Structure Atomique et Ordre Chimique dans les Nanoalliages CoPt

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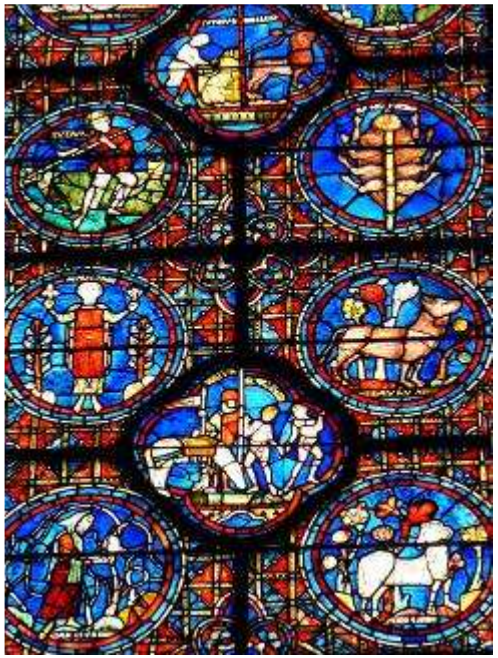
Atelier multi-échelle 2010, CIRM, Marseille – Luminy.



Une façon empirique d'utiliser les Nanoalliages:

- vitraux, arts du verre
- photographie argentique
- pétrochimie (catalyse)

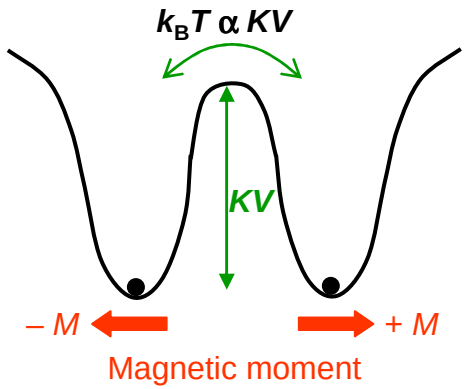
… contrôle des propriétés ⇔ contrôle de la structure et du mode d'élaboration

vers une étude de la **relation structure-propriétés** :

- catalyse hétérogène
- propriétés optiques (plasmonique)
- magnétisme (enregistrement ultra-haute densité)

Propriétés Magnétiques de Nanoparticles / superparamagnétisme

Néel relaxation time in the Néel-Arrhenius model :



$$\tau = \tau_0 e^{\frac{KV}{k_B T}}$$

K : magnetic anisotropy
V : volume
T : temperature

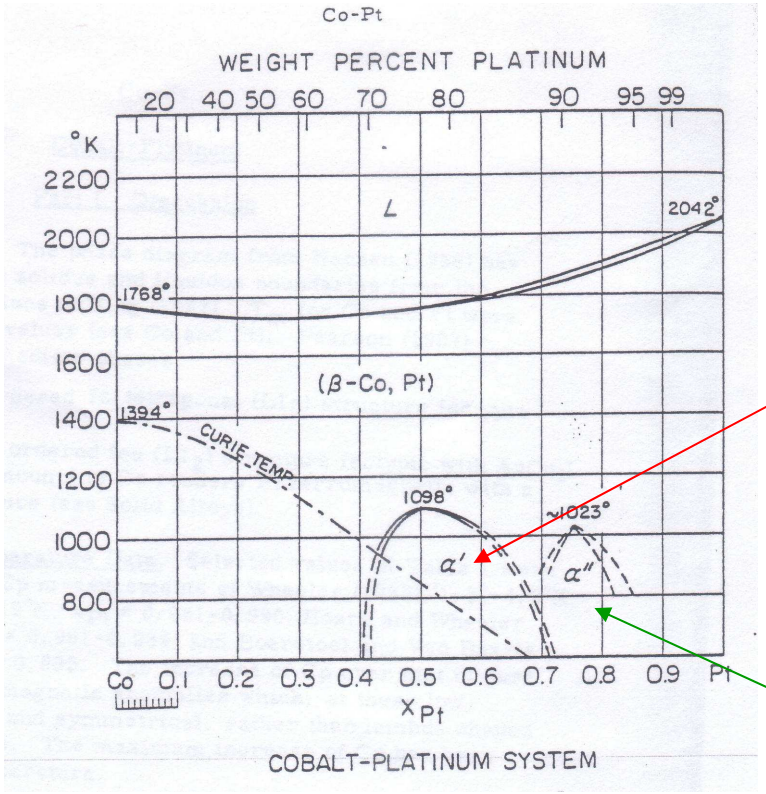
As V ↘, find a way to ↗ K

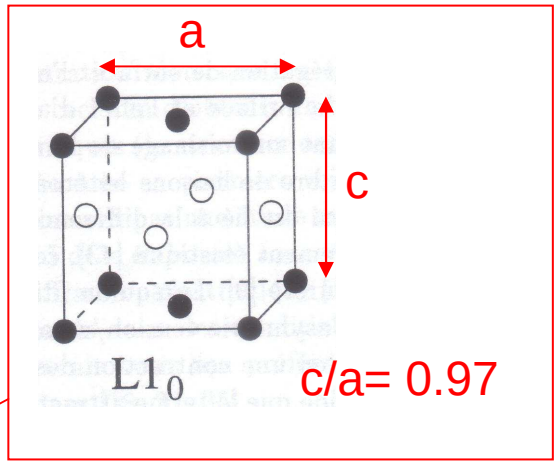
Allier un métal 3d magnétique à un métal 4 ou 5d avec un fort couplage spin-orbit : FePt, FeRh, CoPt, CoRh, … en utilisant la phase ordonnée $L1_0$.

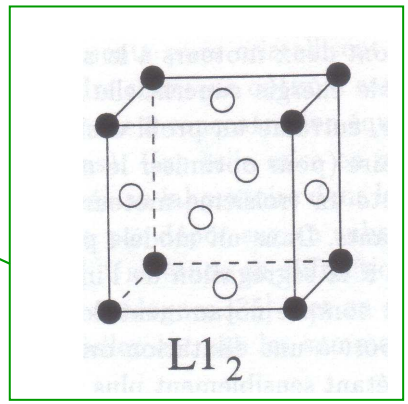
Cependant, si la structure atomique change par rapport à celle de volume (Ih, Dh, …) la multiplicité de symétrie ↘ K

Structures hors équilibre: formes anisotropes, blocage cinétiques, … dépendant du mode d'élaboration.

CoPt bulk alloy







Plan de l'exposé:

- **Potentiel SMA pour les alliages**

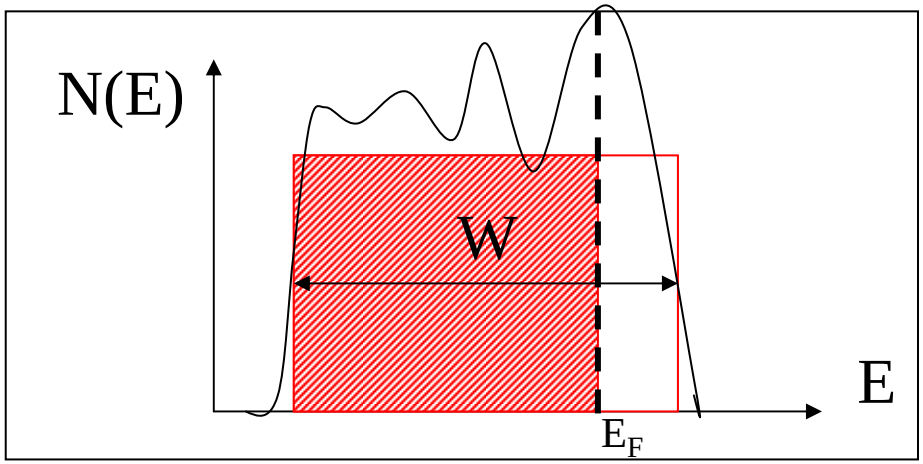
- **Transition A1 → $L1_0$ (FCC) /** *Monte Carlo – SMA potential*

- **Transition Ih → Dh → TOh (FCC) /** *Monte Carlo – QMD – SMA potential*

- **Autres symétries: taille < 1nm /** *Global Opt. – SMA potential + DFT*

→ Comparaison avec les expériences

Tight-Binding Many-Body Potential : Second Moment Approximation (SMA)



$$E_{pot.} = \sum_i \left(-\sqrt{\sum_j \xi^2 e^{-2q\left(\frac{r_{ij}}{r_0}-1\right)}} + \sum_j A e^{-p\left(\frac{r_{ij}}{r_0}-1\right)} \right)$$

A,p,q,ξ are fitted on bulk properties :

- cohesive energy
- lattice parameter
- elastic constants

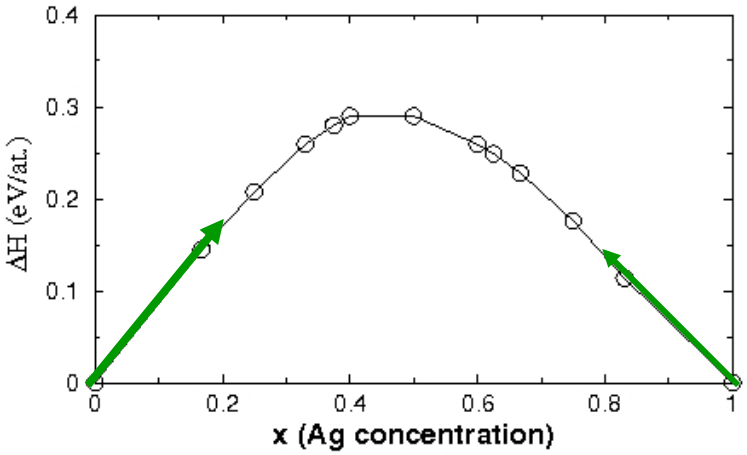
How to fit the hetero-atomic interactions

- Fit on the enthalpy energy ΔH and in particular the dissolution energy $\Delta H^B(A)$, $x_A \longrightarrow 0$
- mixing pair interactions: $V=(V_{AA}+V_{BB}-2V_{AB})/2$, $V_{ij} < 0$

2 different cases :

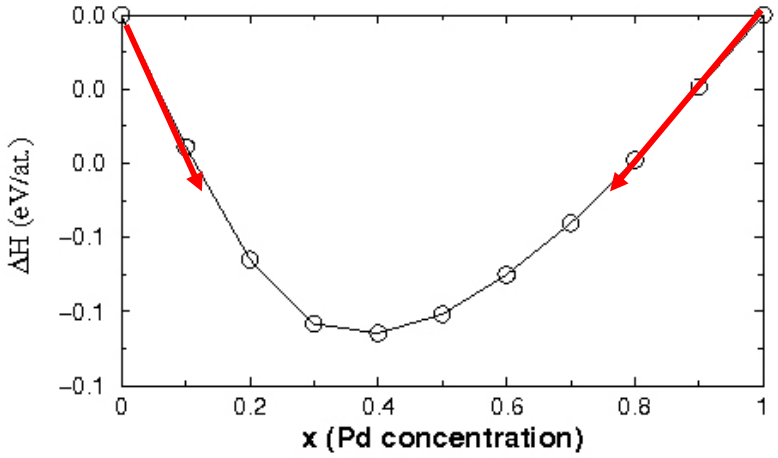
Demixion : $\Delta H > 0$, $V < 0$

$Co_{1-x}Ag_x$



Ordering : $\Delta H < 0$, $V > 0$

$Au_{1-x}Pd_x$



Co-Pt system

• **Alloy interaction**: V > 0

	$\Delta H^{Pt}(Co)$ (eV)	$\Delta H^{Co}(Pt)$ (eV)	ΔH_{A1} (eV)	ΔH_{L1_0}(eV)	ΔH_{L1_2}(eV)
Calc.	-0.472	-0.657	-5.258	-5.327	-5.624
Exp.	-0.47	-0.65	-5.155	-5.296	-5.634

• **Surface energy difference**:

Surface energies (J/m^2) (eV/at.)	TB-SMA	DFT	Exp.
$\gamma^{Pt} - \gamma^{Co}$	0.12 0.16	-0.27 -0.06	-0.07 0.19

• **Misfit** : $\frac{r_{Pt} - r_{Co}}{r_{Co}} = 10\%$

• **Order/disorder transition temperature**: $T_c(L1_0 / A1)$= **900K** (1100K, exp.)

• **tetragonalization of the $L1_0$ phase** : c/a = **0.93** (0.97, exp.)

Metropolis Monte Carlo - method

In canonical ensemble: $N=N_A+N_B$, P, T

- *displacement* of one atom
- *exchange* between two atoms

$$P_{new} = Min\left\{ 1 \ , \ e^{-\frac{\Delta E}{kT}} \right\}$$

- box size *expansion*

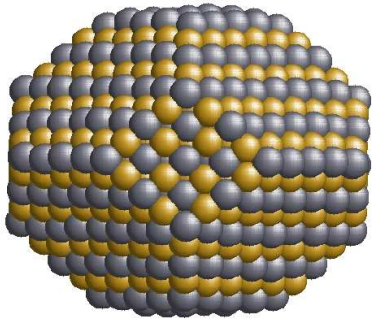
$$P_{new} = Min\left\{ 1 \ , \ e^{-\frac{\Delta E + P\Delta V - NkT\Delta \ln V}{kT}} \right\}$$

$$M_{MC} = N_{macro}\left(Nn_{disp} + Nn_{ex} + n_{box}\right)$$

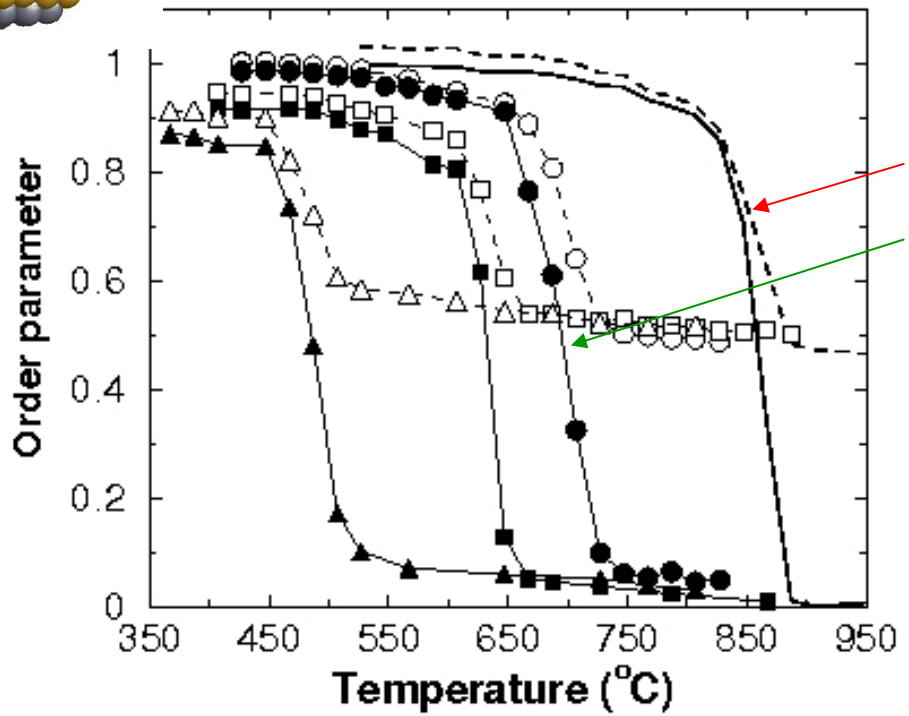
Having a rejected rate around 50% of the trials

Transition ordre / désordre dans les NPs CoPt

Monte Carlo canonique – potentiel SMA



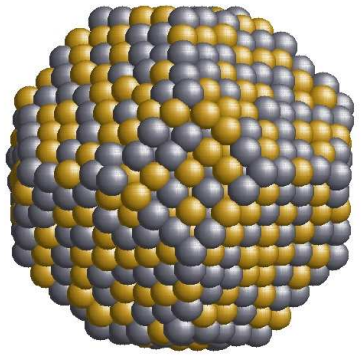
$$\begin{cases} \text{LRO} = max\{ |\eta_x|, |\eta_y|, |\eta_z| \},\ \eta_i=(p_A-c_A)+(p_B-c_B),\ i=x,y,z \\ \text{SRO} = 1-\dfrac{m-m_0}{c-m_0}\ ,\ \text{m (m}_0\text{), number of mixed bonds} \end{cases}$$



SRO (- - -) ; LRO (——)

Bulk

FCC TOh : 3 nm (○ ●), 2.5 nm (□ ■), 2 nm (△ ▲)



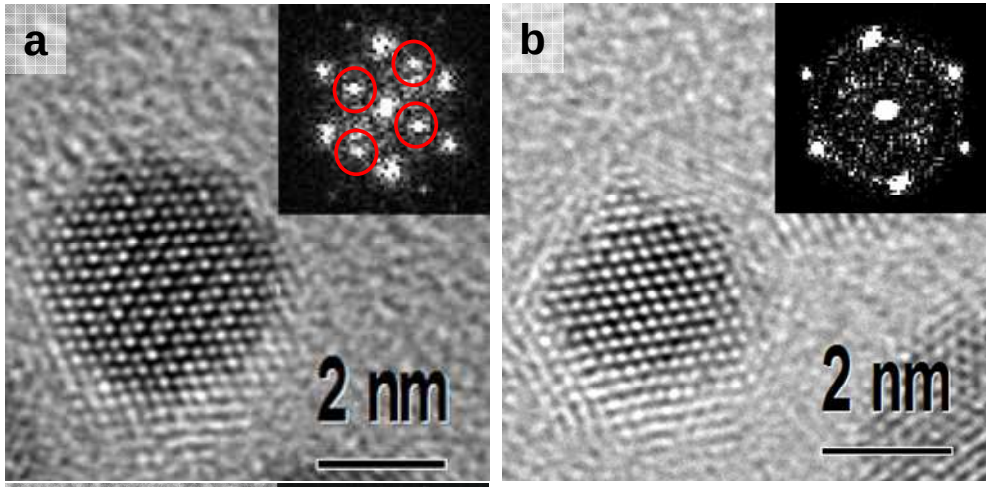
D. Alloyeau, C. Ricolleau, C. Mottet, T. Oikawa, C. Langlois, Y. Le Bouar, N. Braidy, A. Loiseau, Nature Materials 8, 940 (2009) *« Size and shape effects on the order-disorder phase transition in CoPt nanoparticles ».*

Evidence expérimentale de cette transition par HRTEM

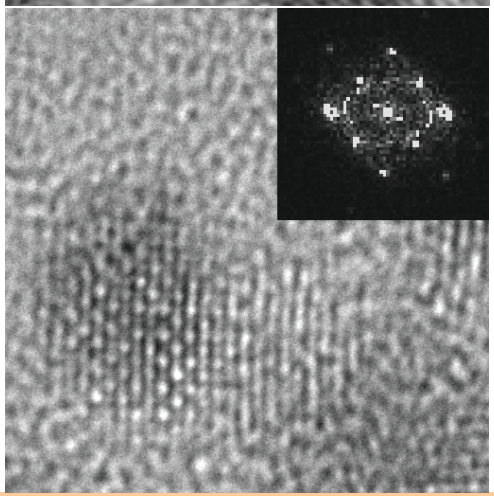
CoPt Pulsed Laser Deposition / amorphous Al_2O_3

$T < T_c$ $T > T_c$

Recuit d'1h à 750℃



Recuit de 16h à 500℃



Pour les NPs de taille < 3nm, la phase $L1_0$ n'est obtenue que si la température de recuit est inférieure à la température standard (650-750℃)

Alloyeau, Ricolleau, Oikawa, Langlois, Le Bouar, Loiseau, Ultramicroscopy 108 (2008)
STEM nanodiffraction technique for structural analysis of CoPt nanoparticles.

D. Alloyeau, C. Ricolleau, C. Mottet, T. Oikawa, C. Langlois, Y. Le Bouar, N. Braidy, A. Loiseau, Nature Materials 8, 940 (2009) *« Size and shape effects on the order-disorder phase transition in CoPt nanoparticles ».*

Forme et structure *in-situ* d'une collection de NPs par diffusion de rayons X

GIWAXS/GIXD

Grazing incidence
wide angle X-ray scattering

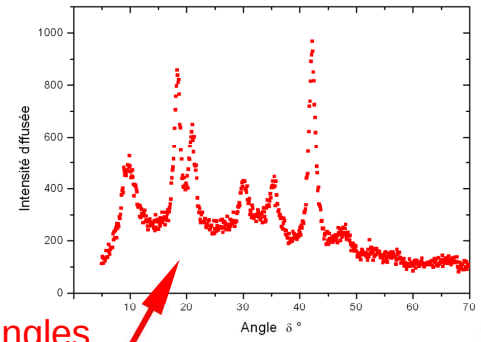
Structure
Icosahedra, decahedra, fcc, chemical order/disorder

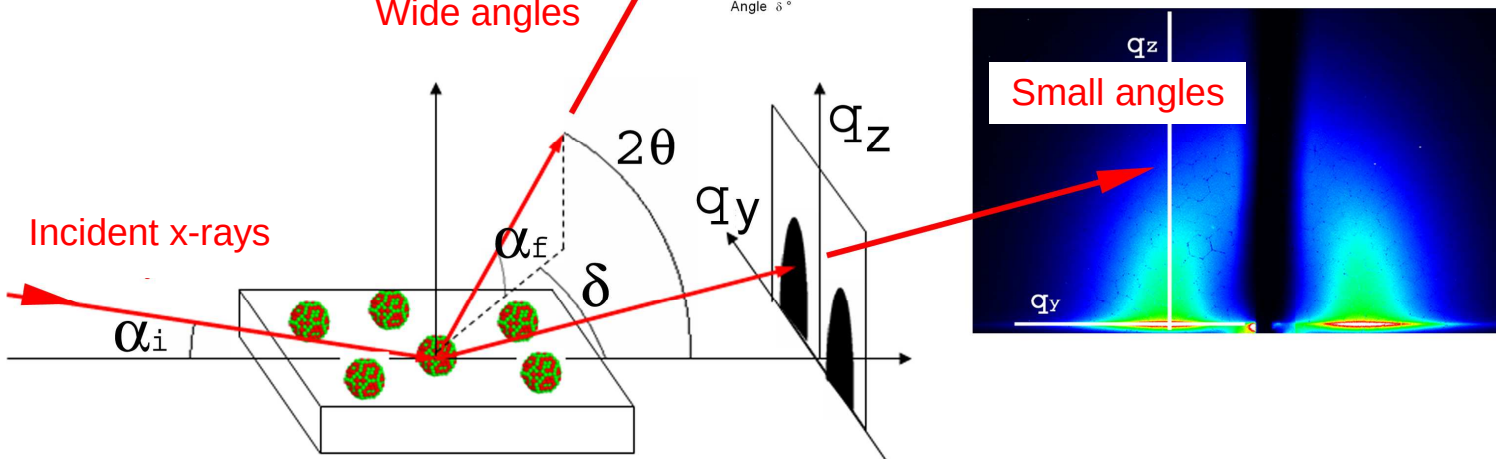
GISAXS

Grazing incidence
small angle X-ray scattering

Size-Shape
(Diameter-Height)

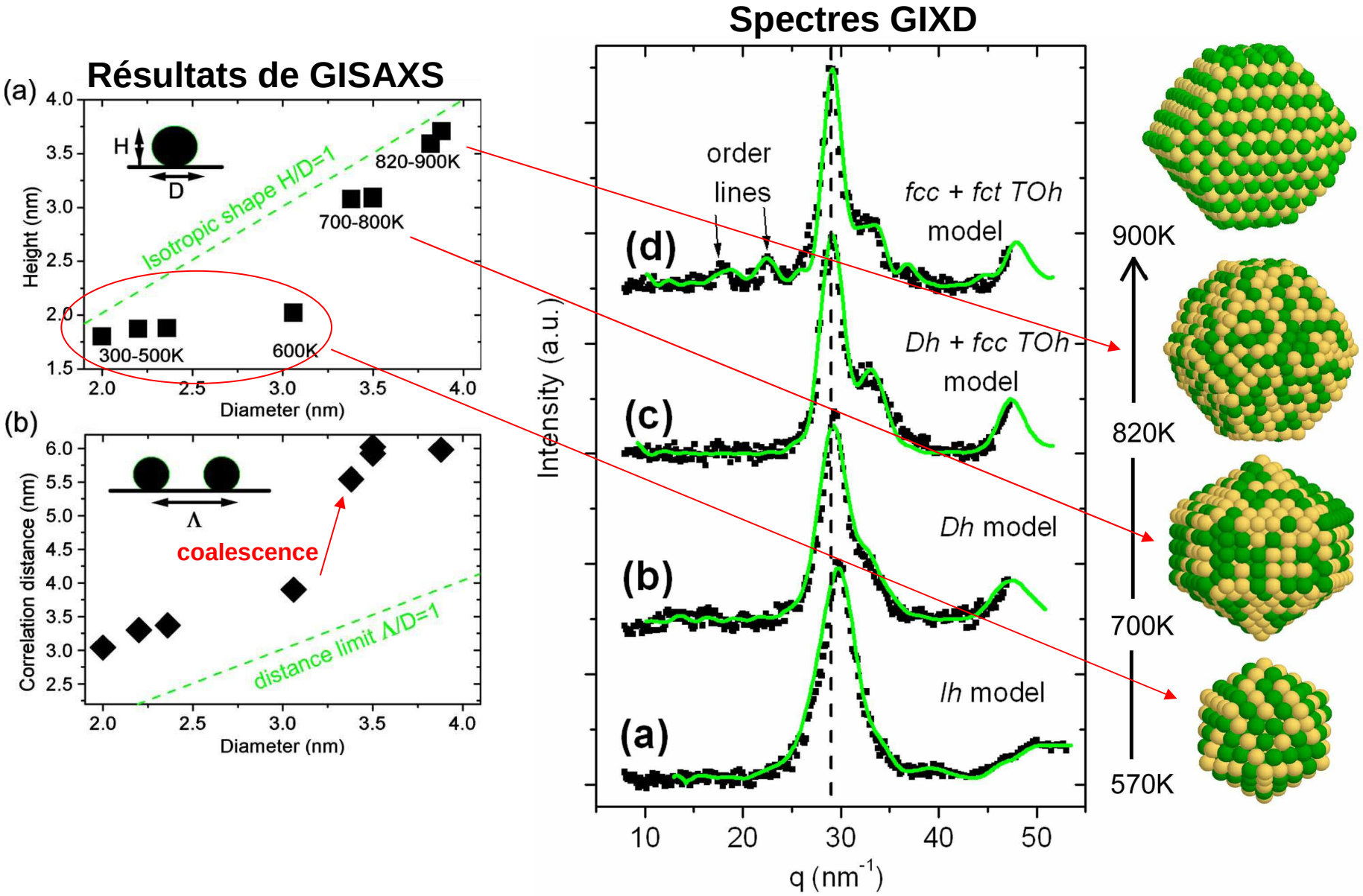
Interparticle distance





une incidence (grazing), deux détections (small and wide angles)

GISAXS et GIXD de NPs de CoPt *in situ* et sous recuit



Andreazza, Mottet, Andreazza-Vignolle, Penuelas, Tolentino, De Santis, Felici, Bouet, PRB 82, 155453 (2010)

Probing nanoscale structural and order/disorder phase transitions of supported Co-Pt clusters under annealing

Stability criterion

To compare nanoalloys with - different sizes

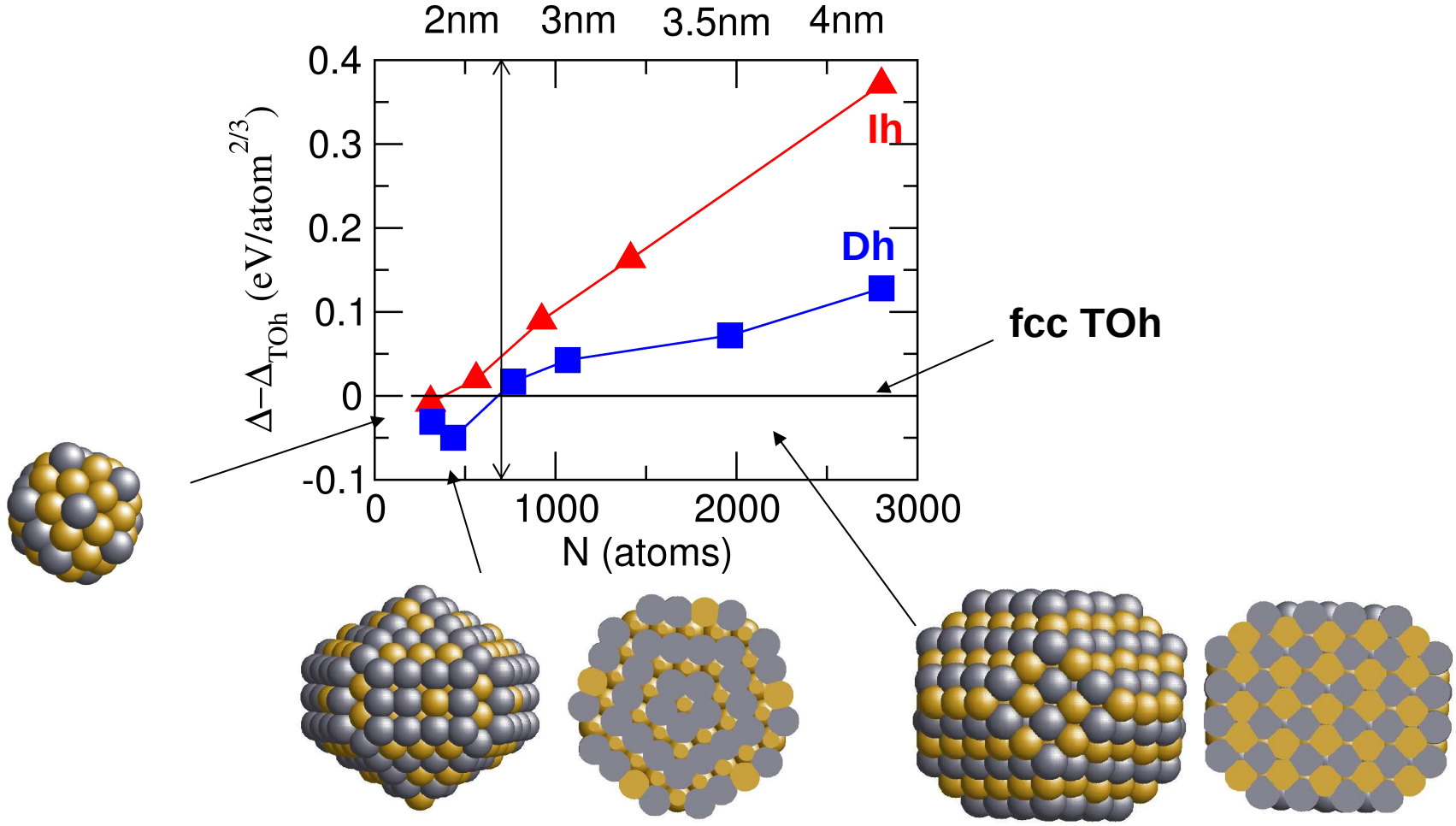
- different compositions

$$\Delta = \frac{E_{tot}^{Co_n Pt_m} - nE_{coh}^{Co} - mE_{coh}^{Pt}}{N^{2/3}}$$

Stable configurations ⟷ low Δ

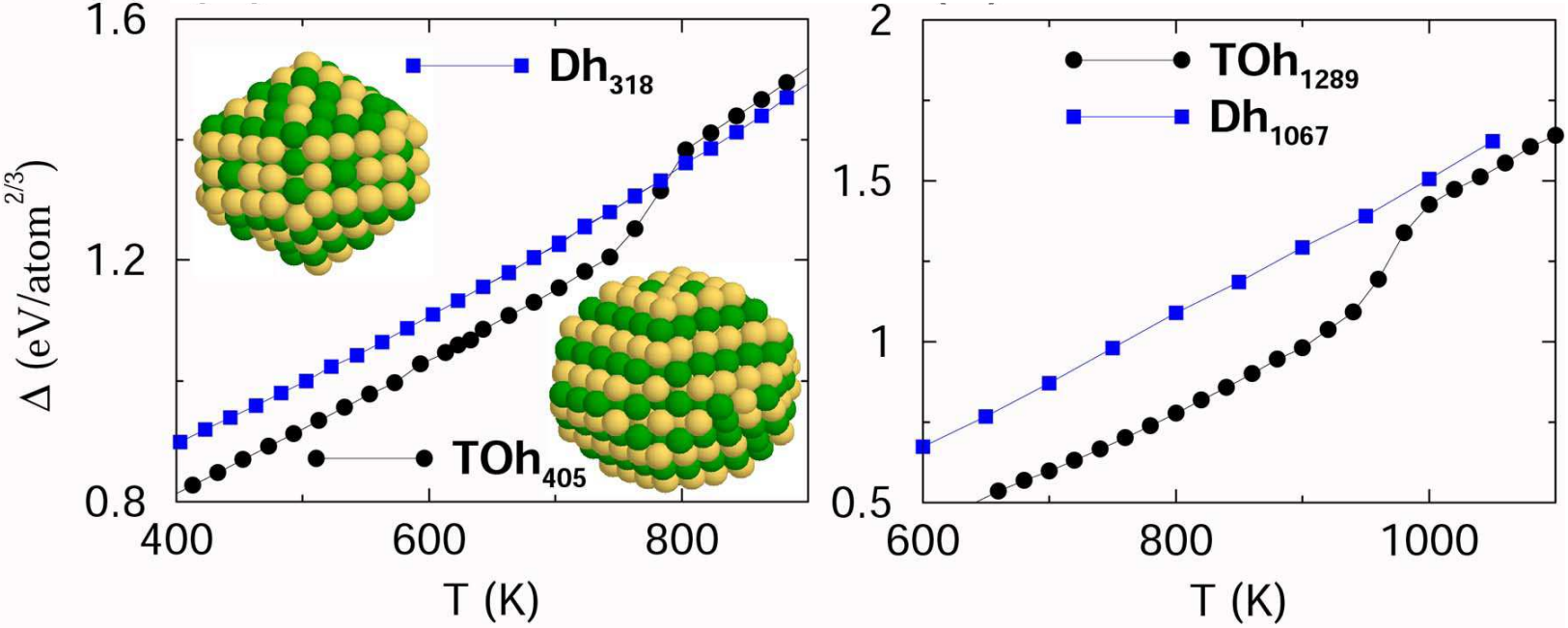
Monte Carlo + Dynamique Moléculaire Trempée de NPs CoPt

État fondamental à OK



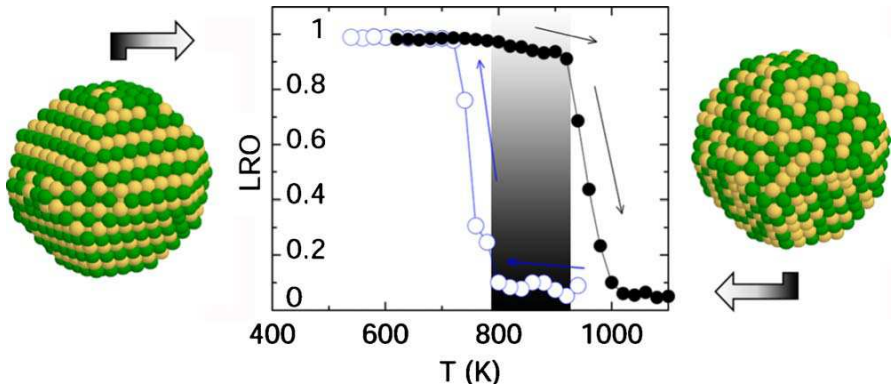
Simulations Monte Carlo de recuits de NPs CoPt

Compétition possible, à température finie, entre Dh et TOh chimiquement désordonnés



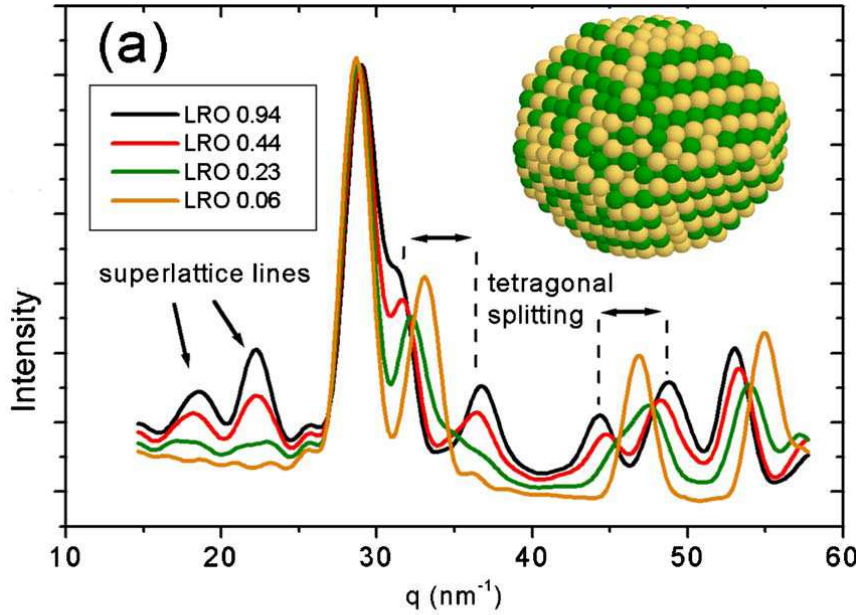
Bistabilité autour de 900K: transition du 1er ordre des nanoalliages

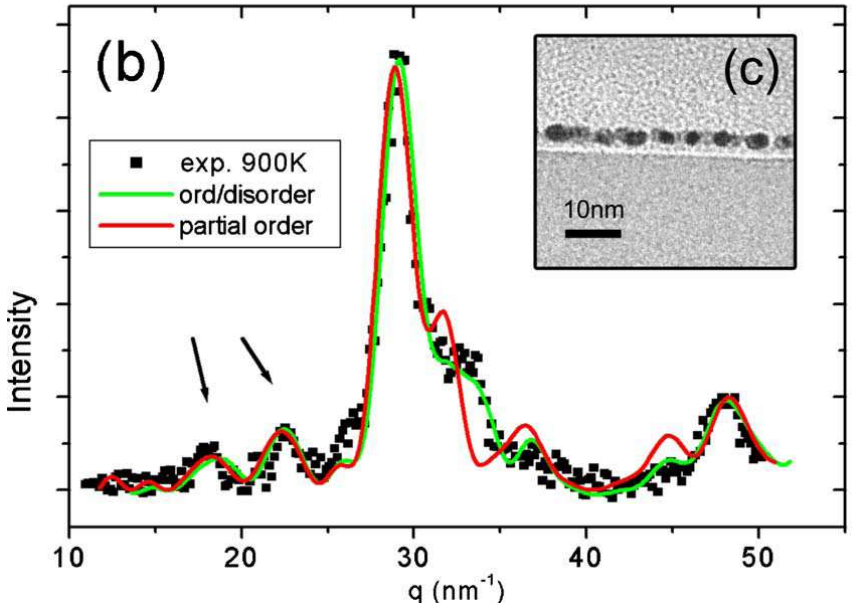
Simulations Monte Carlo



Spectres GIXD:

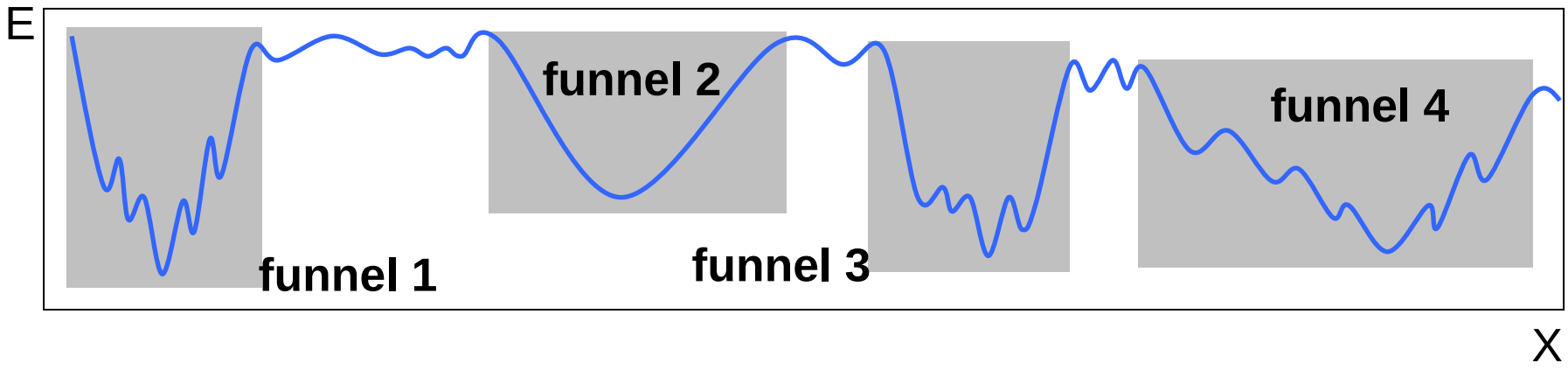
expérimental / calculés





Global optimisation – concept

Potential energy surface (PES) with local minima :



PES is often a multiple-funnel surface

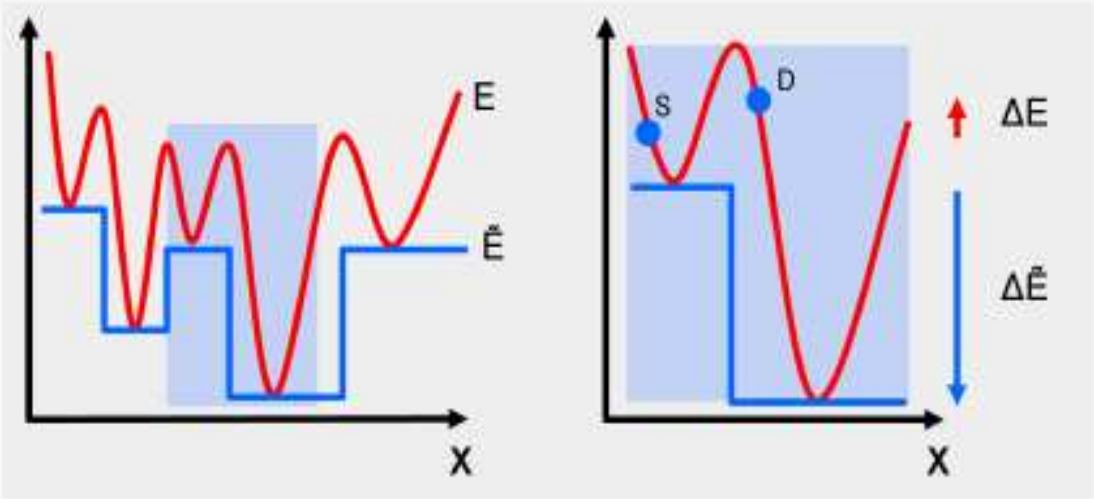
- high barriers among funnels
- low barriers among the minima laying in the same funnels
- one funnel, one structural motif

What a global optimisation algorithm is supposed to do?

- to locate all the different funnels
- to find the lowest lying minimum of each funnel

Global optimisation – method

Basin-hopping method is based on a PES transformation



$$\tilde{E} = min(E)$$

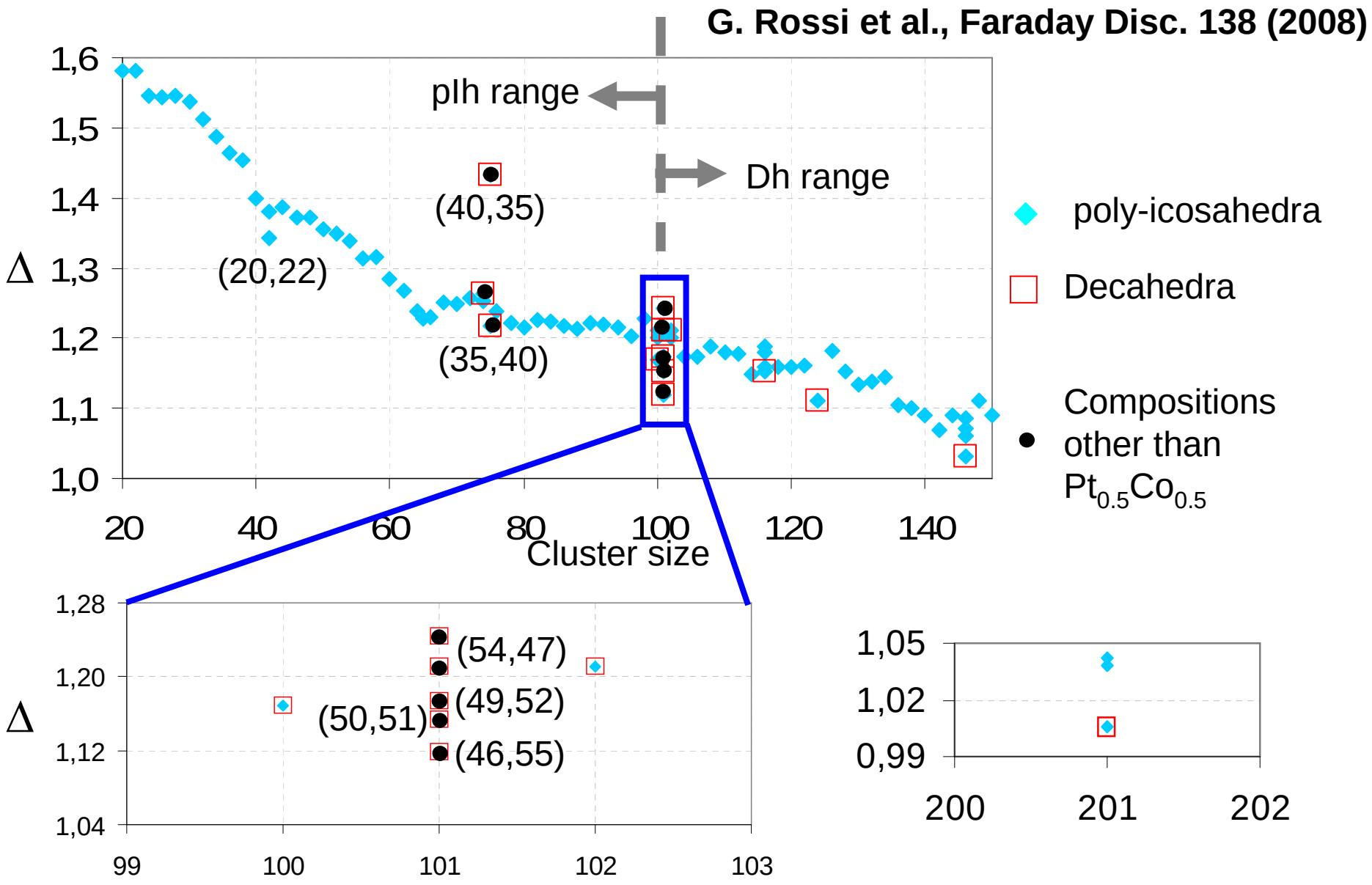
Each point in the configuration space is assigned the energy of its closest local minimum

• a set of six different moves (= shaking of cluster structure) is implemented to guide the search through the PES

• a Monte Carlo – Metropolis rule is applied to accept/reject the moves from the starting configuration, ***S***, to the destination configuration, ***D***

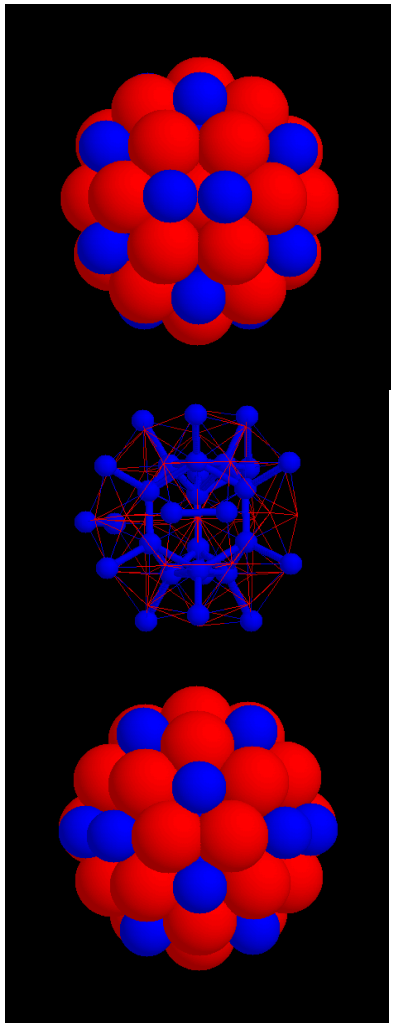
$$\begin{aligned} &\text{if} \quad \tilde{E}_D \leq \tilde{E}_S \quad \longrightarrow p = 1 \\ &\text{if} \quad \tilde{E}_D > \tilde{E}_S \quad \longrightarrow p = e^{-\left(\tilde{E}_D - \tilde{E}_S\right)/K_B T} \end{aligned}$$

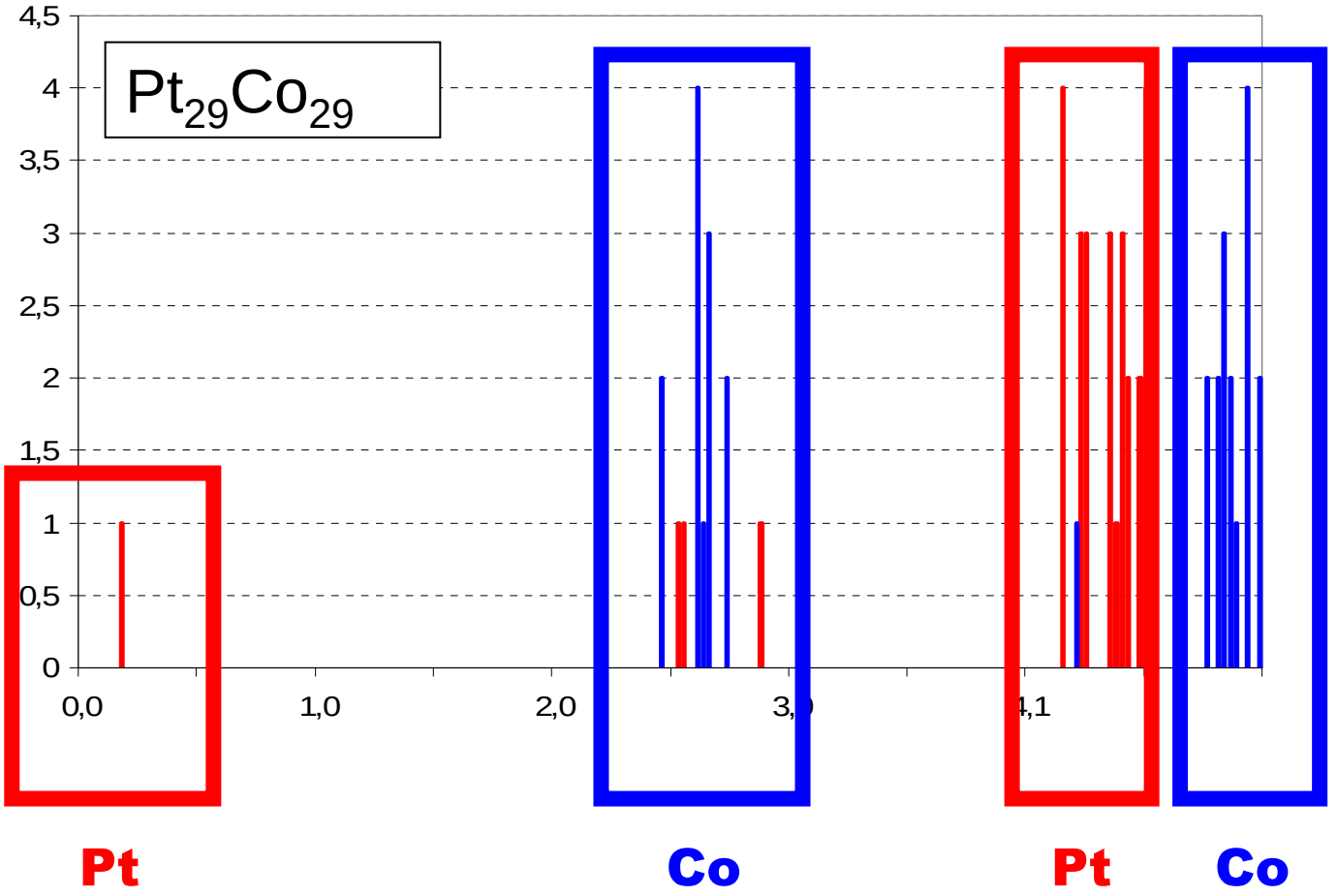
Optimized structures at OK



PIh with alternative Pt/Co shell tendency

N < 100 – Cobalt segregates at the “extrem” surface of the cluster

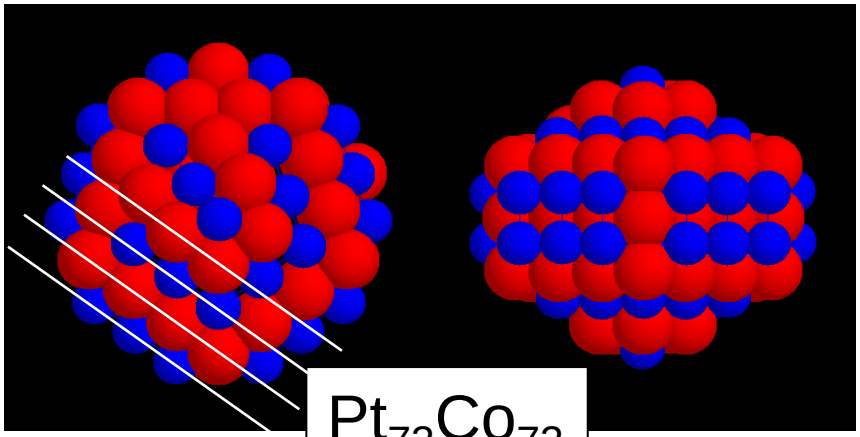




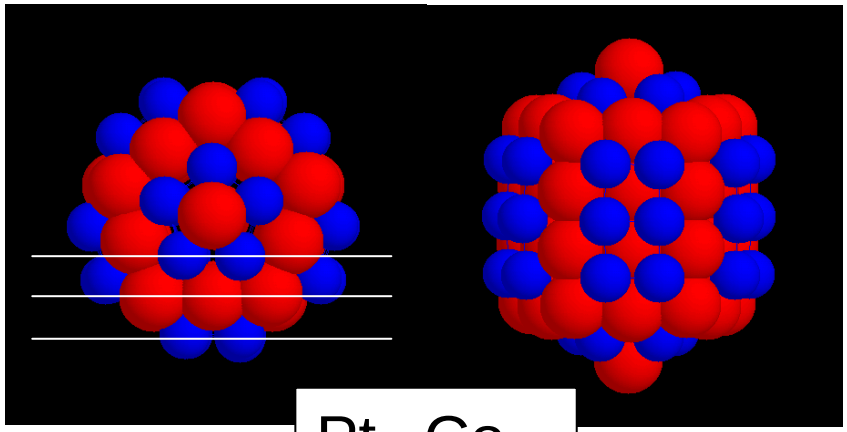
G. Rossi et al., Faraday Disc. 138 (2008)

Dh with $L1_0$ phase ordering tendency

N > 100 – Decahedral clusters



$Pt_{73}Co_{73}$



$Pt_{46}Co_{55}$

Decahedral arrangement allows to alternate Co and Pt planes

-along the (100)-like directions

-along the fivefold symmetry axis

Like in the $L1_0$ bulk alloy !

Co occupy the external (100) facets

plh → N ~ 100 → **Dh**

Conclusions:

- ❖ **caractérisation de la transition ordre-désordre dans les nanoalliages CoPt**
- ❖ **diagramme de phases à OK pour les nanoalliages CoPt**

Perspectives:

- ❖ **autres compositions,**

  … vers un diagramme de phases de nanoalliages

- ❖ **modèle d'interactions au 4ieme moment (cf. J. Los)**

Remerciements à :

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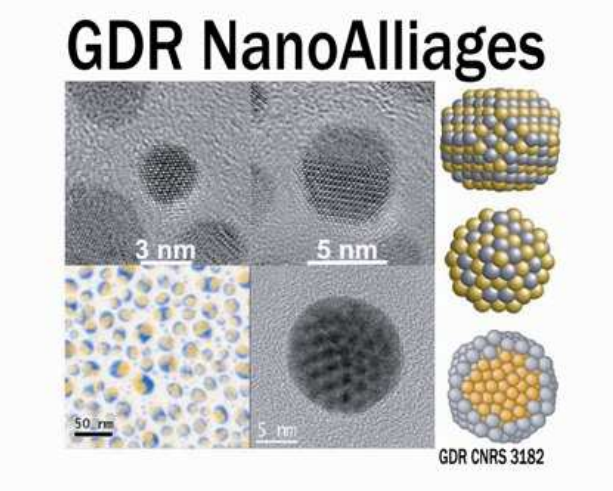
ANR-08-NANO-003-01 program PNANO: Sim_NanA



Et merci de votre attention !!!