Vacancy thermodynamics and diffusion-controlled processes in intermetallics for functional and construction material technologies

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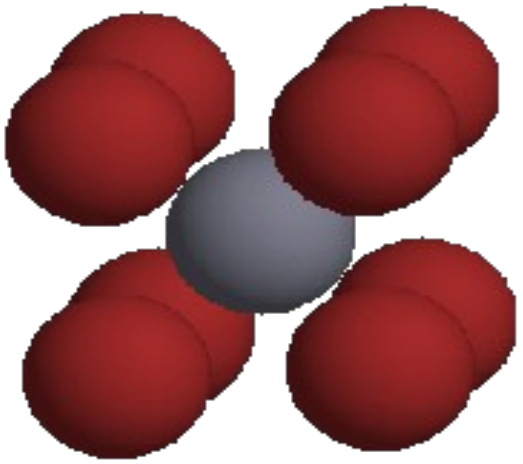
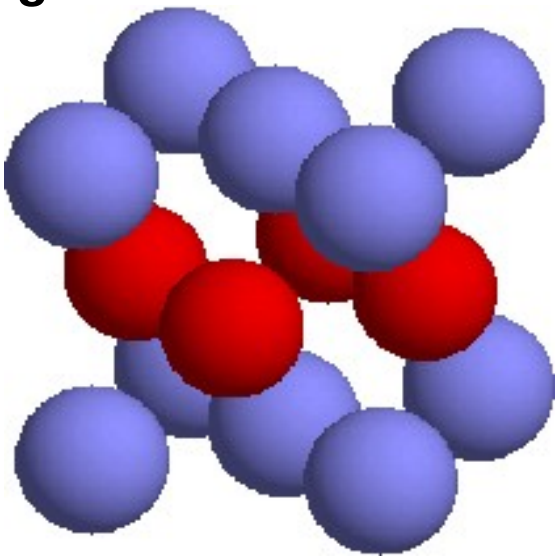
Recently studied systems

BCC-based **B2**
construction material



NiAl
Research by means of modeling - A. Biborski

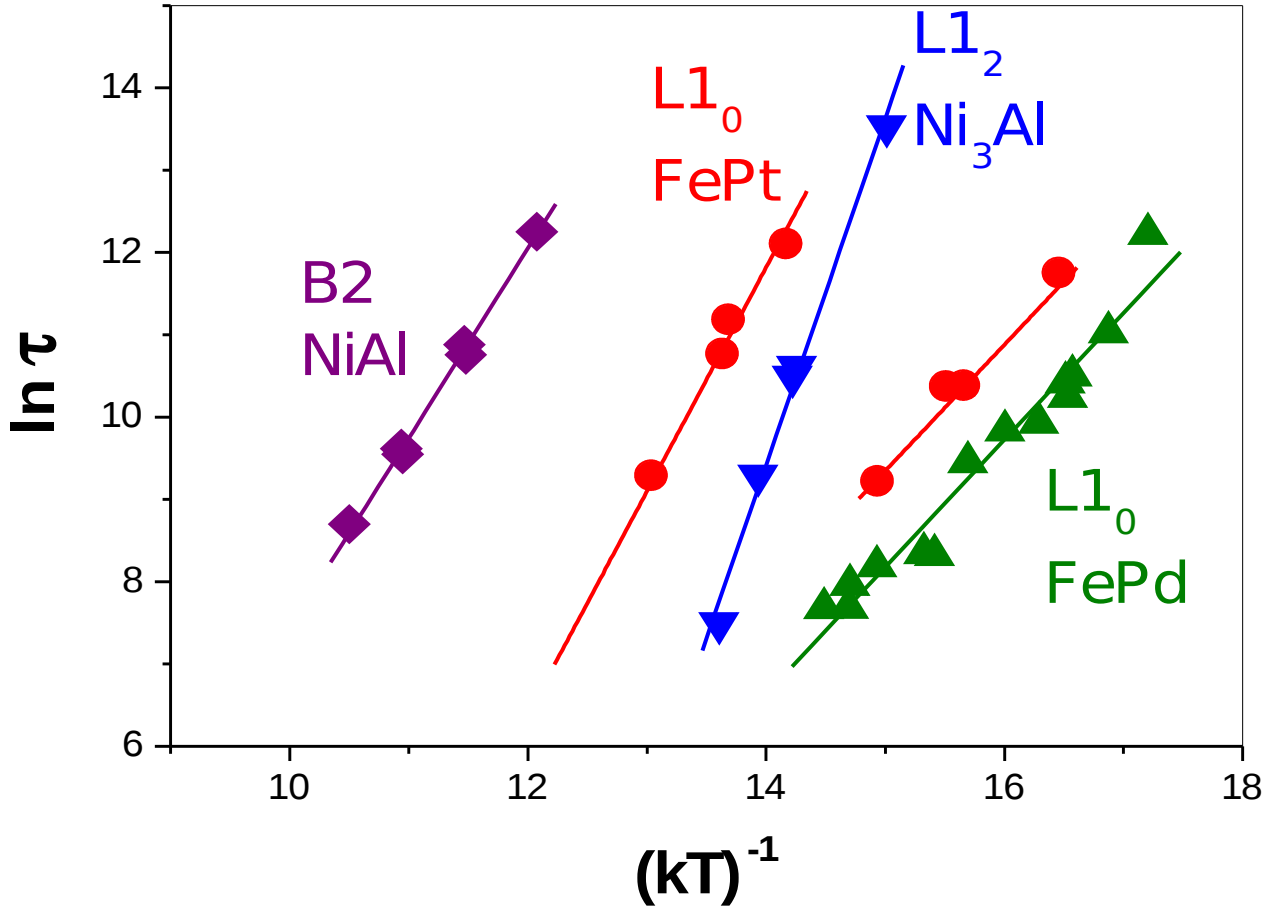
FCC-based **$L1_2$**
magnetic functional material



FePt
Research by means of modeling - M. Kozlowski

General experimental and modeling research of intermetallic systems carried out in group of prof. R. Kozubski IF,UJ

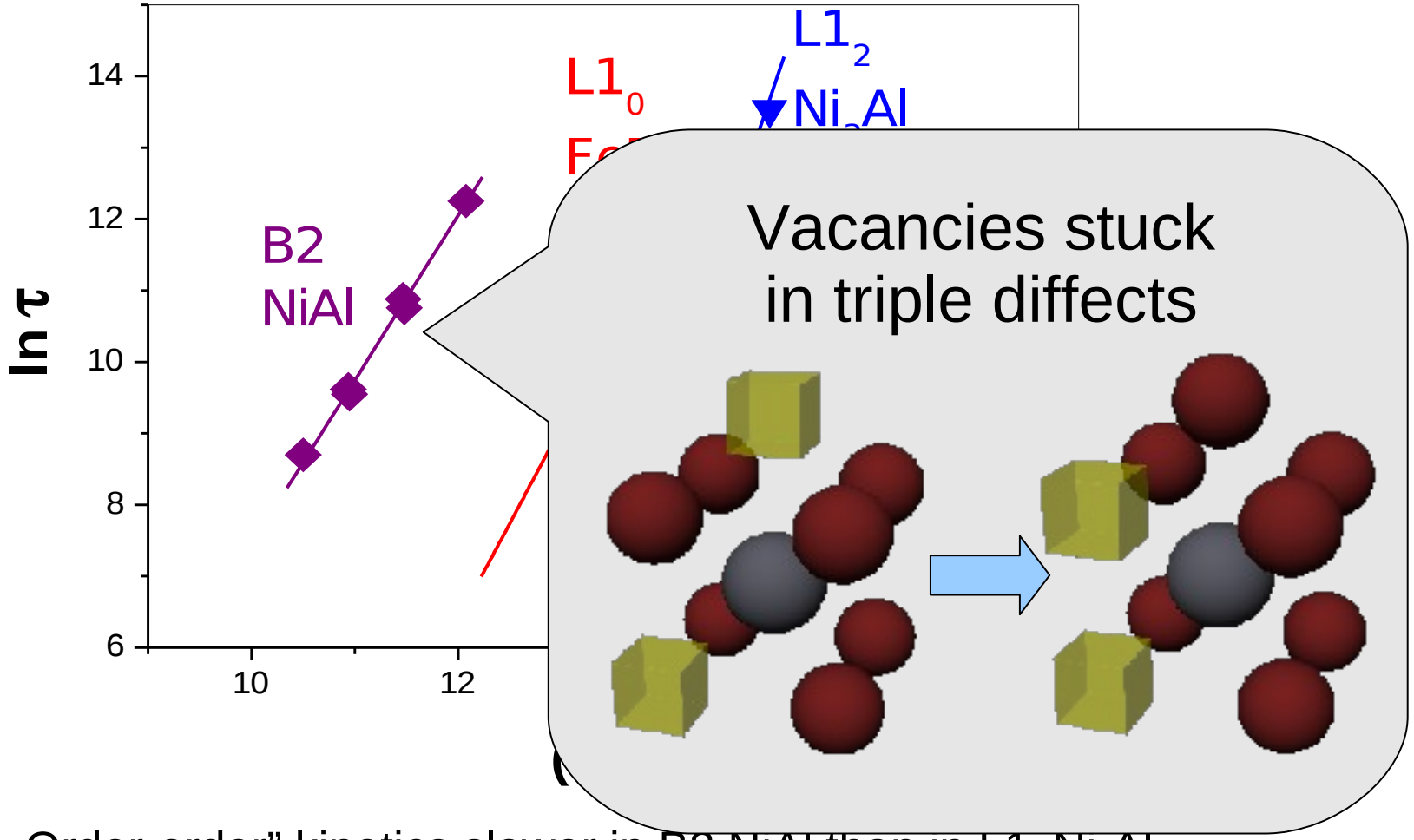
Phenomena studied in B2



„Order-order" kinetics slower in B2 NiAl than in $L1_2$ Ni_3Al experimental observations (Kozubski et al.).

But equilibrium vacancy concentration being around 5 orders of magnitude higher in B2 phase – up to ~10^{-2} (Scheafer et al.)

Phenomena studied in B2



„Order-order" kinetics slower in B2 NiAl than in $L1_2$ Ni_3Al experimental observations (Kozubski et al.).

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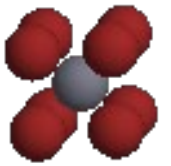
B2 model approach



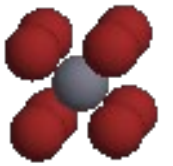
Modeling of „order-order” kinetics in triple-defect type B2 superstructure at equilibrium vacancy concentration

Set model interatomic potentials that promote triple defect

Determine chemical potentials that result in equilibrium vacancy concentration

„Order-order” kinetics via vacancy mechanism

B2 model approach



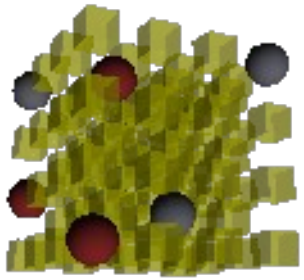
Set model interatomic potentials that promote triple defect

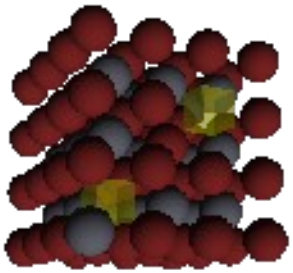
Selected pair-wise interactions promoting triple-defect behaviour:

$$V_{AB} = -0.125 \; V_{AA} = -0.120 \; V_{BB} = -0.050 \;\; [eV]$$

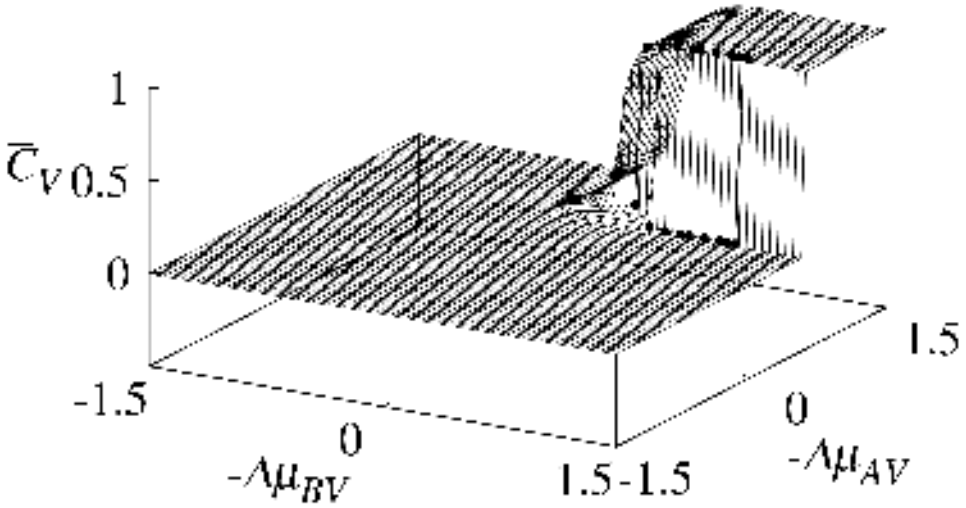
$$V_{VV} = -0.000 \; V_{AV} = 0.040 \; V_{BB} = -0.040 \;\; [eV]$$

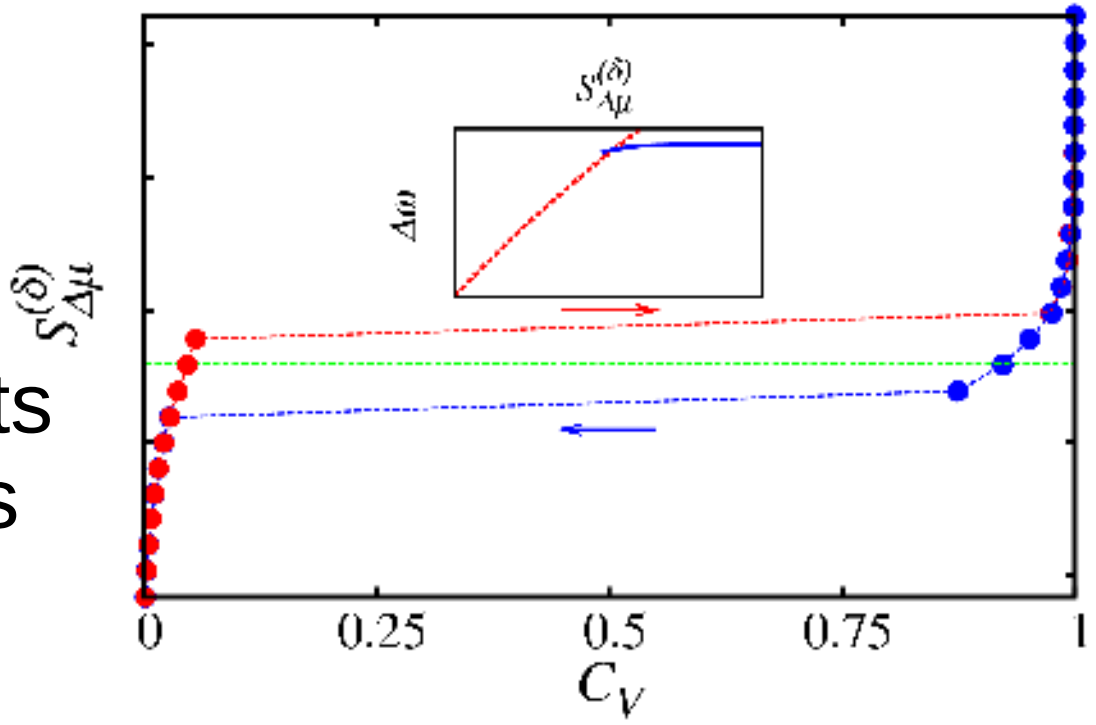
Lattice-gas decomposition SGCMC simulations





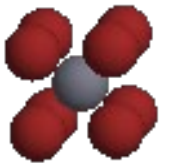
Desired system presents co-existance of phases



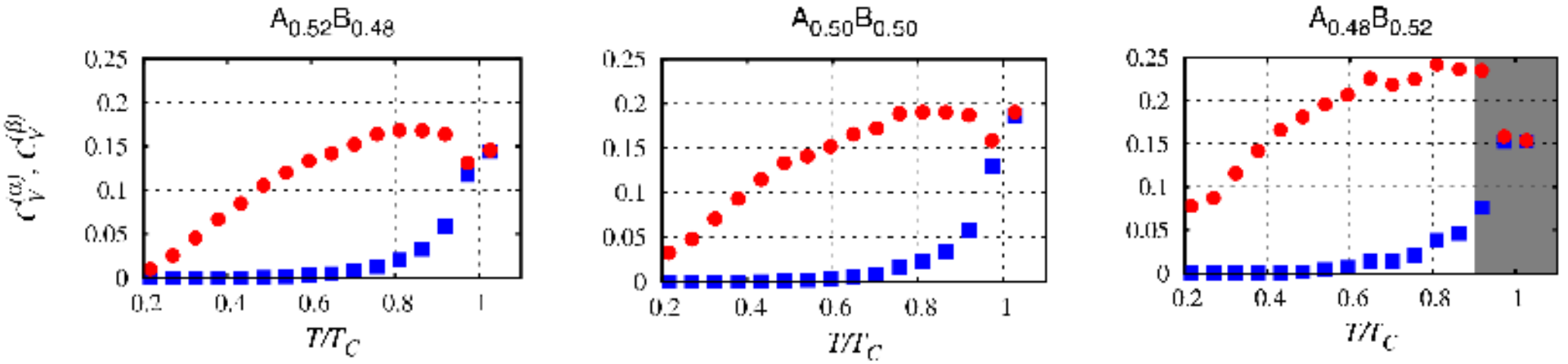


Refining procedures performed successfully resulting in equilibrium thermal vacancy concentration as a function of temperature

Lattice-gas decomposition
SGCMC simulations

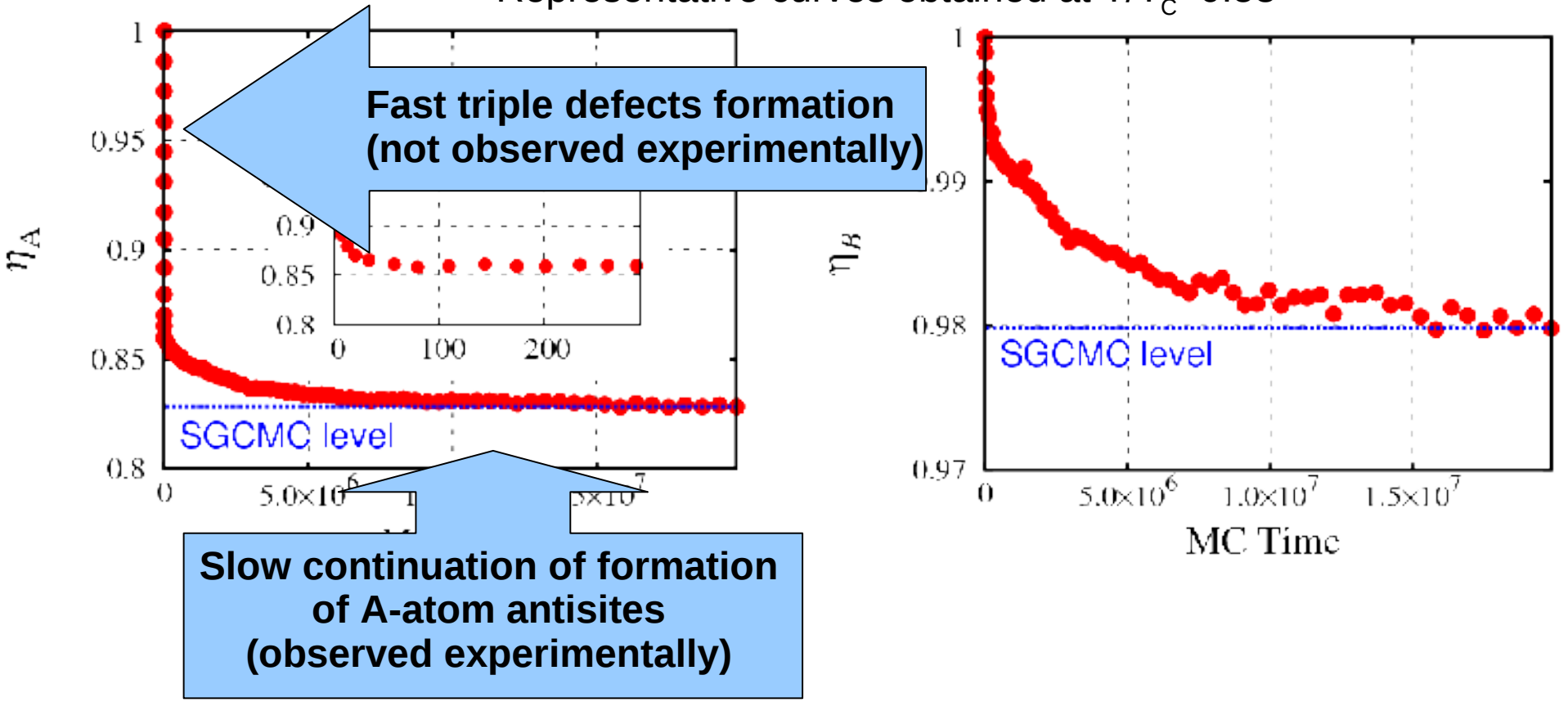


Atom-rich solution (crystal at thermal and chemical equilibrium)



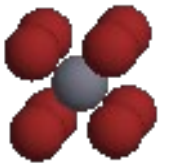
„Order-order” kinetics
Kinetic Monte-Carlo simulations

Representative curves obtained at $T/T_c=0.53$



LRO evolution

B2 model - conclusion



SGCMC with **phase decomposition procedure** is the successful method for determination of **equilibrium vacancy concentration** in binary systems.

It is possible to adjust energies in the system to generate **triple-defect** and observe **“order-order” kinetics** similar to the **experimental**

Perspective – use realistic potentials and generate quantitative agreement with experiment.

Atomic ordering in $L1_0$ FePt thin layers

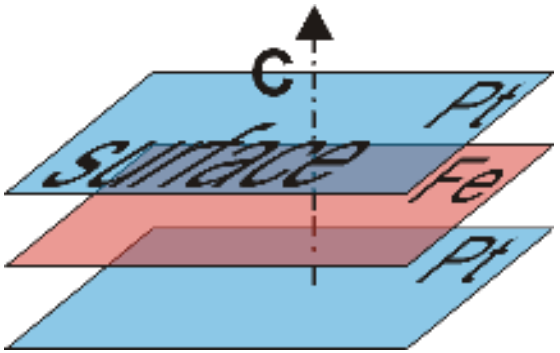
$L1_0$ FePt layers – basic concepts

Two models:

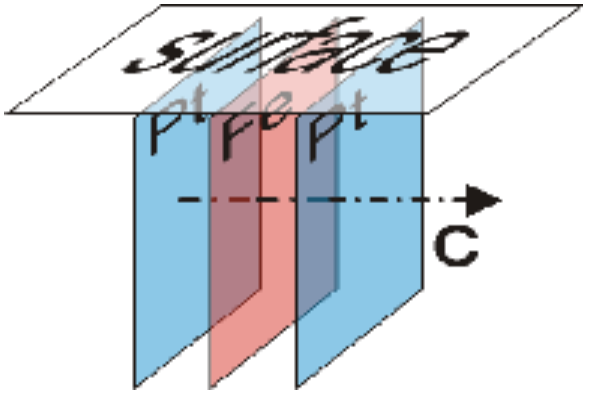
ISING-type – discrete pair interactions based on CEM

ABOP – advanced many-body interactions MD-like

Superstructure variants:

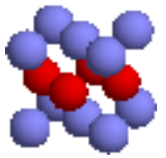


c-variant



a(b)-variant

ISING model Monte Carlo simulations

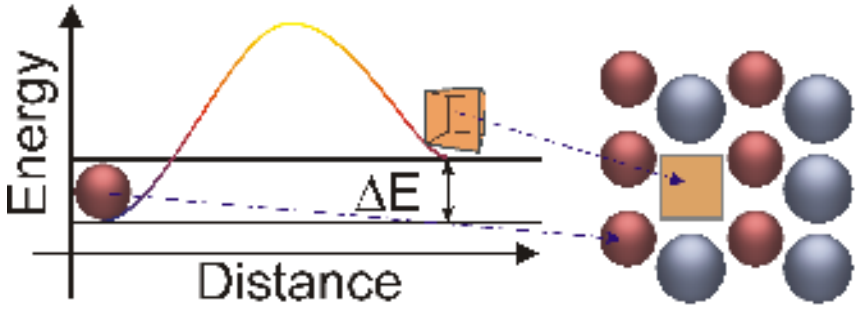


- **Ising** system with pair interaction energies up to the second nearest neighbour.

$$E_{Conf} = \sum_{i,j,r} N_{ij} V_{ij}(r)$$

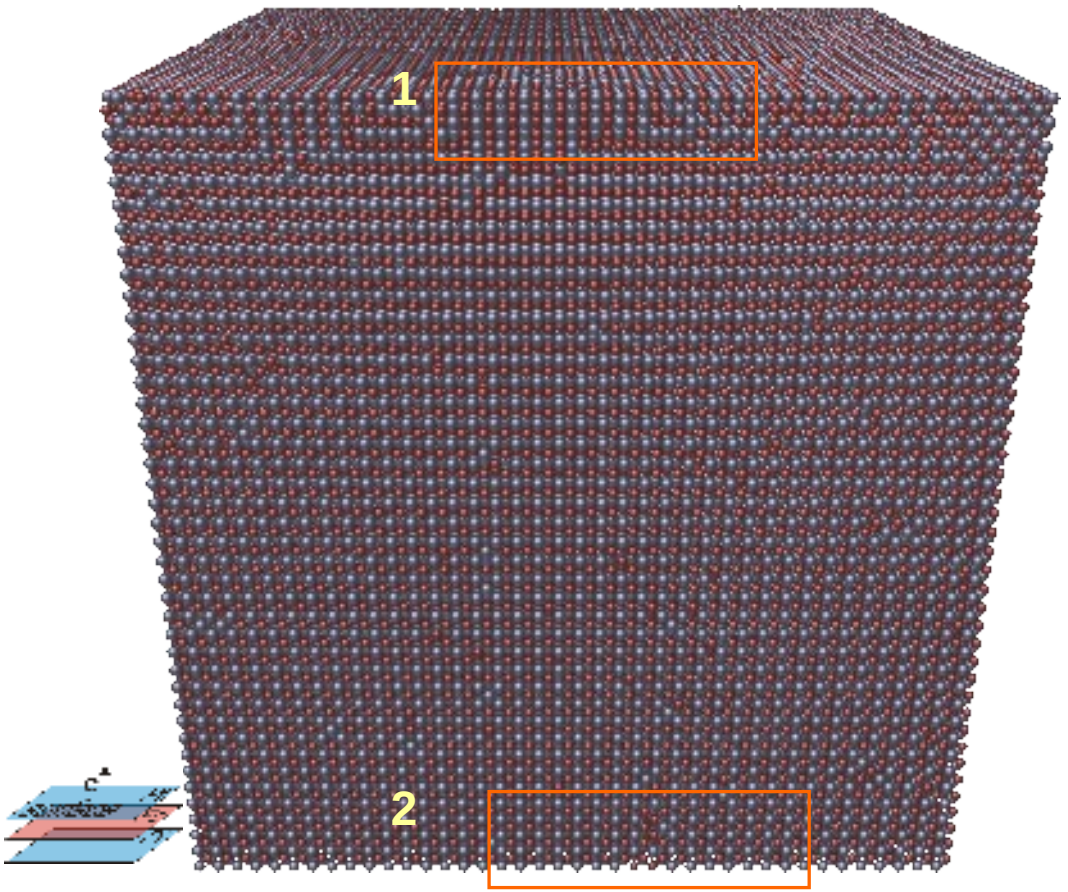
- Potentials developed CEM (Cluster Expansion Method)
- Atomic migration simulated by **jumps to nn vacancies** with probabilities determined within **Glauber** dynamics.

$$P_{i \to j} = \frac{\exp\left(-\frac{\Delta E}{k_B T}\right)}{1+\exp\left(-\frac{\Delta E}{k_B T}\right)}$$

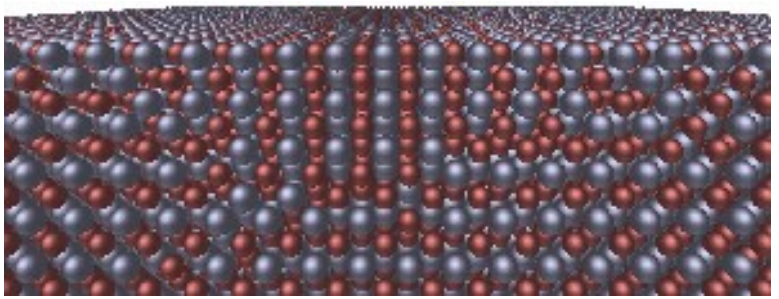


ISING model - $L1_0$ FePt c-variant layers

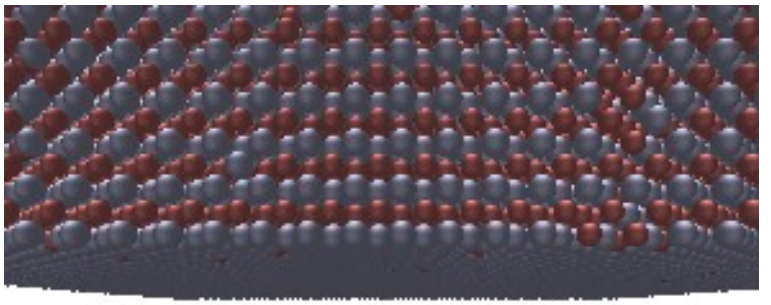
FePt $L1_0$ c-variant → a-variant superstructure reorientation



1 Fe-covered surface



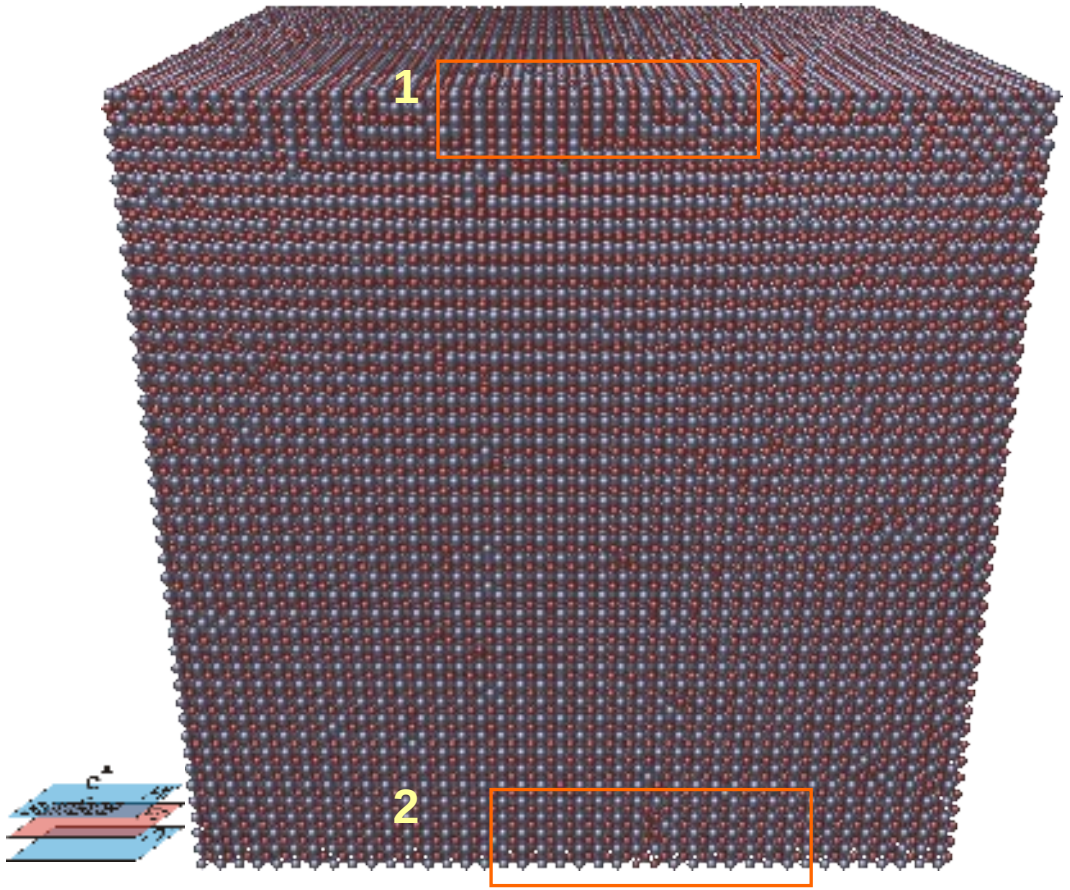
2



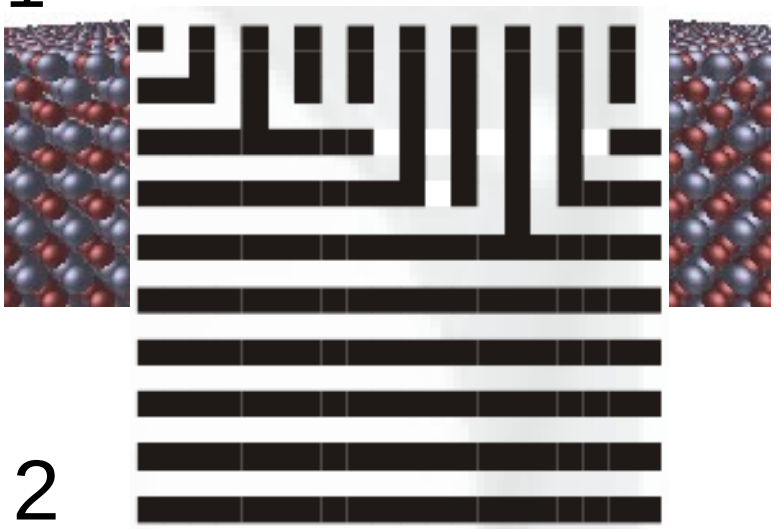
Pt-covered surface

Simulated $L1_0$ FePt c-variant layer
after 5×10^7 MC steps at T = 1000K
- Fe, - Pt, - vacancy.

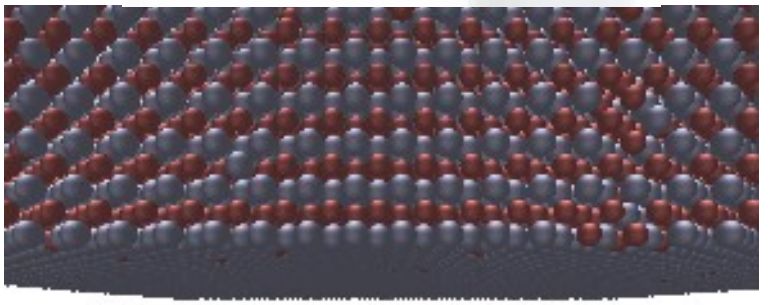
ISING model - $L1_0$ FePt c-variant layers



1 Fe-covered surface

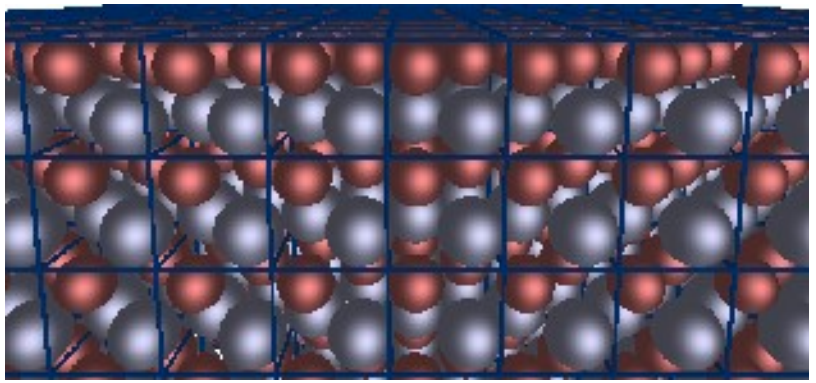


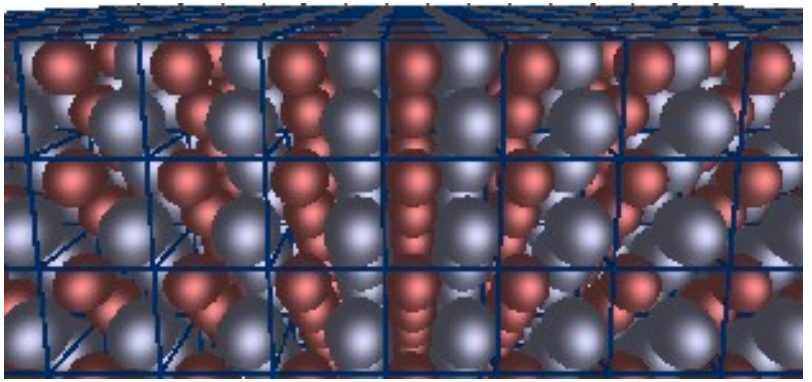
2

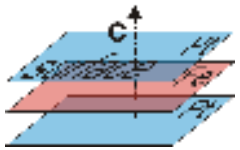


Pt-covered surface

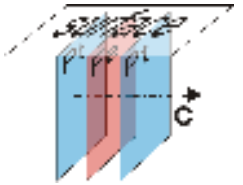
Energetic instability





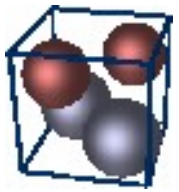


c-variant
c ⊥ surface



a(b)-variant
c || surface

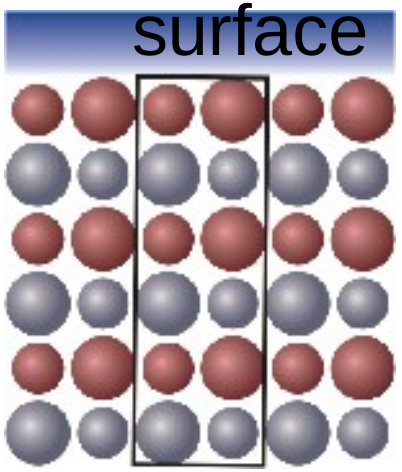
$$\Delta E_{uc} = 2V_{FePt} - V_{FeFe} - V_{PtPt} < 0$$

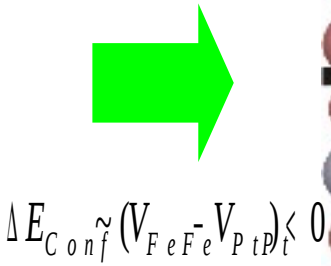


- FePt $L1_0$ unit cell

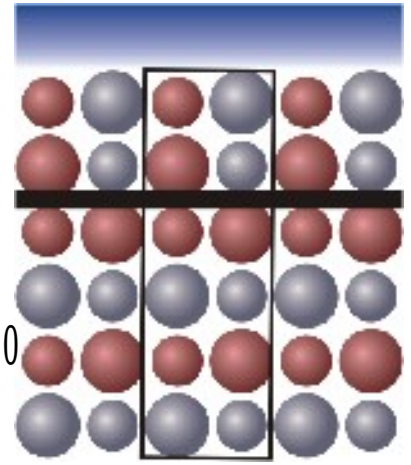
Driving force

Energetically **favorable** reorientation at **Fe** surface



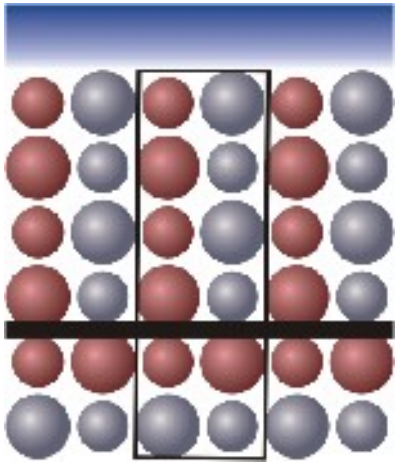


$\Delta E_{Conf} \sim (V_{FeFe} - V_{PtPt}) < 0$

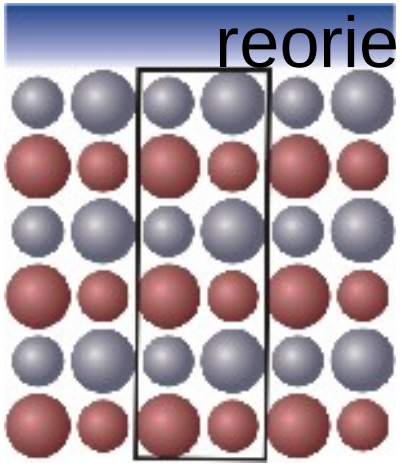


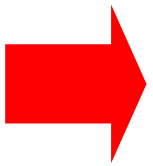
No energy **change** during domain **growth**

$\Delta E = 0$

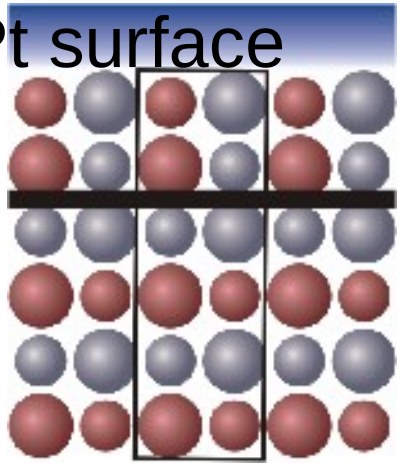


Energetically unfavorable reorientation at Pt surface

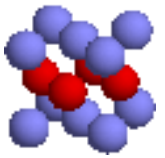




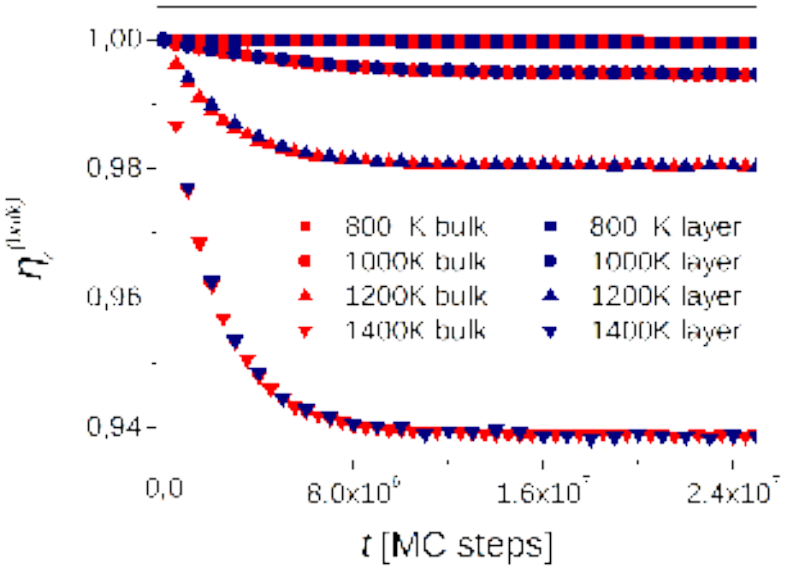
$\Delta E_{Conf} \sim (V_{PtPt} - V_{FePt}) > 0$

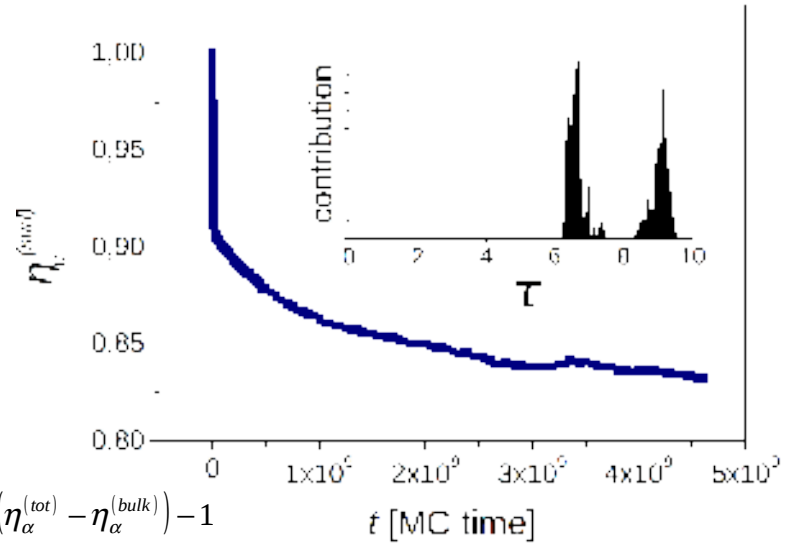


Reorientation kinetics

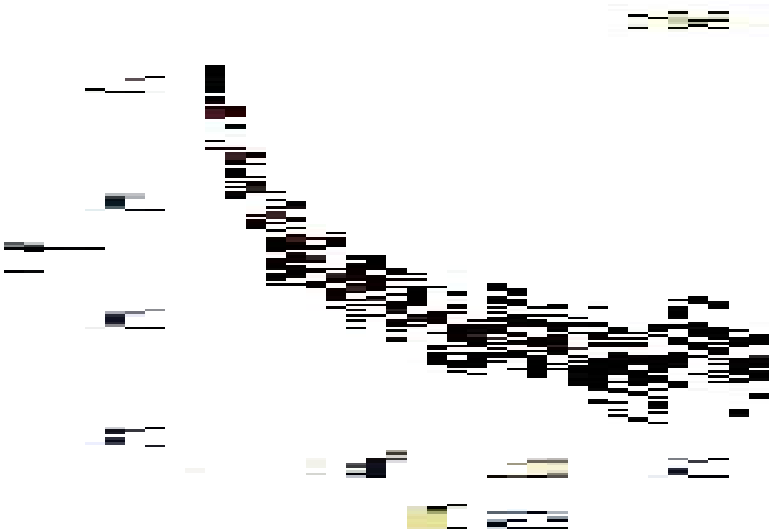


0. homogeneous disordering (generation of antisite defects).
1. nucleation of a- and b-variant $L1_0$ domains within the surface layer of the $L1_0$ unit cells
2. growth of the nucleated a- and b-variant $L1_0$ domains inward the layer
3. relaxation of the microstructure of a- and b-variant $L1_0$ domains





$$\eta_\alpha^{(surf)} = \left(\eta_\alpha^{(tot)} - \eta_\alpha^{(bulk)}\right) - 1$$

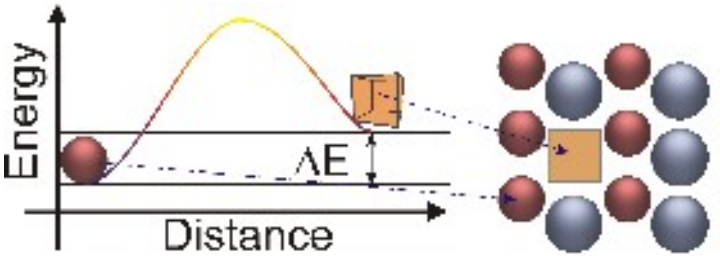


ABOP – MC/SR simulations

Monte Carlo / Static Relaxations (MS + Lattice optimization)

MC – atomic migrations by means of Glauber algorithm.

$$P_{i\to j} = \frac{\exp\left(-\frac{\Delta E}{k_B T}\right)}{1+\exp\left(-\frac{\Delta E}{k_B T}\right)}$$

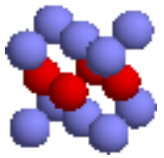


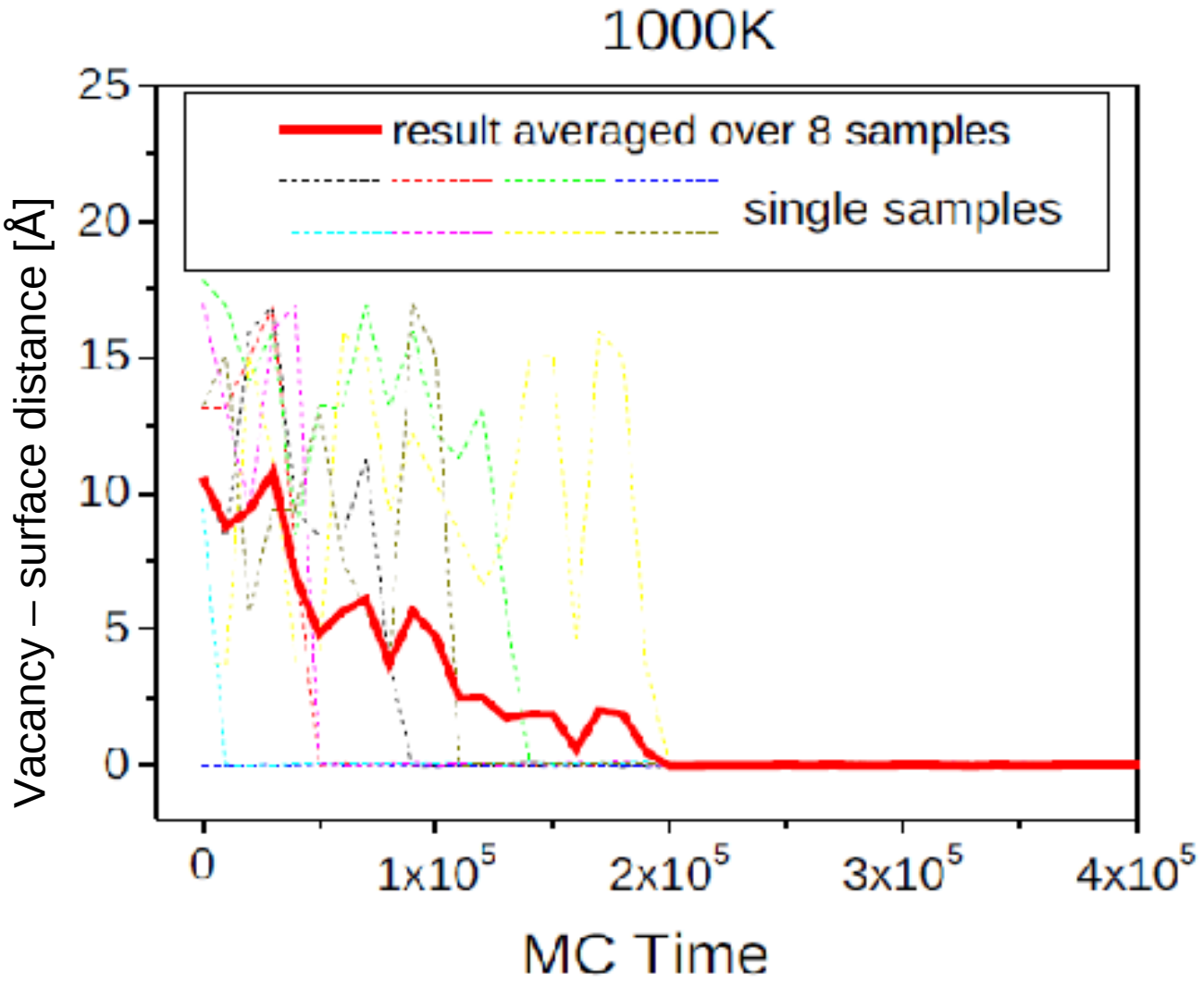
MS – molecular statics for surface relaxations

$$E = \sum_{i<j} f_{ij}^{c}(r_{ij}) \left[V_{ij}^{R}(r_{ij}) - \frac{b_{ij}+b_{ji}}{2} V_{ij}^{A}(r_{ij}) \right]$$

Lattice optimization – evolution of tetragonal distortion

ABOP model results – FePt $L1_0$ layers



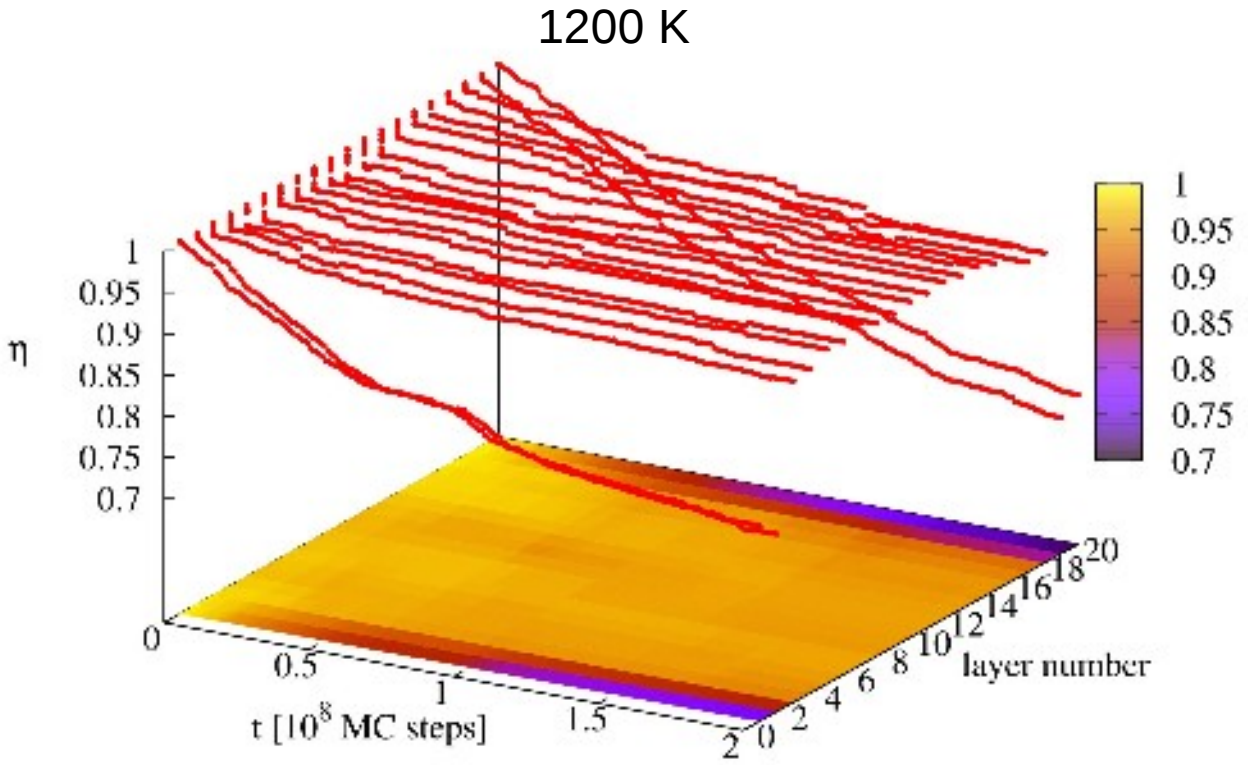


Vacancies stay at the surface

ABOP model FePt c-variant $L1_0$ layers

Samples 10x10x10 unit cells, initially c-variant $L1_0$,1 vacancy.

Isotermal simulation. Results averaged over 8 runs

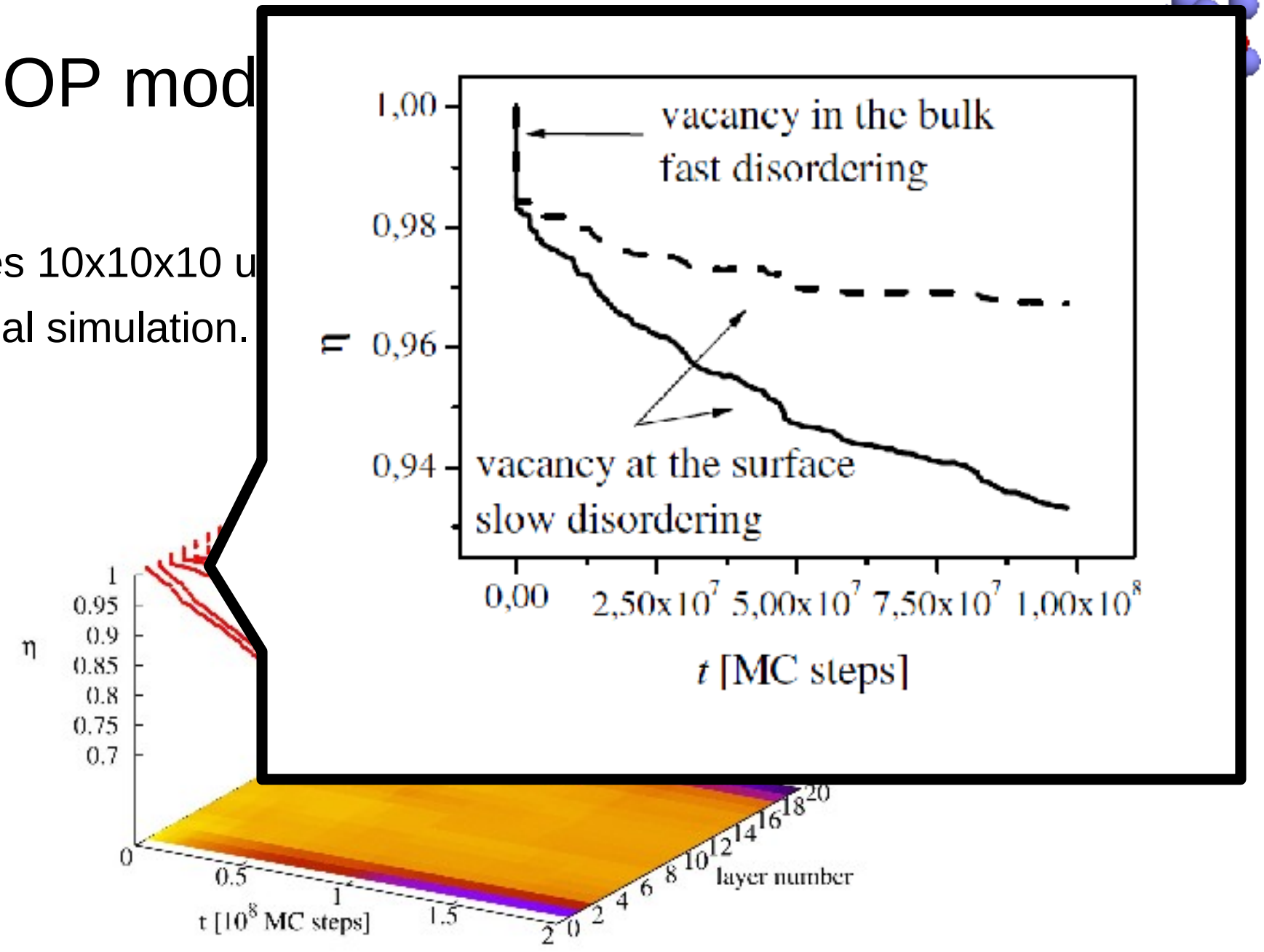


Metastable superstructure – localized surface disordering

ABOP mod

Samples 10x10x10 u

Isotermal simulation.

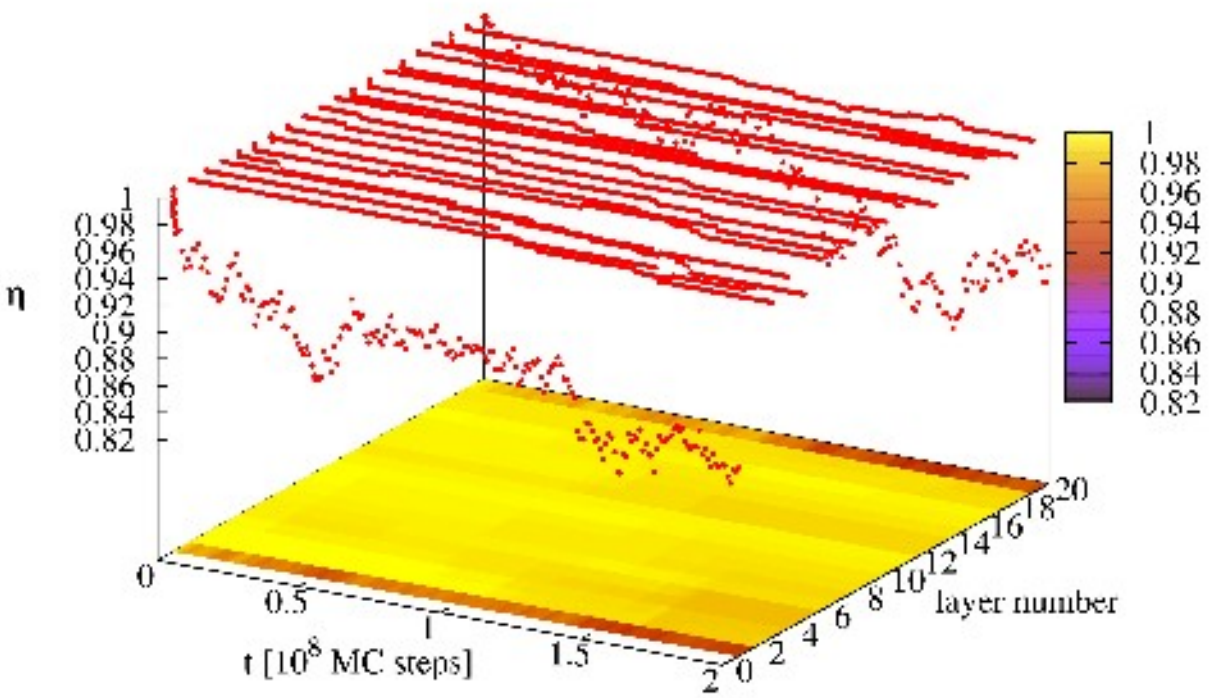


Metastable superstructure – localized surface disordering

ABOP model FePt a-variant $L1_0$ layers

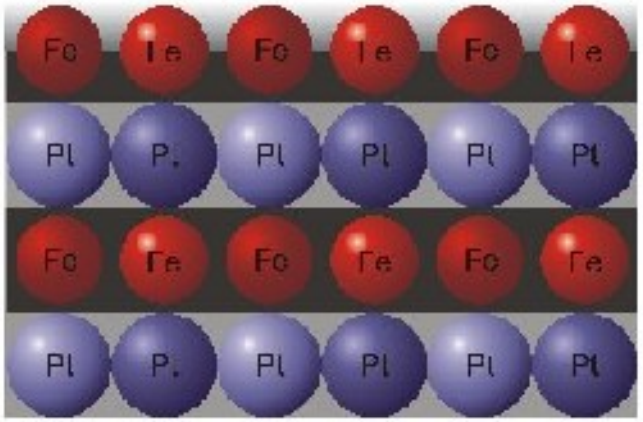
Samples 10x10x10 unit cells, initially a-variant $L1_0$,1 vacancy.
Isotermal simulation. Results averaged over 8 runs

1200 K



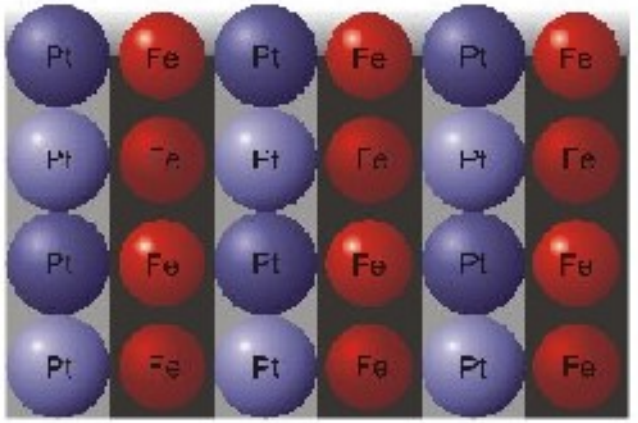
Stastable superstructure – localized surface disordering

$L1_0$ FePt layers summary I



c-variant

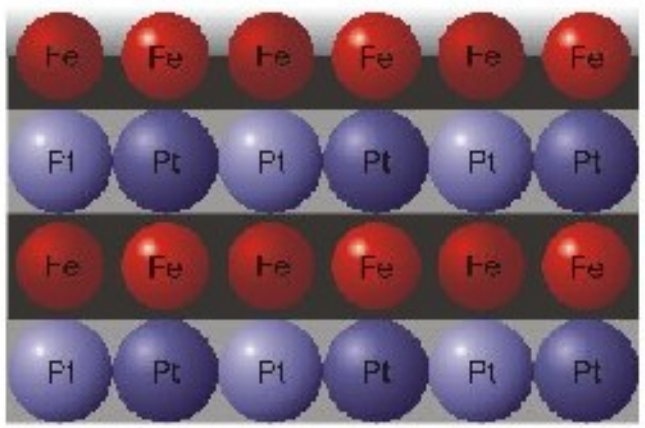
$E_c > E_a$



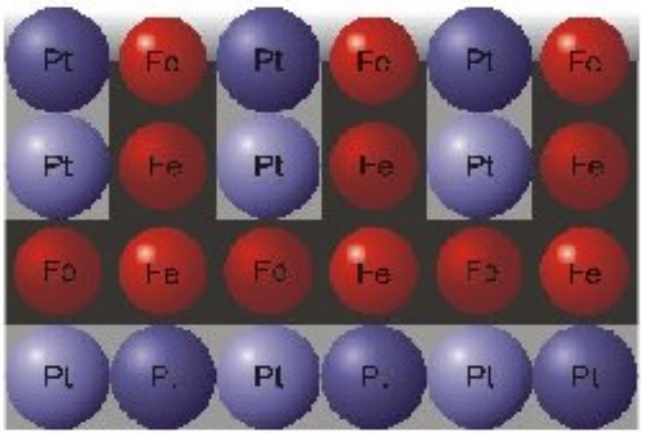
a-variant

In all considered models configurational energy of c-variant $L1_0$ ordered FePt layer is lower than in a-variant layer.

$L1_0$ FePt layers summary II



$$\Delta E_{AP_{surf}}$$



c-variant

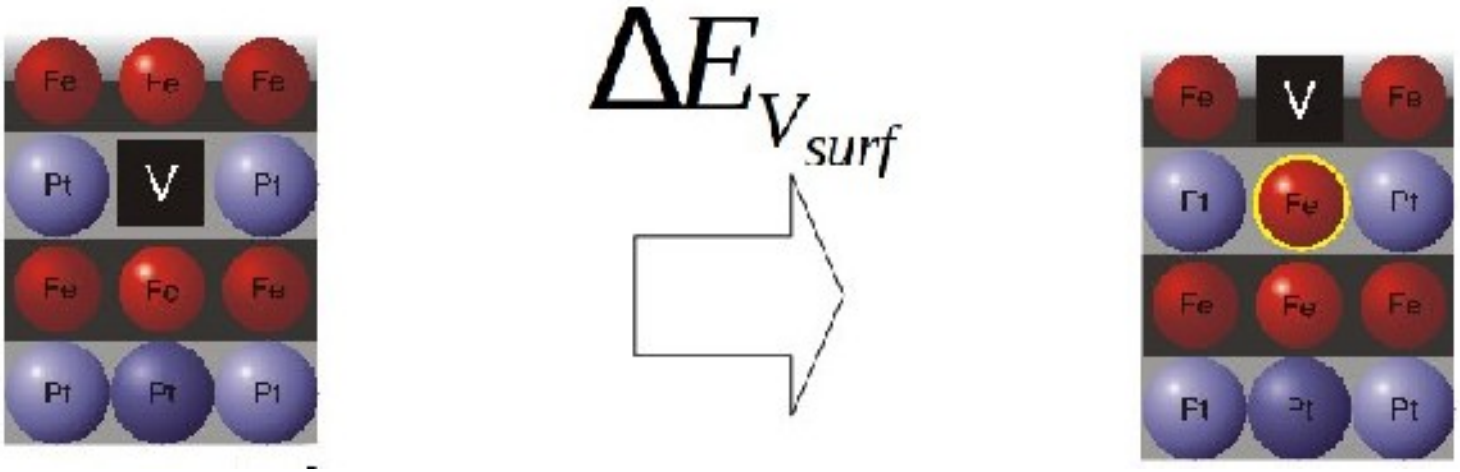
a-variant
at the surface of
c-variant

ISING: $\Delta E_{APsurf} < 0$

ABOP: $\Delta E_{APsurf} > 0$

Only in ISING model
nucleation of a-variant at the surface of c-variant is energetically favorable.

$L1_0$ FePt layers summary III

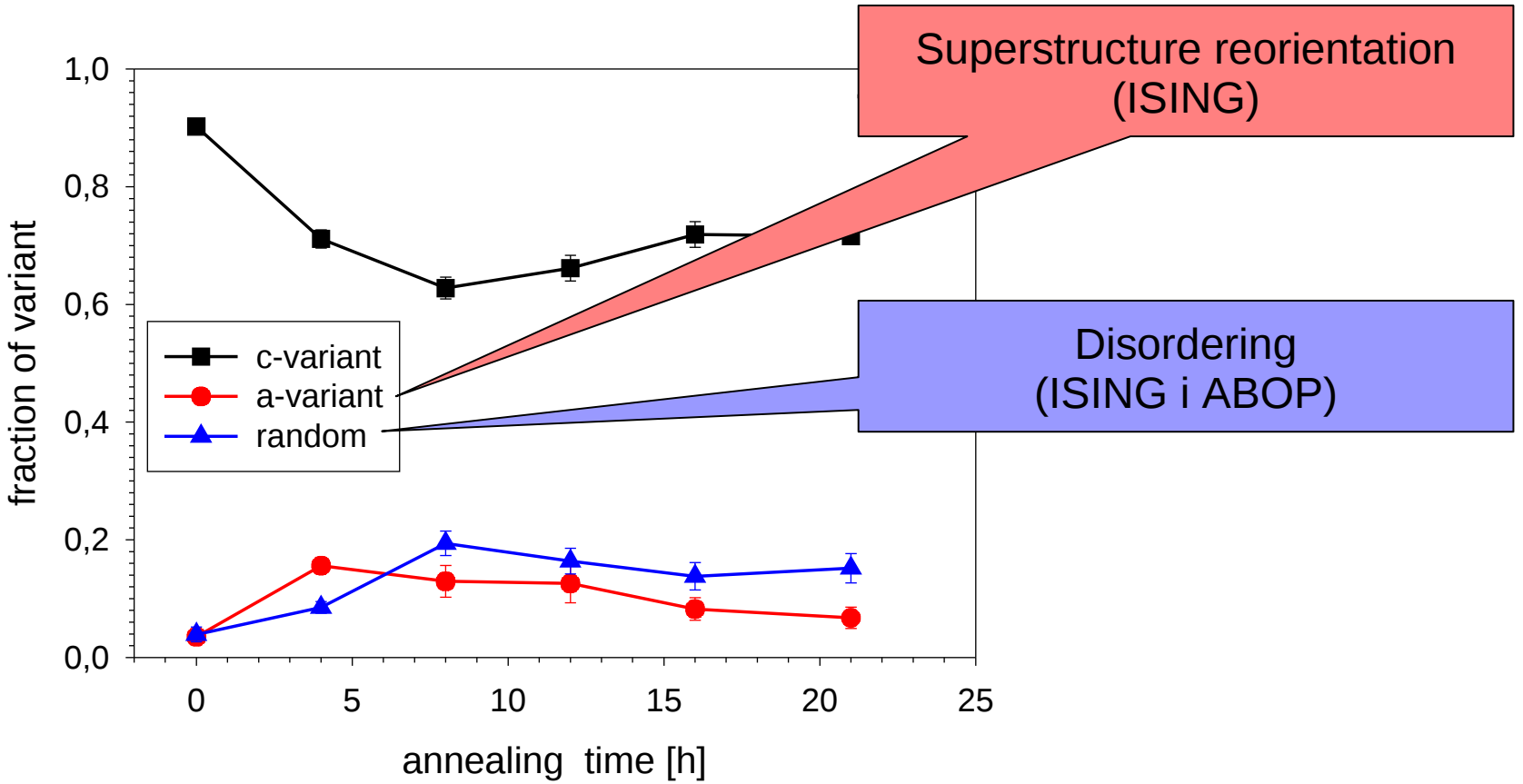


ISING: $\Delta E_{Vsurf} < 0$

ABOP: $\Delta E_{Vsurf} < 0$

In ABOP model energy of vacancy migration towards the surface determines the ordering kinetics.

Experimental data instead of conclusion



CEMS-measured evolution of concentration of particular $L1_0$ variants in FePt layered sample annealed at 773°C.

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Thank you for your attention