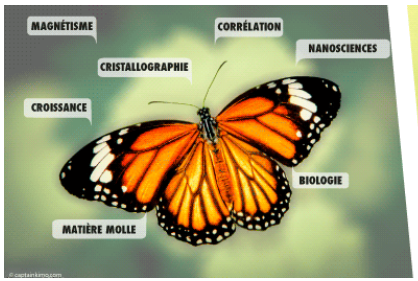
Nanostructures and symmetries, nano-objects

F. Tournus

“Magnetic Nanostructures” group

Institut Lumière Matière,
UMR 5306 CNRS & Univ. Lyon 1

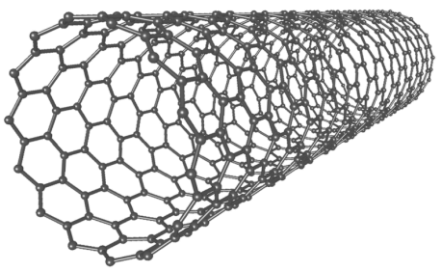


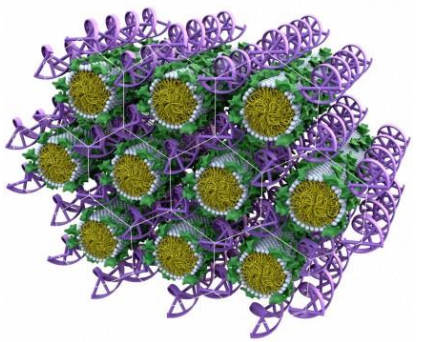
Nanostructures?

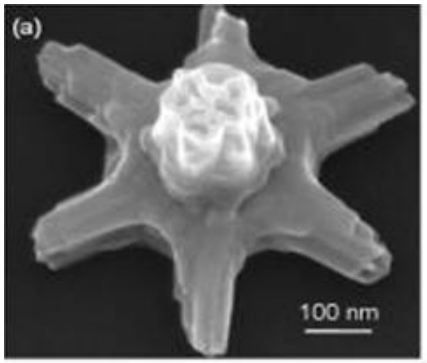
Great variety of nanostructures

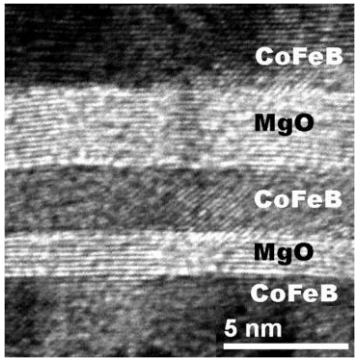
Nanometer dimension along
1, 2 or 3 directions

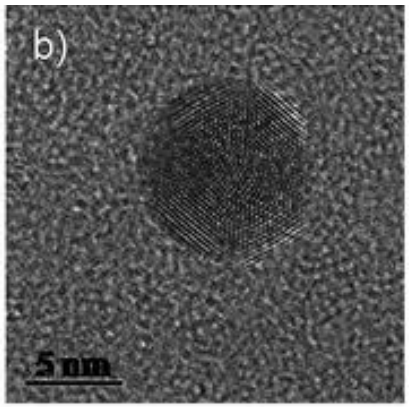
From molecular systems to “large” system
(hundreds of nanometers)

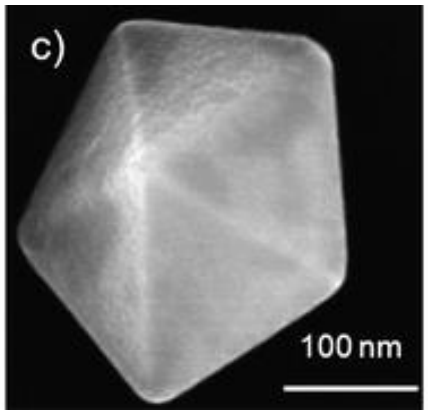


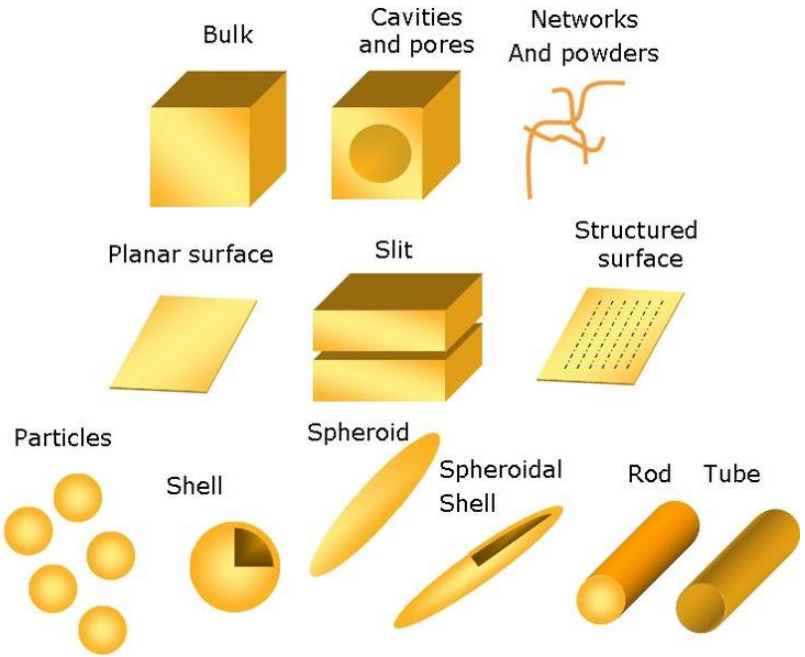






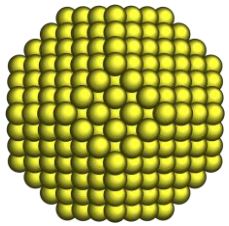






Nanostructures?

(My research = metallic nanoparticles)



2.7 nm diameter cluster (586 atoms):
45% of the atoms on the surface

Here, we will focus on “small” nano-objects, with a size below 10 nm

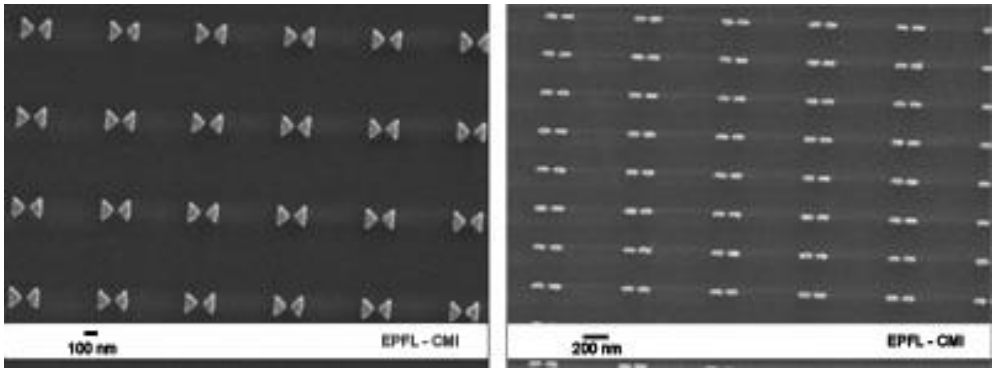
Major importance of the surface

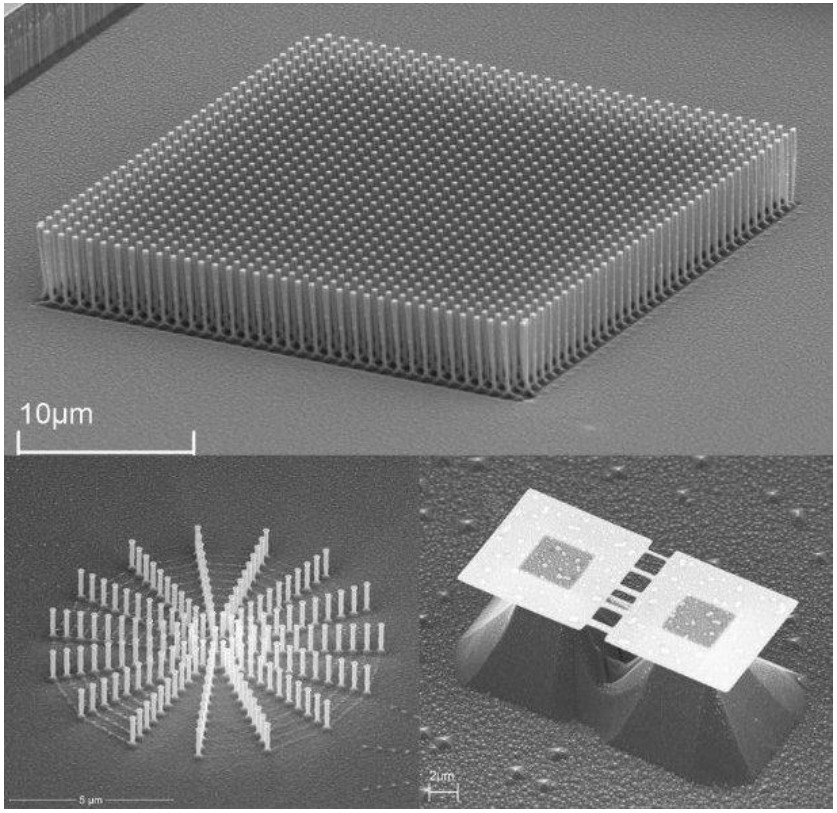
⟹ Properties can differ from the bulk ones

Restriction to bottom-up elaboration

Top-down elaboration (nano-fabrication)

⟹ Essentially like the bulk material, but systems with chosen shape and organization (symmetries)

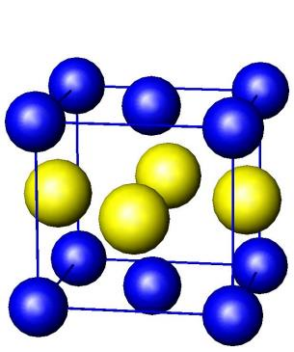


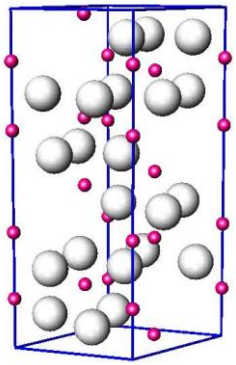


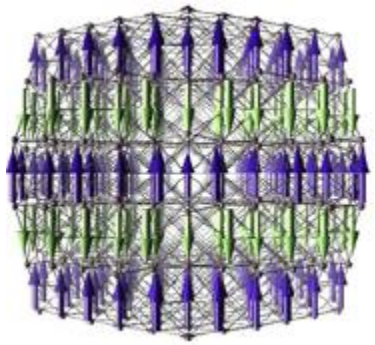
Symmetries?

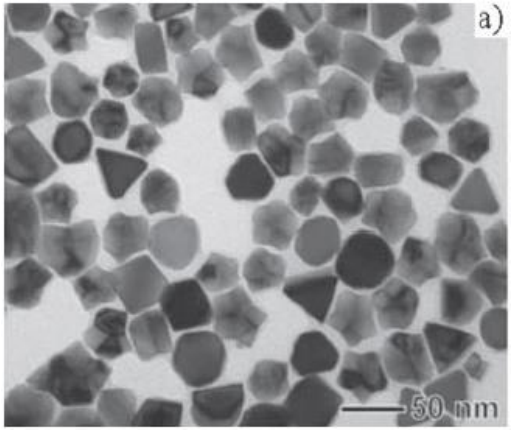
Several levels of symmetry for nano-objects

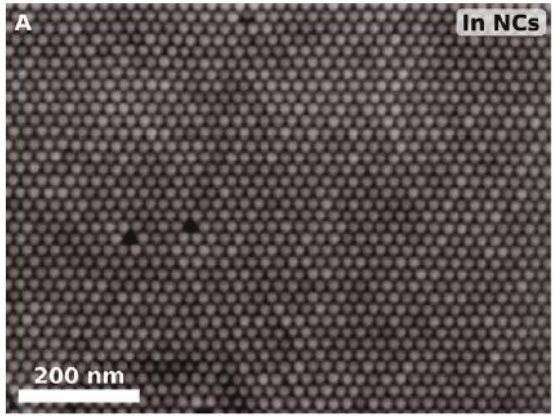
- ✓ Atomic structure, inside the objects (and chemical arrangement)
- ✓ Magnetic order
- ✓ Shape of the objects
- ✓ Organization of the objects (assembly)







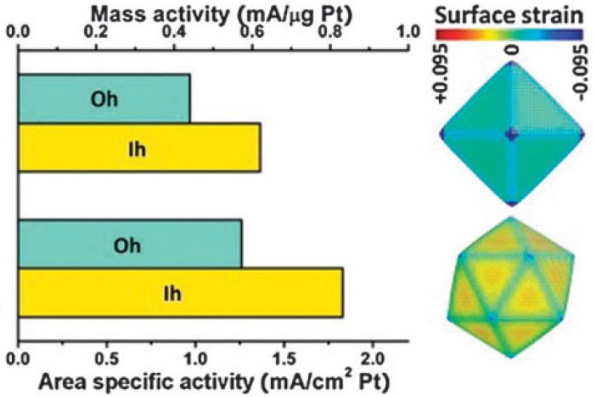




Why does symmetry matter?

To control the properties ⟹ The physical properties reflect the system symmetries

Strain induced enhancement of oxygen reduction for Pt_3Ni particles



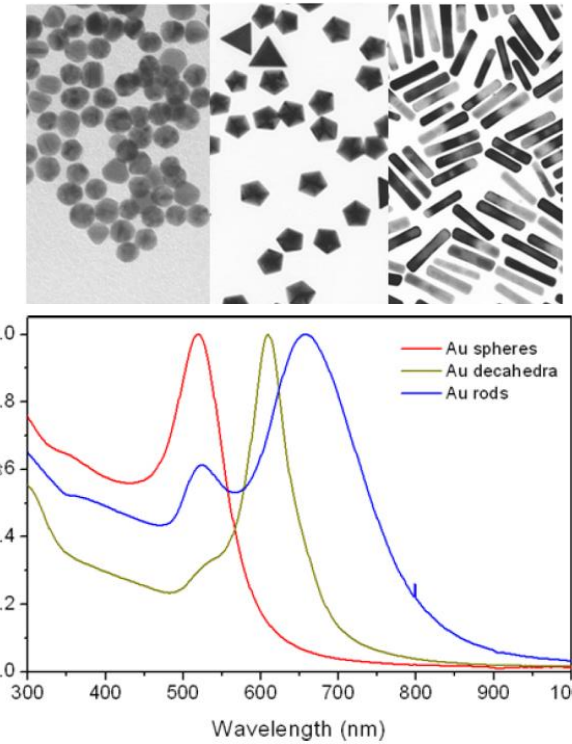
J. Wu et al., Chem. Soc. Rev. **41**, 8066 (2012)

We can expect specific features at nanoscale (for instance new phases…)

For applications in various domains:

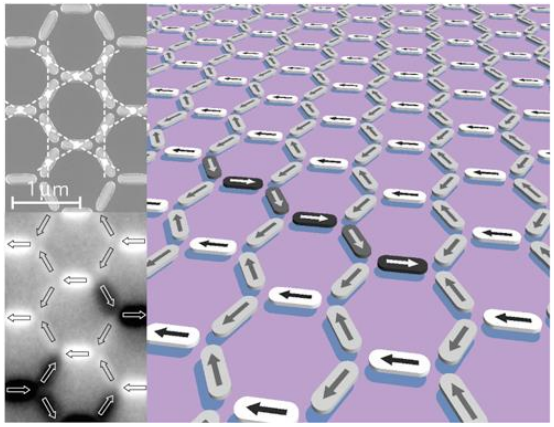
- Optics
- Electronics and magnetism
- Catalysis

Influence of the morphology on the absorption (plasmon) of gold particles



L. M. Liz-Marzan, SPIE Newsroom (doi:10.1117/2.1200707.0798)

Artificial spin ice, with a kagome lattice of nanomagnets

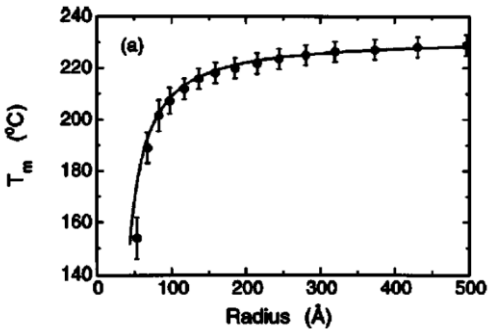


E. Mengotti et al., Nature Physics **7**, 68 (2011)

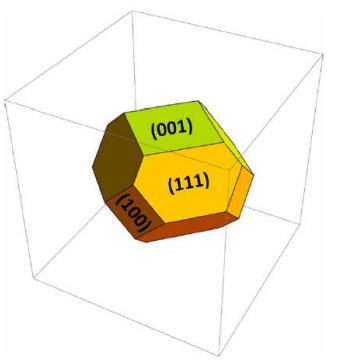
Model systems, to study interactions and collective behaviors…

⟹ Playground for physicists

Outline



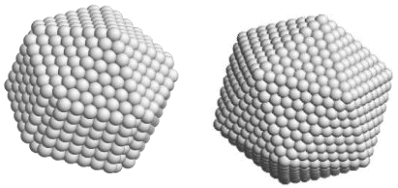
Some specificities of nanoparticles, related to symmetry

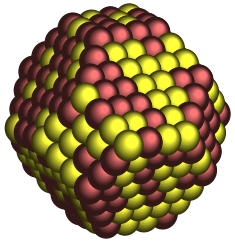


✓ Finite size and phase diagrams

✓ Shape of nanoparticles

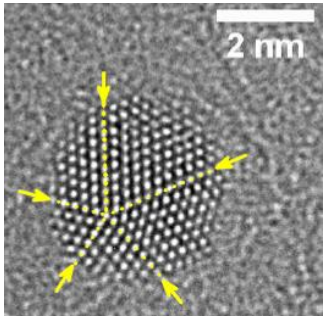
→ Faceting and non-crystalline structures (with 5-fold symmetries)



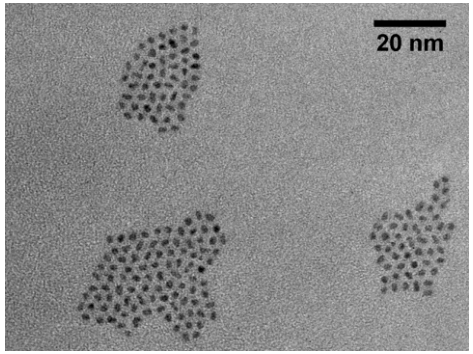


✓ Bi-metallic particles, chemical arrangement

→ Example of CoPt and FePt particles



✓ Non-ideal symmetries, relaxation



✓ Magnetic order: one short example

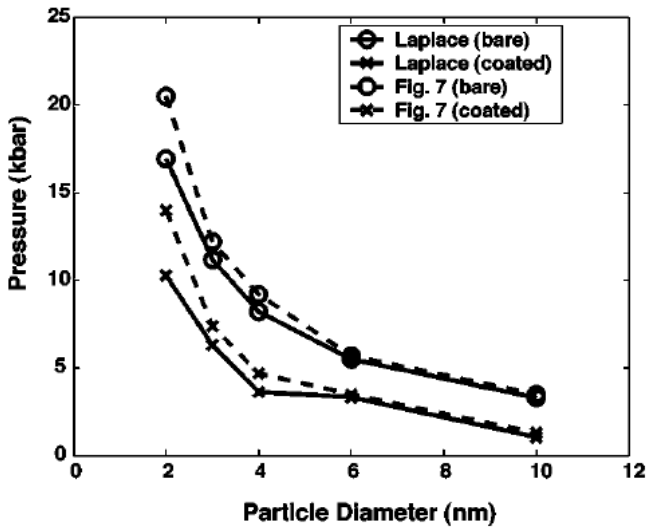
✓ Self-organization of nanoparticles

A lot of electron microscopy images…

Finite size and thermodynamics

Continuous description (not atomic)

Internal pressure for Si particles



T. Hawa et al., J. Chem. Phys. **121**, 9043 (2004)

Surface energy term

$$\mu = \mu_{sphere} = \mu_{\infty} + \mu_{\Sigma} = \mu_{\infty} + \frac{2\gamma V_m}{r}$$

Variation of the internal pressure with the size

Strain, modification of inter-atomic distances

Influence of the size on phase transitions (solid-liquid or solid-solid)

Phase diagram modification

The stable phase, and hence the symmetry, will depend on the size!

Decrease of melting temperature at small sizes

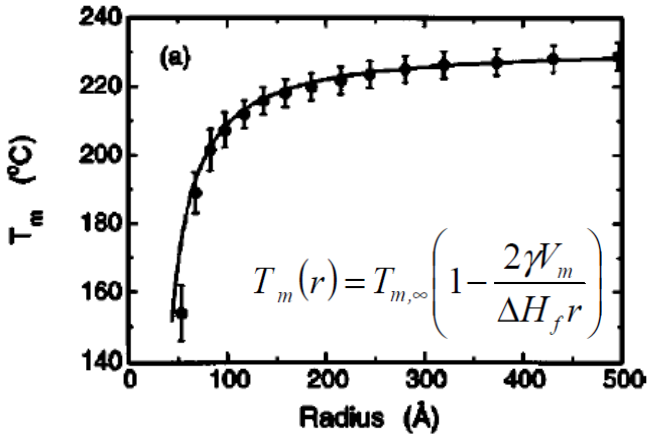


FIG. 26. Comparison of theoretical and experimental melting points of supported tin clusters: ●, experiment; solid line, the fitting by means of Eq. (42). From Lai *et al.*, 1996.

F. Baletto et al., Rev. Mod. Phys. **77**, 371 (2005)

Finite size and thermodynamics

Ex.: For a given pressure, the stable phase vary with the nanoparticle size

Modification of the transition pressure due to finite size

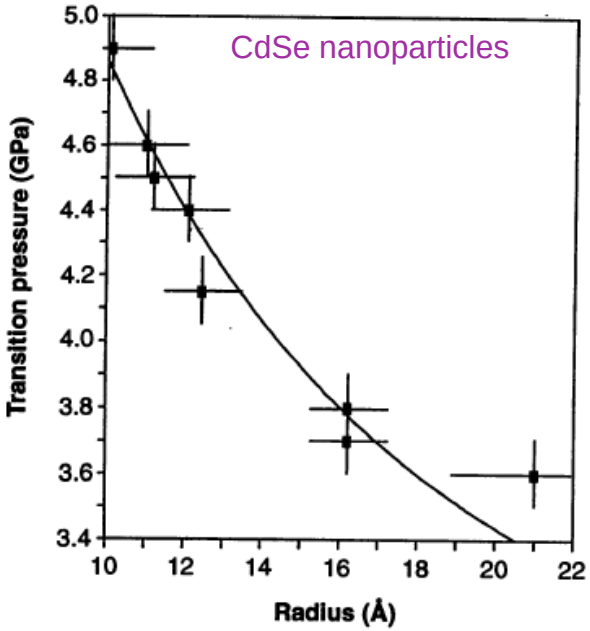
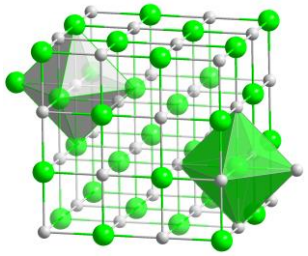
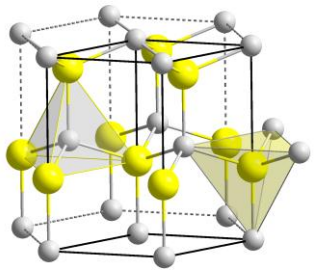


Fig. 4. Wurtzite–to–rock salt transformation pressure as a function of nanocrystal radius.

S. H. Tolbert et al., Science **265**, 373 (1994)



Rock salt (cubic)



Wurtzite (hexagonal)

Difference of surface energy
=> pressure shift of the transition

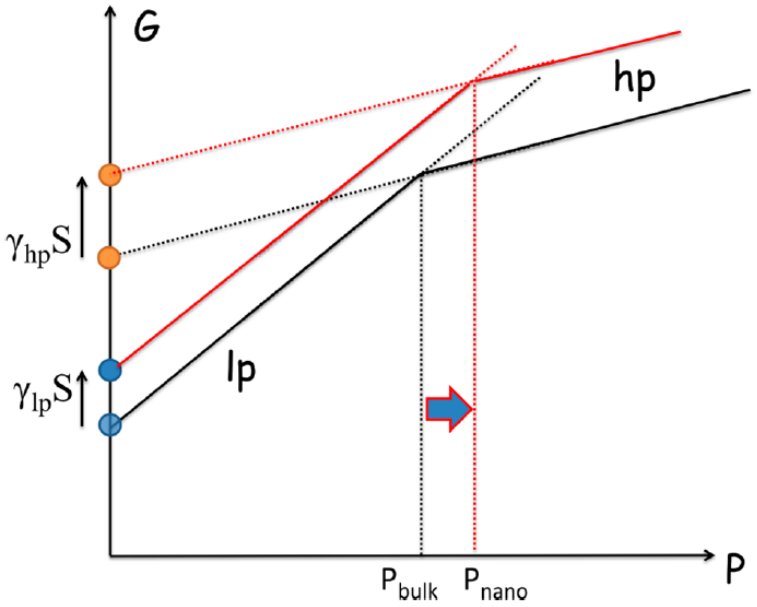


Figure 1. Effect of the surface energies on the phase stability. The pressure of the phase transition in bulk material is given by the cross over between the Gibbs energy function for each phase. In the case of nanoparticles, this Gibbs energy must be corrected by a surface-related term ($\gamma_i S$) for each phase i (lp for low-pressure and hp for high-pressure phases, respectively). Usually, the surface tension is higher in the high-pressure phase than in the low-pressure one. This leads to a predicted shift of the transition pressure to higher value.

D. Machon et al., Nano Lett. **14**, 269 (2014)

Finite size and crystal truncation

Atomic description of the surface

Crystal = periodic arrangement of the atoms

Translation symmetry, only if the crystal is infinite

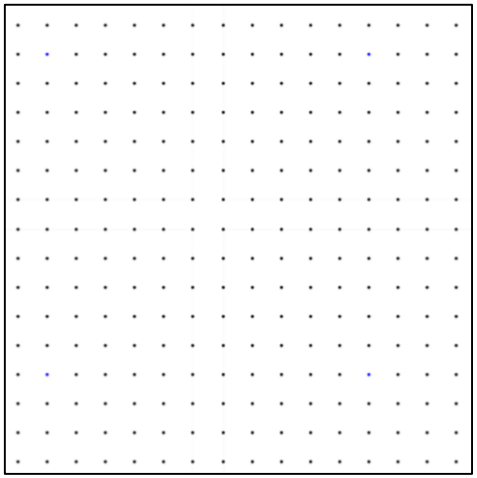
⟹ Finite size breaks the translation symmetry!

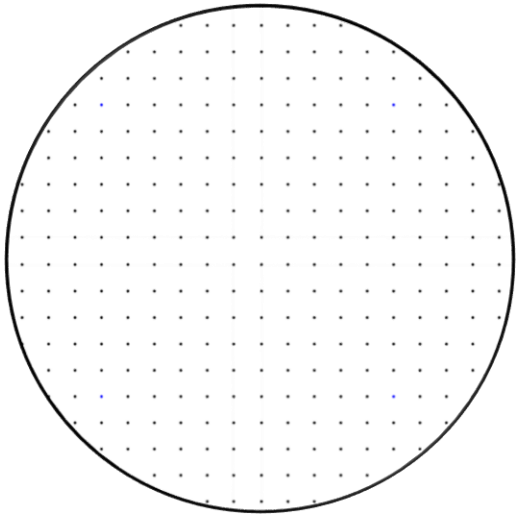
How can we cut a crystal?

Creating a surface has an energy cost…

Finite size and crystal truncation

For a continuous description (as a liquid), the spherical shape minimizes the surface energy

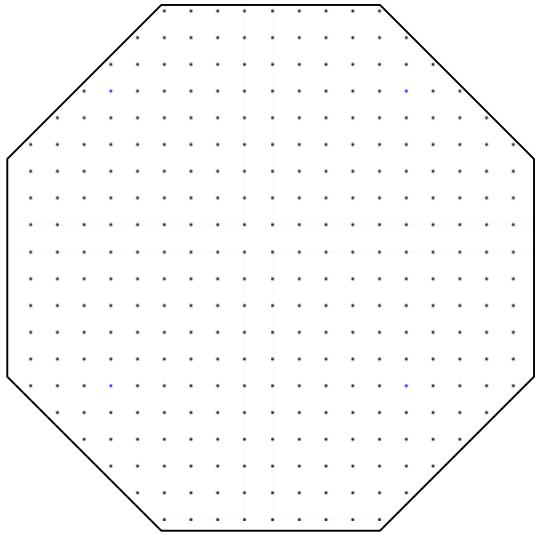


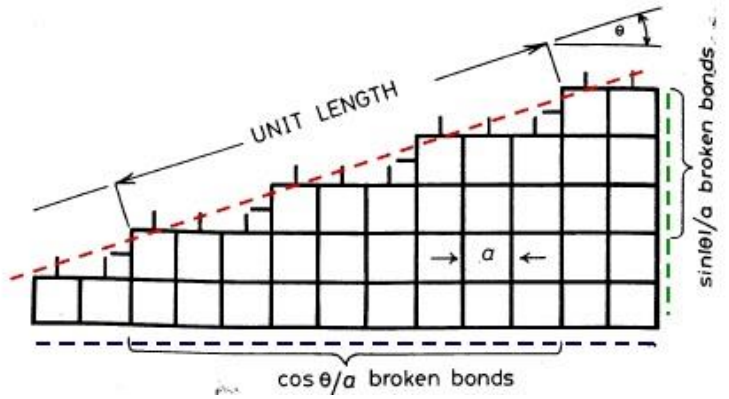


Simple model: evaluation of the surface energy with the number of broken bonds

$$E_{surf} = (\cos\theta+\sin\theta)\varepsilon_b/(2a^2)$$

Best choice for a crystal?

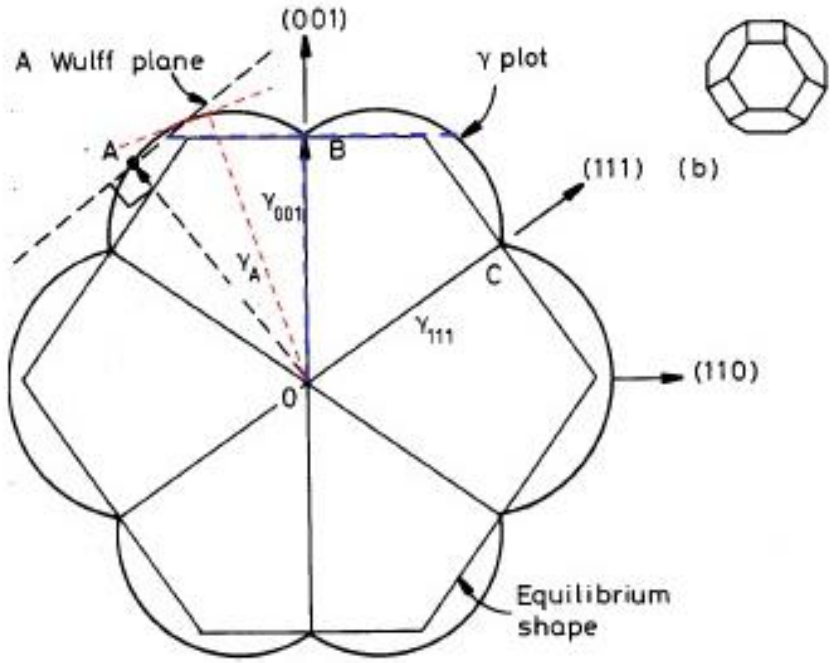


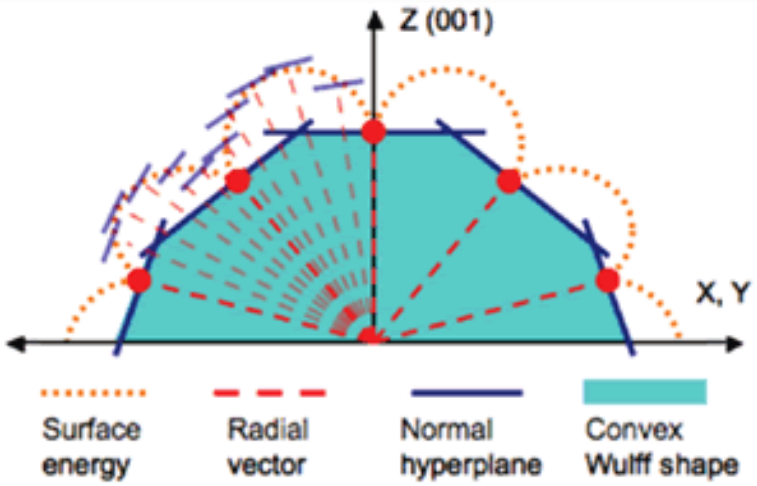


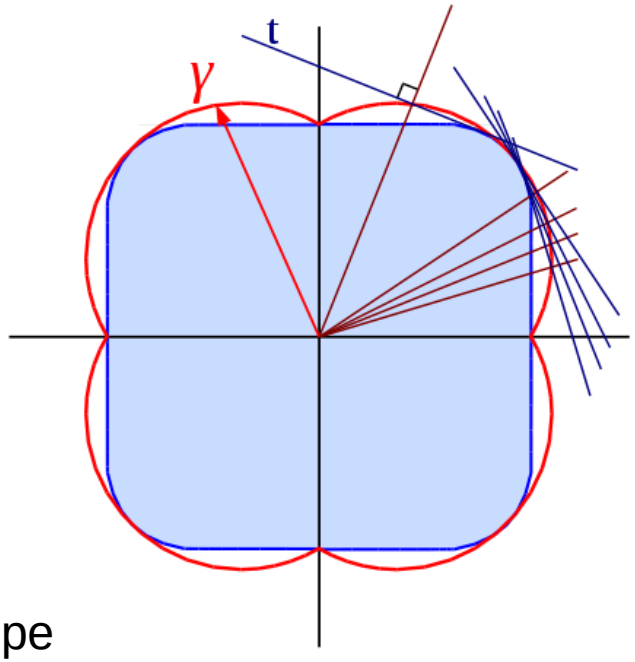
→ The energy of a facet depends on its angle with respect to the crystallographic directions

Crystal truncation: equilibrium shape

Wulff construction







h_j = distance from the center of the particle to a facet j

γ_j = surface energy of a facet j

Minimizing the energy (with a fixed volume) corresponds to: h_j proportional to γ_j.

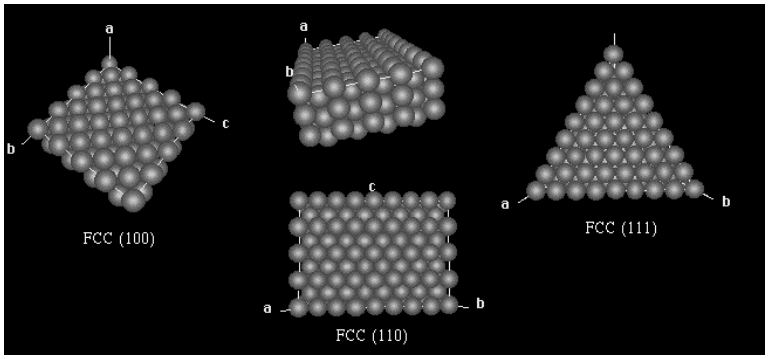
Construction using a polar plot of the surface energy $\gamma(\theta)$

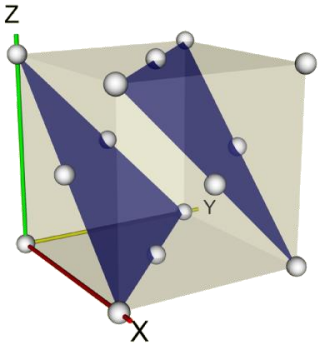
⟹ The equilibrium shape is given by the convex envelope

Equilibrium shape for a fcc crystal

The surface ratio between (100) and (111) facets depends on $\gamma_{111}/\gamma_{100}$

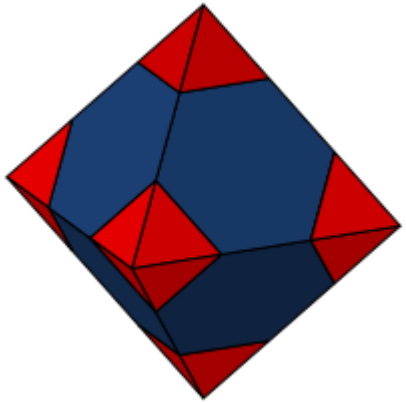
(111) surface is more compact
⟹ Lowest surface tension





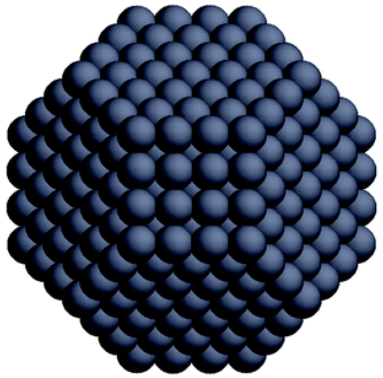
(111) planes

With only (111) facets: octahedron, where the surface/volume ratio is too large (too far from a spherical shape) ⟹ A compromise has to be found (Wulff construction)



Octahedron

Truncated-octahedron



Truncated-octahedron

(Non-favorable)

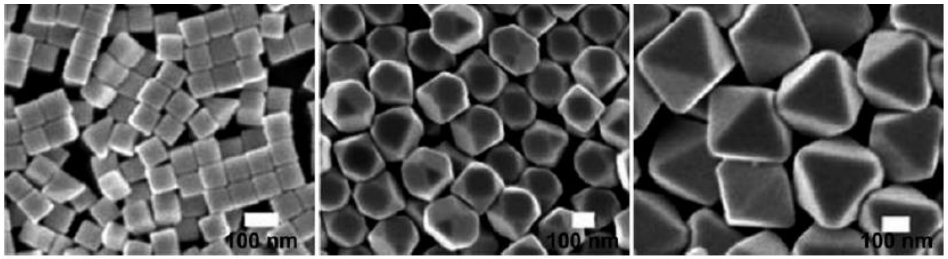
cuboctahedron

Beyond the Wulff model

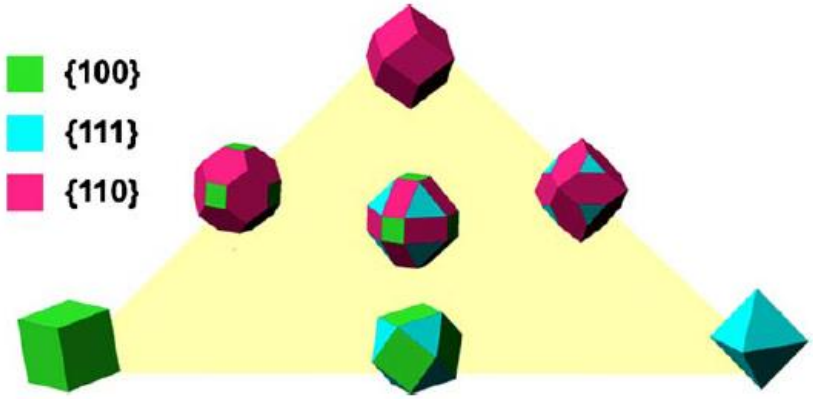
Wulff construction gives the equilibrium shape

⟶ Thermodynamic equilibrium not granted

The morphology of a crystal can influenced by kinetic factors



Ag nanoparticles



W. Niu et al., Nano Today **6**, 265 (2011)

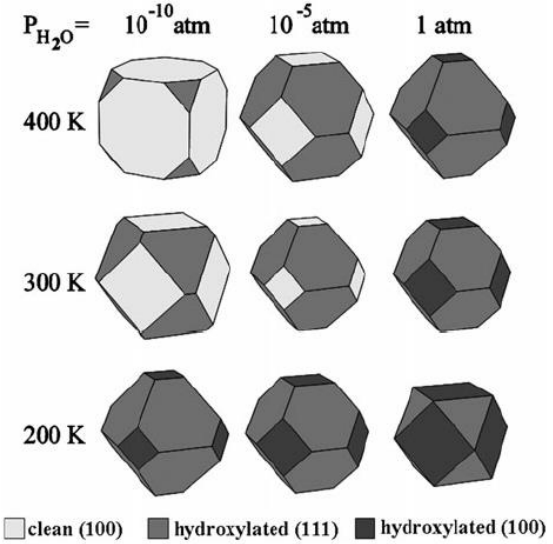


Fig. 4 Wulff equilibrium shapes of MgO crystallites as a function of the temperature and pressure. Light grey: clean MgO(100) facets, medium grey: hydroxylated MgO(111) facets, dark grey: hydroxylated MgO(100) facets. Only the three low-index surfaces were taken into account in the Wulff construction.

P. Geysermans et al., Phys. Chem. Chem. Phys. **11**, 2228 (2009)

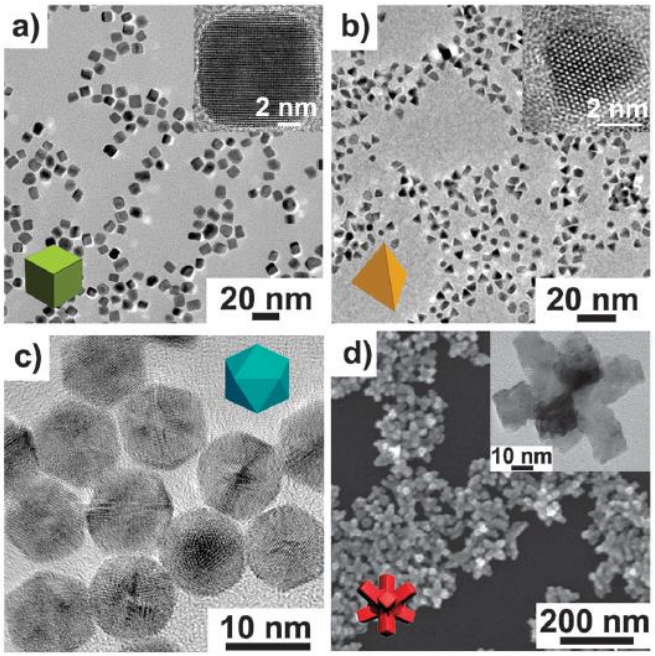
A control is also possible through the nanoparticles environment

⟶ For a given material, a variety of shapes can in fact be obtained

Beyond the Wulff model

With chemical syntheses, there are a lot of possibilities to control the nanoparticle symmetry

Pt-Pd particles



Cube	Continuous growth	Capping agents strongly bind on {100} facets
Tetrahedron / Octahedron	Continuous growth	Capping agents strongly bind on {111} facets
Icosahedron	Continuous growth	Slow reduction rate; capping agents strongly bind on {111} facets
Rod	Continuous growth	Surfactant-formed templates
Multi-pod	Continuous growth	Facet-specific oxidative etching

J. Gu et al., Chem. Soc. Rev. **41**, 8050 (2012)

The Wulff construction is somehow limited

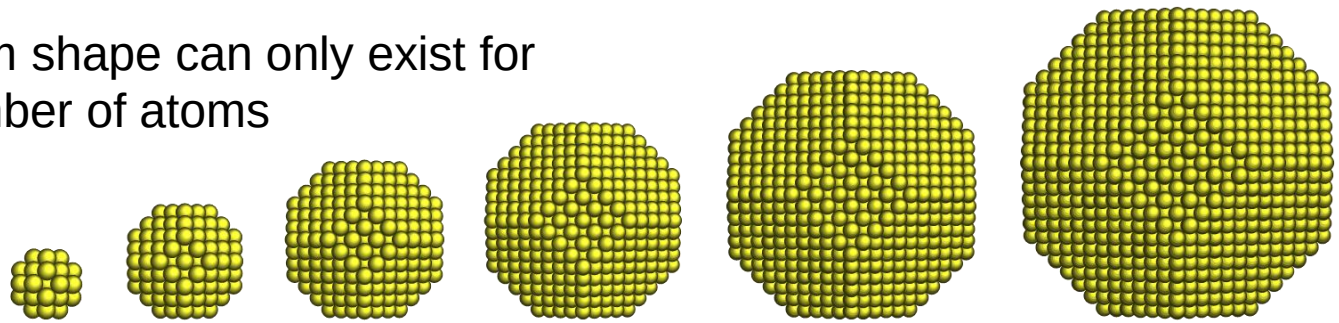
- ✓ The surface energies must be known (they can vary with the size…)
- ✓ There is also a contribution from the edges: $E_{\mathrm{Tot}} = E_{\mathrm{Bulk}} + E_{\mathrm{Surf}} + E_{\mathrm{Edge}}$
- ✓ The bulk crystal structure is assumed (while we can have relaxations or non-crystalline structures)

Non-perfect crystal shapes

The nanoparticle morphology reflects the crystal symmetry **but…**

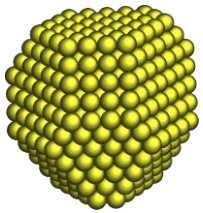
✓ The Wulff equilibrium shape can only exist for some particular number of atoms

Regular truncated octahedra (Oh symmetry)



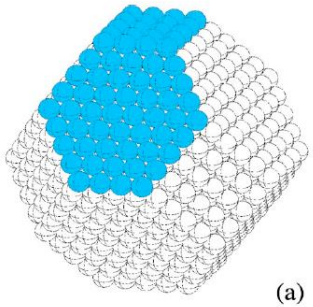
Number of atoms:	38	201	586	1289	2406	4033

For other numbers of atoms, there will be additional facets or incomplete facets

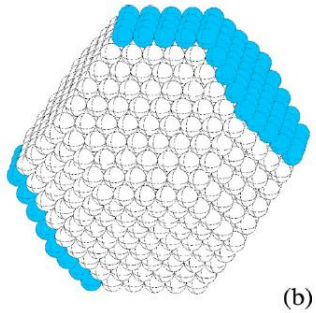


→ The symmetry is then lowered

Ex.: Major influence of additional facets on the magnetic anisotropy of Co clusters



K_{ani} = 160 kJ/m^3



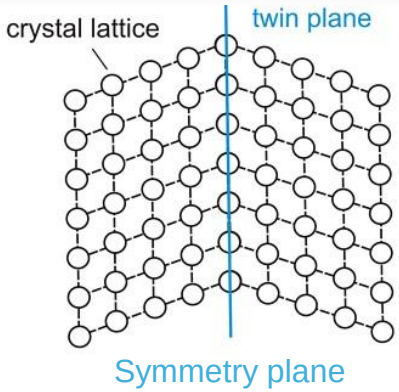
K_{ani} = 300 kJ/m^3

K_{ani} = 0 kJ/m^3 for a regular cluster (Oh)

M. Jamet et al., Phys. Rev. B **69**, 024401 (2004)

Non-crystalline structures

Multiply-twinned particles

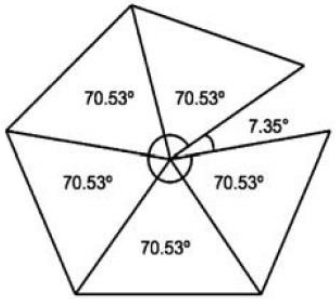


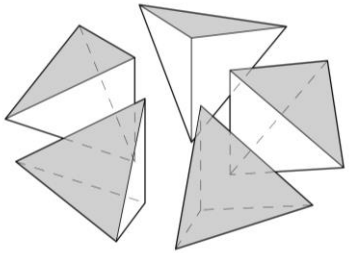
➡ Particles are constructed by joining tetrahedra of fcc crystals, forming twins

The idea is to have only (111) facets, which is favorable for the surface energy

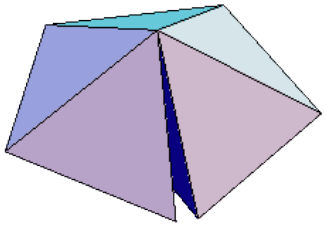
A **decahedron** (pentagonal dipyramid) or an **icosahedron** can be formed

➡ 5-fold symmetry

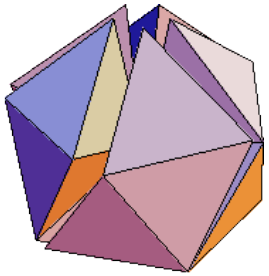




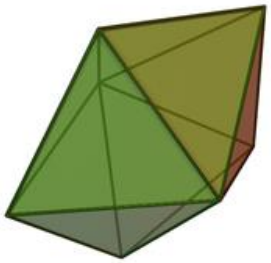
(a)



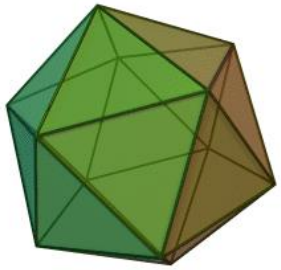
(b)



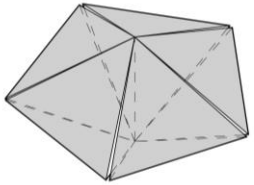
Dh



Ih



When joining the crystal pieces, there remains a small gap



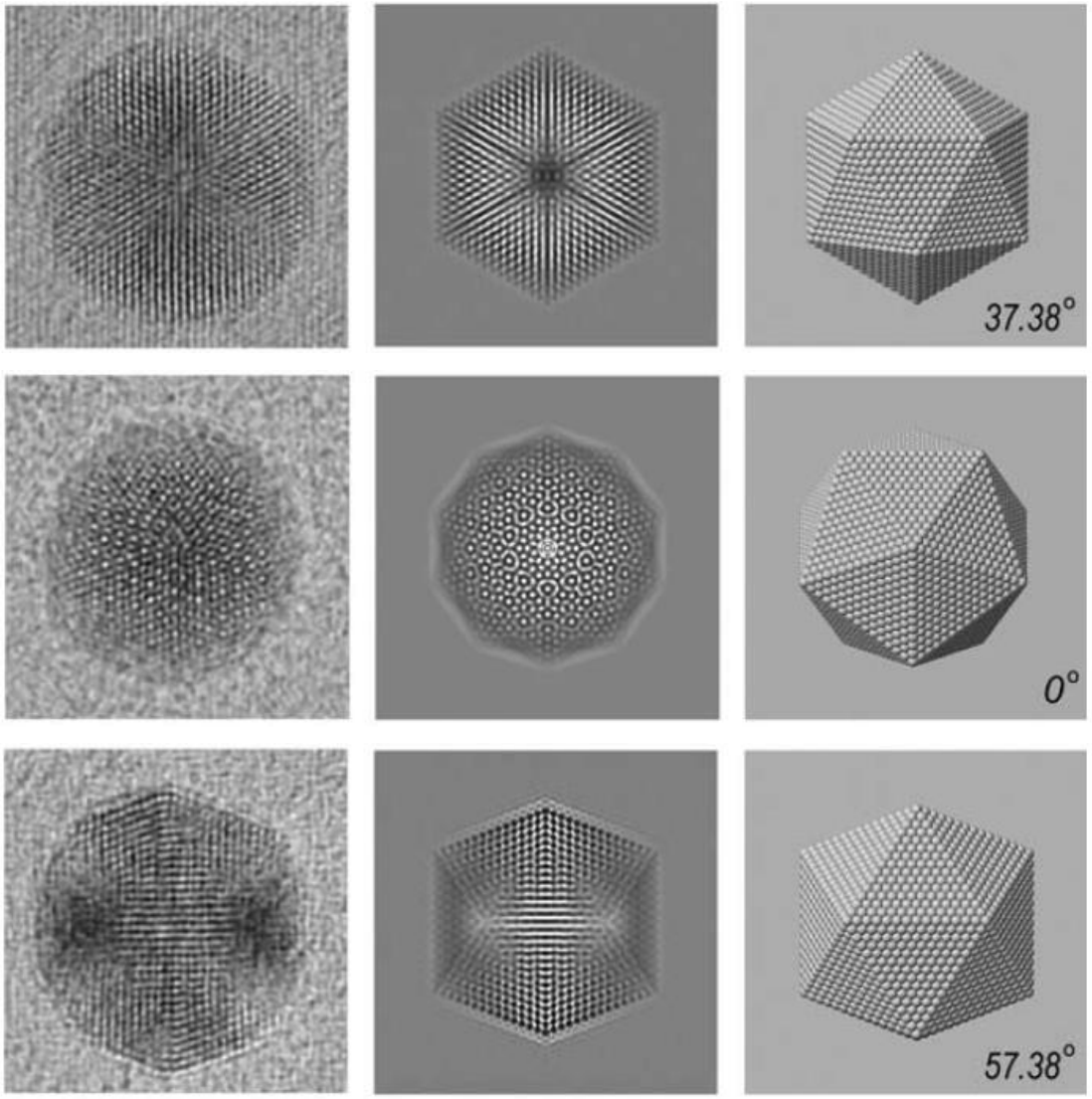
➡ Deformation to “close” the structure: they are non-crystalline

Low surface energy, but large strain energy

Observation of Icosahedra

Identification of icosahedral particles with HRTEM

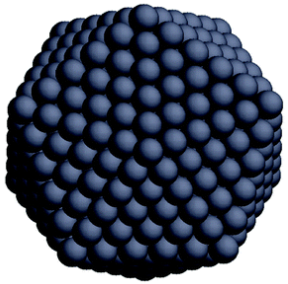
Au particles

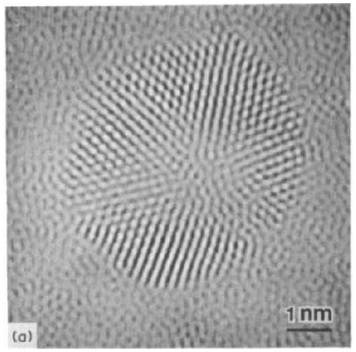


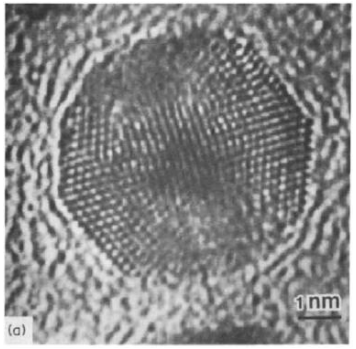
3-fold

5-fold

2-fold





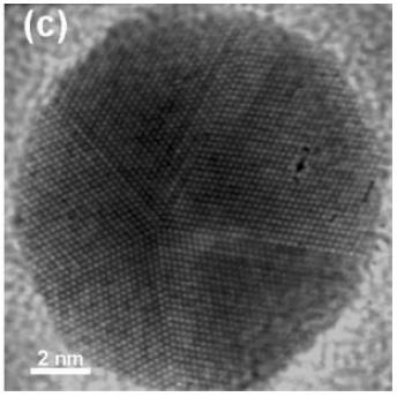


K. Koga et al., Surf. Sci. **529**, 23 (2003)

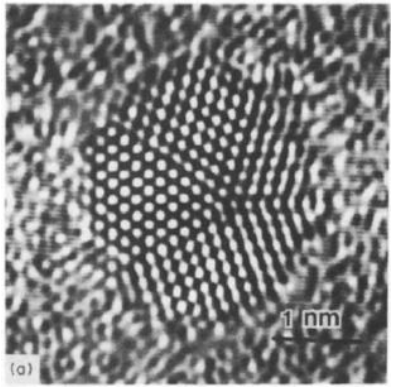
S. Tehuacanero et al., Acta metall. mater. **40**, 1663 (1992)

Observation of decahedra

Decahedra are also easily observed with HRTEM



J. L. Elechiguerra et al., J. Mater. Chem. **16**, 3906 (2006)



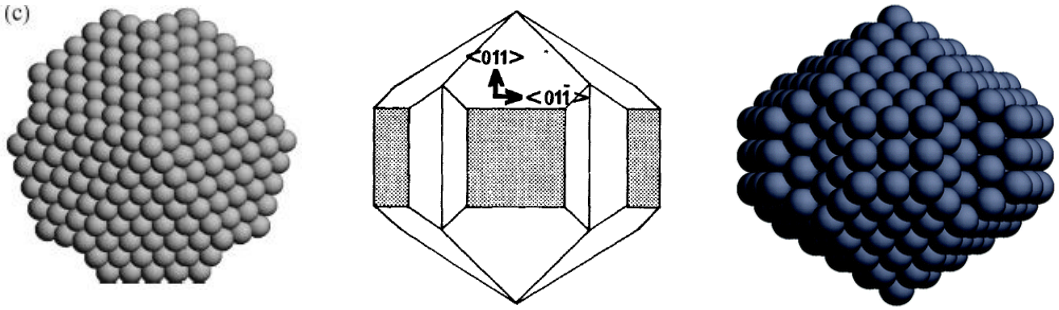
S. Tehuacanero et al., Acta metall. mater. **40**, 1663 (1992)

Decahedral symmetry, but with (100) facets

⟹ Less flattened shape

Additional faceting to reduce the energy

⟹ Marks decahedron

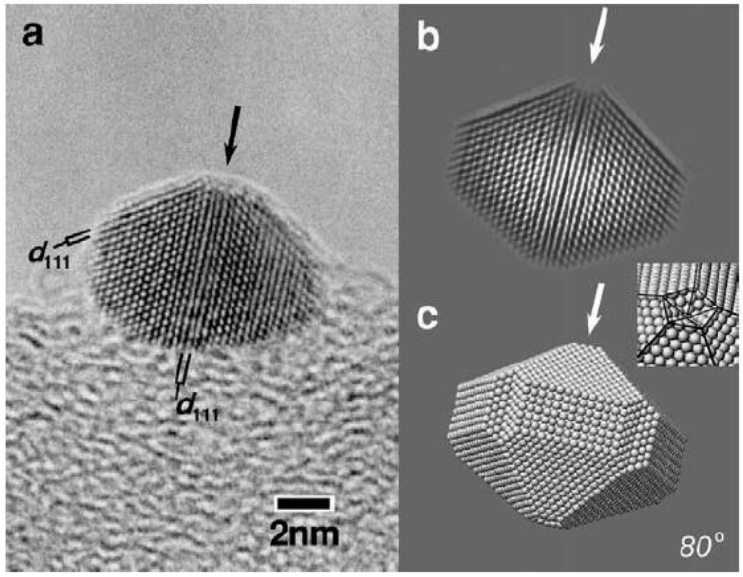


L. D. Marks, Phil. Mag. A **49**, 81 (1984)

From a fcc crystal to a 5-fold symmetry structure

⟹ **Specificity of nano-sizes**

(5-fold symmetry is incompatible with translation symmetry)

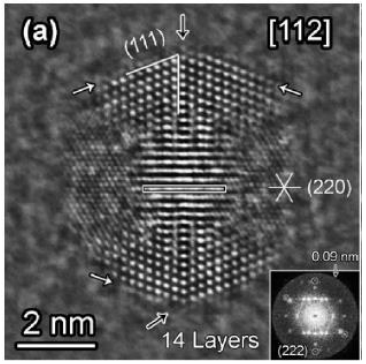


K. Koga et al., Surf. Sci. **529**, 23 (2003)

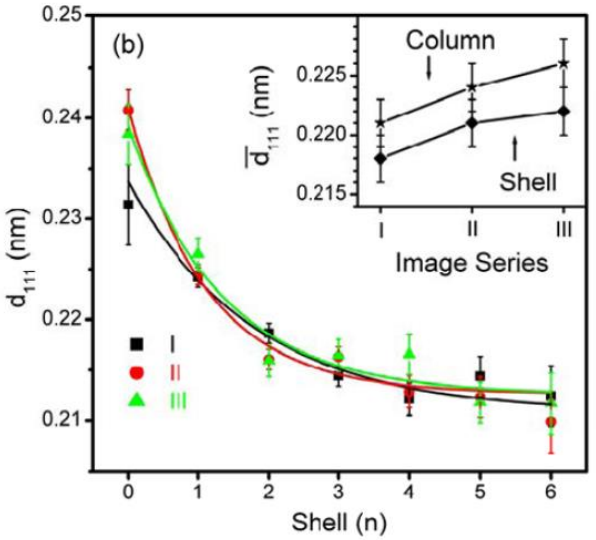
Icosahedra and decahedra: strain

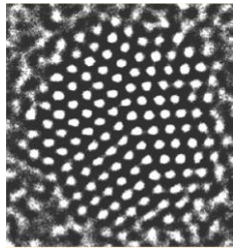
R. M. Wang et al., Phys. Rev. Lett. **100**, 017205 (2008)

Strain determination, from HRTEM images

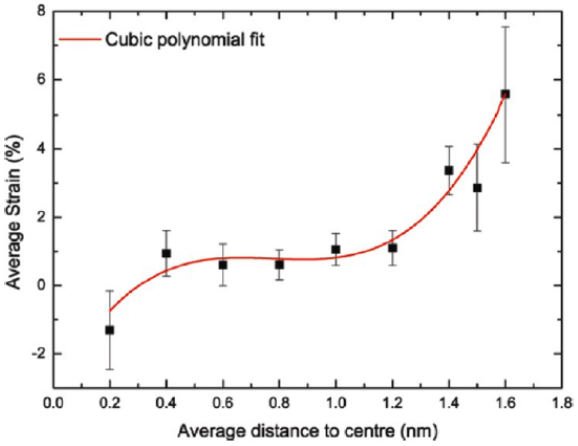


FePt cluster (Ih)



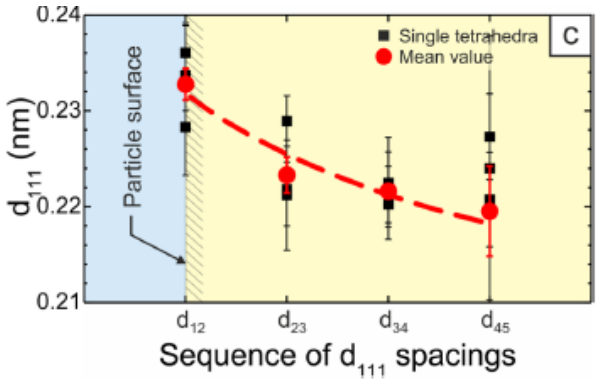


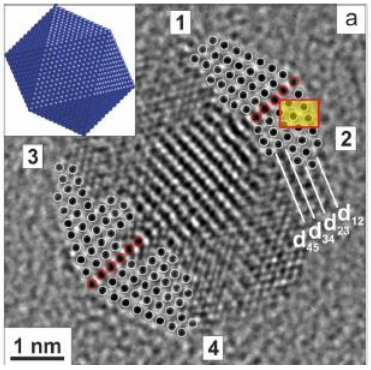
Au cluster (Dh)



M. J. Walsh et al., Nano Lett. **12**, 2027 (2012)

FePt cluster (Ih)





This strain can have important repercussion on the properties…

D. Pohl et al., Nano Lett. **14**, 1776 (2014)

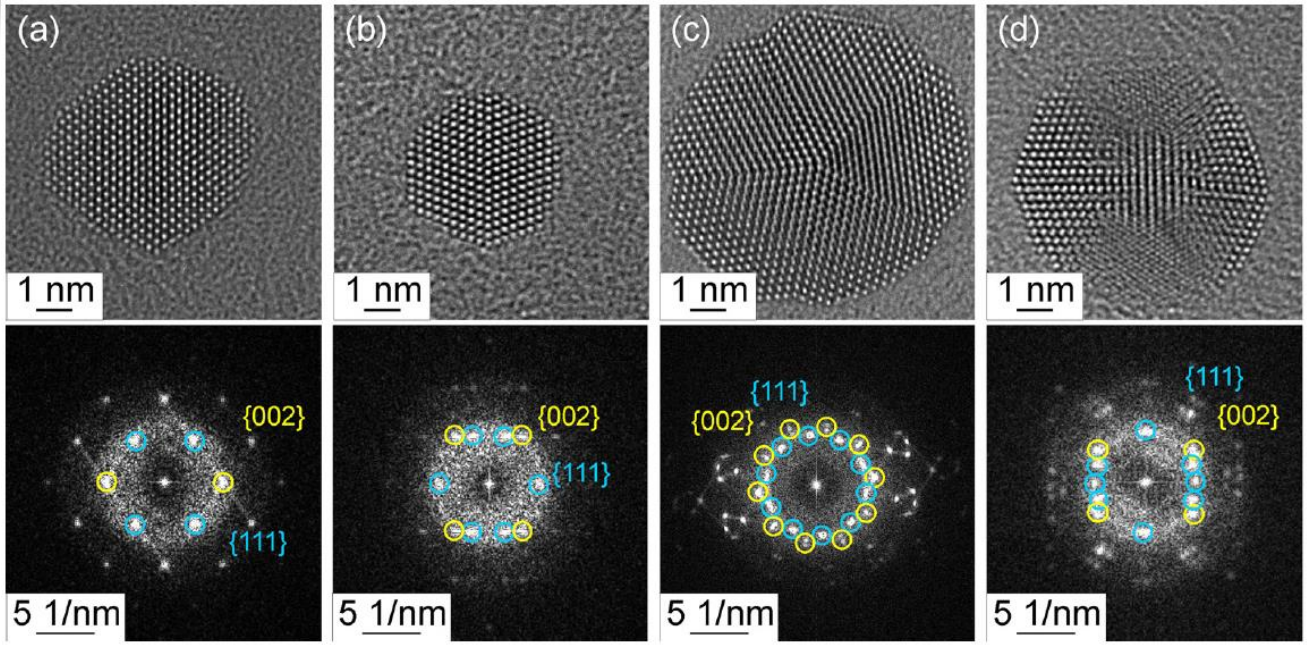
Coexistence of structures

Au clusters

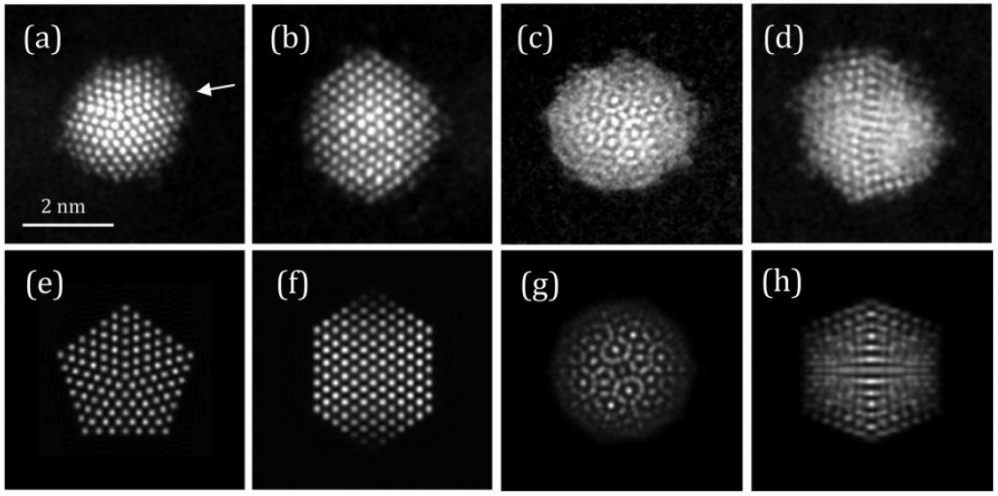
D. Pohl et al., Appl. Phys. Lett. **101**, 263105 (2012)

Various geometries can be observed for small particles

Coexistence of structures with different symmetries



Au clusters



The most favorable structure depends on the size

→ Compromise between surface and strain energy

Ih: low surface energy, large strain
Oh: no strain but larger surface energy
Dh: intermediate case

Z. W. Wang et al., Phys. Rev. Lett. **108**, 245502 (2012)

Most favorable structures

F. Baletto et al., Rev. Mod. Phys. **77**, 371 (2005)

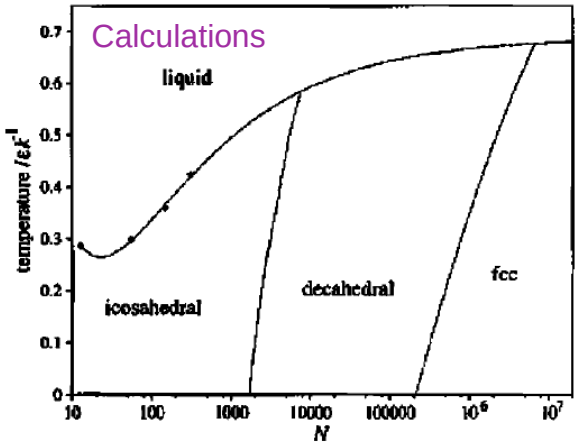
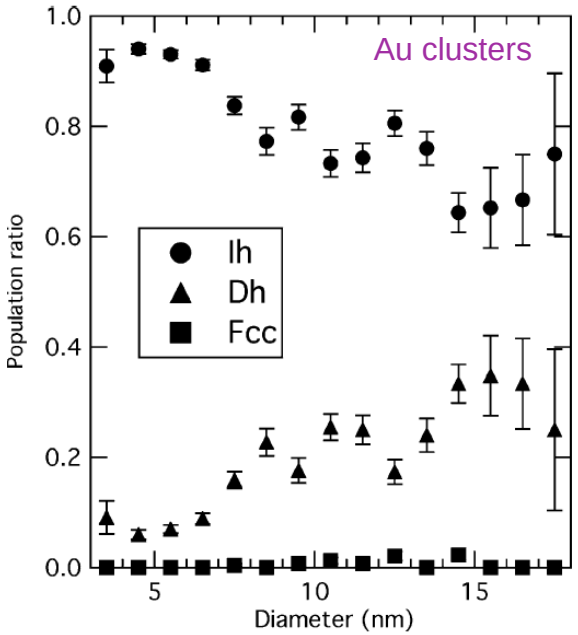


FIG. 20. Structural phase diagram in the N,T plane for Lennard-Jones clusters in the harmonic superposition approximation. From Doye and Calvo, 2002.

Transition with size:

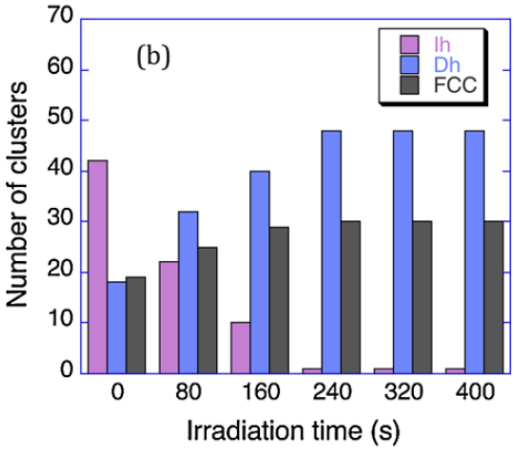
From icosahedra to truncated octahedra (fcc crystals)

K. Koga et al., Surf. Sci. **529**, 23 (2003)



Coexistence of different structures and evolution under electron beam or with the environment…

Au clusters



Z. W. Wang et al., Phys. Rev. Lett. **108**, 245502 (2012)

D. Pohl et al., Appl. Phys. Lett. **101**, 263105 (2012)

Au clusters

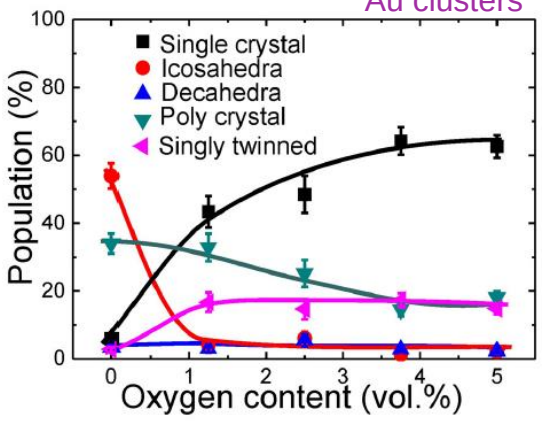
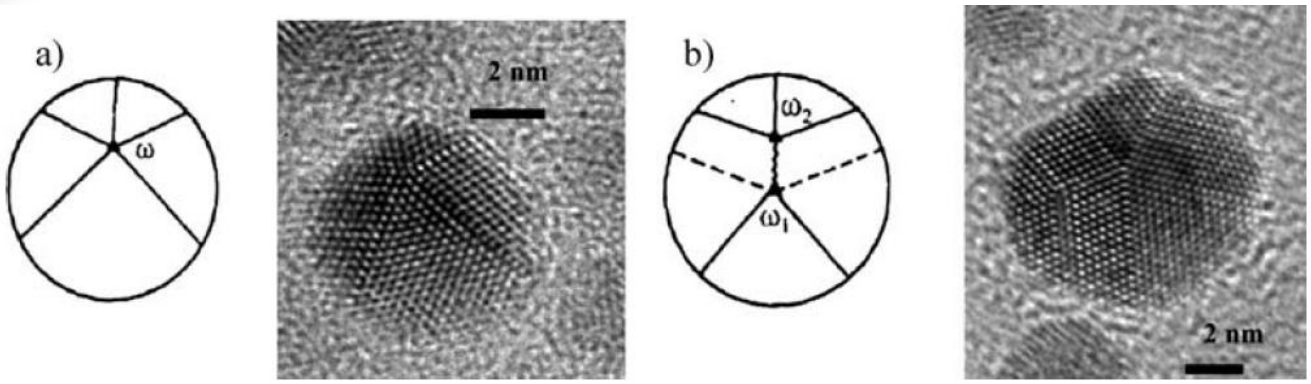


FIG. 3. Au nanoparticle morphology distribution as a function of the oxygen content in the sputtering gas. The solid lines are guide to the eyes.

Large decahedral particles

Decahedral particles incompatible with a crystalline order

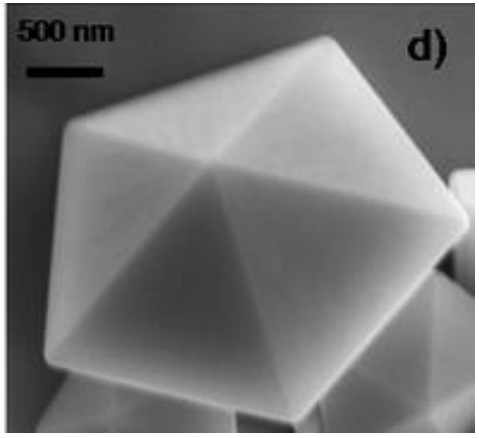


A. Mayoral et al., Nanoscale **2**, 335 (2010)

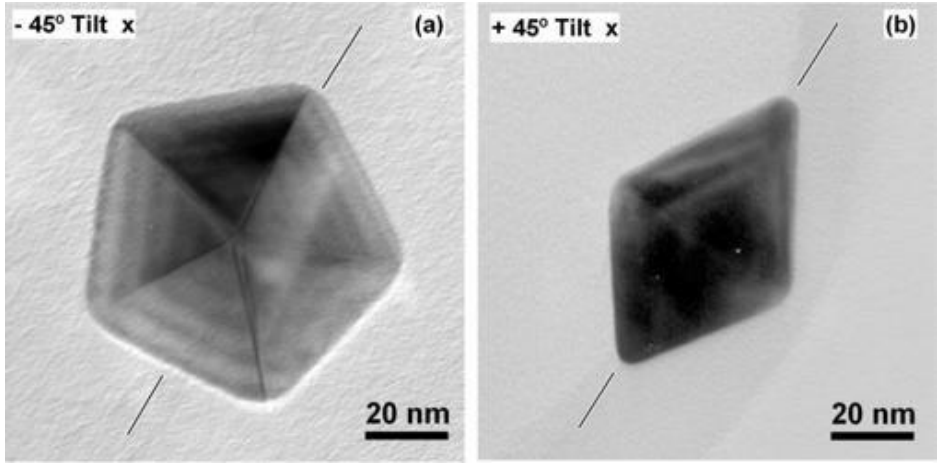
Mechanisms of stress relief

➡ Enable 5-fold symmetry at larger particle sizes

Also, importance of kinetics of growth…



A. Mayoral et al., Nanoscale **2**, 335 (2010)

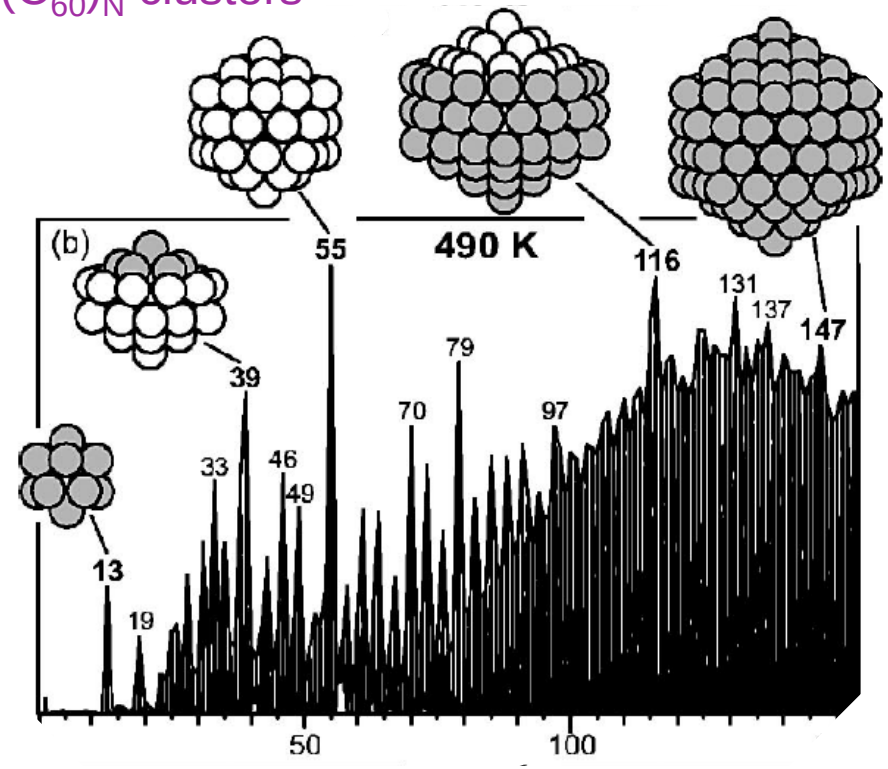


Magic numbers

Higher relative stability for structures with complete facets

⟹ Visible in mass abundance spectra: “Magic numbers”

$(C_{60})_N$ clusters



F. Baletto et al., Rev. Mod. Phys. **77**, 371 (2005)

The magic numbers sequence gives indications about the symmetry (decahedra, icosahedra, truncated-octahedral)

Ex. with $(C_{60})_N$ clusters, where N = 13, 55, 147 correspond to perfect icosahedra

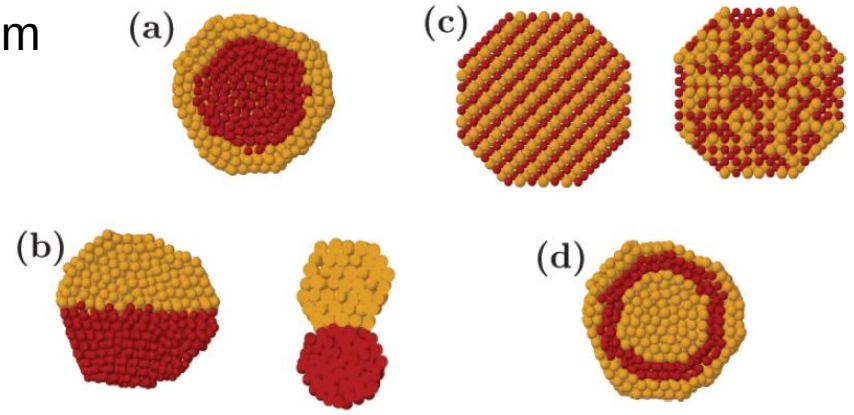
This is only valid for non-directional bonding (VdW, metallic)

Bi-metallic nanoparticles

R. Ferrando et al., Chem. Rev. **108**, 845 (2008)

Two types of atoms: additional degree of freedom

⟹ **Tailoring of the properties**

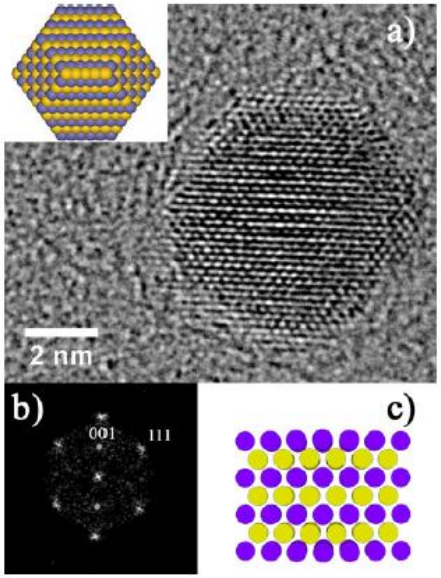


Symmetry of the lattice
+ chemical occupation

Specific features for nanoalloys
(different structures)

A variety of chemical arrangements are possible, with exotic chemical orders

Ex.: Detection of $L1_0$ chemical order in FeAu alloy nanoparticles, while Fe and Au are immiscible in the bulk…



A. Hillion, PhD thesis

D. Bochicchio et al., Phys. Chem. Chem. Phys. **16**, 26478 (2014)

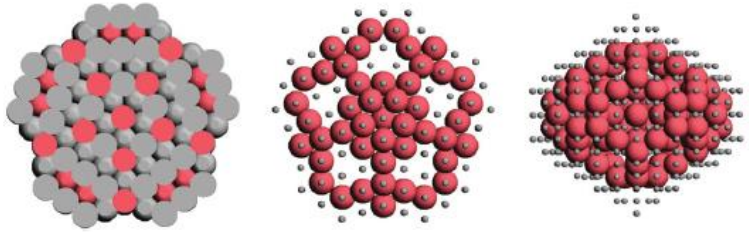
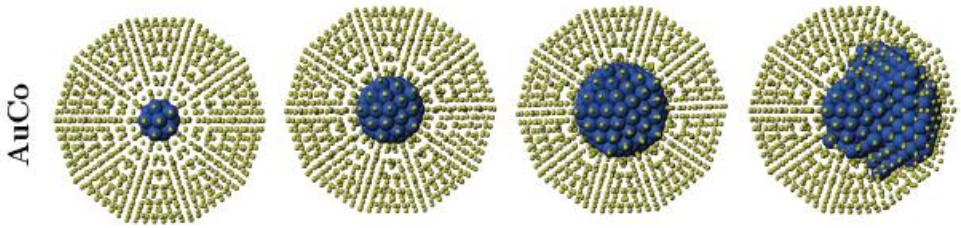


Fig. 3 Decahedral structure with highly symmetric chemical ordering found for composition $Ag_{341}Pd_{93}$. Symbols as in Fig. 2.

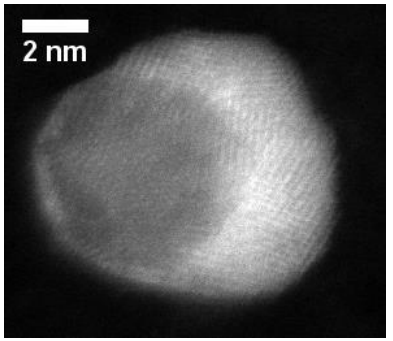
Bi-metallic nanoparticles

The most favorable structure results from a compromise, and depends on chemical mixing energies, surface energies, strain energy…

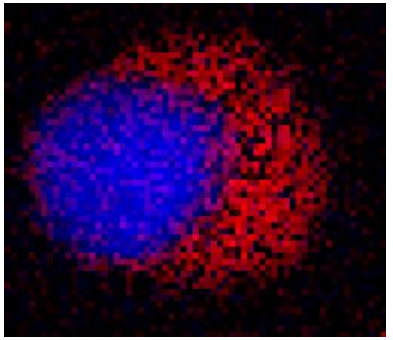
Kinetics and environment also play a major role.



D. Bochicchio et al., Phys. Rev. B **87**, 165435 (2013)



HAADF
(Z contrast)



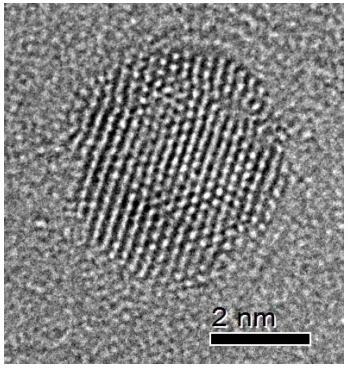
Co

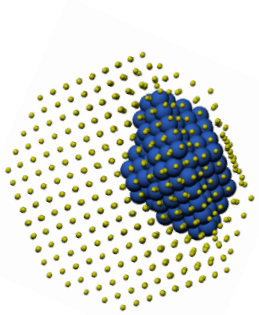
Au

EELS map

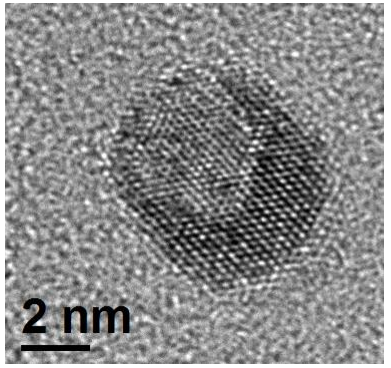
Ex.: CoAu nanoparticles, with an off-centered Co core and Au shell

⟹ Symmetry can be broken



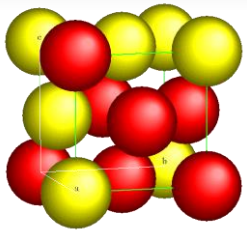


Observations in agreement with theoretical predictions



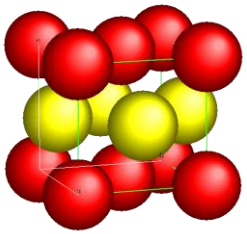
F. Tournus, unpublished

The case of CoPt and FePt nanoparticles



A1 phase

- Chemically disordered
- fcc cell

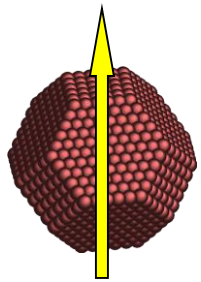


$L1_0$ phase

- Chemically ordered
- tetragonal cell (c/a < 1)

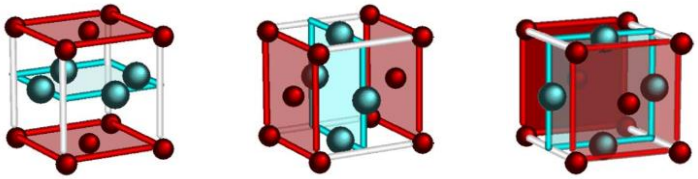
The $L1_0$ phase has a huge magnetic anisotropy constant (K_{eff}~ 5 MJ/m^3)

⇒ Interesting for magnetic storage applications



The $L1_0$ phase is stable at room temperature, but A1 is metastable

⇒ Chemical ordering obtained by annealing

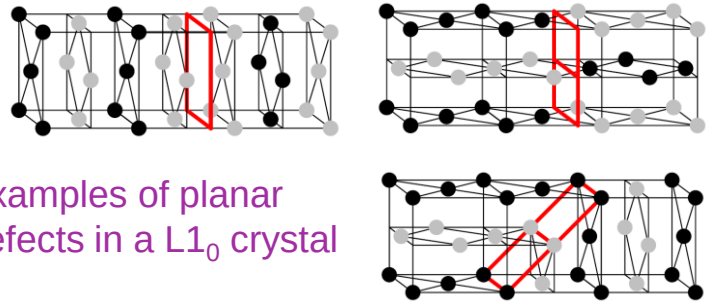


From cubic to tetragonal: 3 equivalent directions for the chemical order (variants)

Antiphase, c-phase or twin boundaries between different $L1_0$ domains

⇒ Observed in films and large particles

Are they met in small particles?

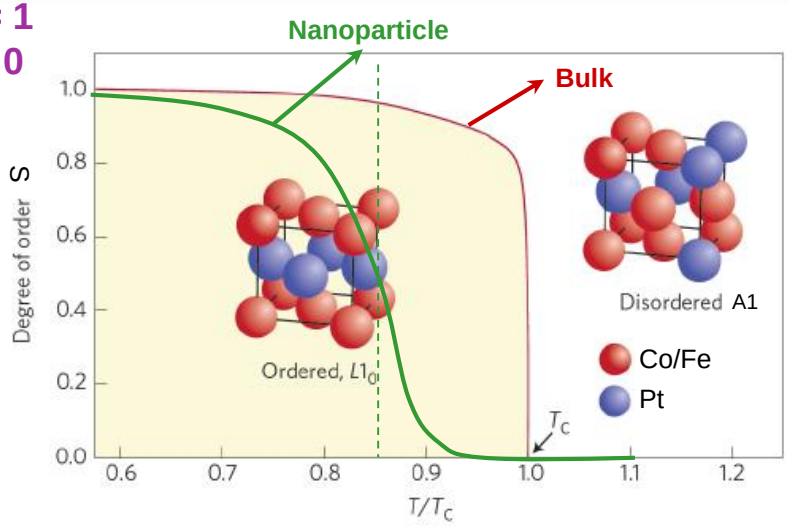


Examples of planar defects in a $L1_0$ crystal

A. Alam *et al.*, Phys. Rev. B **82**, 024435 (2010)

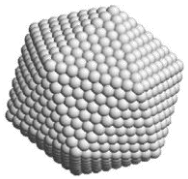
CoPt/FePt: Structure and size reduction

$L1_0$: S = 1
A1: S = 0

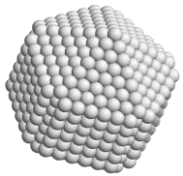


• Chemical order phase transition shifted and smoothed

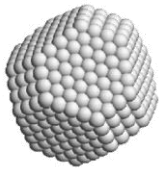
➡ Threshold size for $L1_0$ stability?



Icosahedron



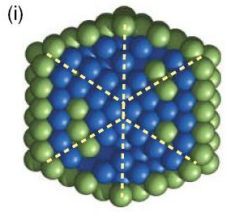
Decahedron



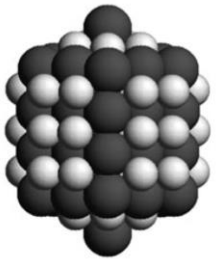
Truncated-octahedron

• As a function of particle size, competition between different geometries

➡ Multiply-twinned particles



Core–shell icosahedron with depleted subsurface shell



M. Grüner *et al.*, *Phys. Rev. Lett.* **100**, 087203 (2008)

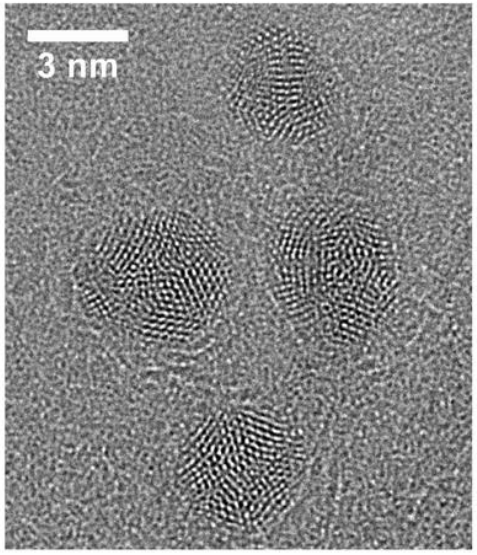
G. Rossi *et al.* *Faraday Discuss.* **138**, 193 (2008)

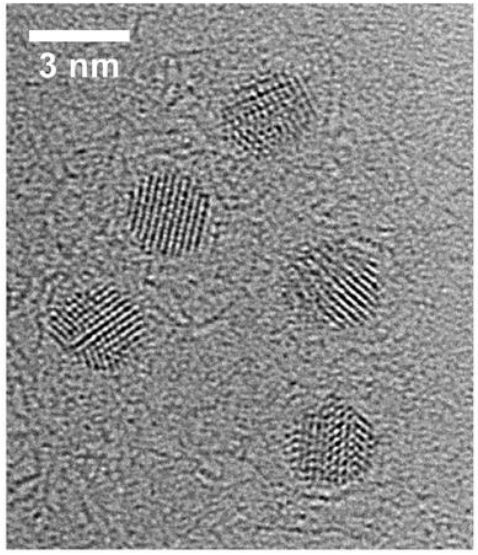
• Various theoretical predictions

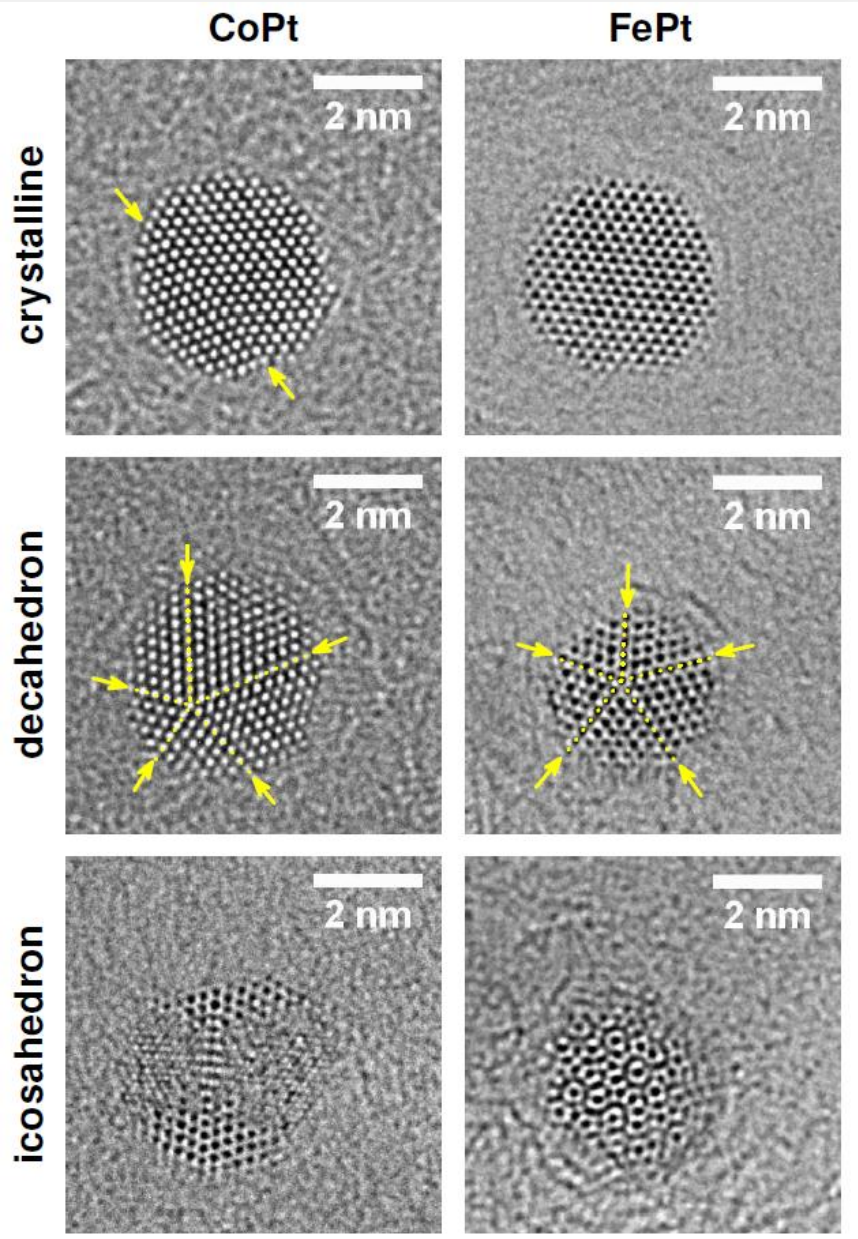
➡ $L1_0$ ordered decahedron should be favorable

CoPt/FePt: nanoparticle geometries

- No chemical order before annealing (disordered alloy, A1 phase)
- Coexistence of different particle structures
- Consistent with theoretical calculations
  ⇒ Small energy differences (twins)
- Structure identification is not trivial
  ⇒ No quantitative population analysis





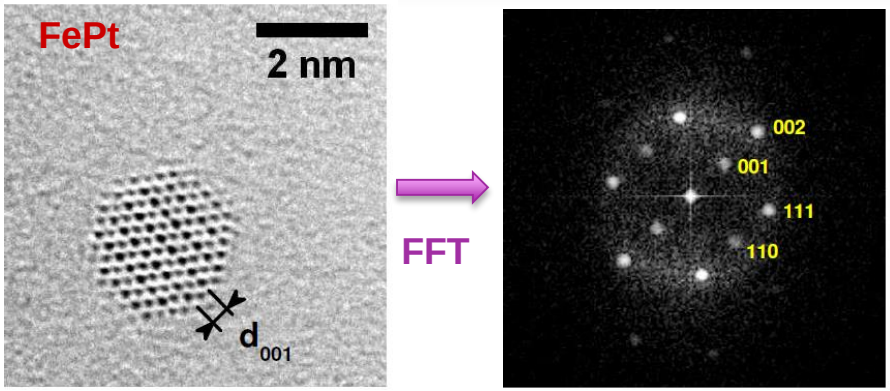


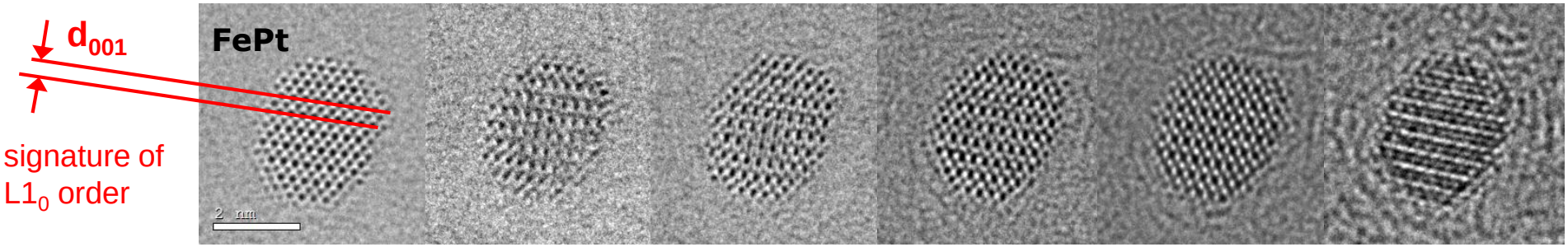
F. Tournus *et al.*, Phys. Rev. Lett. **110**, 055501 (2013).

$L1_0$ ordered particles

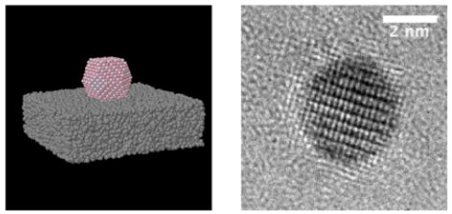
✓ $L1_0$ contrast ([001] peak) after annealing, even for the smallest particles

✓ Particles with a single $L1_0$ domain



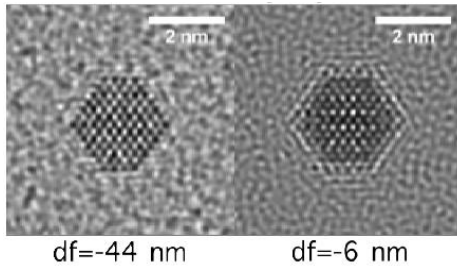


Through-focus HRTEM images of a chemically ordered fcc FePt particle.



Quantification of the chemical order parameter for a single nanoparticle (S ~ 1)

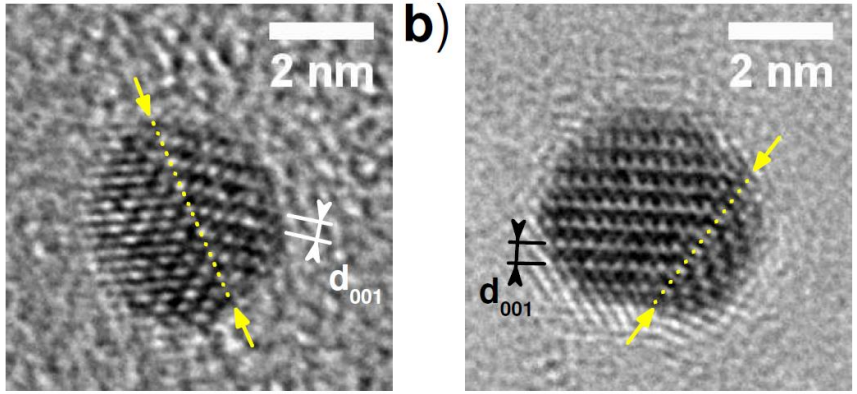
N. Blanc *et al*., Phys. Rev. B **83**, 092403 (2011)



But, chemical order is **not necessarily visible** (particle orientation, defocus)

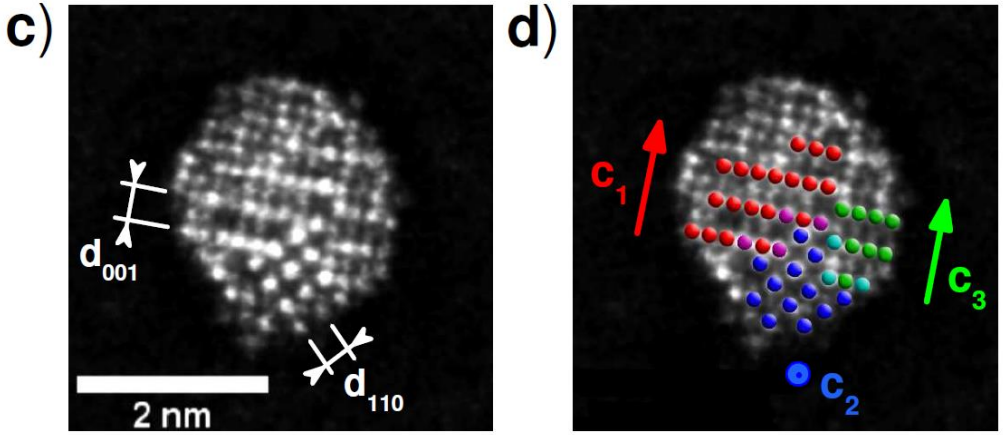
✓ Challenging observations!
✓ Not a statistical method

Particles with several $L1_0$ domains

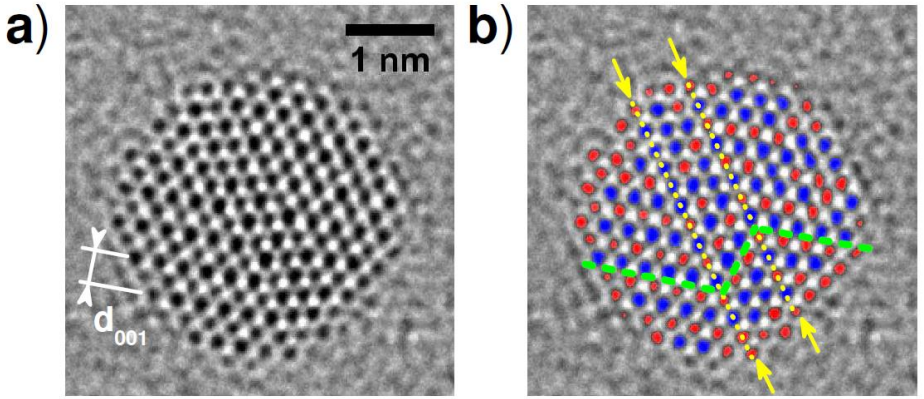


- The chemical order is preserved across (111) twins

STEM HAADF image of a CoPt particle



- Twinned particles with two $L1_0$ domains



HRTEM image of a CoPt particle (atoms are colored according to their size)

- Coexistence of several $L1_0$ variants (with antiphase boundaries)

In a single crystal particle of 2 nm diameter!

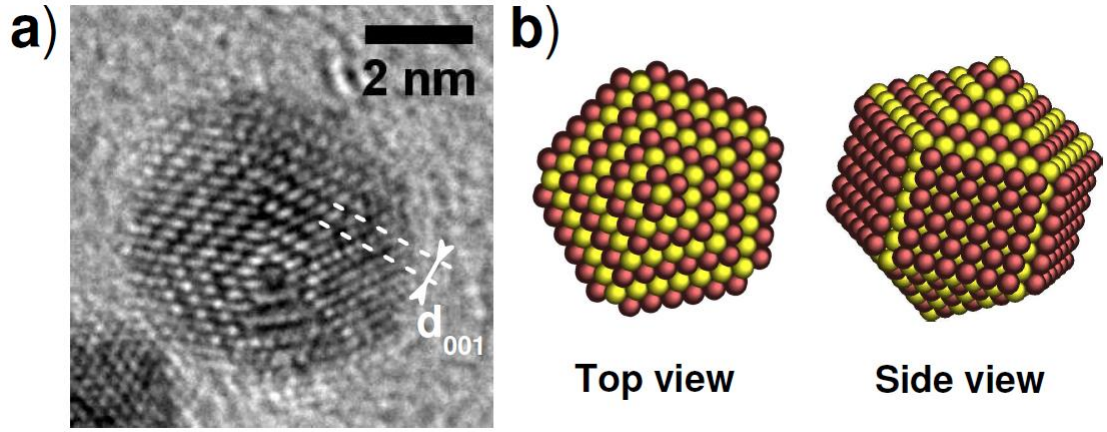
F. Tournus *et al.*, Phys. Rev. Lett. **110**, 055501 (2013).

Chemically ordered decahedra

- ✓ Multiply-twinned particles
- ✓ Fivefold symmetry

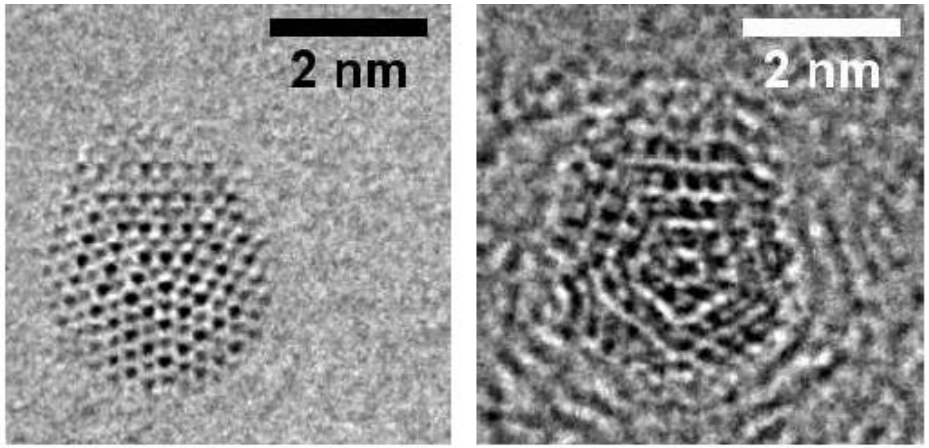
⇩

Chemically ordered CoPt and FePt decahedral particles

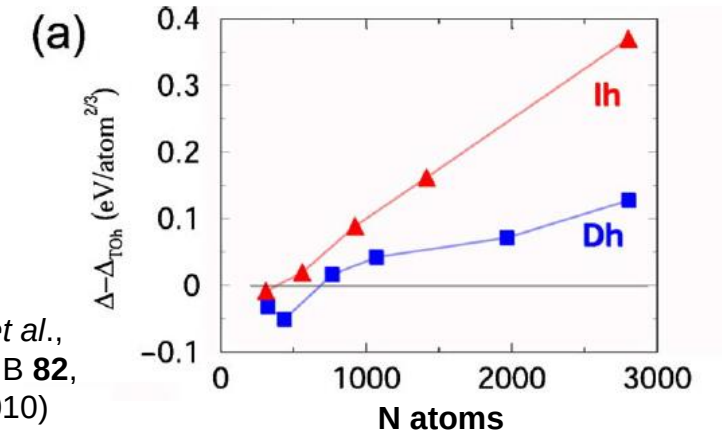


Five $L1_0$ domains with different c-axis orientations

⟹ Will dramatically lower the magnetic anisotropy



Cs-corrected HRTEM image of a FePt particle, for different defocus values



Andrezza *et al.*, Phys. Rev. B **82**, 155453 (2010)

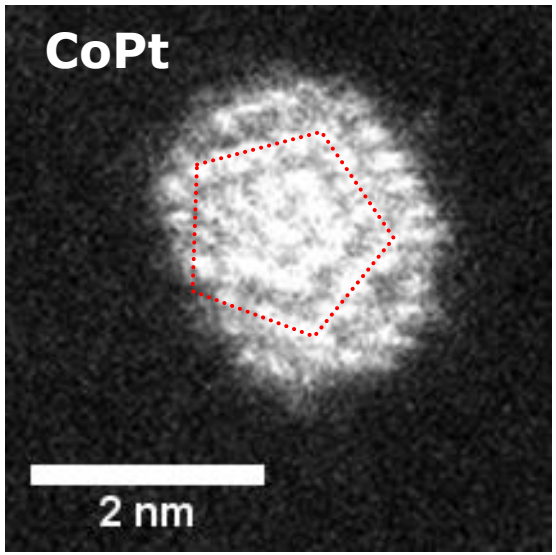
Agreement with the theoretical predictions

Chemically ordered decahedra

Chemical identification of the atomic columns

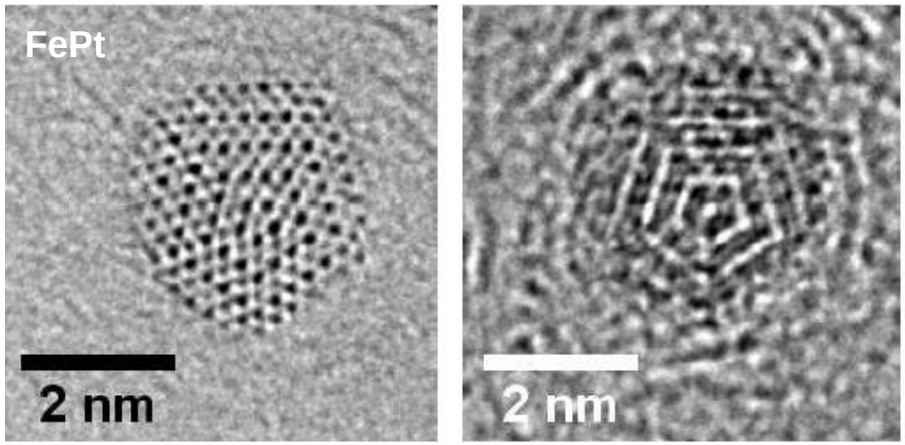
No preferential occupation of one element for the facets or the central atoms

⟹ No indication of segregation

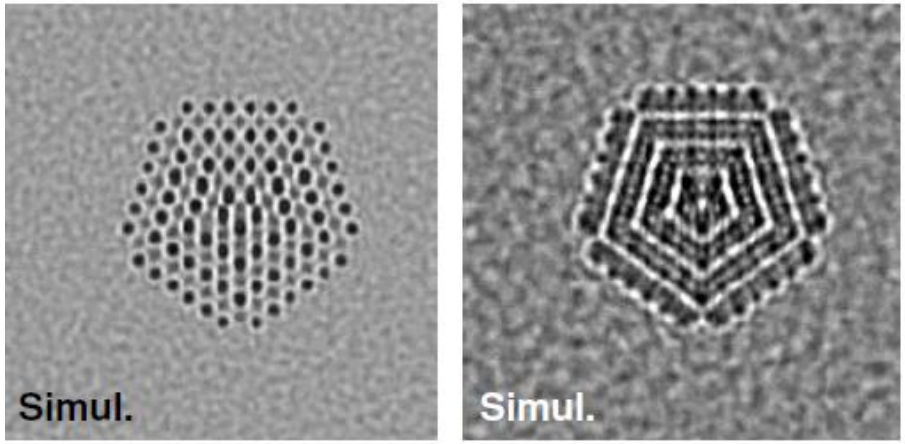


STEM-HAADF image

Experimental HRTEM image



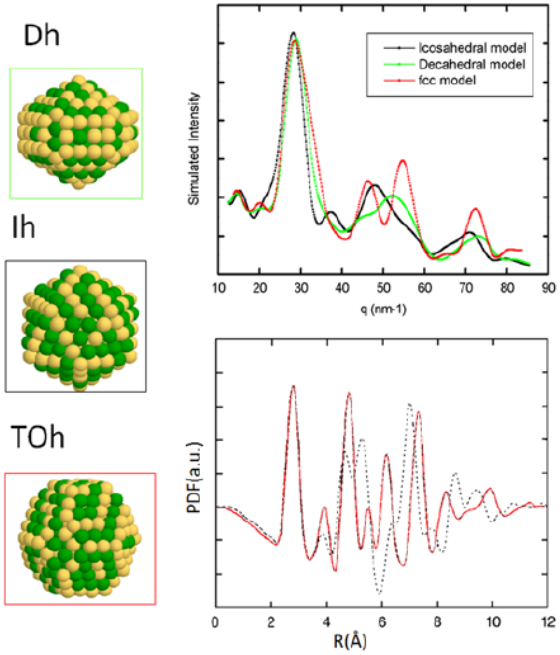
Multislice HRTEM simulations (JEMS)



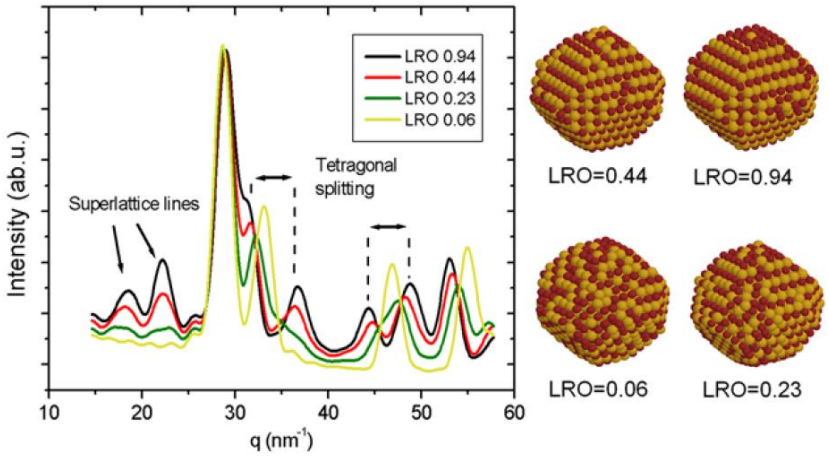
Chemical order in icosahedral particles?

F. Tournus *et al.*, Phys. Rev. Lett. **110**, 055501 (2013).

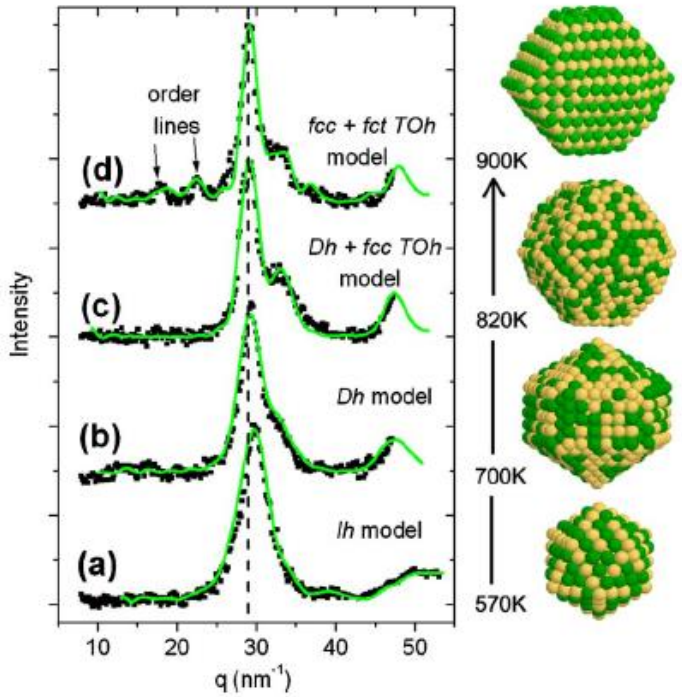
Some other results: XRD



P. Andreazza *et al*., unpublished



X-ray diffraction spectra are also sensitive to the particle symmetry and chemical order



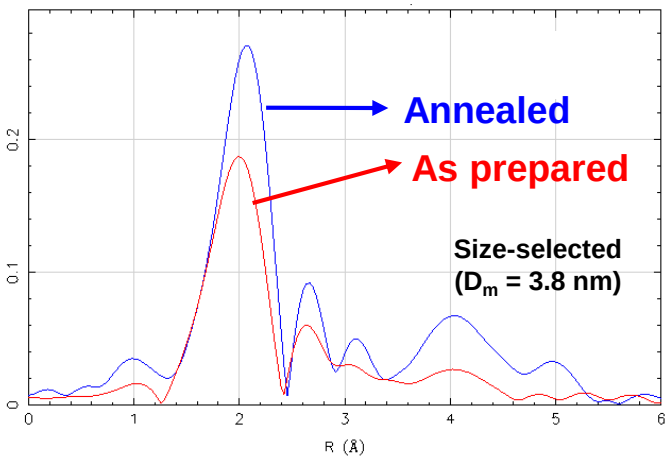
Modelling is necessary

➡ Difficult because coexistence of different geometries and particle sizes (measurement on particle assemblies)

In fact, chemical ordering is possible without changing the particle Dh symmetry

P. Andreazza *et al*., Phys. Rev. B **82**, 155453 (2010)

Chemical order and relaxation

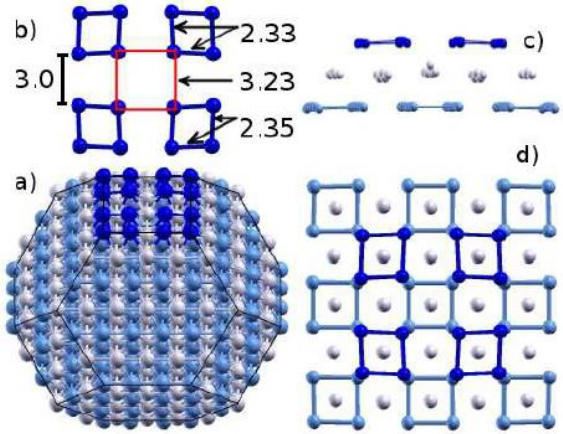


N. Blanc *et al.*, Phys. Rev. B **87**, 155412 (2013)
V. Dupuis *et al.*, Eur. Phys. J. B **86**, 1 (2013)

EXAFS measurements: probe the local environment of one type of atoms

- Drastic change upon annealing
- Evolution of N_{Co}/N_{Pt}

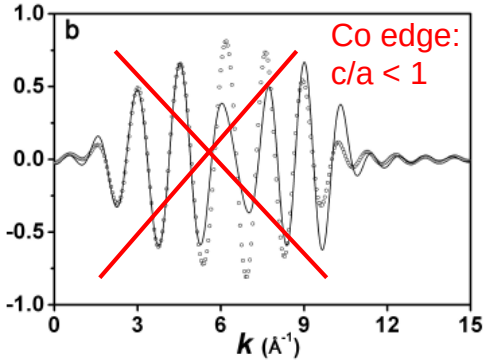
A1 → $L1_0$ transition



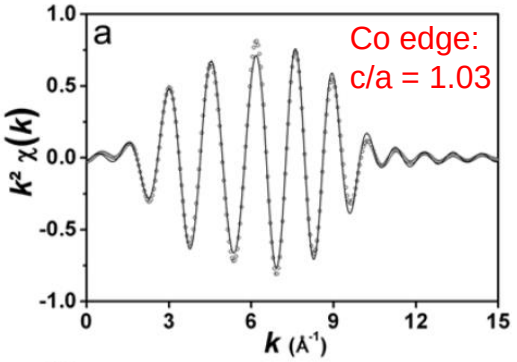
Apparent c/a ratio

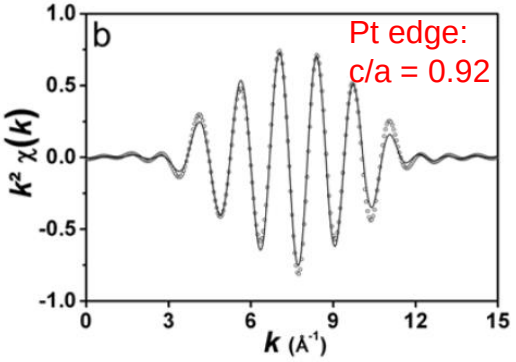
→ Different around Co and Pt atoms:
$d_{Pt\text{-}Pt} \neq d_{Co\text{-}Co}$

DFT calculations: "$L1_0$ like" structure
→ Strong relaxation of the Co-Co distances



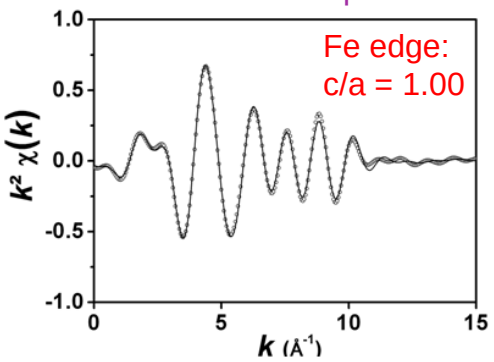
Tetragonalization different from the bulk

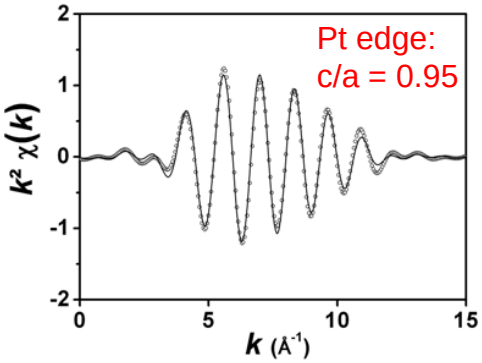




Chemical order and relaxation

EXAFS for FePt particles





Dispersion of nearest-neighbor distances, with the position, and the chemical nature

The particles are not “crystals”

Relaxation ($d_{Fe\text{-}Fe} \neq d_{Pt\text{-}Pt}$)

Indirect indication of Pt segregation for icosahedral FePt

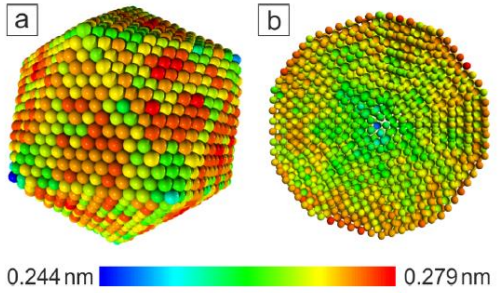
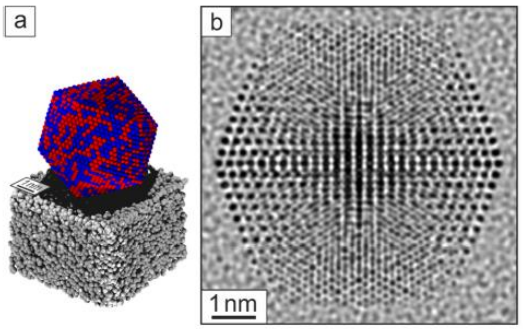
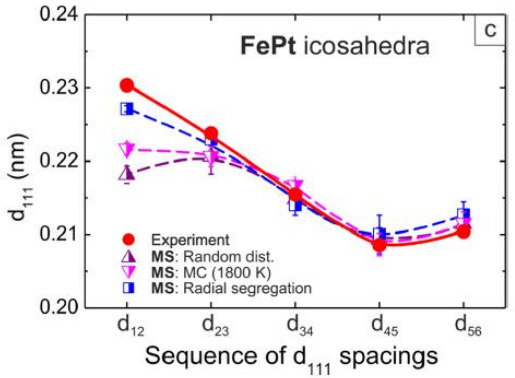


Figure 7. Color-coded image of the variation of the next nearest neighbor distances across a disordered FePt icosahedron of 8217 atoms after structural relaxation through MS simulations. (a) Perspective image of the particle. (b) Cross section through the particle center as seen along one of its five-fold symmetry axes.

FePt cluster (Ih)





Imperfect symmetry:
relaxation, non-regular shapes, defects…

Variability of the nano-objects in an assembly, with coexistence of different structures…

⟹ Dispersion of the properties (for instance, the magnetic anisotropy)

D. Pohl et al., Nano Lett. **14**, 1776 (2014)

Magnetic order: one example

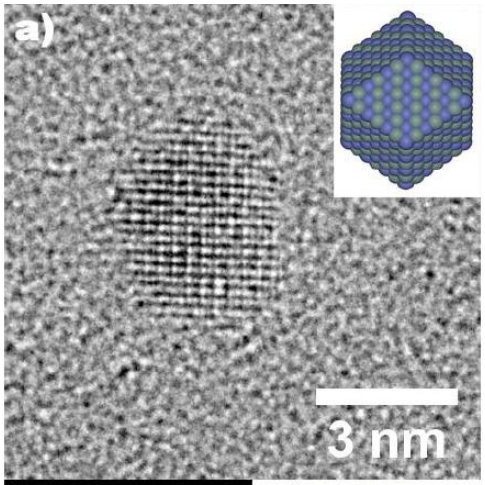
The magnetic order can be influences by the size reduction

➡ Example: FeRh nanoparticles

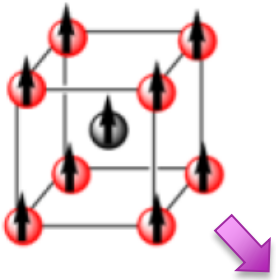
Chemically ordered particles (B2 phase), after annealing

The particles are ferromagnetic, down to 2 K, instead of anti-ferromagnetic

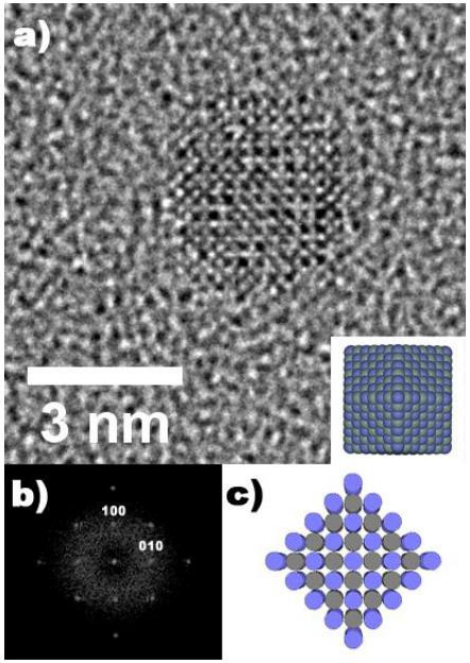
Chemically ordered FeRh particle

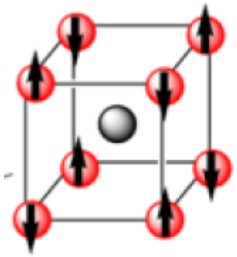


FM order

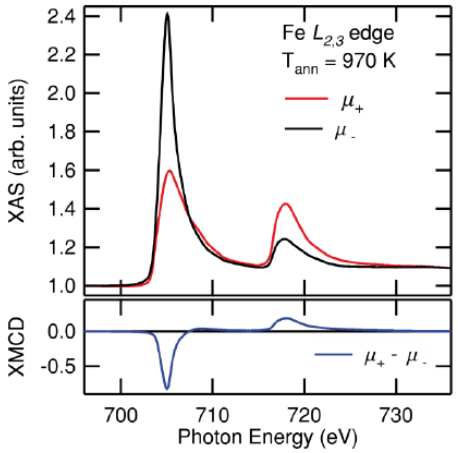


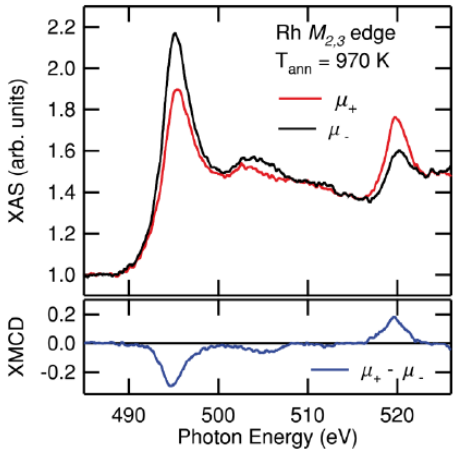
Chemically ordered FeRh particle





AF order





A. Hillion et al., Phys. Rev. Lett. **110**, 087207 (2013)

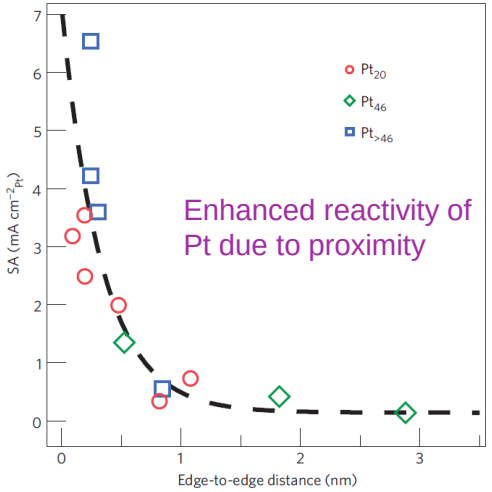
XMCD measurements at Fe and Rh edges

Supra-crystals, arrays of nanoparticles

Bottom up approach ➡ Self-organization

Motivations:

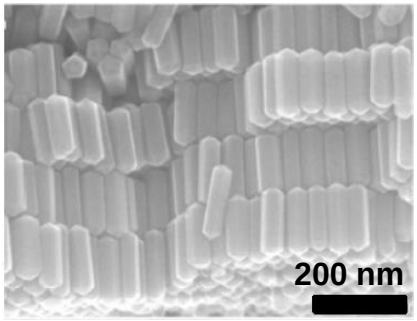
- ✓ Optimal packing (inter-particle coupling, resonance)
- ✓ Same environment for all particles
- ✓ Particle localization (for ex. for information storage)
- ✓ Mechanisms of self-organization (particle-particle and particle-substrate interactions)



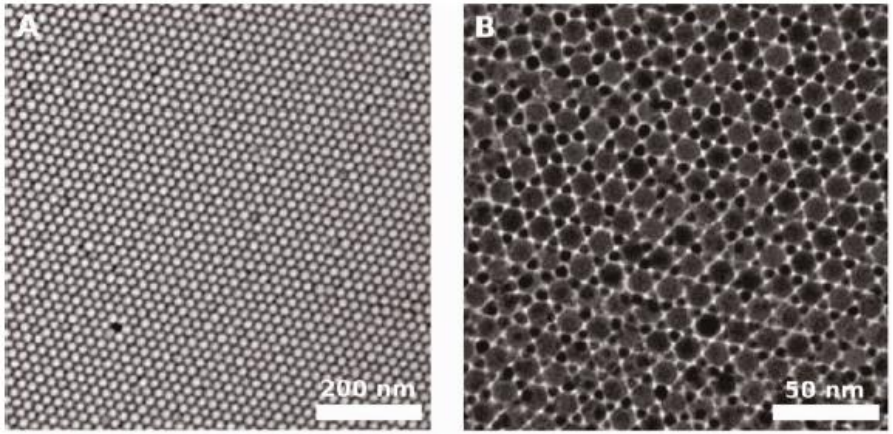
M. Nesselberger et al., Nat. Mater. **12**, 919 (2013)

Mostly from colloidal particles

➡ Very nice results (not bare particles), with good order over large ranges



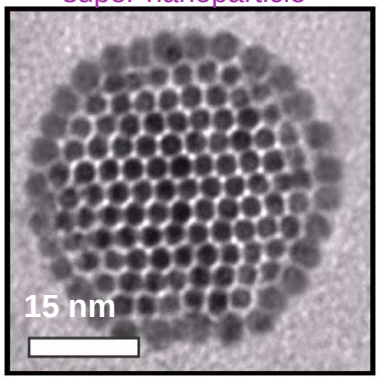
B. Pietrobon et al., ACS Nano **3**, 21 (2009)



S. Pichler et al., ACS Nano **5**, 1703 (2011)

Different stacking (hexagonal, cubic), mixed supra-crystals, exotic structures…

CdSe-CdS Core-shell super-nanoparticle



O. Chen et al., Nat. Commun. **5**, 5093 (2014)

Compact structures

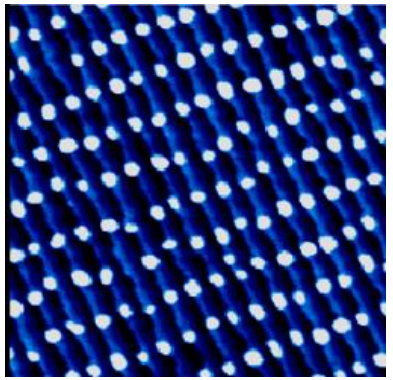
➡ Particle agglomeration due to VdW interactions (+ electrostatic, chemical…)

Self-organization with a physical route

Atomic deposition on template surfaces (UHV conditions)

⇒ • Good organization for pure clusters
• Importance of the atom and particle/surface interaction

Preformed cluster deposition, an alternative approach ⇒ Not the same morphology as with atomic deposition

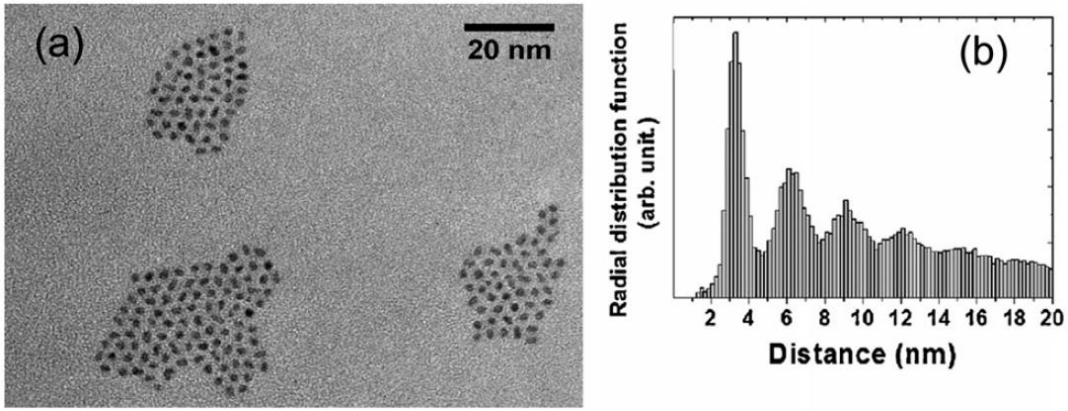


Co nanoparticles on Au(788)
V. Repain *et al*.
Euro. Phys. Lett. **58**, 730 (2002)

Ex.: size-selected FePt clusters deposited on graphite

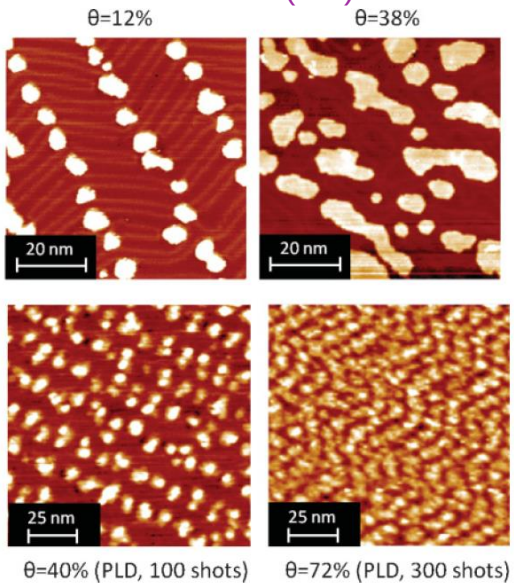
⇒ Local hexagonal symmetry (correlation length)

Key ingredients = same size, diffusion, attraction with short-range repulsion



L. Bardotti et al., Phys. Chem. Chem. Phys. **16**, 26653 (2014)

Pd/Au(111)



Atomic deposition

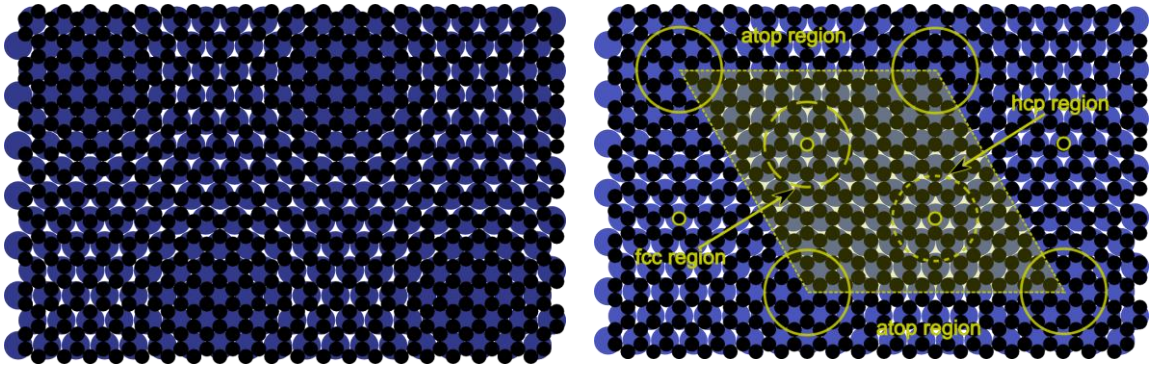
Cluster deposition

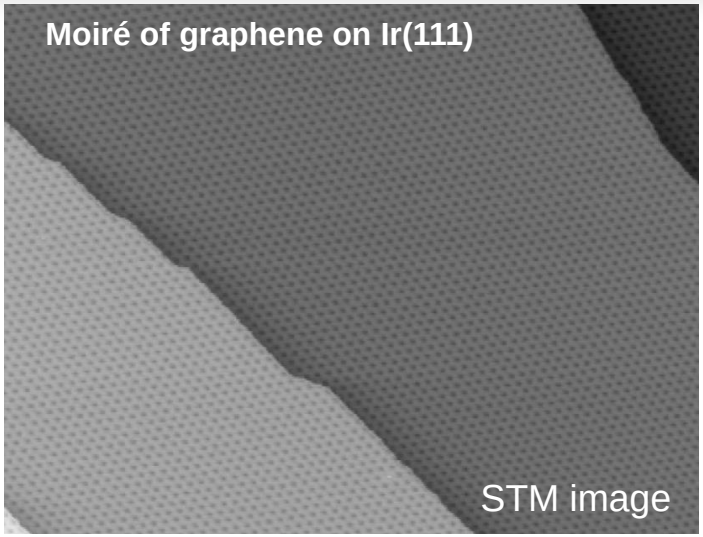
Casari et al., Phys. Rev. B **84**, 155441 (2011)

Cluster deposition on graphene / Ir(111)

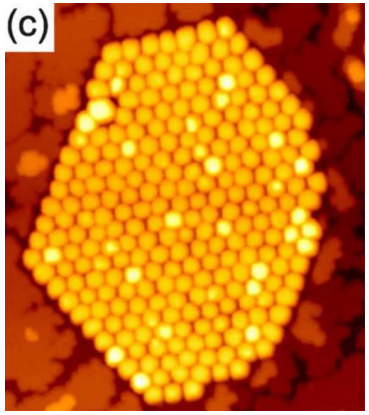
Idea: use the **moiré lattice** of graphene epitaxially grown on Ir(111) to obtain **arrays of particles**

Lattice mismatch produces a moiré
⇒ specific sites with a 2.5 nm periodicity





J. Coraux *et al*., Nano Letters **8,** 565 (2008).



✓ Organized growth of dots with atomic deposition

✓ Self-organization using deposition of preformed clusters?

⇒ Deposition of clusters (D ~ 1.5 nm)

N'Diaye *et al*., New J. Phys. **11,** 103045 (2009); Phys. Rev. Lett. **97**, 215501 (2006).

Collaboration with G. Renaud

NMGEM
NanoMagnetisme sur Graphène Epitaxié sur Métaux

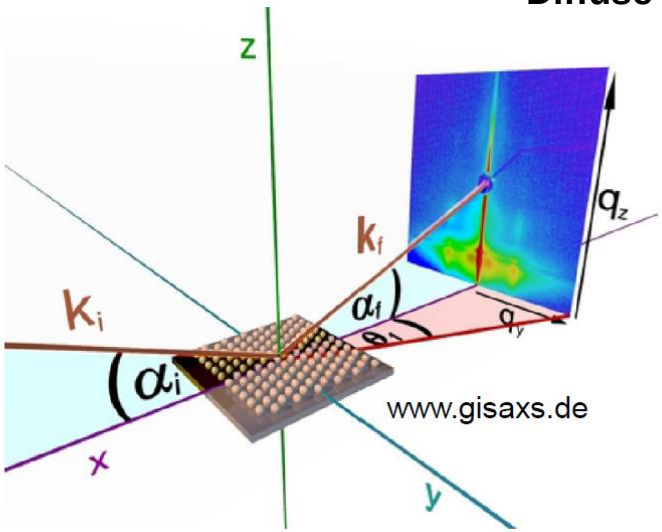
ANR-2010-BLAN-1019-NMGEM

Clusters on graphene: GISAXS results

Information about the shape and distribution of particles

Grazing Incidence Small Angle Scattering (Decoupling approximation)

$$I(\boldsymbol{q}) = |\langle F(\boldsymbol{q})\rangle|^2 \times S(\boldsymbol{q}) + \underbrace{\langle |F(\boldsymbol{q})|^2\rangle - |\langle F(\boldsymbol{q})\rangle|^2}_{\text{Diffuse term}}$$



$I(\boldsymbol{q})$: *Scattered Intensity*

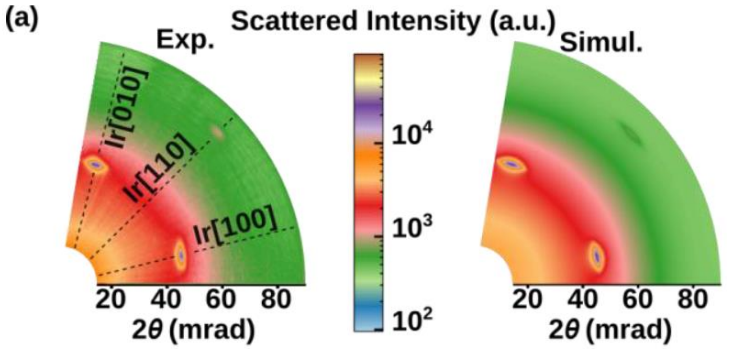
$F(\boldsymbol{q})$: *Form factor*

$S(\boldsymbol{q})$: *Interference function*

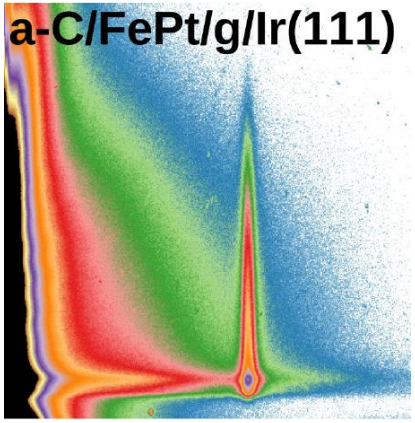
Hexagonal lattice of Pt clusters (lattice parameter = 2.5 nm)

➡ Pt clusters pinned on a specific moiré site

S. Linas et al., submitted

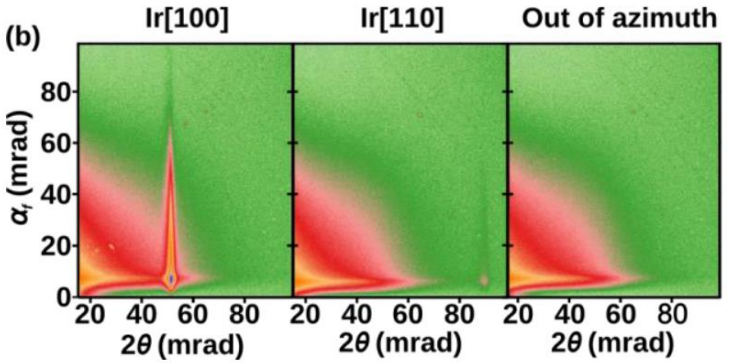


a-C/FePt/g/Ir(111)



Coherence but imperfect symmetry: some clusters are not on the moiré lattice

Same feature with FePt particles…

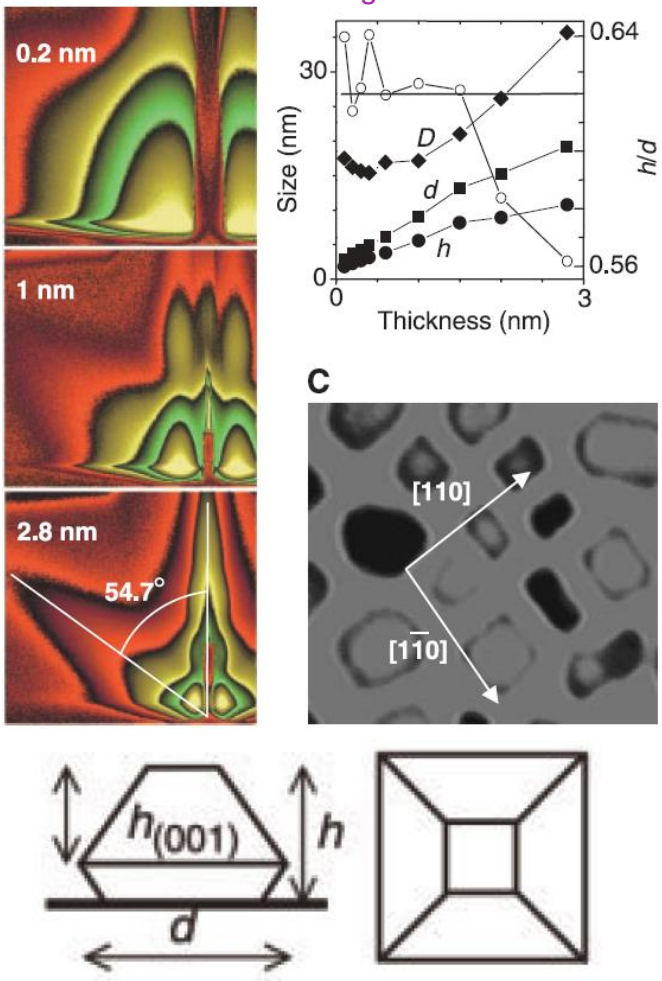


GISAXS and signature of symmetry

Probe for 2 different levels of symmetry

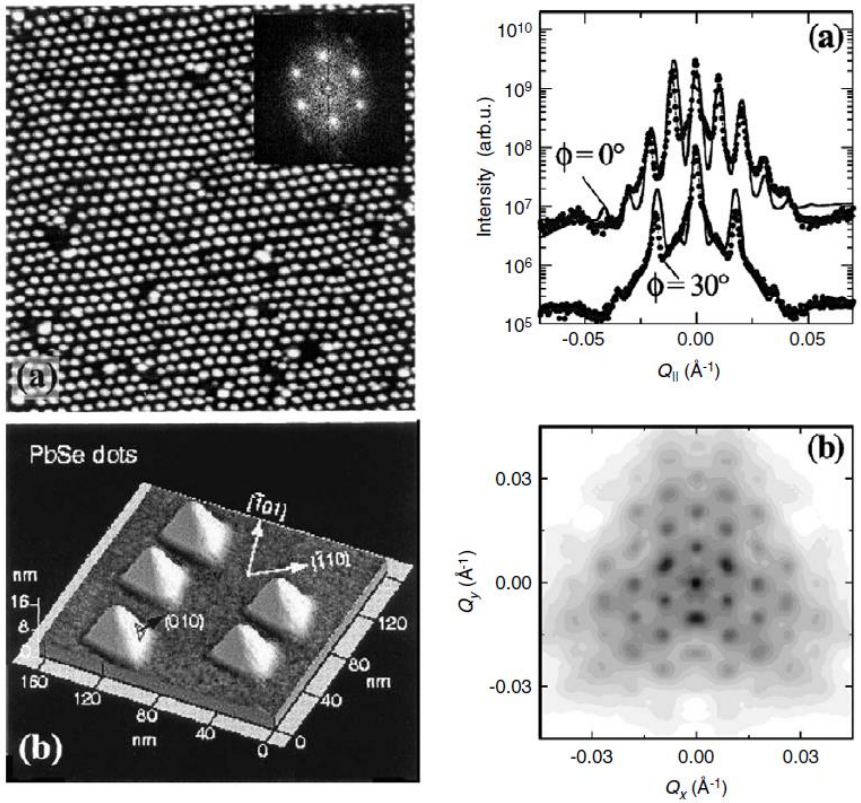
➡ Size and **shape** of the particles + interference between particles (**organization**)

Pd dots/MgO



G. Renaud et al., Science 300, 1416 (2003)

PbSe dots/PbEuTe



G. Renaud et al., Surf. Sci. Rep. 64, 255 (2009)

Well suited for nanostructrures, complementary to local probe microscopy (STM/AFM)

Summary and conclusion

- ✓ There are several levels of symmetry in a nano-system
  - ⟹ Crystal phase, shape, magnetic order, organization…
- ✓ Phase diagrams are modified by finite size (symmetries can be different from the bulk)
- ✓ For nanoparticles, non-crystalline structures can be favorable (in particular with a 5-fold symmetry)
- ✓ The symmetry of a nanostructure is often (always?) imperfect (defects, relaxation, variability in an assembly…)
- ✓ Controlling the symmetry at different levels is a challenge
  - ⟹ Control of the particles structure, morphology, orientation and location
- ✓ Some techniques are well-suited for the study of symmetry

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