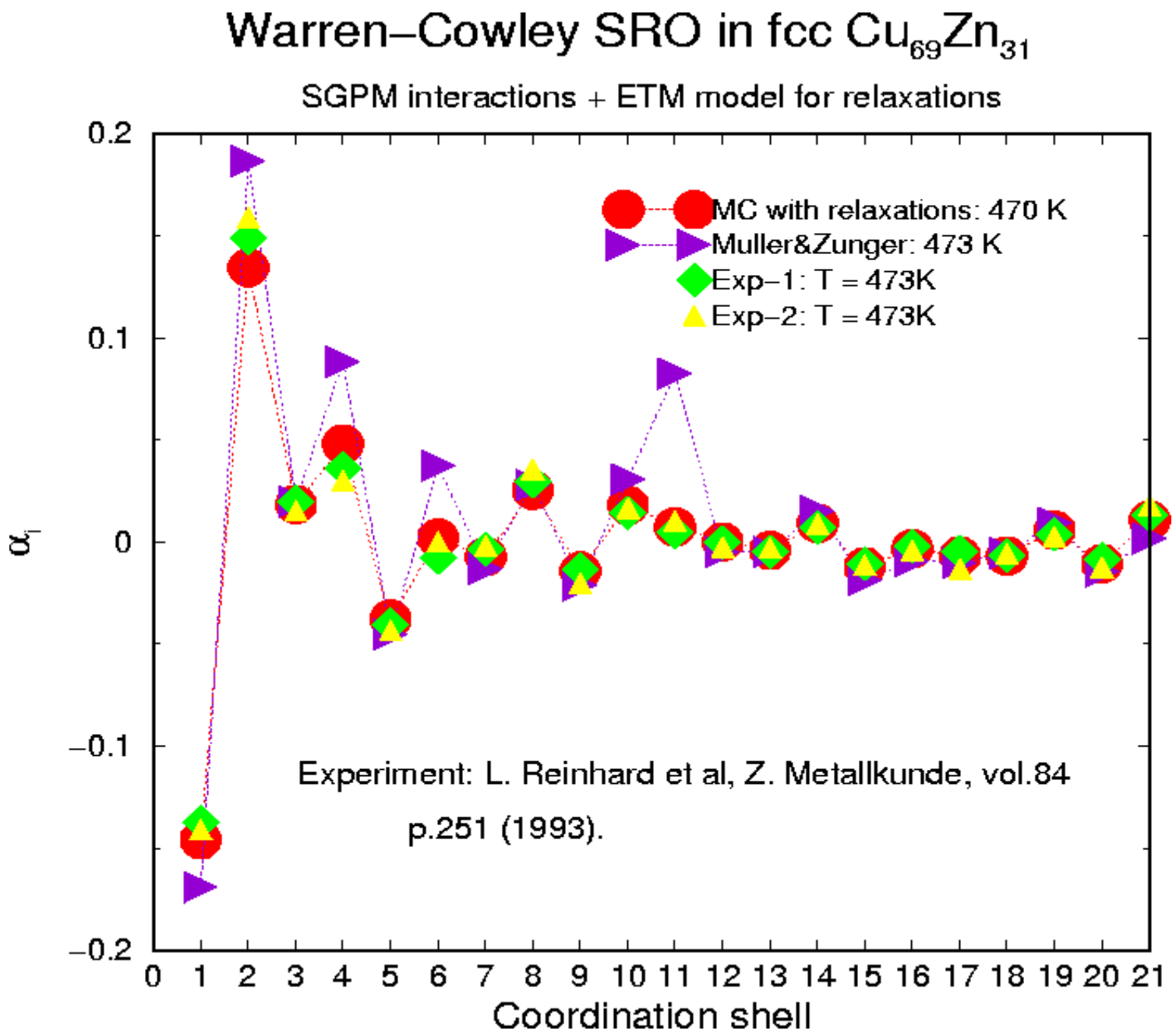
GPM: Present results

FP-PAW: Full-potential, VASP

PP: Pseudopotential

Include up to 50 shells for coverged ordering energy, cf. short-range order in α-brass




Warren–Cowley SRO in fcc $Cu_{69}Zn_{31}$
SGPM interactions + ETM model for relaxations
MC with relaxations: 470 K
Muller&Zunger: 473 K
Exp–1: T = 473K
Exp–2: T = 473K
Experiment: L. Reinhard et al, Z. Metallkunde, vol.84
p.251 (1993).
α_l
0.2
0.1
0
–0.1
–0.2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Coordination shell

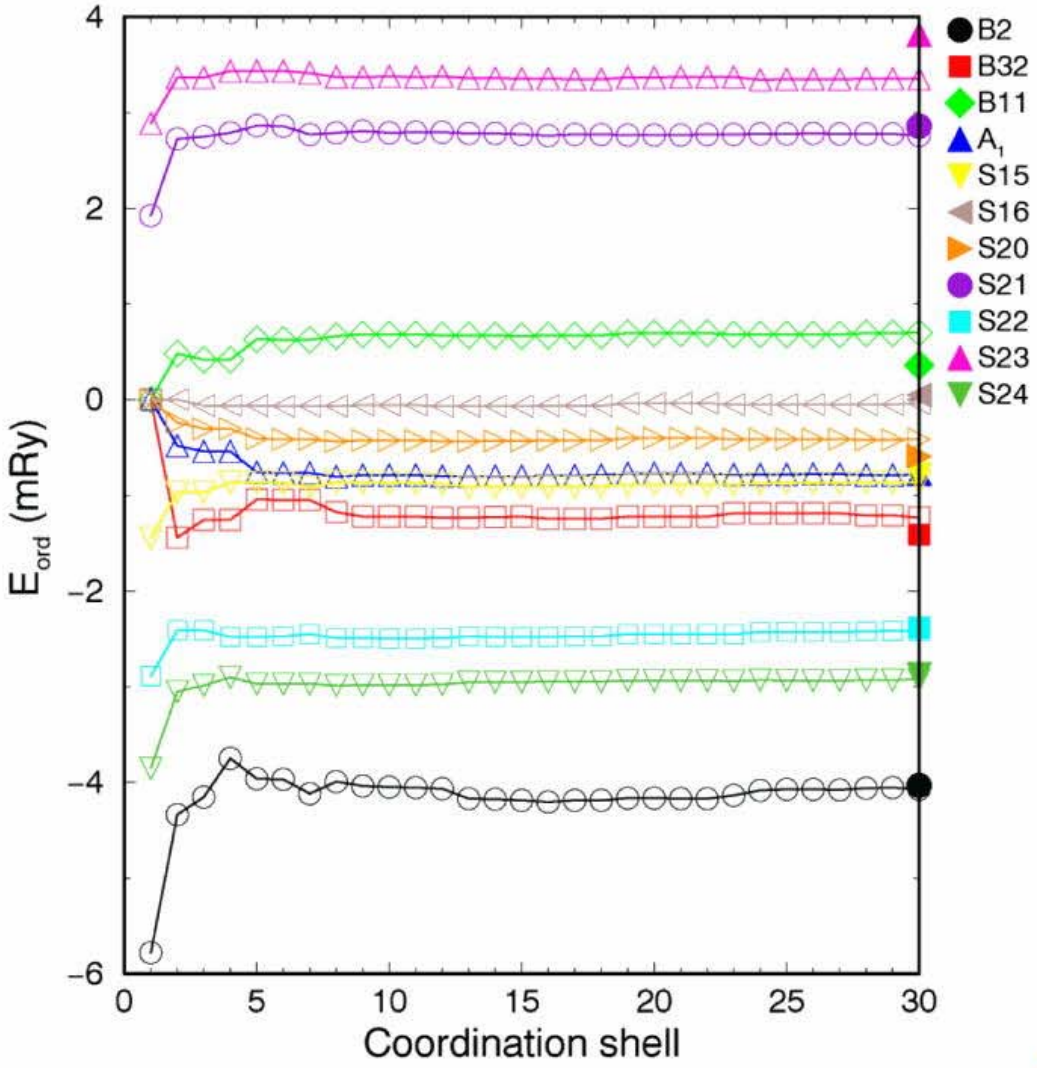
Ordering energies in bcc CuZn

Ordering energy:

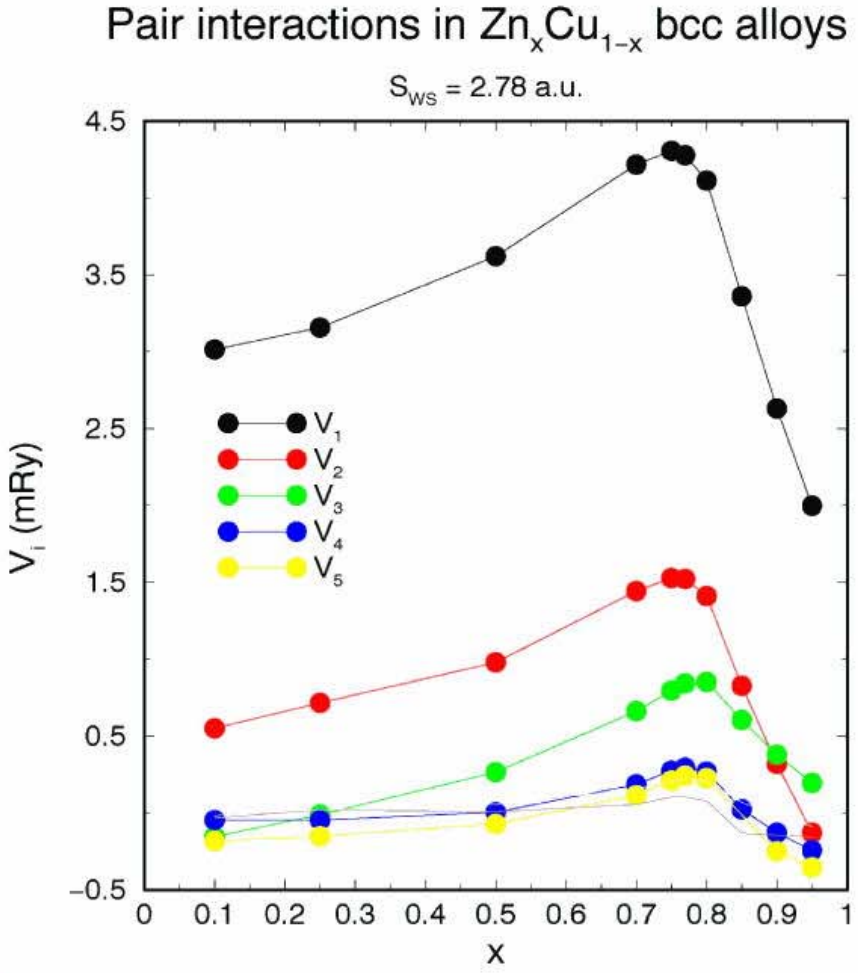
$$E_{ord} = \tfrac{1}{2} c(1-c) \sum_R \alpha_R V_R$$

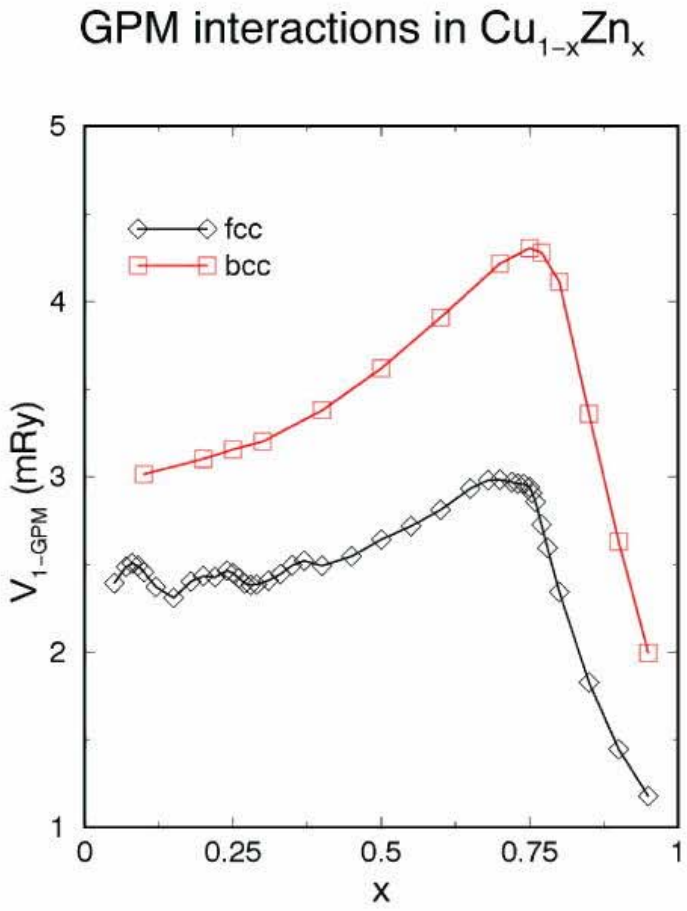
SGPM result versus full-potential calculations (Fp-PAW, VASP)

Include only up to 10 to 15 shells for coverged ordering energy



Pair potentials: Concentration dependence

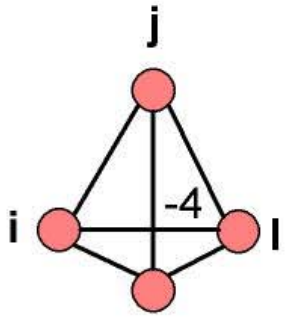




Effective tetrahedron model for local lattice relaxtions

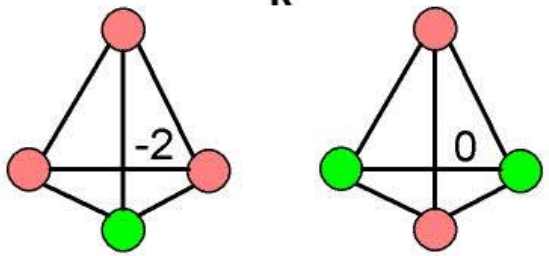
Tetrahedra of configuration:

$$\Sigma = \sigma_i + \sigma_j + \sigma_k + \sigma_l$$



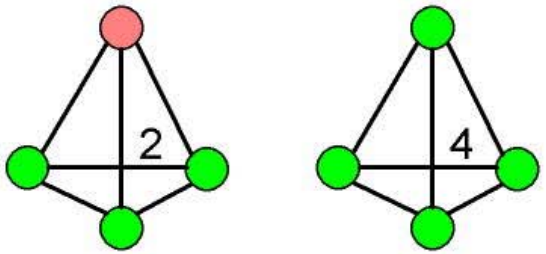
Volume relaxation energy:

$$V_{elast}^{\Sigma} = E^{\Sigma}(\Omega(\Sigma)) - E^{\Sigma}(\Omega_{alloy})$$



Ω_{alloy} : Volume used in Monte Carlo

$\Omega(\Sigma)$: Volume from spring model



Spring model of lattice relaxations

Given spring constants and distances:

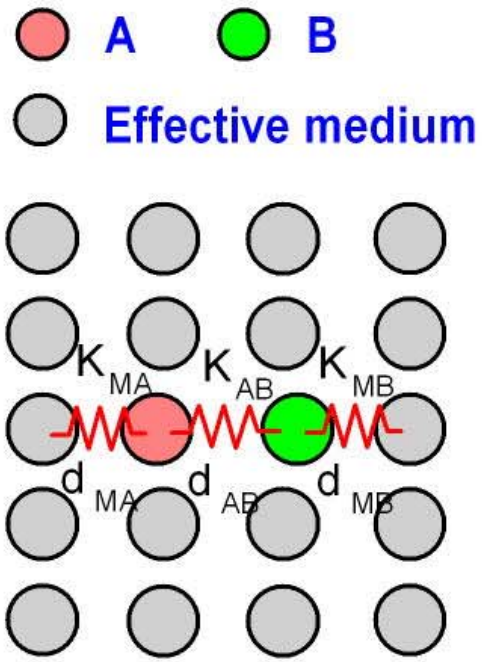
K^{*}_{AA} d^{0}_{AA} (A, fcc)

K_{BB} d^{0}_{BB} (B, fcc)

K_{AB} d^{0}_{AB} (AB, $L1_0$)

K_{MM} d^{0}_{MM} (AB, random)

* K ~ Bulk modulus



Derived:

$$K_{MA} = \frac{1}{2}(K_{MM} + K_{AA})$$

$$d_{MA} = \left[\frac{1}{2}(d^{0}_{MM})^{3} + (d^{0}_{MM})^{3}\right]^{1/3} \quad \text{(Zen's law)}$$

$$d_{AA} = d^{0}_{AA} + 2(d^{0}_{MM} - d^{0}_{AA})/(2B_A/B_M+1)$$

$$d_{AB} = d^{0}_{AB} + 2(d^{0}_{MM} - \frac{1}{2}(d^{0}_{AA} + 2d^{0}_{AB} + d_{BB})/(B_{AB}/B_{MB} + B_{AB}/B_{MA}+1)$$

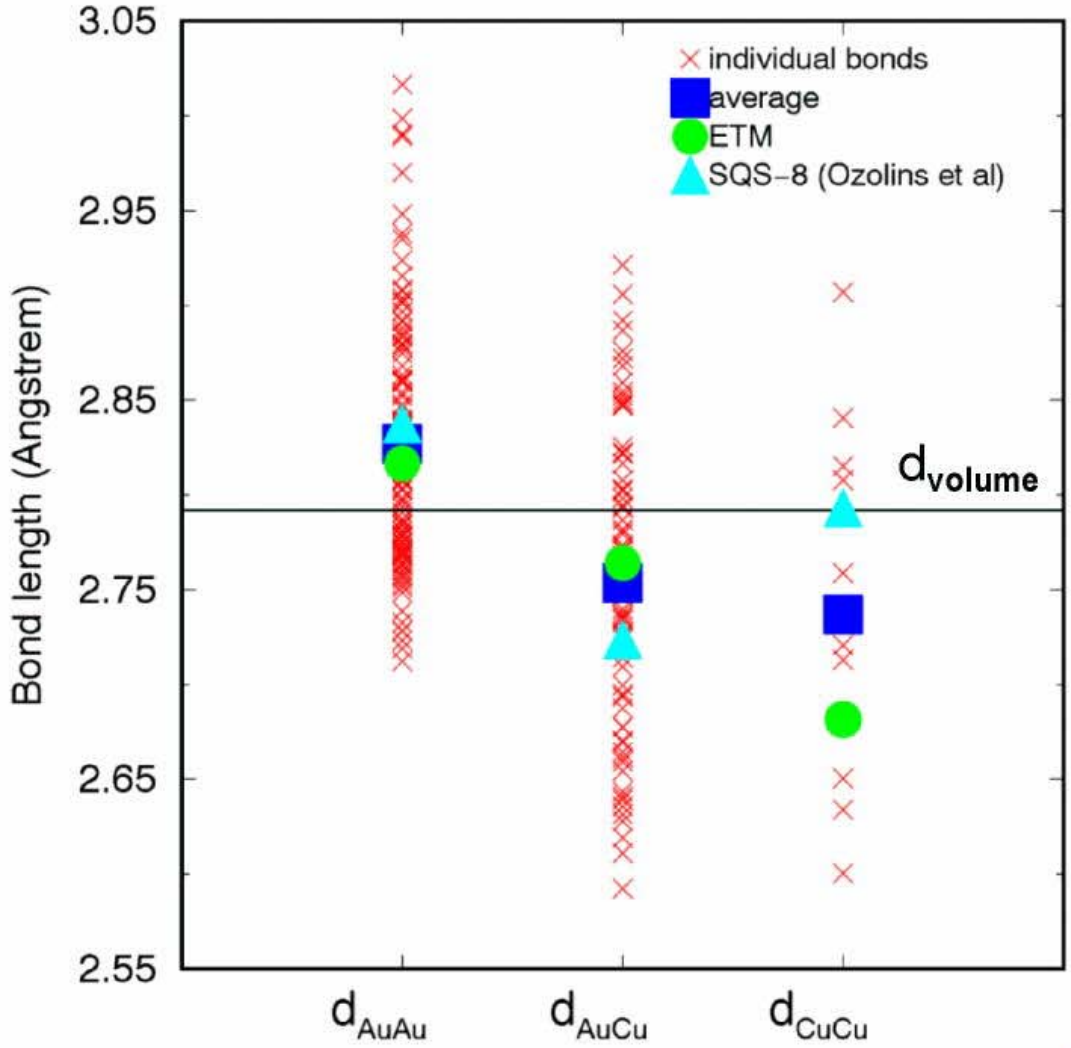
Interatomic distances in $Au_{75}Cu_{25}$

ETM versus full-potential calculations(FP-PAW)

X: Full-potential (FP-PAW), SQS 32

ETM: Effective tetrahedron model

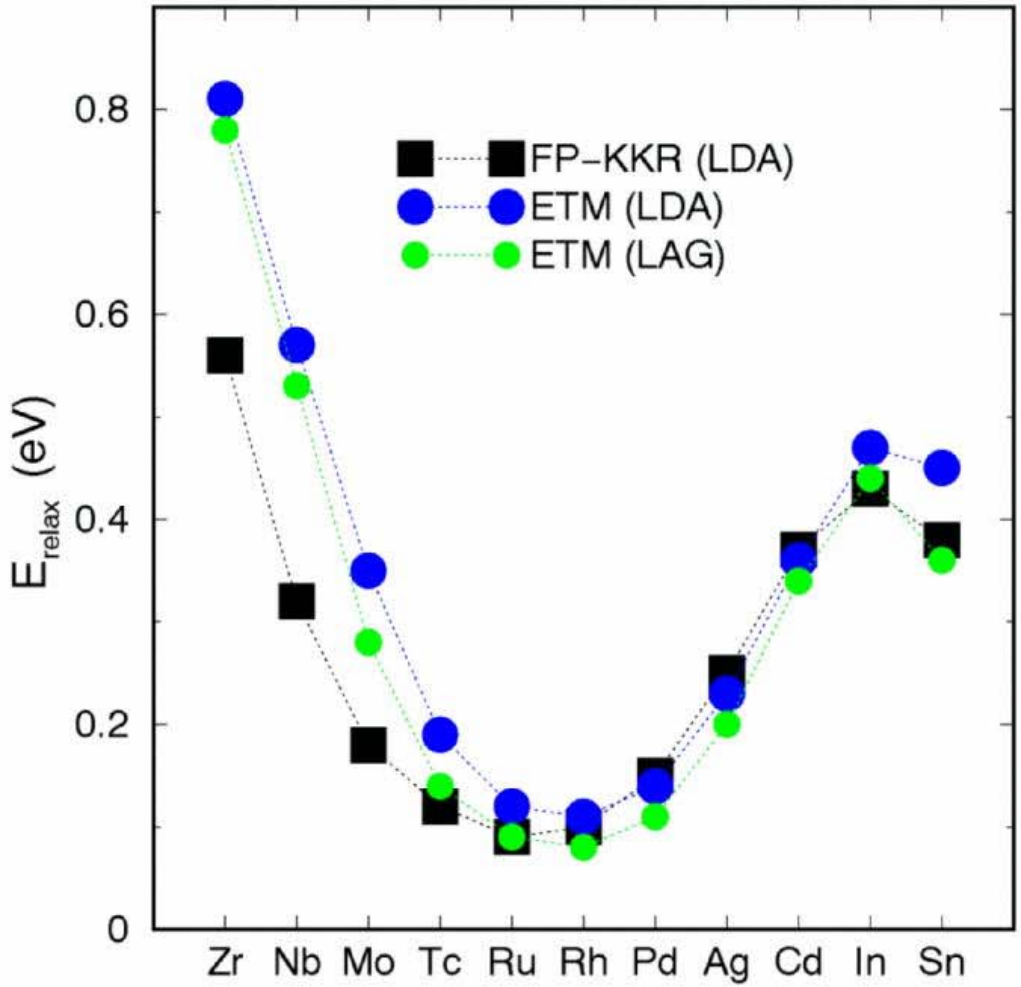
SQS: Special quasi-random structure



Relaxation energies: Impurities in Cu

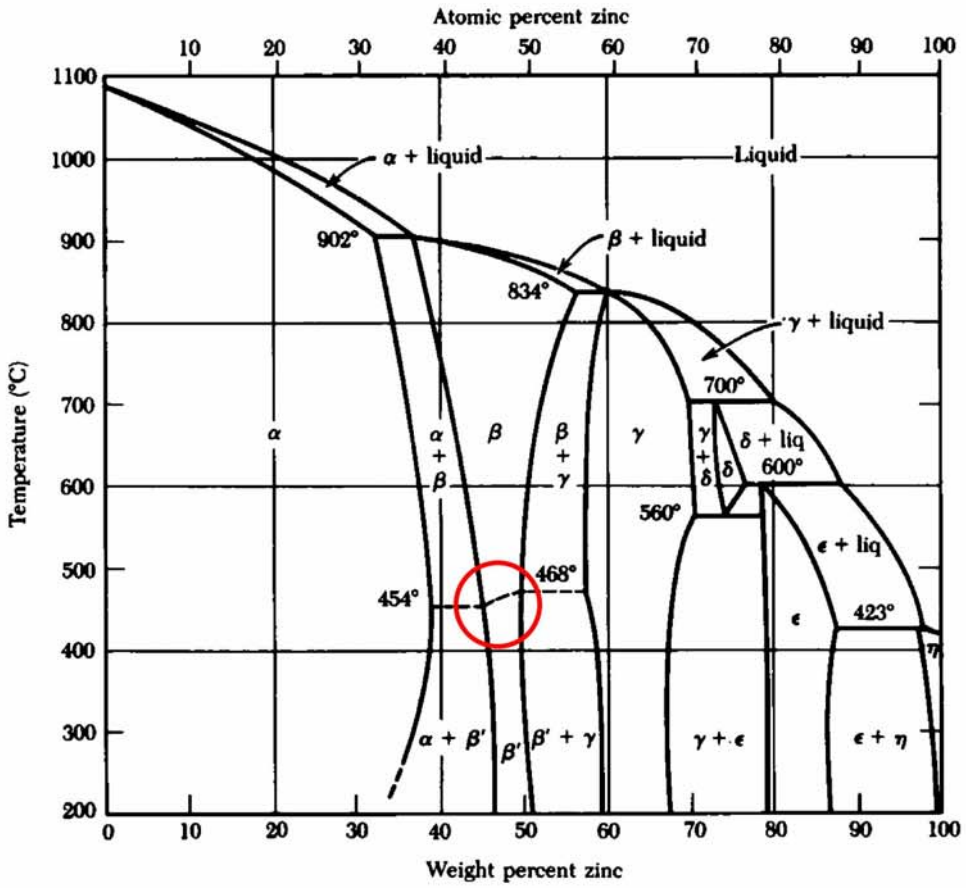
ETM: Effective tetrahedron model

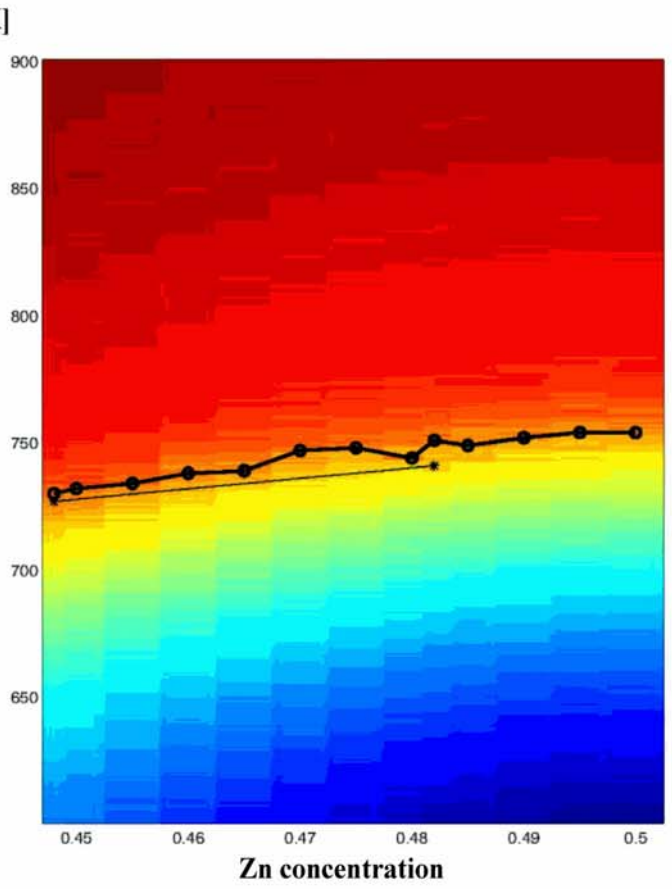
FP-KKR: Full-Potential results*)

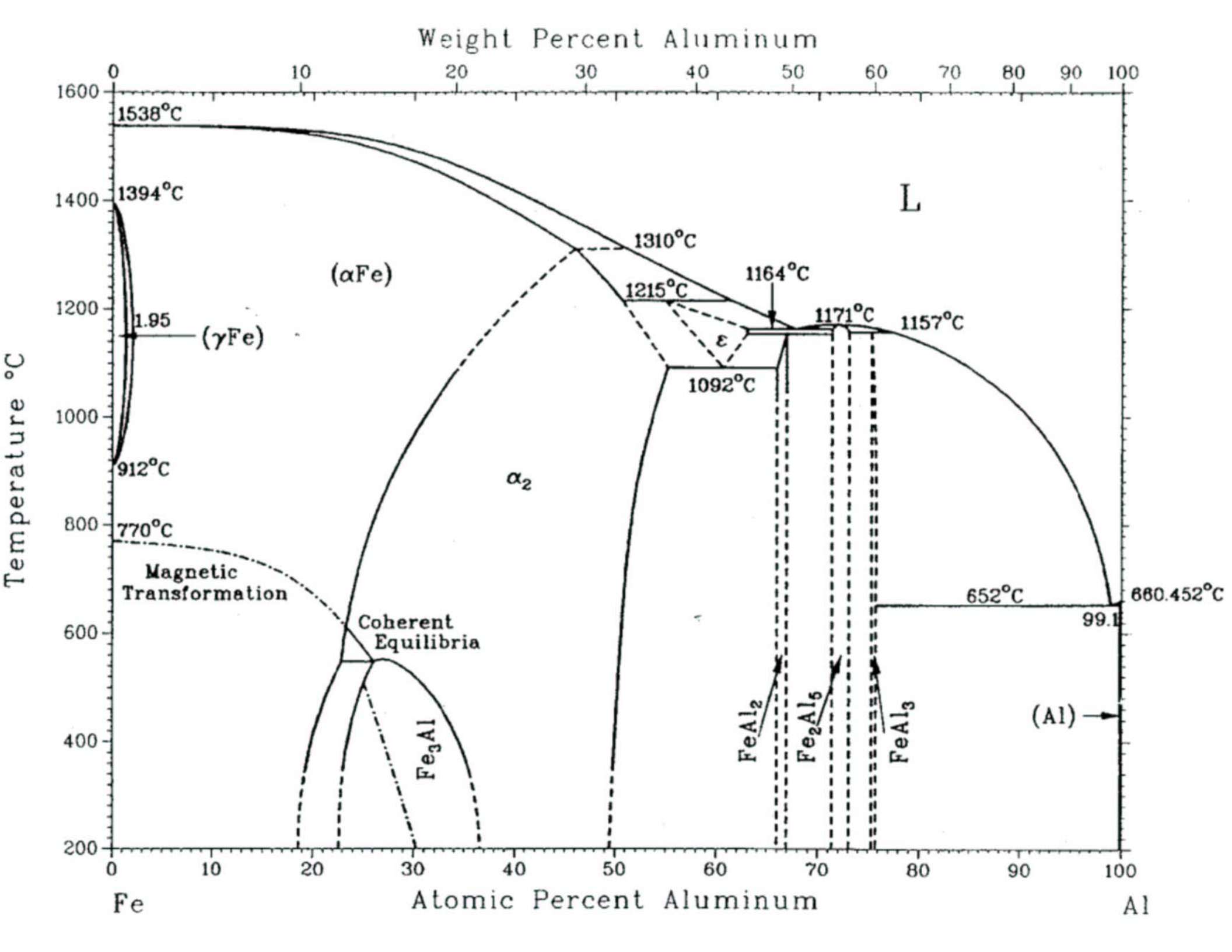


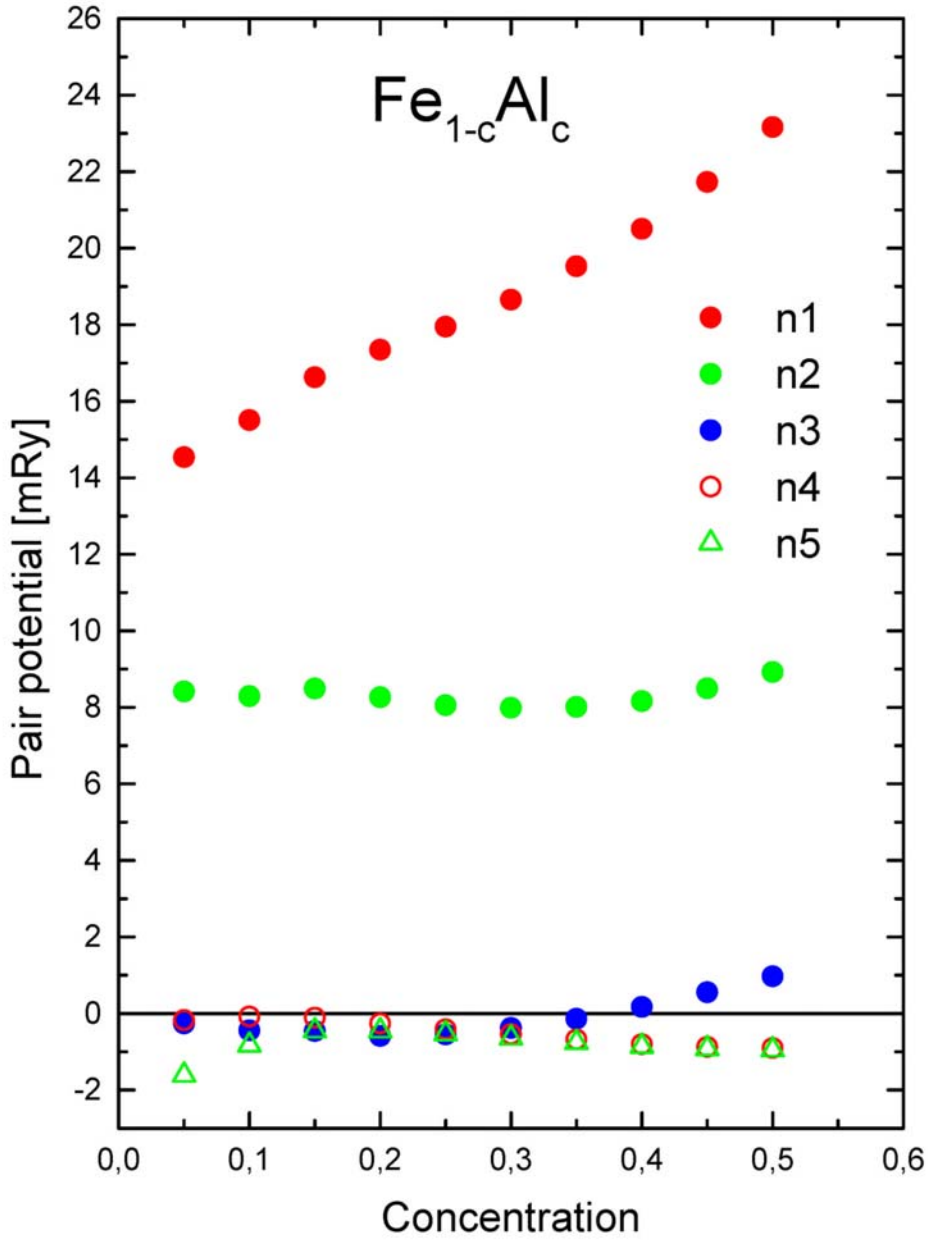
*) Papanikolaou *et al.* , Phys. Rev. B **55**, 4157 (1997)

Monte Carlo simulation of order-disorder transition in β-brass

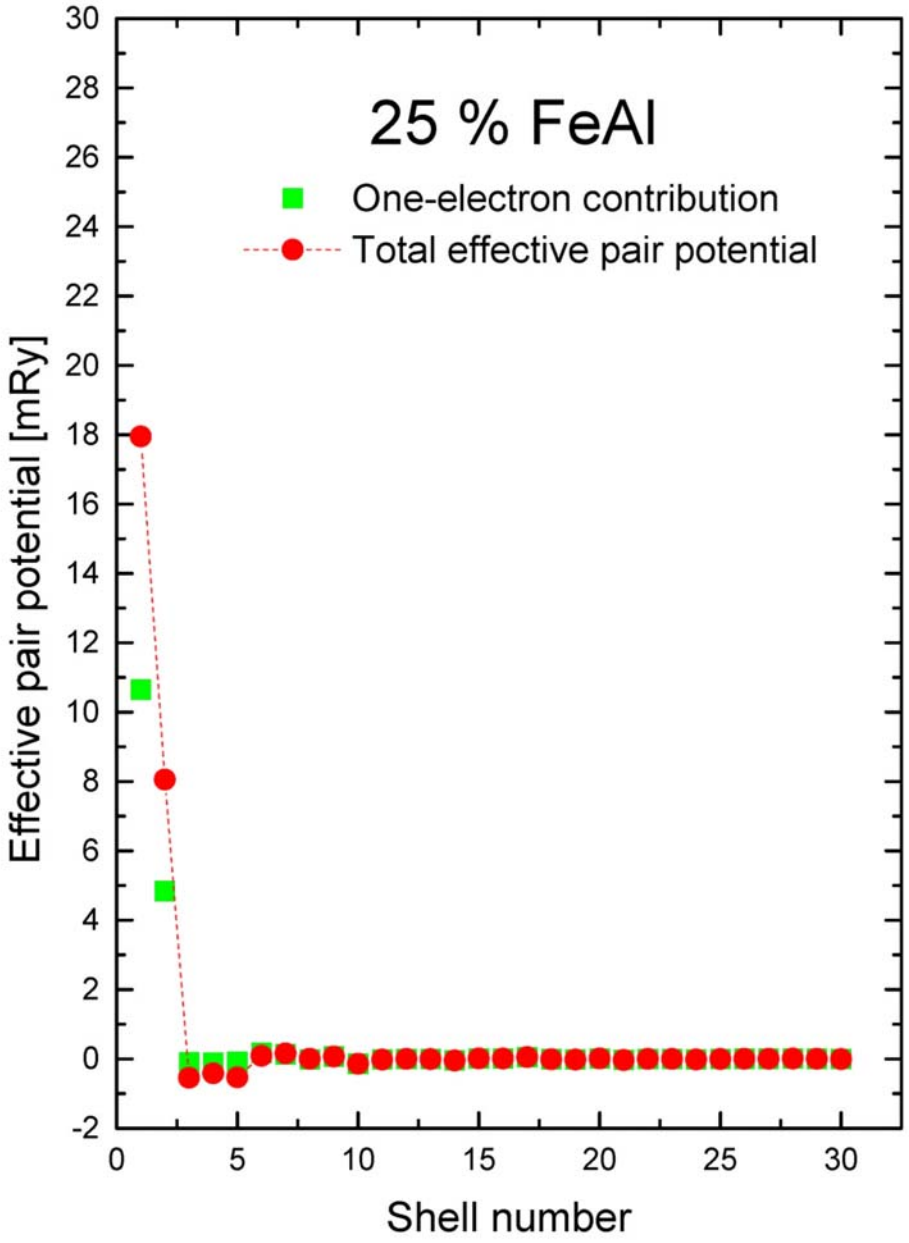


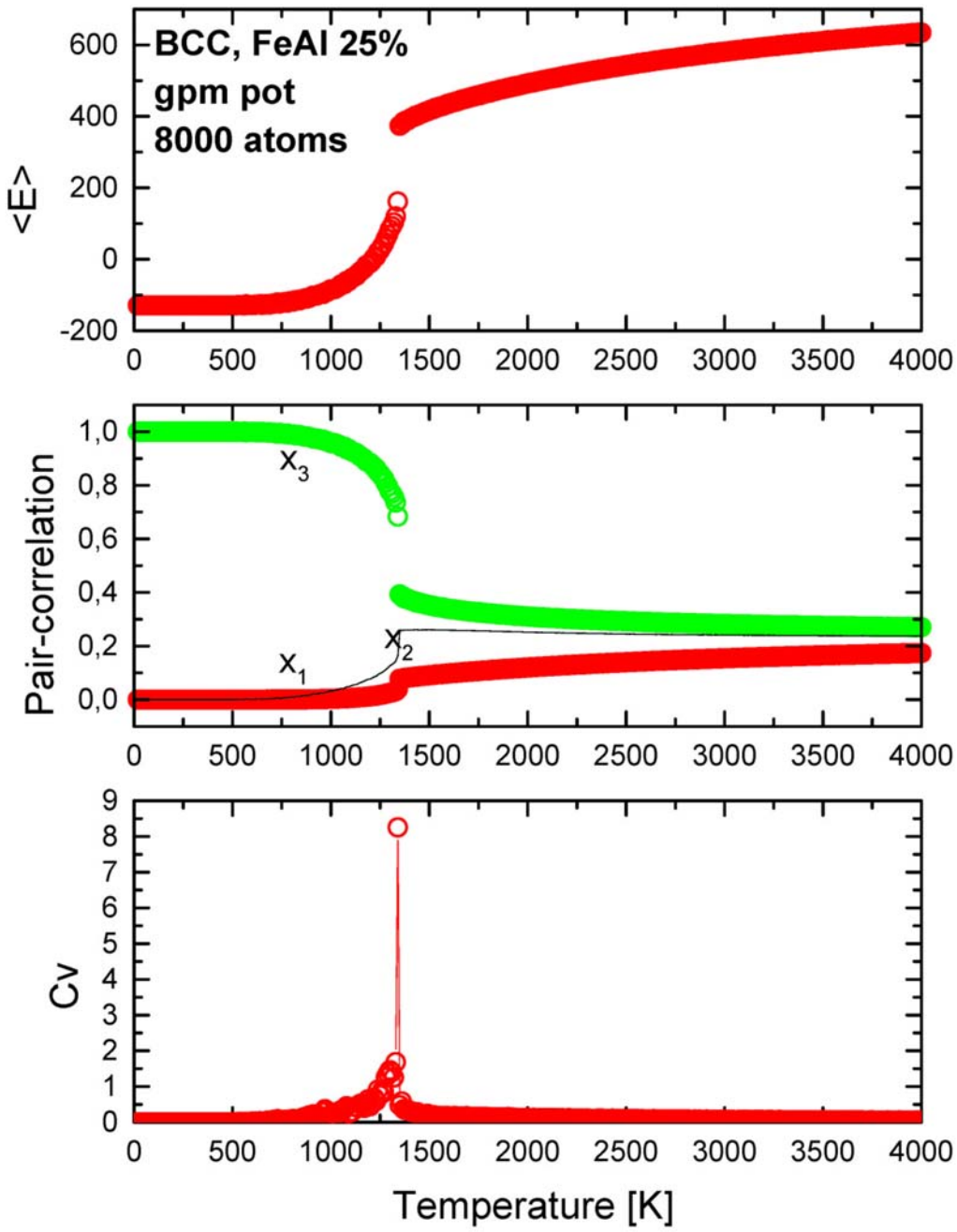


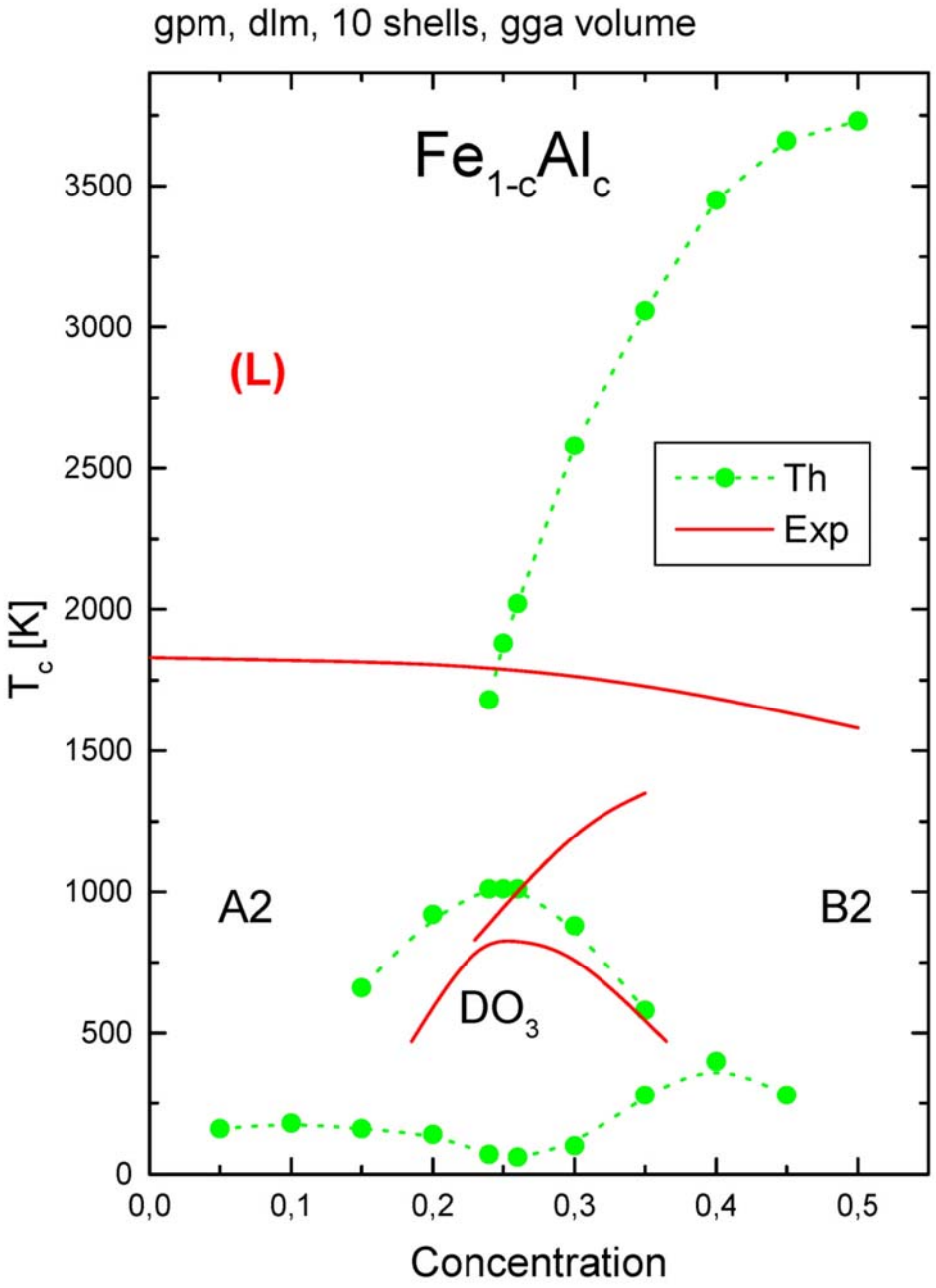

Weight Percent Aluminum
0
10
20
30
40
50
60
70
80
90
100
1600
1400
1200
1000
800
600
400
200
Temperature °C
1538°C
1394°C
1.95
(γFe)
912°C
770°C
Magnetic
Transformation
(αFe)
1310°C
1215°C
1164°C
1171°C
1157°C
ε
1092°C
L
α2
Coherent
Equilibria
Fe3Al
FeAl2
Fe2Al5
FeAl3
652°C
660.452°C
99.1
(Al)
Fe
Atomic Percent Aluminum
Al


Fe1-cAlc
Pair potential [mRy]
Concentration
n1
n2
n3
n4
n5
26
24
22
20
18
16
14
12
10
8
6
4
2
0
-2
0,0
0,1
0,2
0,3
0,4
0,5
0,6

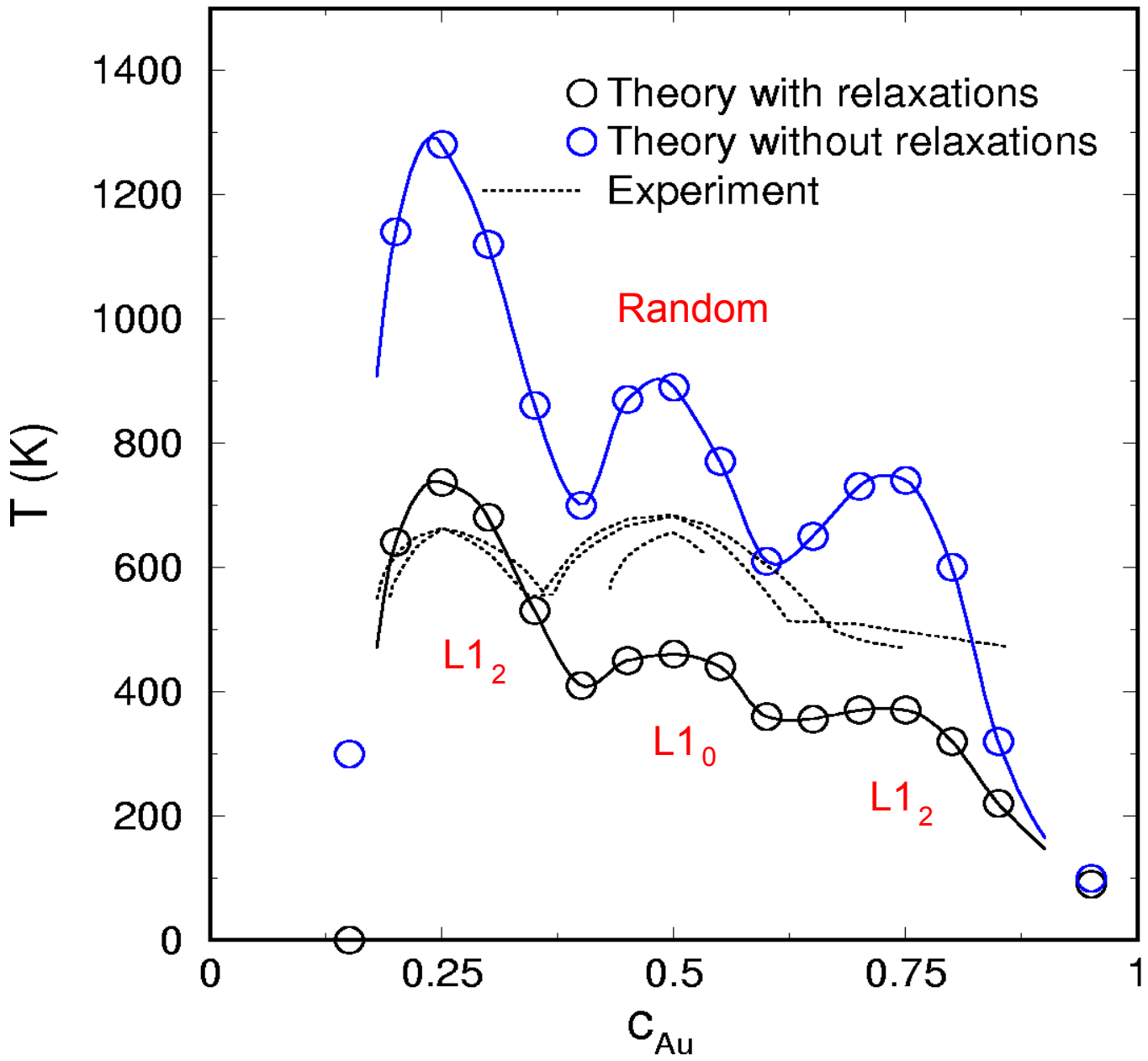
15-05-02 11:23:26

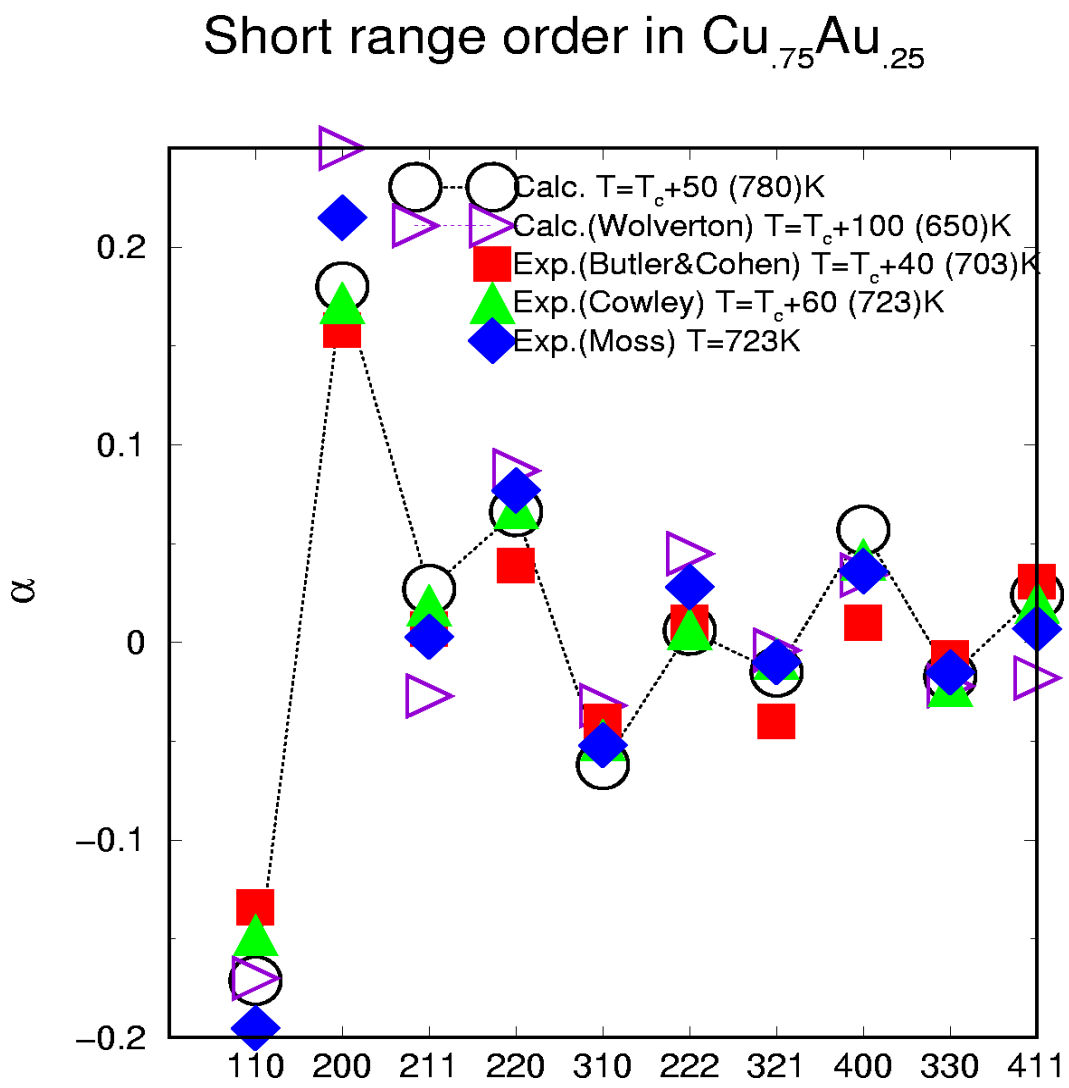



BCC, FeAl 25%
gpm pot
8000 atoms
<E>
600
400
200
0
-200
0
500
1000
1500
2000
2500
3000
3500
4000
Pair-correlation
1,0
0,8
0,6
0,4
0,2
0,0
X3
X2
X1
Cv
9
8
7
6
5
4
3
2
1
0
Temperature [K]

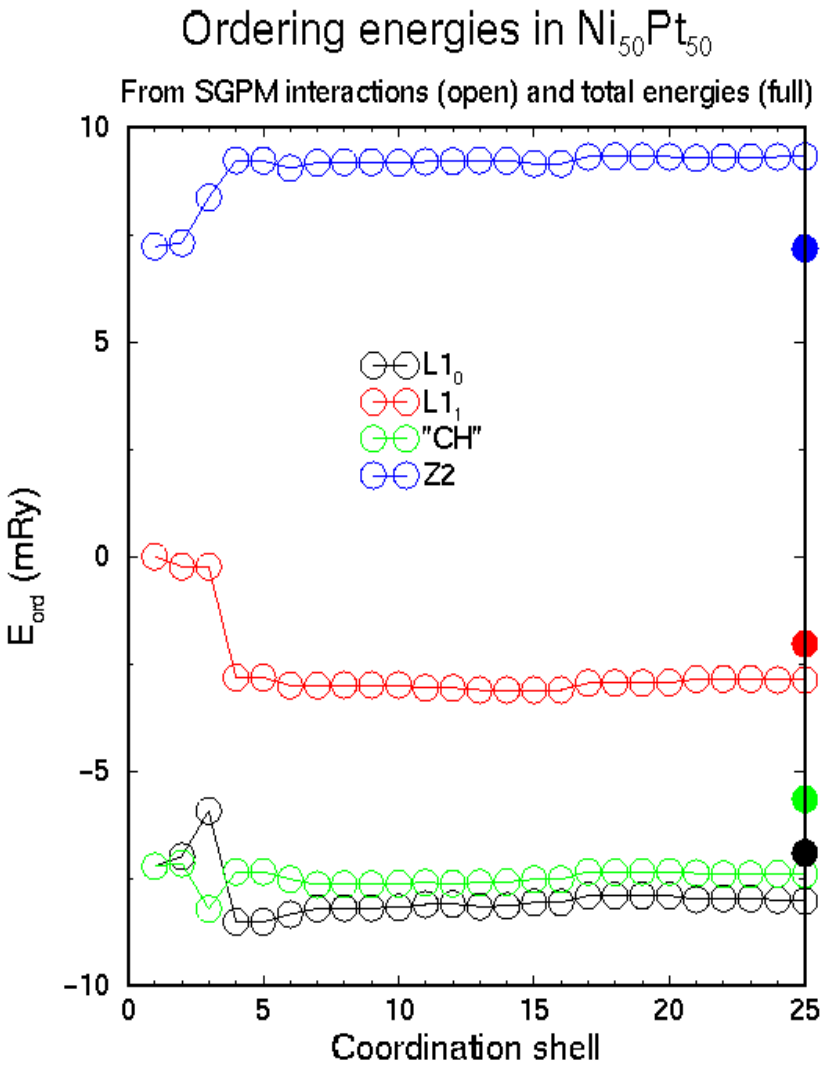

gpm, dlm, 10 shells, gga volume
Fe1-cAlc
(L)
Th
Exp
A2
B2
DO3
Tc [K]
Concentration
0
500
1000
1500
2000
2500
3000
3500
0,0
0,1
0,2
0,3
0,4
0,5

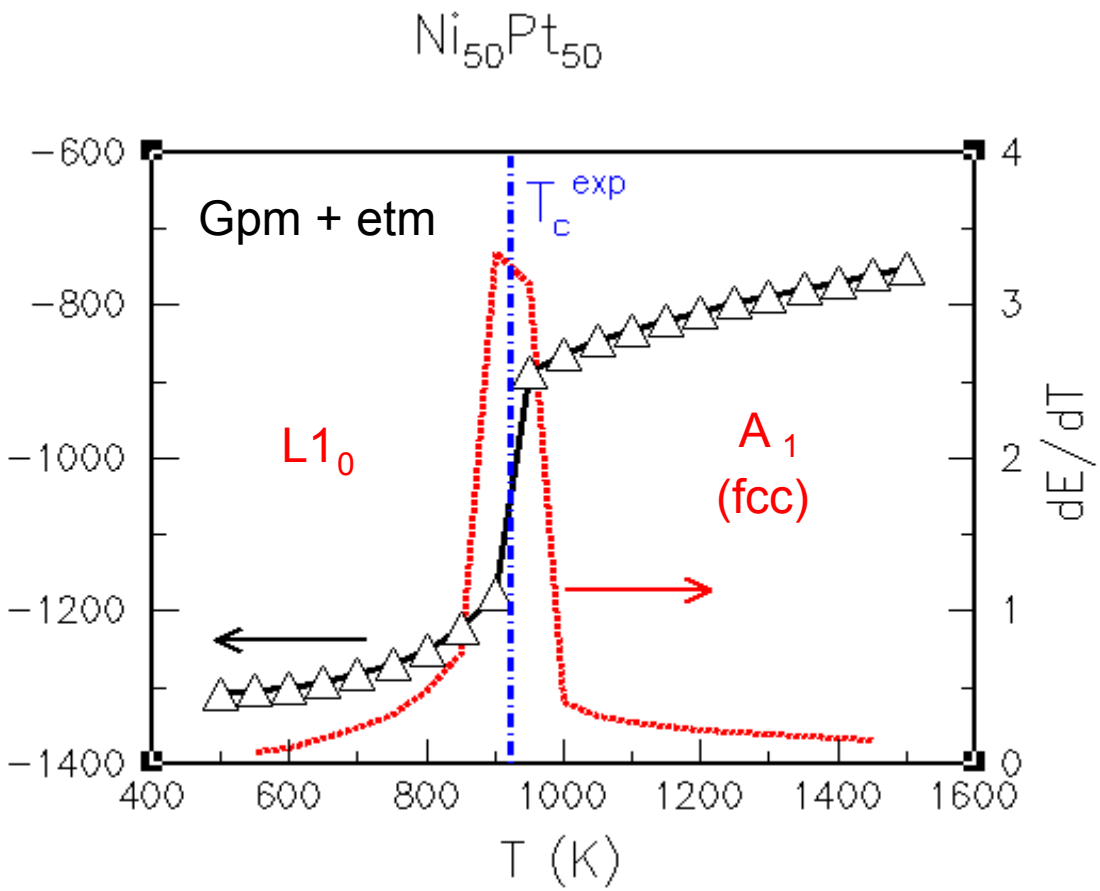
Calculated Cu–Au phase diagram




Short range order in Cu.75Au.25
Calc. T=Tc+50 (780)K
Calc.(Wolverton) T=Tc+100 (650)K
Exp.(Butler&Cohen) T=Tc+40 (703)K
Exp.(Cowley) T=Tc+60 (723)K
Exp.(Moss) T=723K
α
0.2
0.1
0
−0.1
−0.2
110
200
211
220
310
222
321
400
330
411

Ordering in NiPt



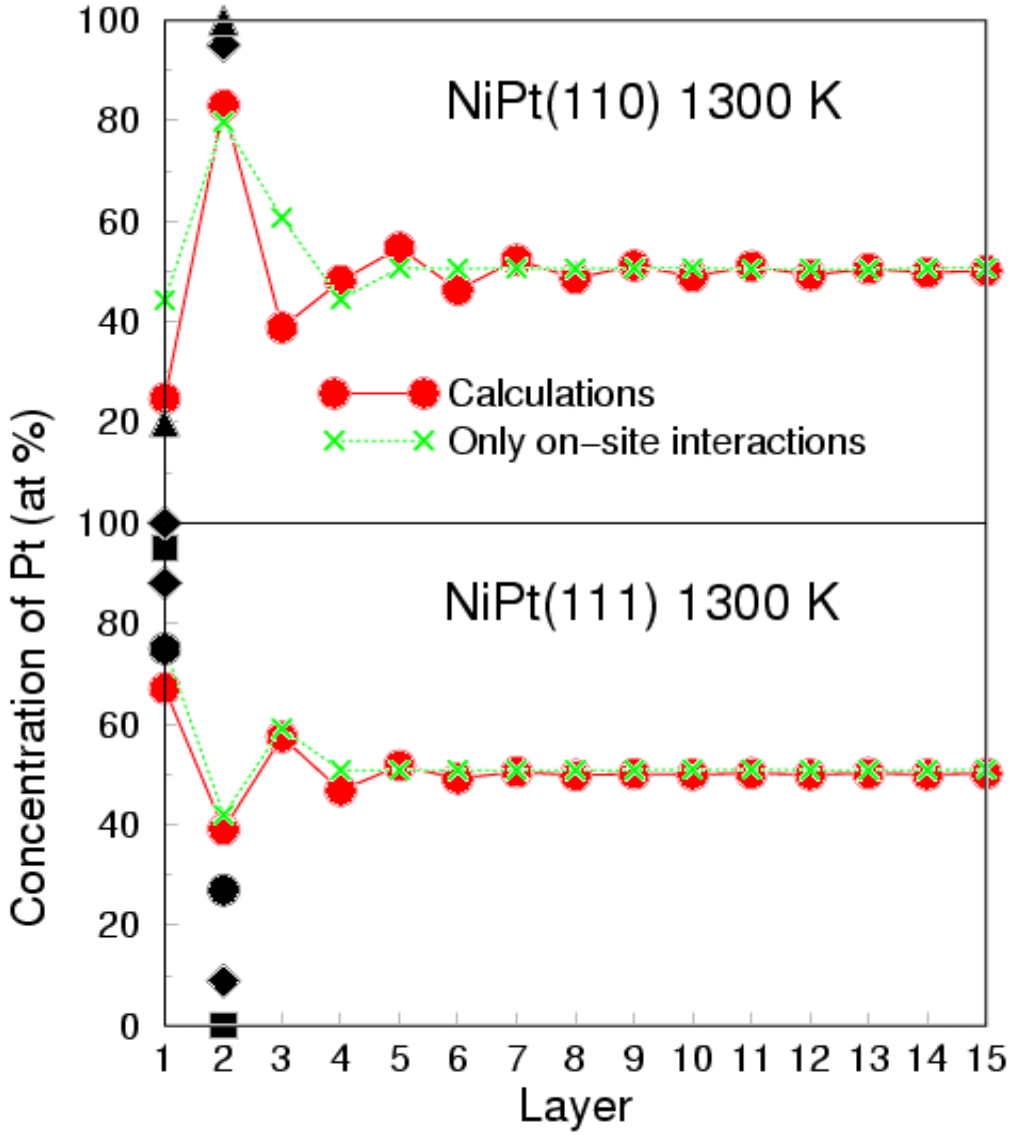


Monte Carlo simulations for NiPt surfaces

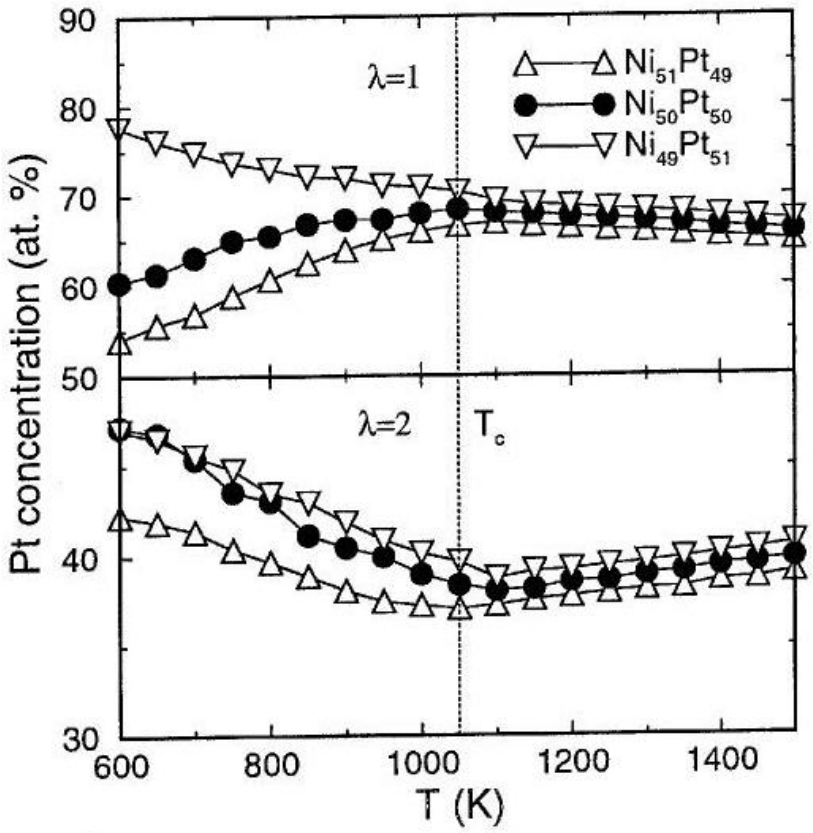
$T > T_{Ordering}$

Segregation reversal:
Pt prefers second layer

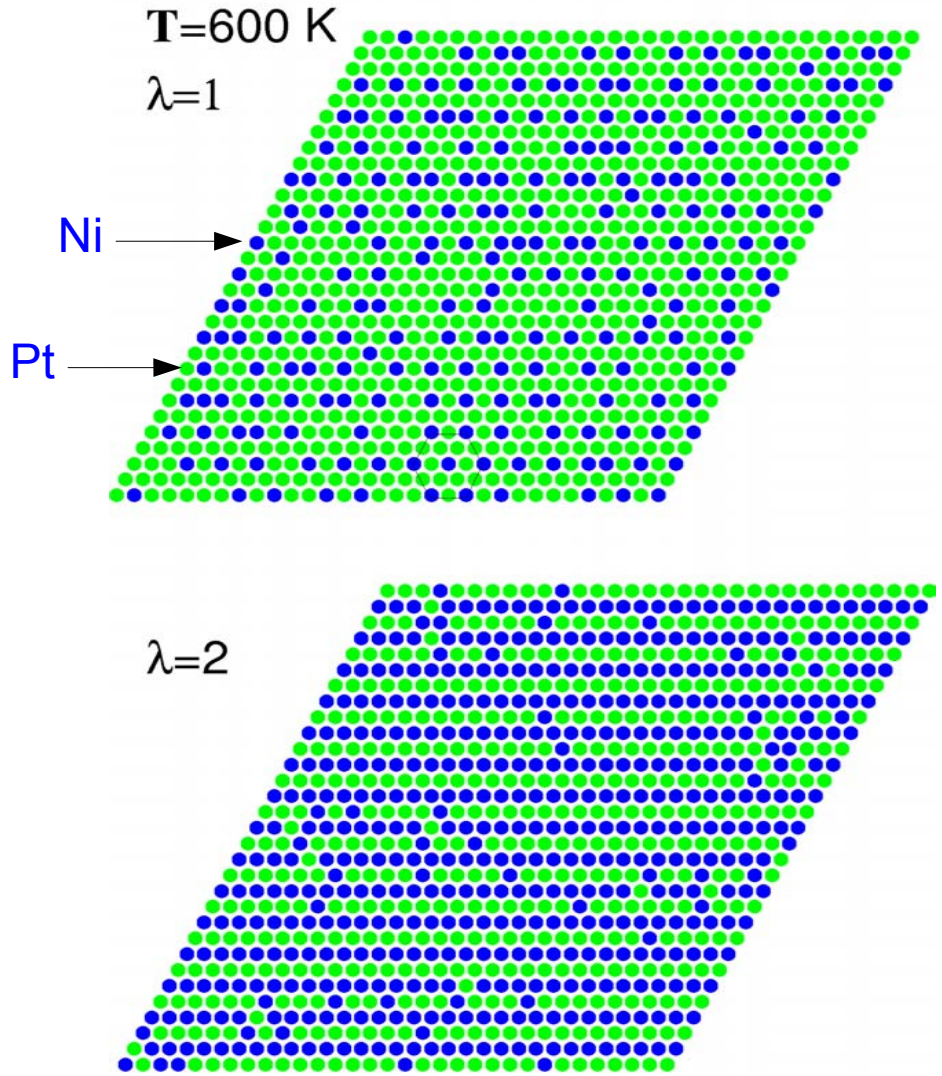
MC: Exchange atoms between surface and bulk requires segregation energy



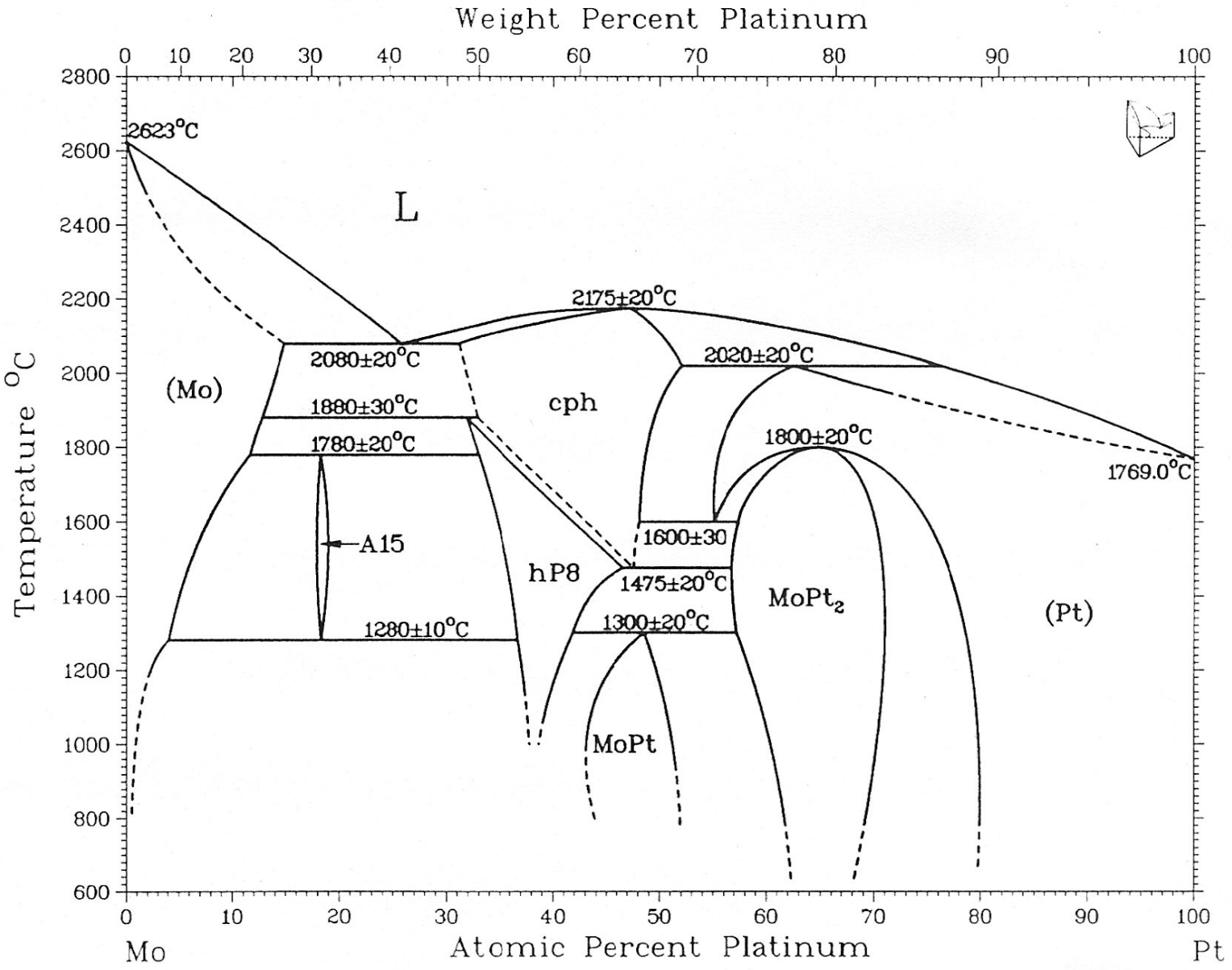
Monte Carlo simulations for NiPt(111)



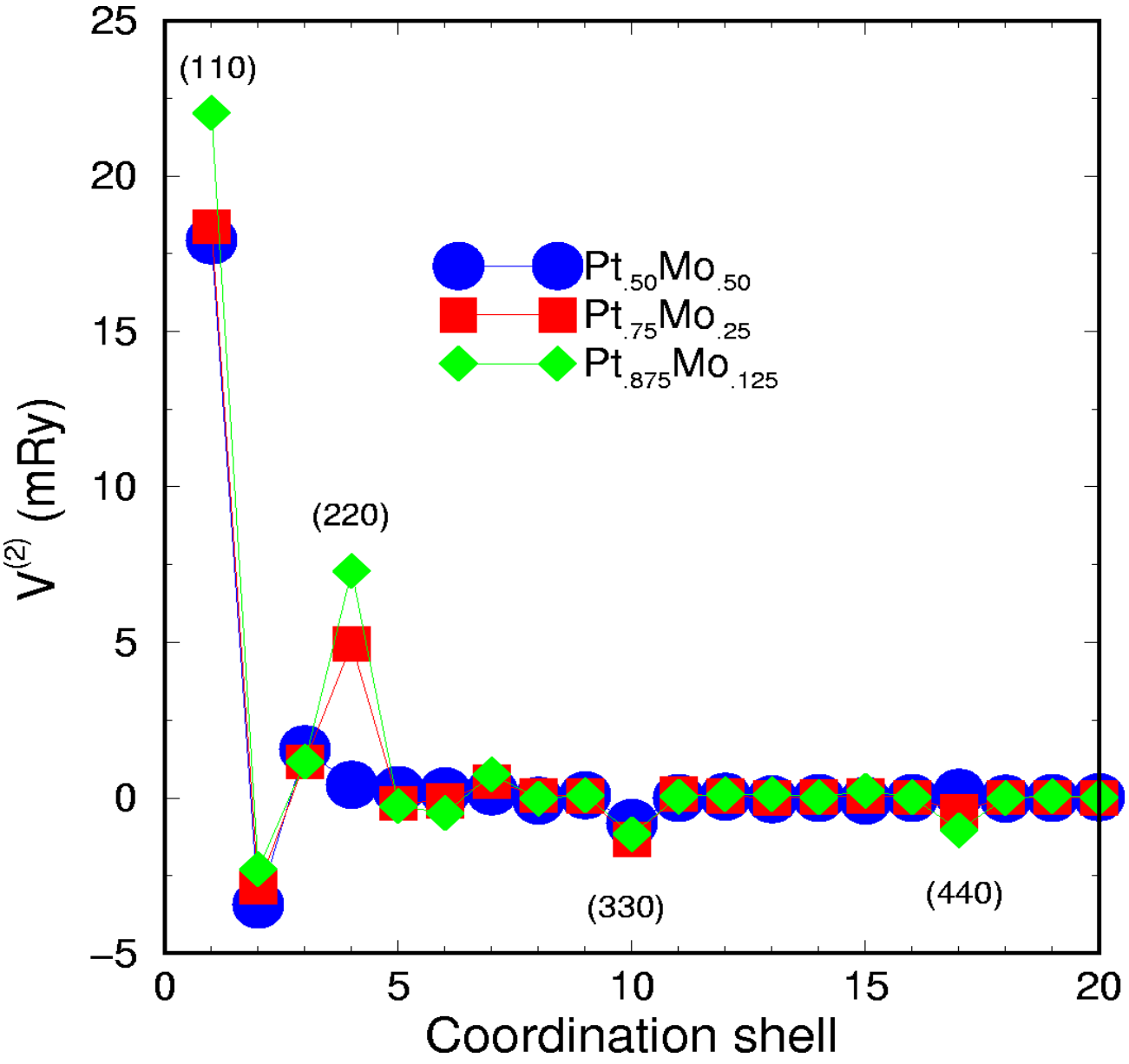
$Ni_{49}Pt_{51}$



Phase equilibria in Pt-rich Pt-Mo alloys



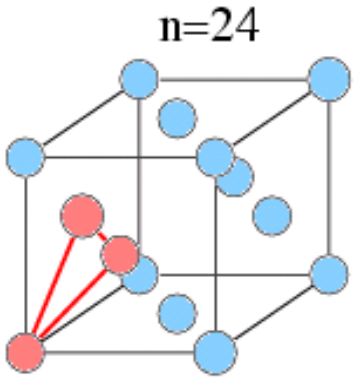
Effective pair interactions in PtMo



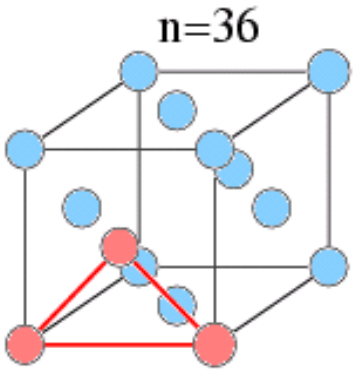
Effective multisite interactions in PtMo (in mRy)

$Pt_{66}Mo_{33}(Pt_{81}Mo_{19})$

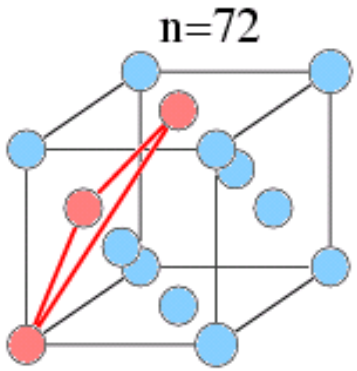
"n" is the number of the corresponding cluster per site;



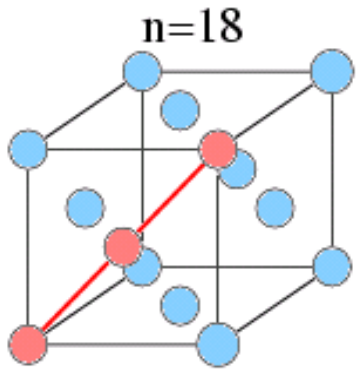
−0.37(−0.76)



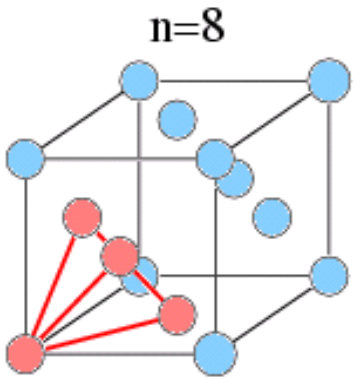
0.28 (0.13)



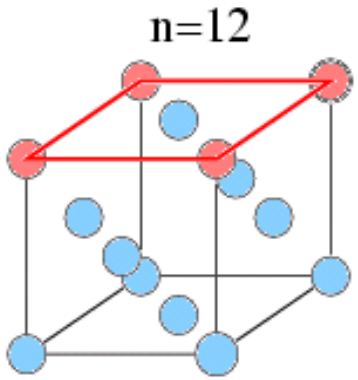
1.40 (1.62)



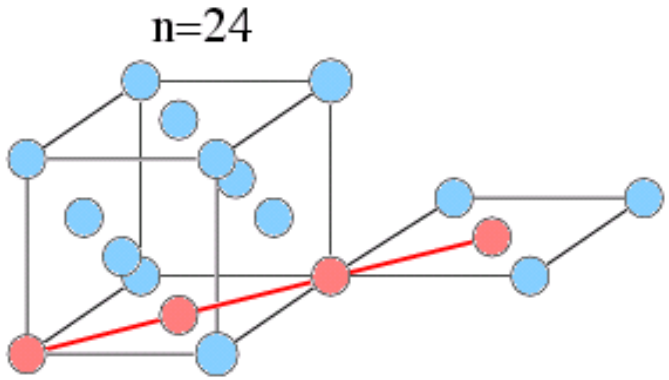
−5.30(−6.01)



1.84 (1.91)



0.79 (0.20)



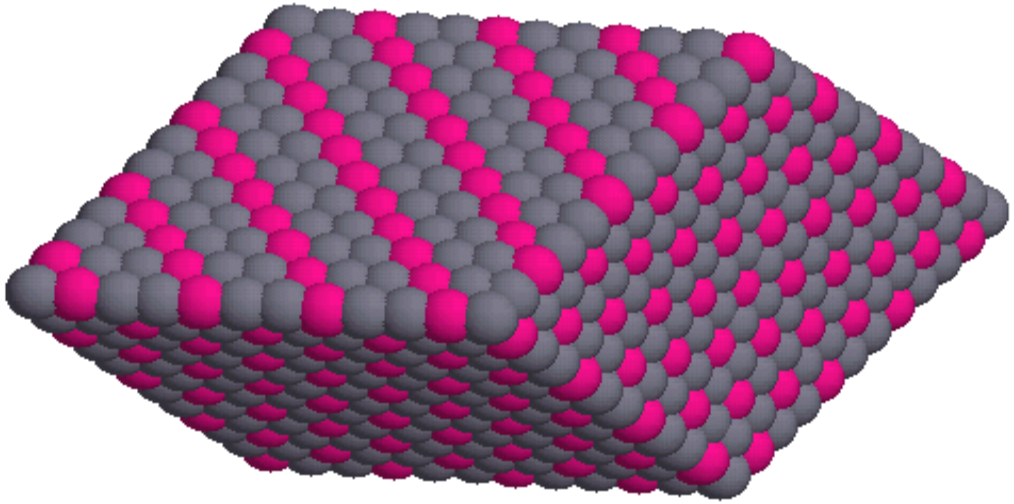
5.81 (8.86)

Pt_2Mo ordered phase

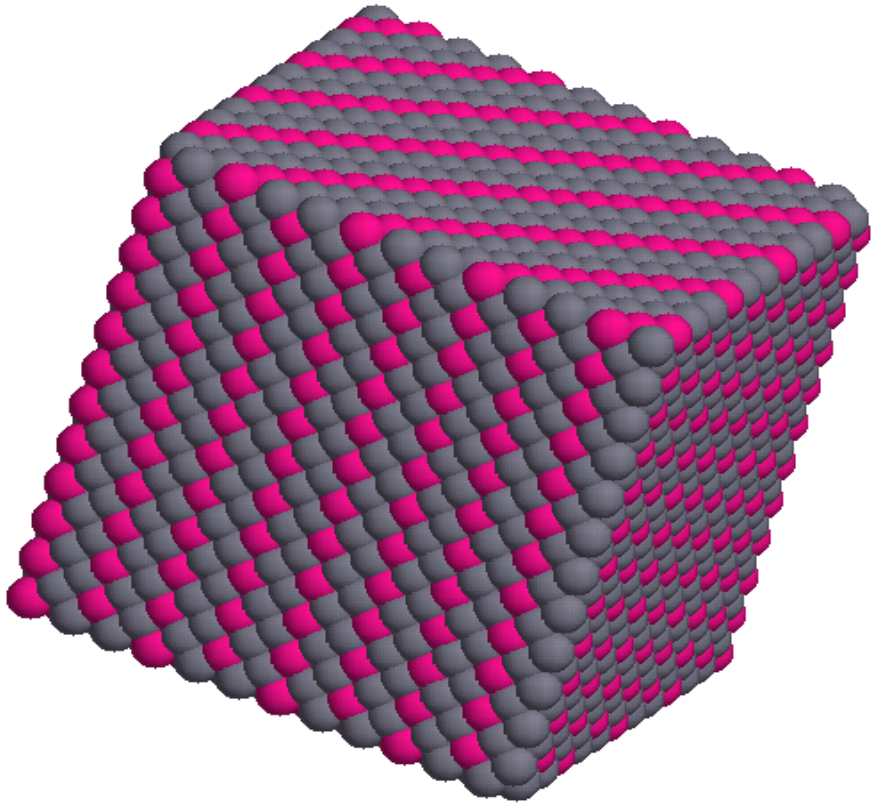
Space group Immm (71)

Order-disorder transition temperature : 2080 K (exp), 2200 K(theor).

$Pt_2Mo(111)$

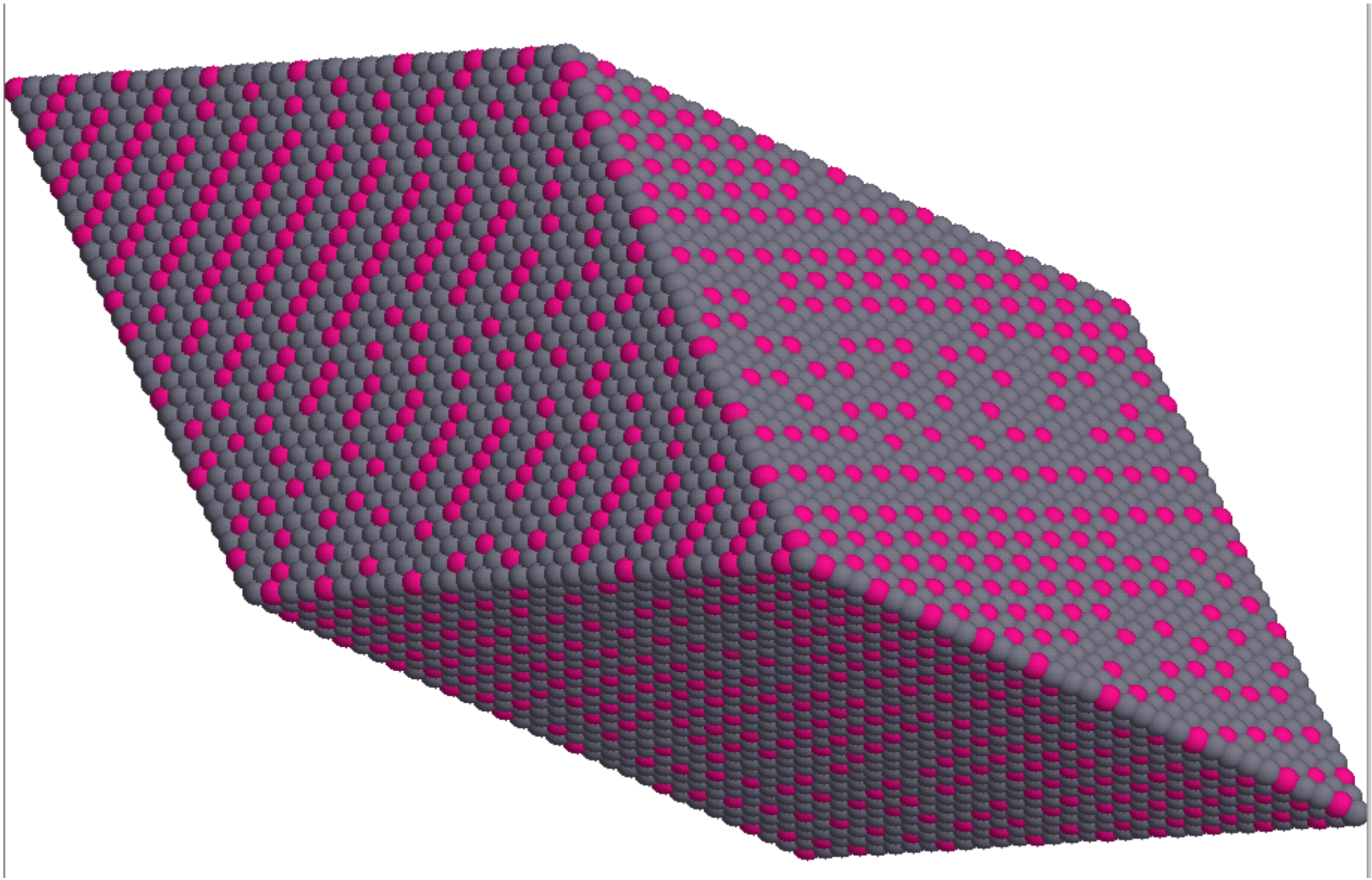


$Pt_2Mo(100)$

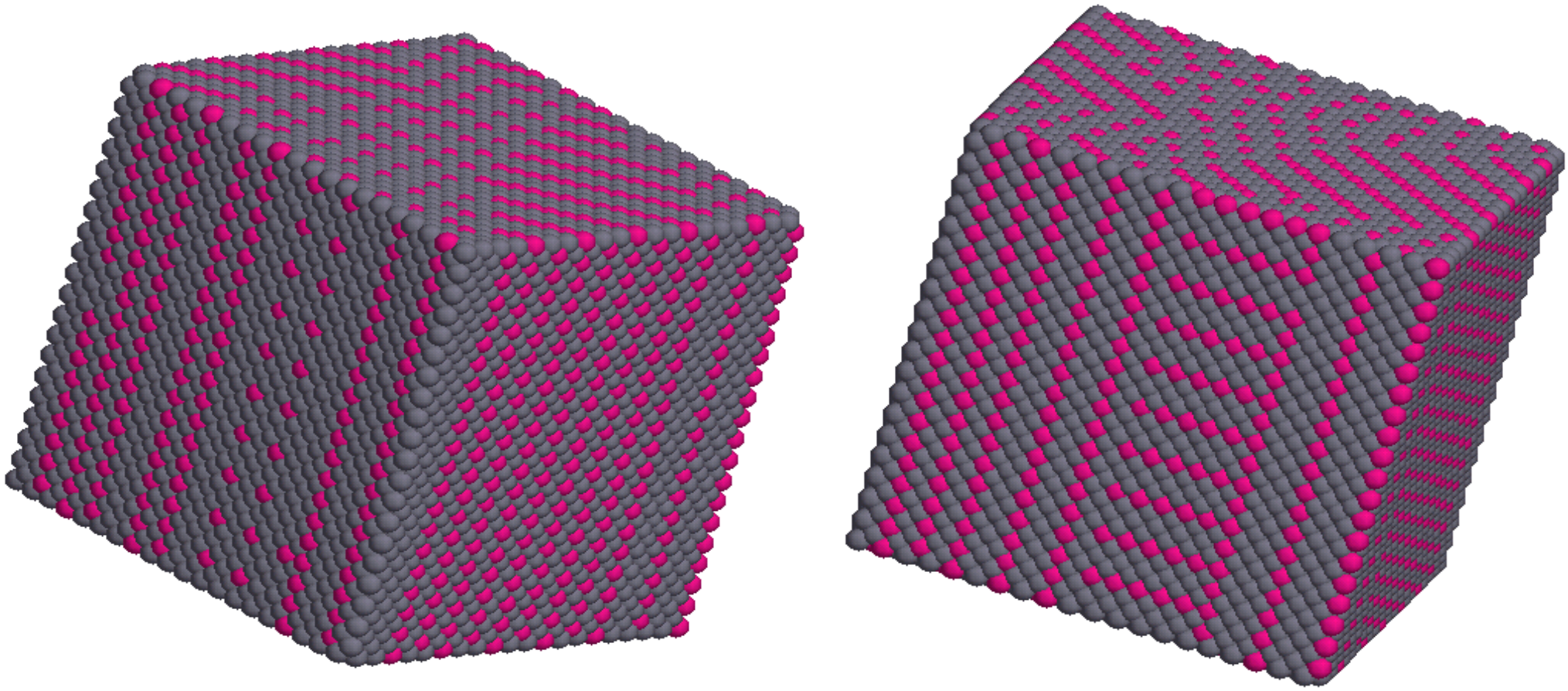


$Pt_{75}Mo_{25}$

A (111)-type snapshot of the ground-state (T=OK) structure



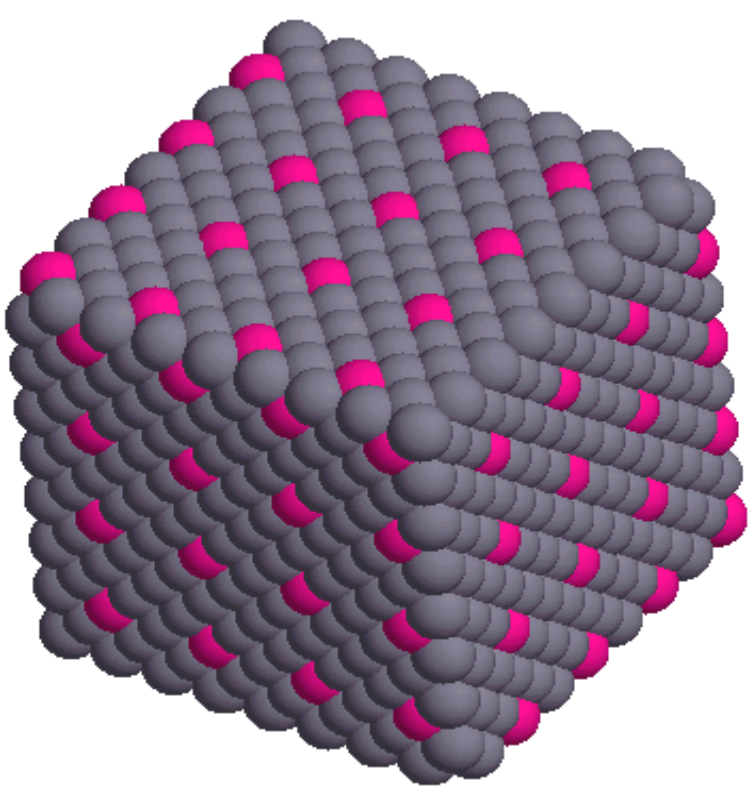
$Pt_{75}Mo_{25}(100)$

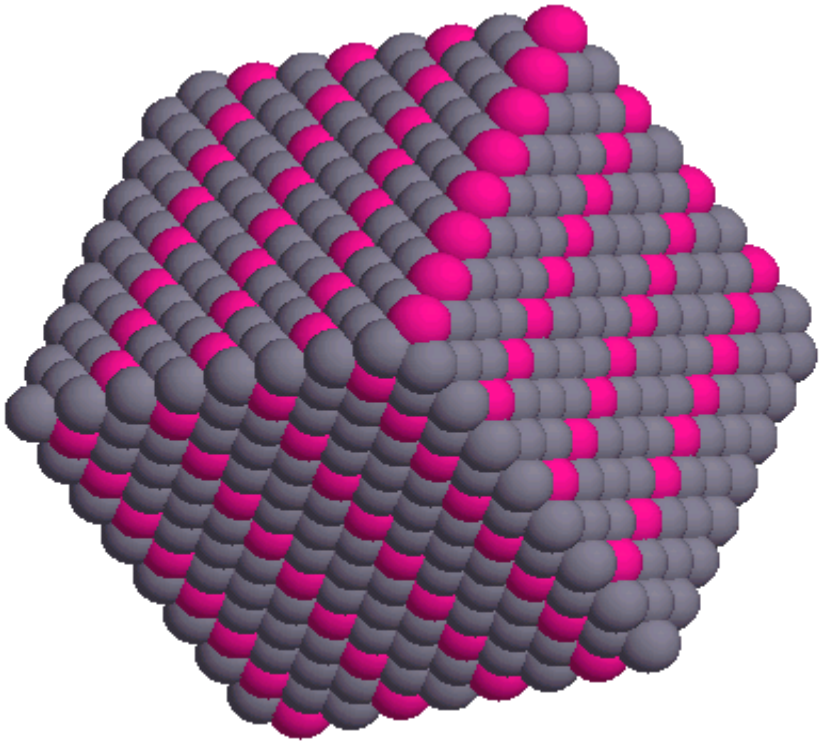


$Pt_{13}Mo_3$

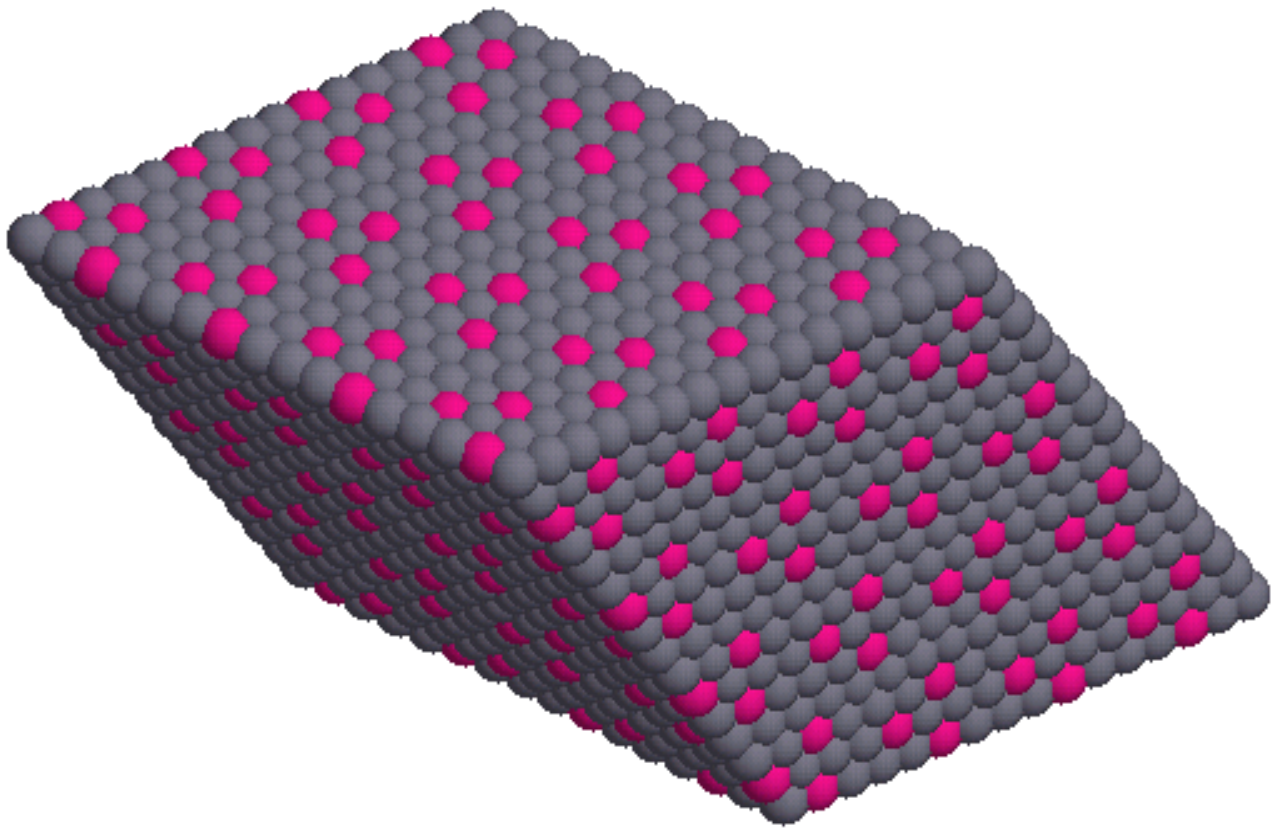
A (100)-type snapshot of the ground state (T=0K) structure

Undergoes the 1st order phase transition at about 2000 K.





$Pt_{13}Mo_3$ (111)

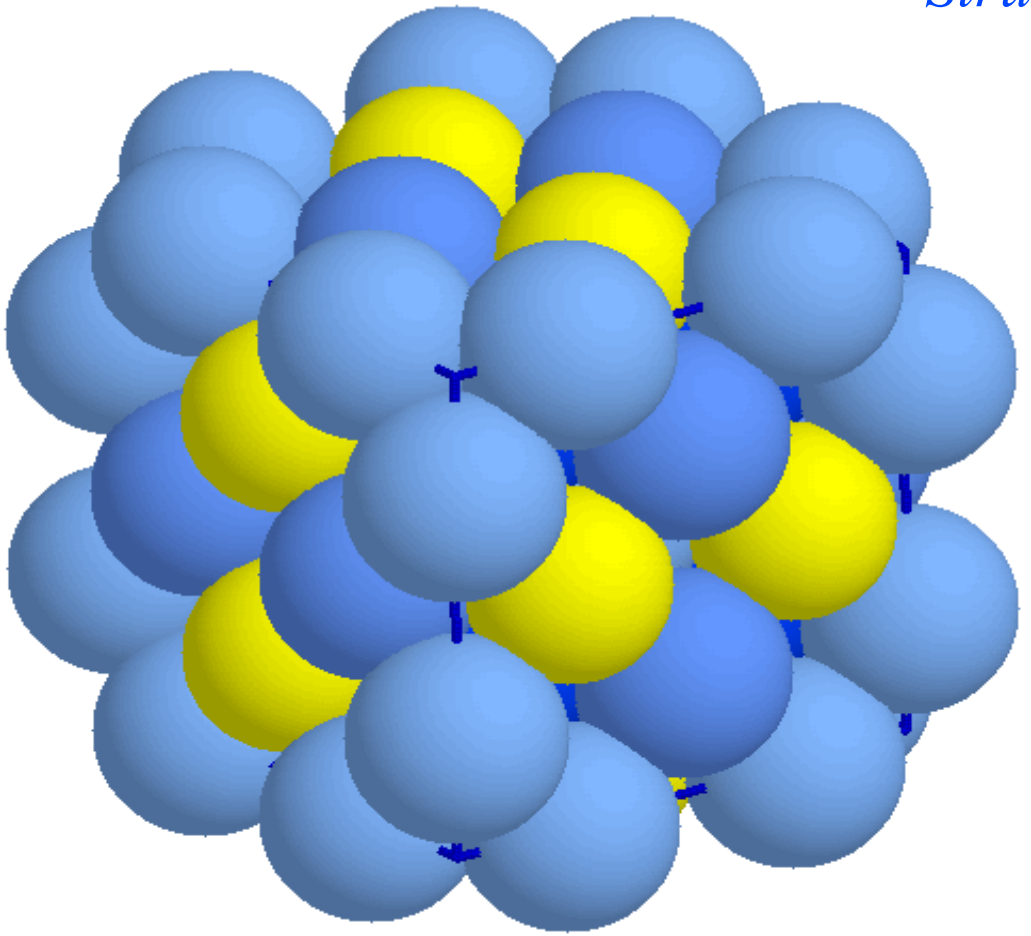


$Pt_{13}Mo_3$ structure

Space group: Pm-3n (223) or O_h^3

Pearson symbol: cP32

Strukturbericht designation: ??



Primitive translations:

(1,0,0)a

(0,1,0)a

(0,0,1)a

Basis:

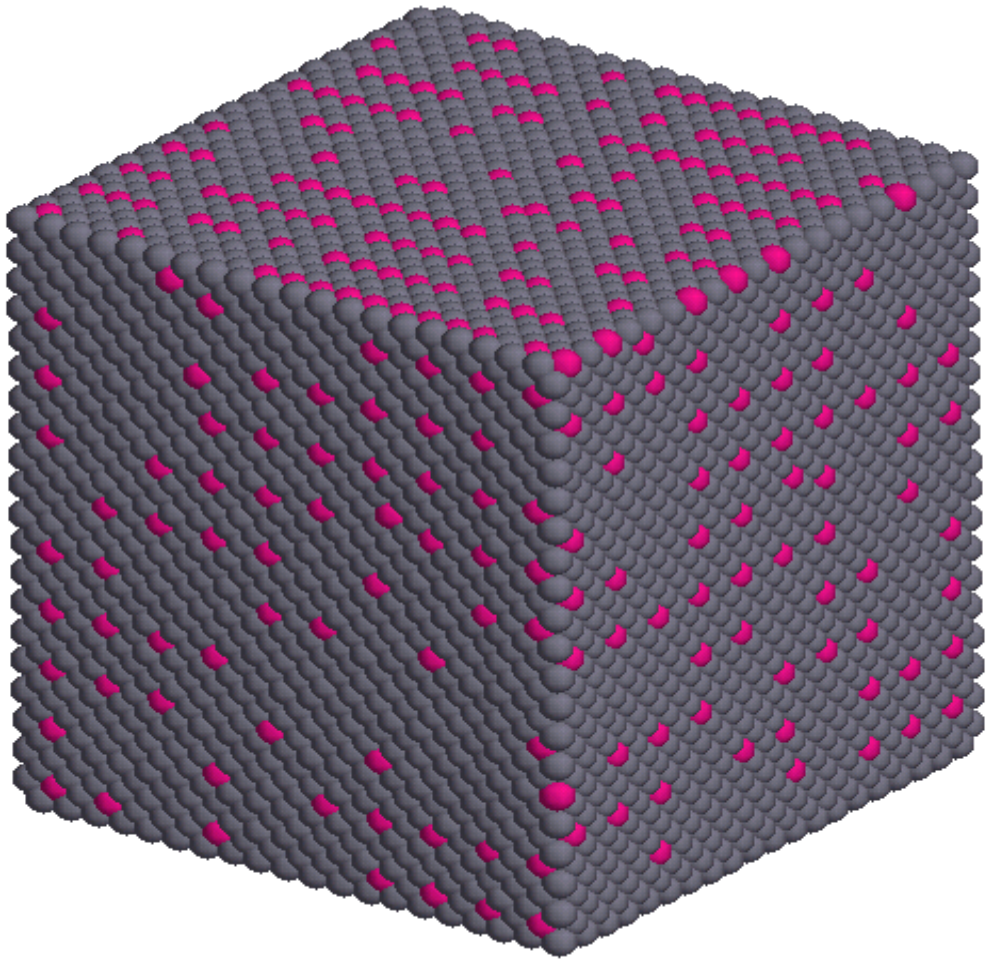
Pt_1 (1/4,0,0)

Pt_2 (1/2,0,1/4)

Pt_3 (1/4,1/4,1,4)

Mo (1/2,1/4,0)

Snapshot of $Pt_{87.5}Mo_{12.5}$ at T= 0K



Phase stability in Pt-rich PtMo alloys