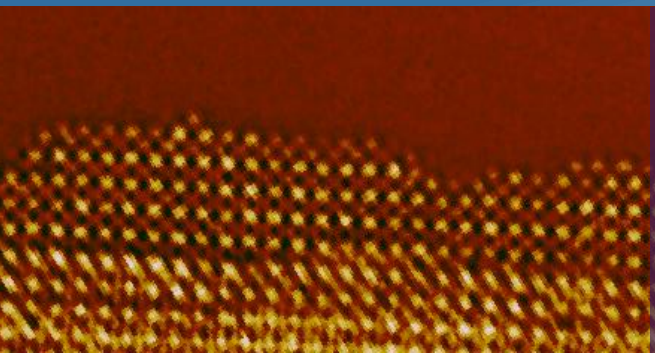
Bi-metallic nanoparticles: A size problem



Magali Benoit, Nicolas Combe, Hao Tang, Nathalie Tarrat, Joseph Morillo

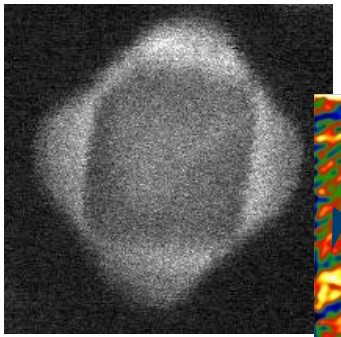
CEMES-CNRS and Université Paul Sabatier, Toulouse, France

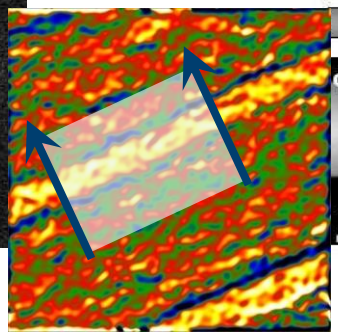
The "Crystalline Materials under Stress" group (MC2)

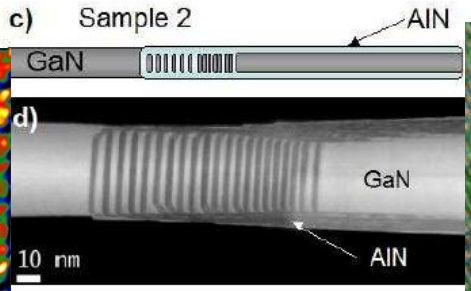
- **Low dimensionality systems**
  - Growth and deformation mechanisms: thin films, self-organisation, interfaces, surface elasticity…
  - Single objects: nanowires, nanoparticles
  - Structure/properties: magnetism, photoluminescence, reactivity …

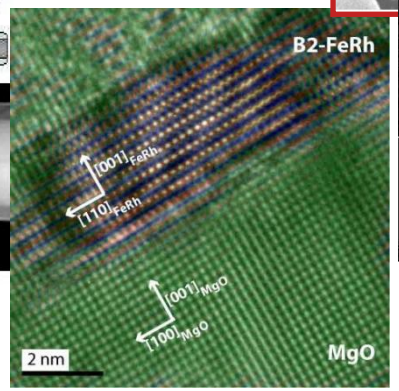
- **Metallurgy and plasticity**
  - Elementary mechanisms of plasticity
  - Materials for aeronautics
  - Plasticity in confined medium

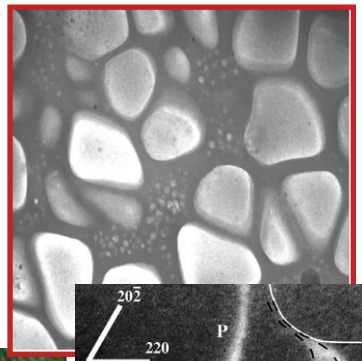
✓ Experiments (TEM…)
✓ Theory
✓ Modelling

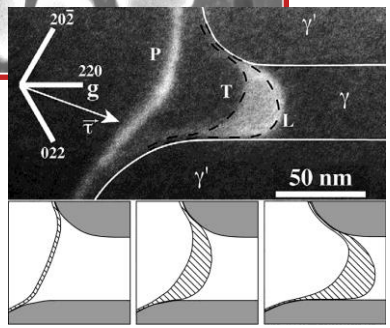






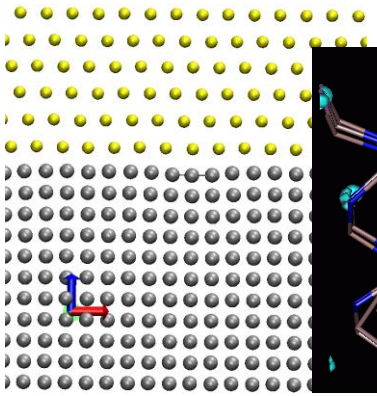


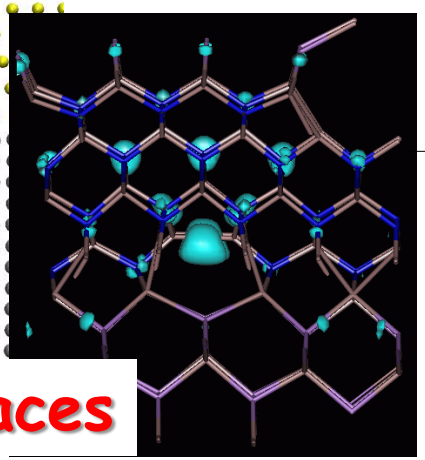




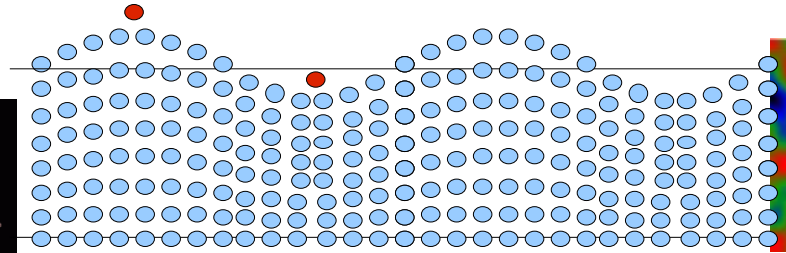
Modelling in the MC2 group

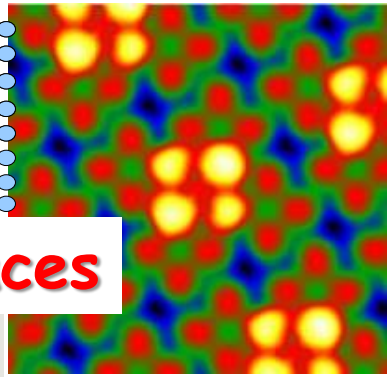
Atomistic Simulations



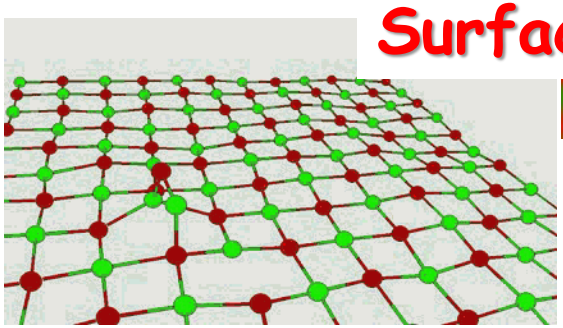


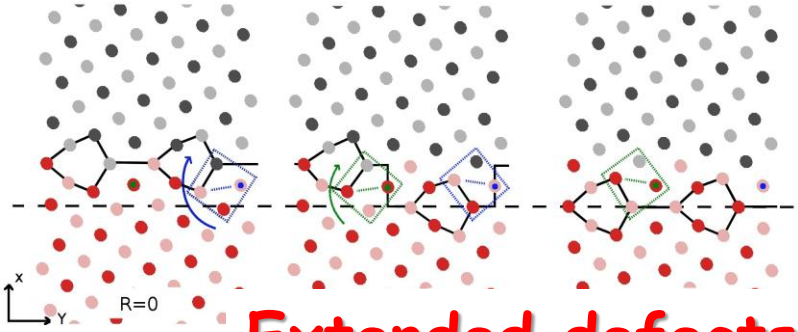
Interfaces



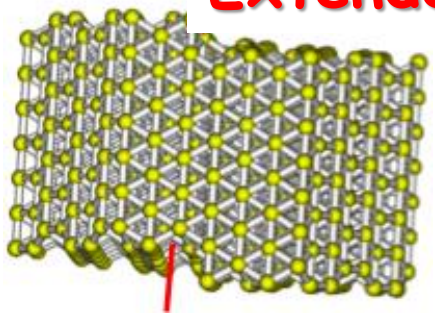


Surfaces

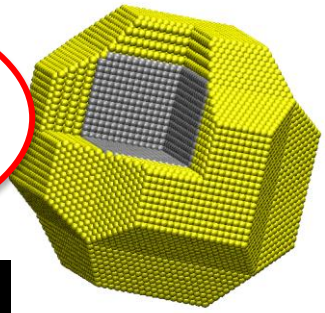


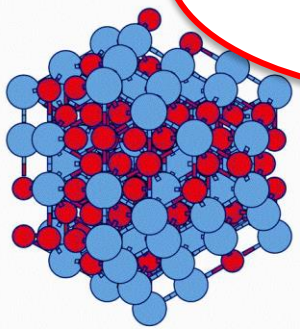


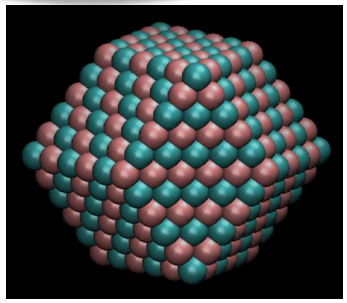
Extended defects



Nanoparticles

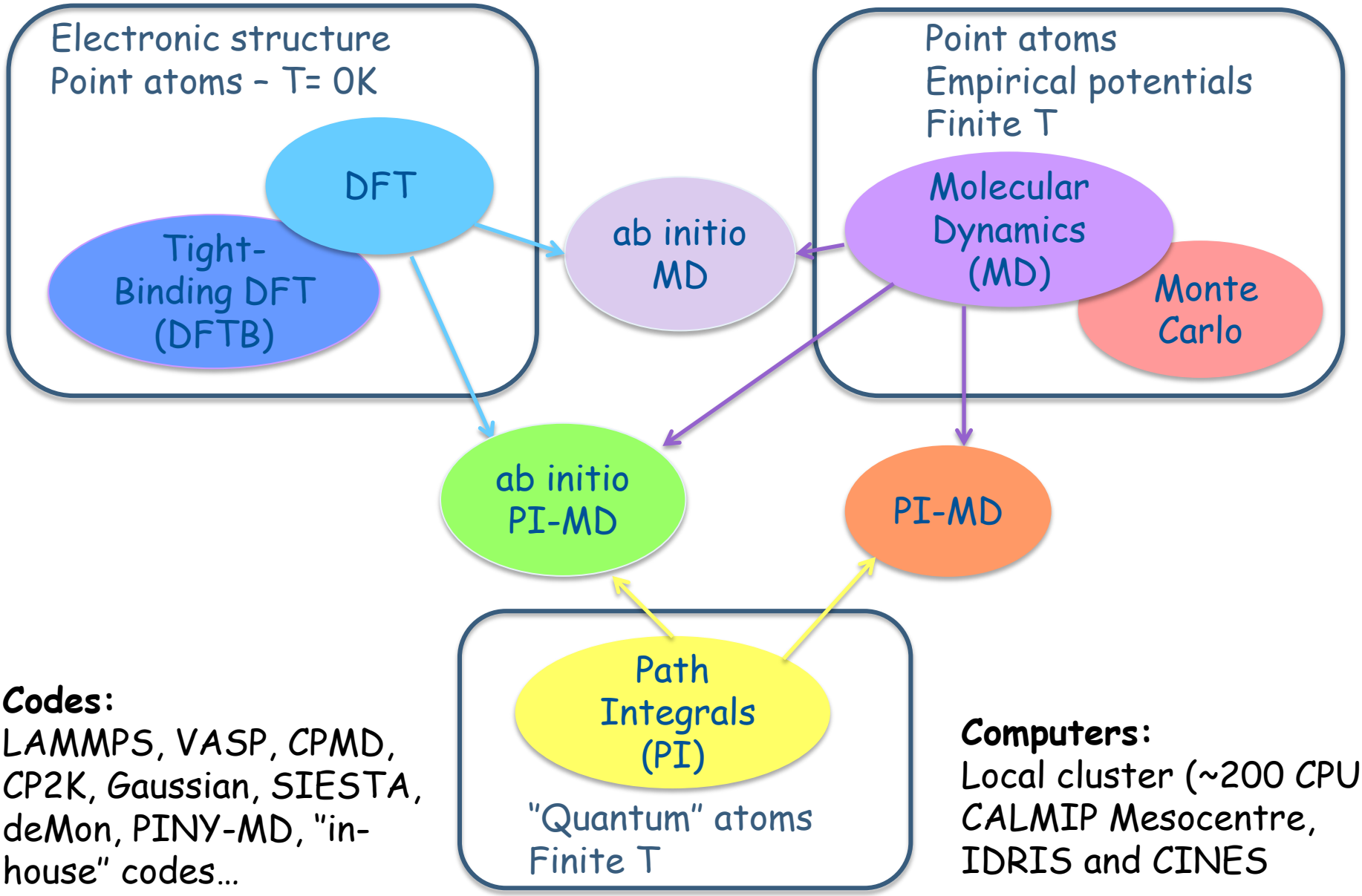






Modelling in the MC2 group

Atomistic Simulations



Codes:
LAMMPS, VASP, CPMD, CP2K, Gaussian, SIESTA, deMon, PINY-MD, "in-house" codes…

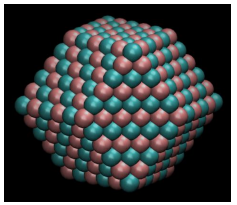
Computers:
Local cluster (~200 CPU), CALMIP Mesocentre, IDRIS and CINES

Bi-metallic nanoparticles

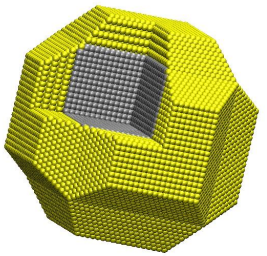
➔ Combine size effects (surface/volume ratio) and chemical order effects (alloy or core-shell)

➔ Numerous potential applications:
- Catalysis
- Optic/Plasmonic
- Magnetic recording
- Biomedical (imaging, vectorization and hyperthermia)
- …

Alloy

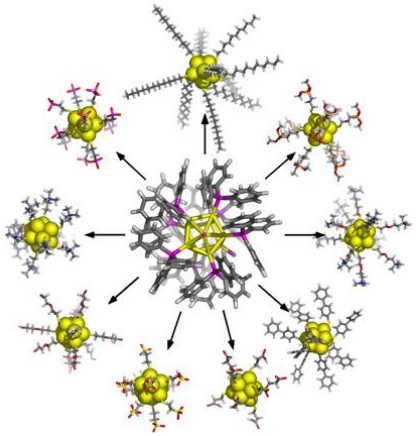


Core-shell

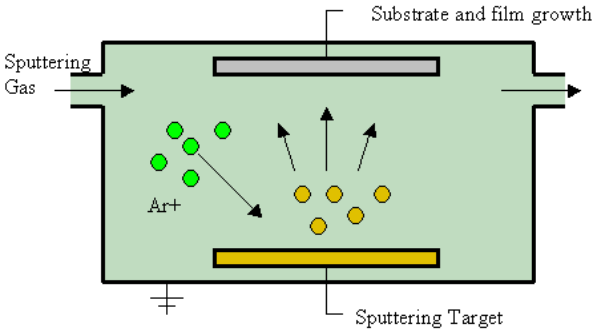


Nanoparticle (NP) synthesis

➢ Chemical route (ligands bound to the NP surface)



➢ Physical route (grown on a substrate)

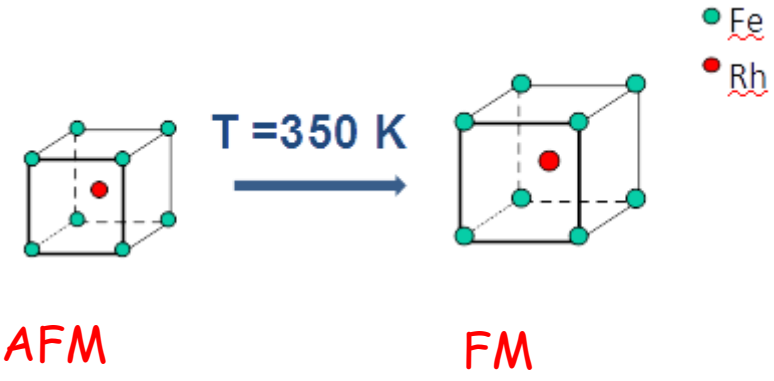


➔ How to control growth ? How does the structure affect the properties? What is the effect of the environment (ligands, solvent, substrate etc.) ?

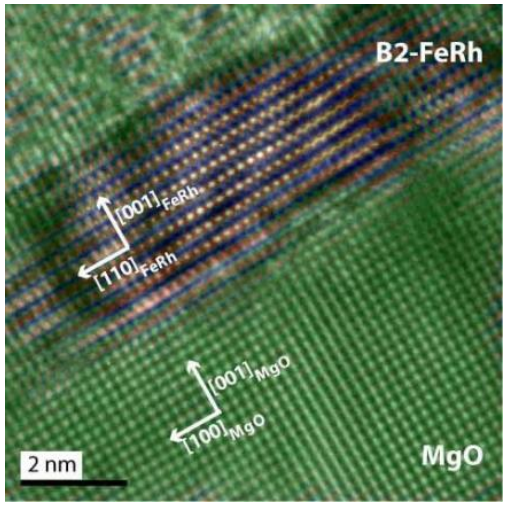
The FeRh nanoparticle: A promising magnetic nanoalloy

H. Tang, M. Liu, J. Morillo et M.-J. Casanove

In the bulk, AFM → FM transition at 350 K
for a small composition range around 50/50



Ordered phase B2



Evolution of the AFM→ FM transition temperature due to size and strain:

- Strain effect: FeRh films in epitaxy on a MgO substrate
- Size effect: small FeRh nanoparticles

➔ DFT modelling of very small FeRh nanoparticles: evolution of the AFM/FM energy difference with the NP size

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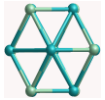
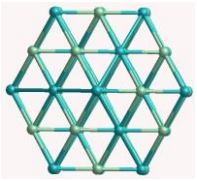
For each NP size:

- 2 compositions around 50/50
- 2 magnetic orderings (FM and AFM)
- Atomic relaxations

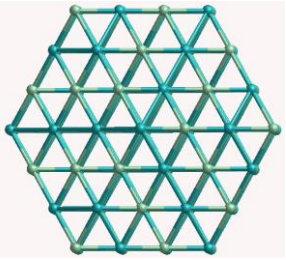
N=15



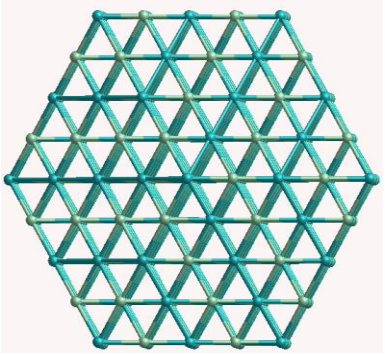
N=60



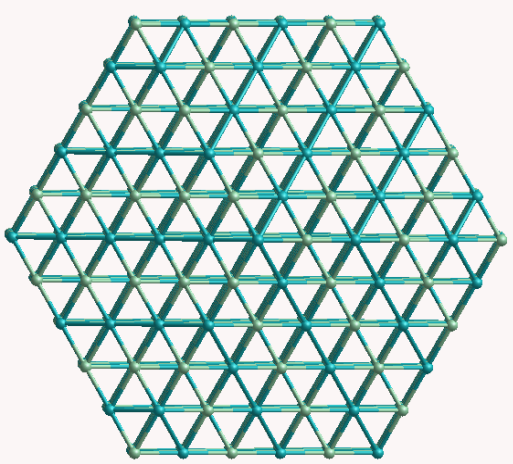
N=175



N=369



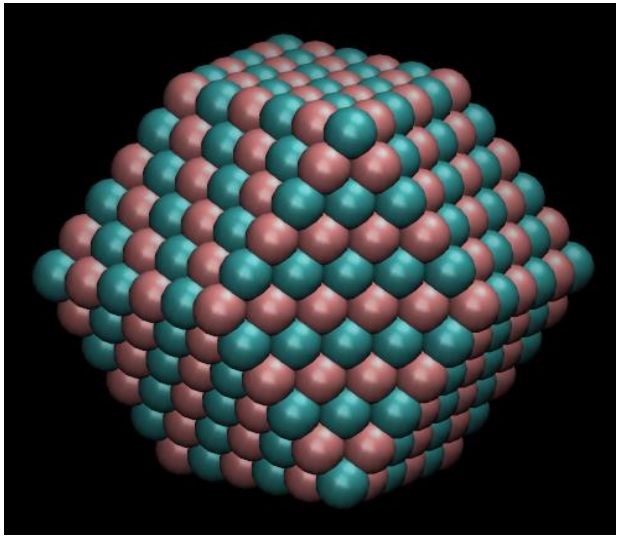
N=671

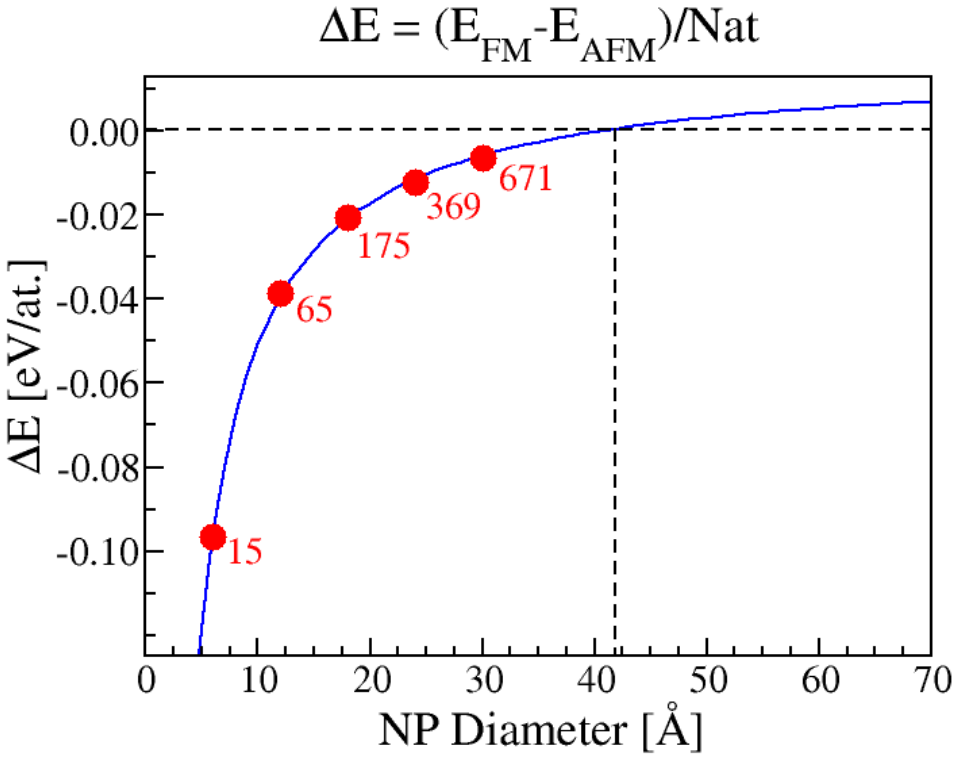


Diam. (nm)	0.6	1.2	1.8	2.4	**3.0**	*3.6*	*4.2*
nb. Tot. atoms	15	65	175	369	**671**	*1105*	*1695*
nb. Surf. atoms	14	50	110	194	**302**	*434*	*590*
nb. Core atoms	1	15	65	175	**369**	*671*	*1105*
% Fe (Rh)	53	50.8	50.3	50.1	**50.07**	*50.05*	*50.03*
% Rh (Fe)	47	49.2	49.7	49.9	**49.93**	*49.95*	*49.97*

The FeRh nanoparticle: A promising magnetic nanoalloy

H. Tang, M. Liu, J. Morillo et M.-J. Casanove





- ✓ For small sizes, the FeRh NPs are preferentially FM at 0K (in agreement with very recent experimental measurements)
- ✓ The FM → AFM transition takes place around 4.2 nm

- ✓ How does the AFM → FM transition temperature evolve with size ?

The FeRh nanoparticle: A promising magnetic nanoalloy

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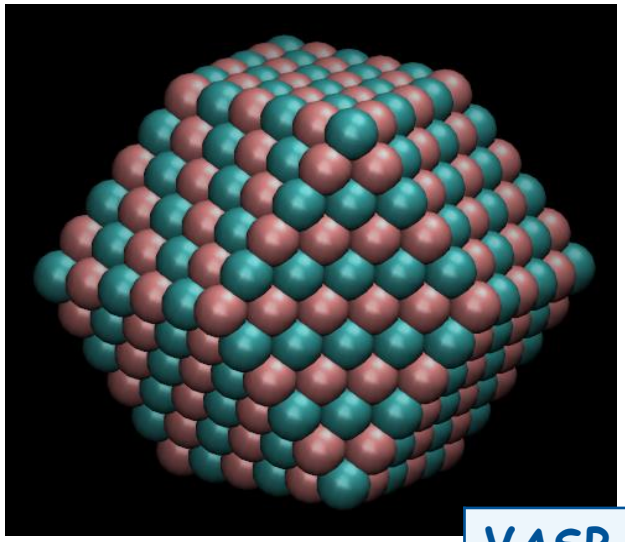


HPC ressources (Hyperion, Calmip):

For a FeRh NP of ∅ 3 nm – VASP code

- # atoms = 671
- # electrons = 5703
- # bands = 3928

VASP version	# PW	RAM	SCF loop	Storage
Γ-point	1098203	4.5 Gb/core	1600 sec.	138 Gb
"normal"	2160921	6 Gb/core	3200 sec.	239 Gb

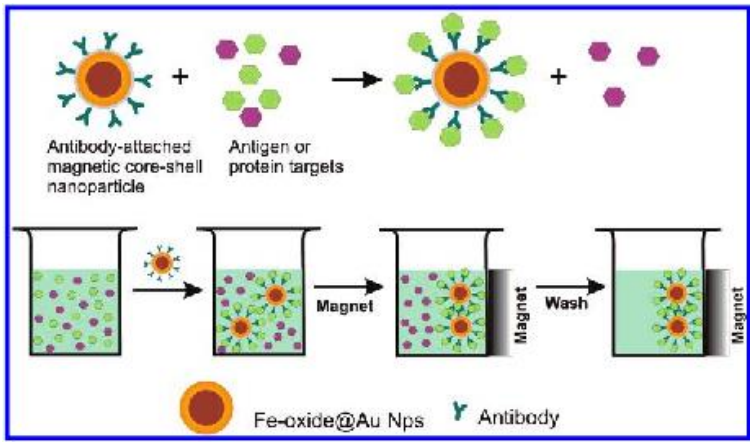
- Need for efficient parallelization (eg, VASP is not really scalable beyond 128 CPU…)
- Need for large RAM

Core-shell Fe@Au Nanoparticles

M. Benoit, N. Combe, N. Tarrat, J. Morillo and M.-J. Casanove

Metallic nanoparticles can be used for biomedial applications:

- ✓Drug delivery
- ✓Medical imaging
- ✓Magnetic hyperthermia



Bio-compatibility ?

The metallic core must be passivated by a biocompatible metal

➔core-shell structure

↳ **Fe and Au:** good candidates for a core-shell Fe@Au chemical order

- low miscibility at room temperature
- Au segregation at the surface

- Are Fe@Au particles experimentally feasible ?
- How is the Fe core modified (magnetism) ?
- Does the gold coating prevent from oxidation ?

Core-shell Fe@Au Nanoparticles

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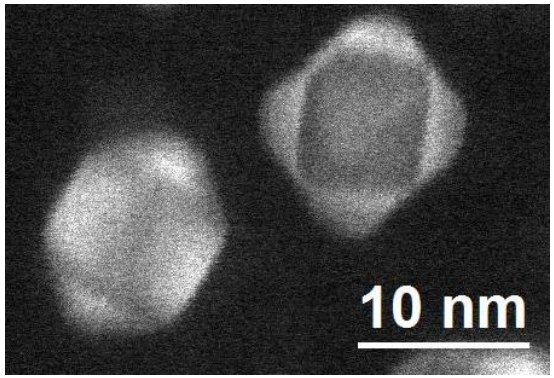
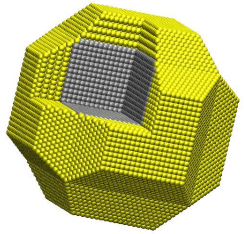
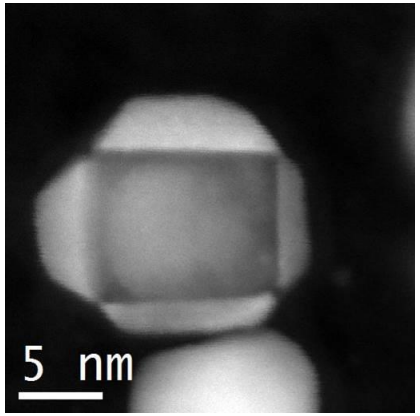
Size of the Fe nanocube: 5- 10 nm



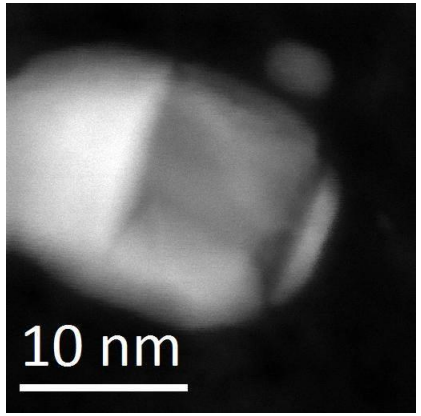
Regular



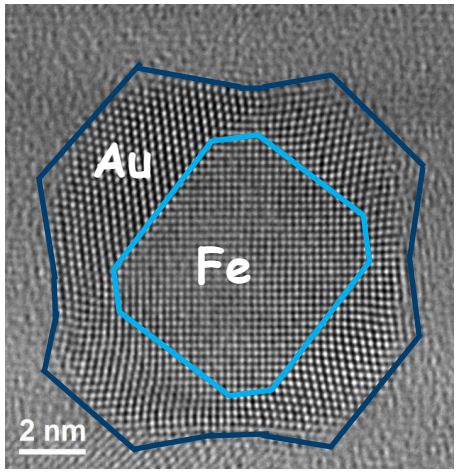
Large nanoparticles



Irregular



Janus



HRTEM Image

- **{001} Fe Facets** : $(001)_{Au}[100]_{Au}//(001)_{Fe}[110]_{Fe}$
- **{110} Fe Facets** :$(111)_{Au}[1\text{-}10]_{Au}//(110)_{Fe}[001]_{Fe}$

What is the equilibrium morphology ?

Is there a critical size ?

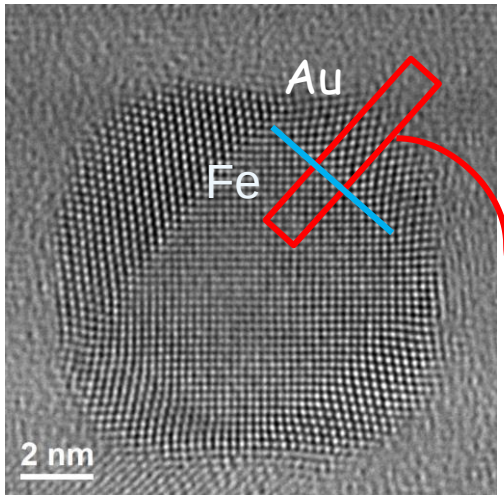
What happens at the interface ?

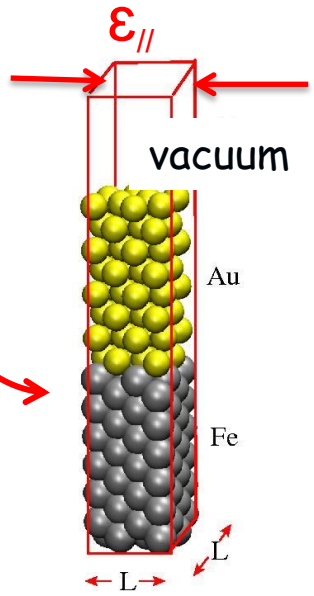
Core-shell Fe@Au Nanoparticles

M. Benoit, N. Combe, N. Tarrat, J. Morillo and M.-J. Casanove

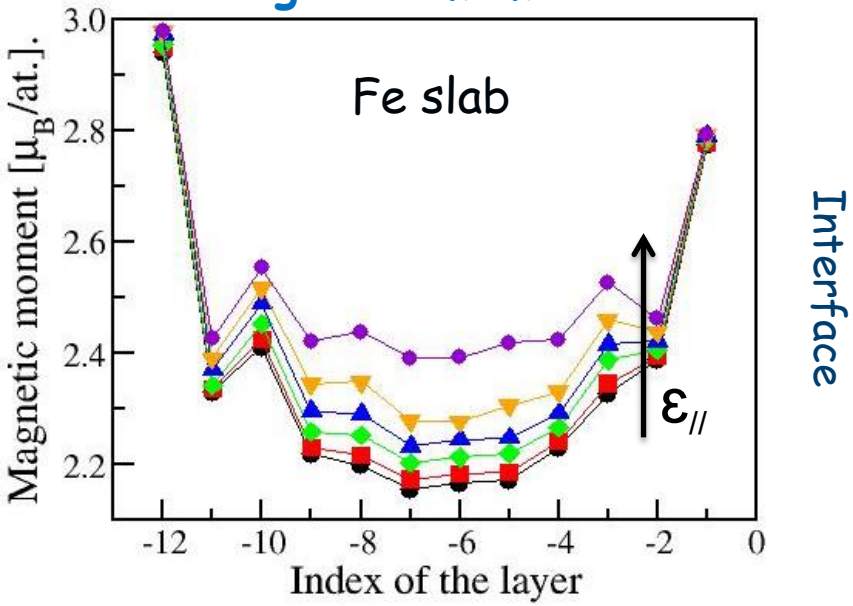
➔ **DFT calculations of the Au(001)/Fe(001) interface (periodic slabs):**

- Number of Au planes
- In-plane strain $\varepsilon_{//}$
  (mismatch between Fe and Au lattice parameters)





Magnetic moments



✓ Enhancement of the Fe magnetic moment at the interface

✓ Small magnetic moment of 0.6 μ_B/at on the Au atoms at the interface

Core-shell Fe@Au Nanoparticles

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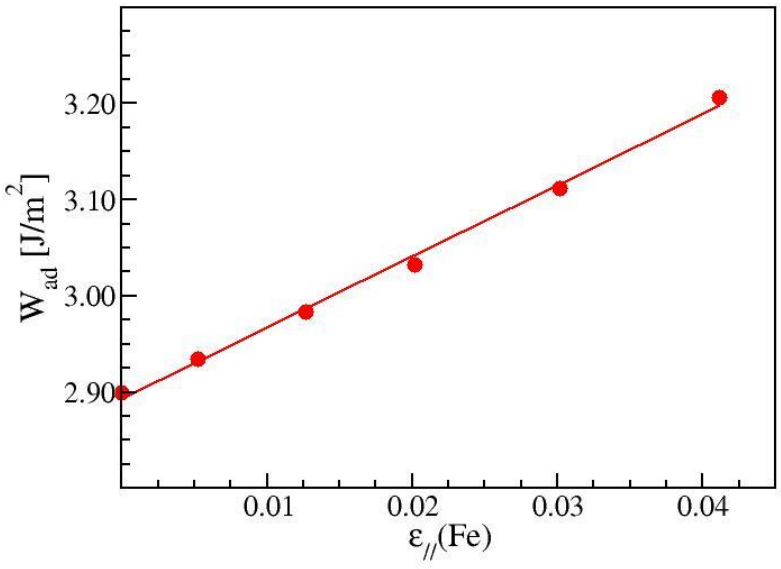
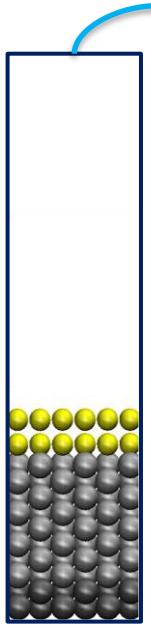
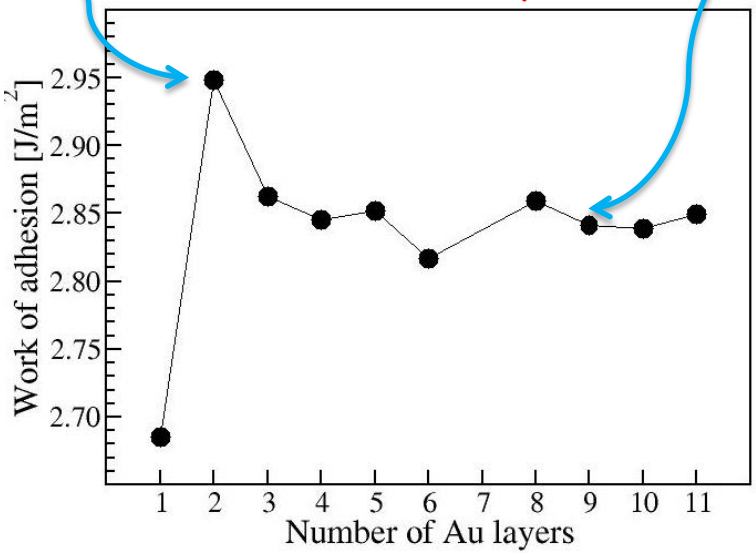
Work of adhesion W_{ad} as a function of the in-plane strain and of the number of Au planes

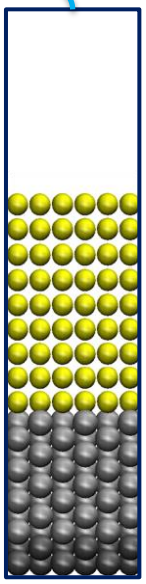
In-plane strain





Number of Au planes





- ✓ W_{ad} increases when the Fe substrate in strained
- ✓ Higher W_{ad} for 2 Au monolayers ➔strong coupling between the interface Fe orbitals and the surface Au orbitals

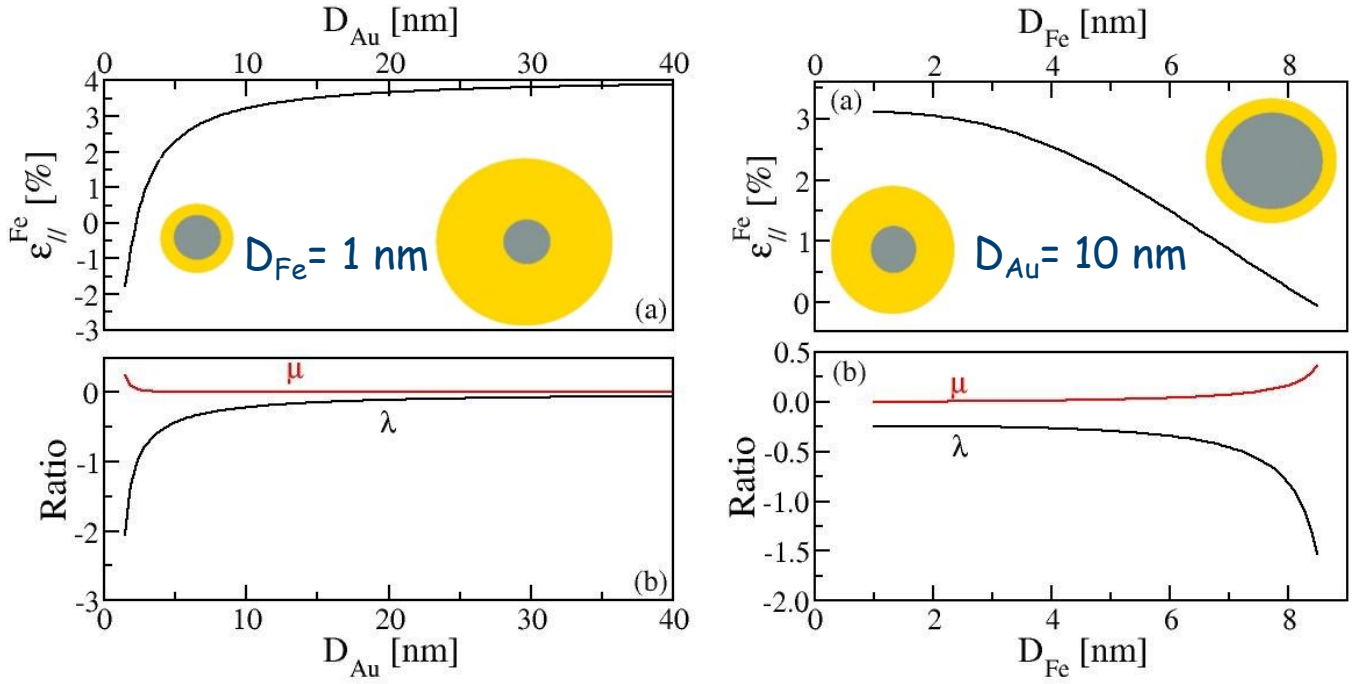
Core-shell Fe@Au Nanoparticles

M. Benoit, N. Combe, N. Tarrat, J. Morillo and M.-J. Casanove

➔DFT evaluation of the surface and interface energies and stresses

Inputs for a simple model:

- ✓ Evolution of the equilibrium strain state of the core as a function of the Fe/Au volume ratio
- ✓ Relative weight of the surface (λ) and interface (μ) elastic contributions



- ✓ Surface elastic effects are important for ∅ smaller 20 nm and are dominant for ∅ smaller than 2.3 nm
- ✓ Interface elastic effects can not be neglected for thin shells

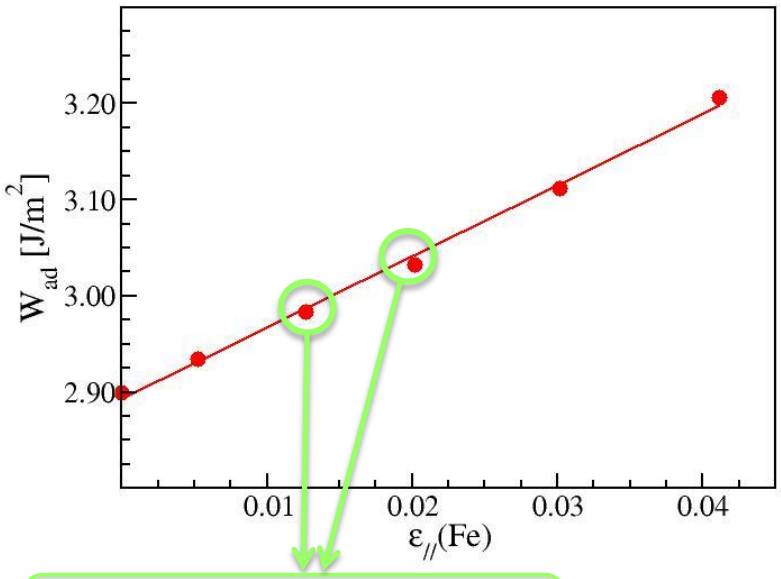
Core-shell Fe@Au Nanoparticles

M. Benoit, N. Combe, N. Tarrat, J. Morillo and M.-J. Casanove

HPC ressources:

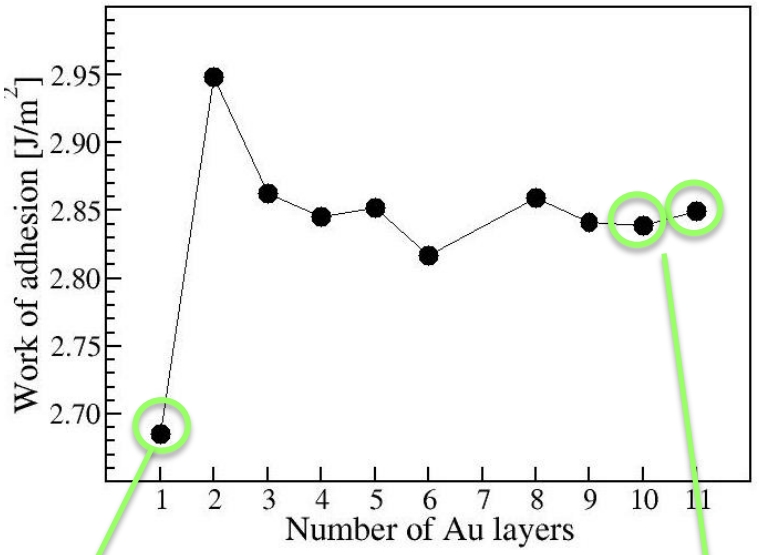
Calculations done on 64 or 128 cores on Hyperion (Calmip) and on Jade (Cines)

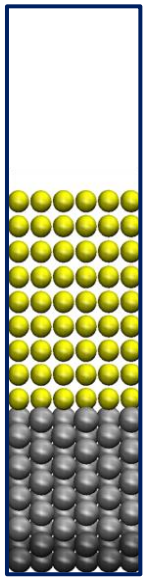
In-plane strain



~ 6000 h CPU (Calmip)

Number of Au planes





~ 2500 h CPU (Calmip)

~ 9000 h CPU (Calmip) and
~ 17 000 h CPU (Cines)

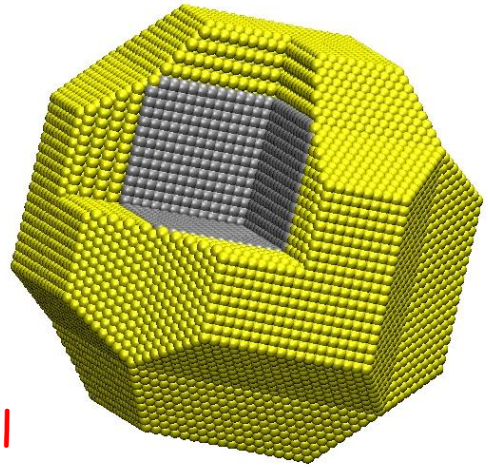
➔ A total of ≈ 100 000 h CPU for these two sets of points

➔ More than 150 000 h CPU for computing surface and interface energies and stresses for all facets

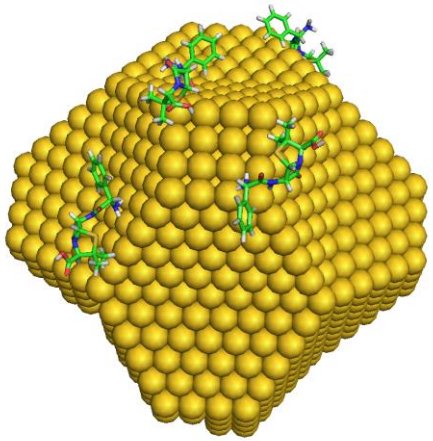
Core-shell Fe@Au Nanoparticles

M. Benoit, N. Combe, N. Tarrat, J. Morillo and M.-J. Casanove

- DFT modelling of an entire nanoparticle ?
  ➔Limited to a few hundred atoms…
- Critical size for the change of equilibrium morphology ~ ∅ 10 nm (≈ 100000 atoms !)



➔ Monte Carlo simulations with a semi-empirical potential
(with F. Calvo, Grenoble)



- DFT modelling of bio-molecules grafted on the NP surface ?
- Large size systems with electronic description

➔ Density-Functional Tight-binding (DFTB) of the NP-molecule system
(with M. Rapacioli, LCPQ, Toulouse)

Conclusion

DFT simulations of metallic nanoparticles:

✓ Access to electronic and magnetic properties

✓ Chemical interaction with the environment (ligands, solvent etc.)

But limited to small sizes !

➔ Because size effects are important around 5-10 nm, need for large scale calculations:

⇒ Large scale DFT calculations ? Localized orbitals ?

⇒ Approximate DFT ? DFTB…

⇒ (much) larger HPC ressources ?

Meanwhile, alternatives are developed ➔ multi-scale approach (electronic → atomistic)

- Fast and easy access to computing ressources is extremely important
- Direct contact with scientific computing engineers is a definite plus

➔ Mesocenters are essential for our work !

THANKS

- **Theory, DFT and DFTB calculations:**
  - Nicolas Combe (CEMES, Toulouse)
  - Hao Tang (CEMES, Toulouse)
  - Nathalie Tarrat (CEMES, Toulouse)
  - Joseph Morillo (CEMES, Toulouse)
  - Mathias Rapacioli (LCPQ, Toulouse)

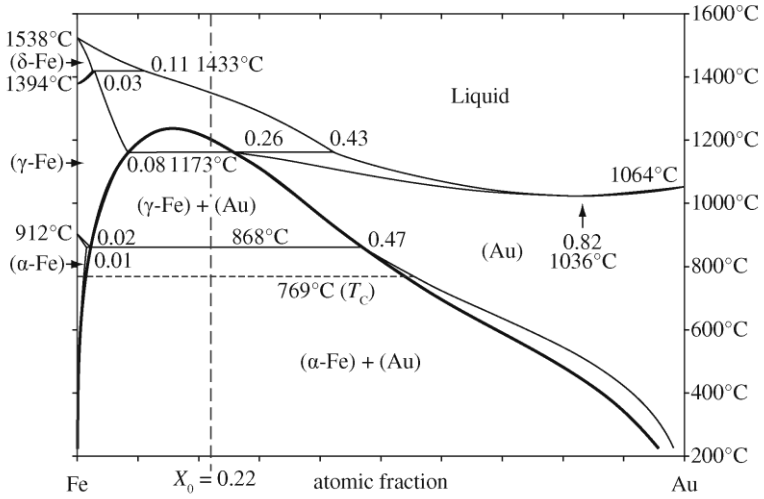
- **CALMIP team:**
  - Nicolas Renon
  - Pierrette Barbaresco
  - Boris Dintrans

- **COST Nanoalloys**
- **ANR SimNaNa**
- **Labex NEXT "CIM3" project**

C E M E S

- **Computer ressources:**
  - CALMIP (Regional center, Toulouse)
  - CINES (National center, Montpellier)
  - IDRIS (National center, Paris)

The Fe-Au system



	Lattice structure	Lattice constant	Atomic number	Average Surface energy
Fe	bcc	2.8665 Å	26	2360 mJ.m^{-2}
Au	fcc	4.0782 Å	79	1540 mJ.m^{-2}

- low miscibility at room temperature
- Au segregation at the surface

↳ *A good candidate for a core-shell Fe@Au chemical order*

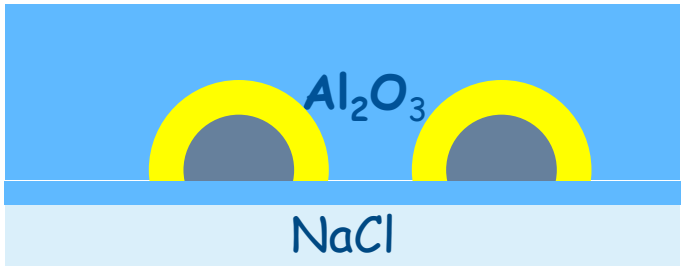
- Are Fe@Au particles experimentally feasible ?
- How is the Fe core modified (magnetism) ?
- Does the gold coating prevent from oxydation ?

Synthesis conditions

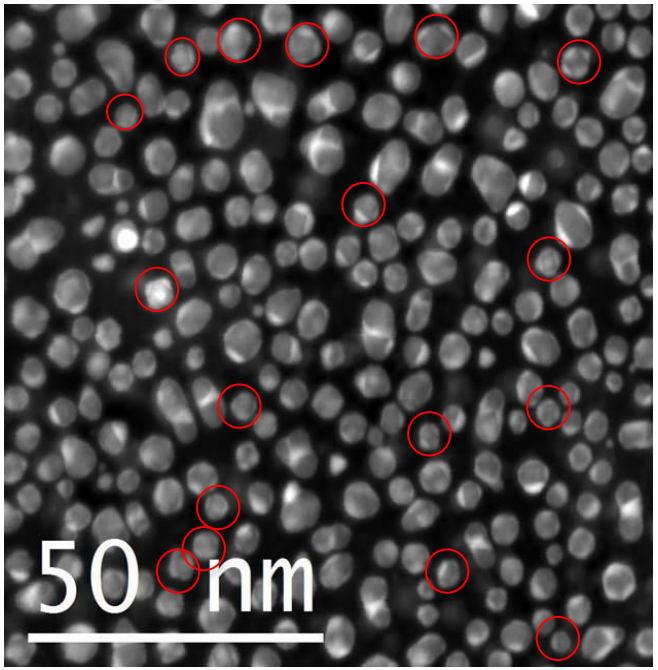
Sequential procedure by dc magnetron sputtering

Substrate : 5 nm Al_2O_3 **amorphous** film on NaCl substrate

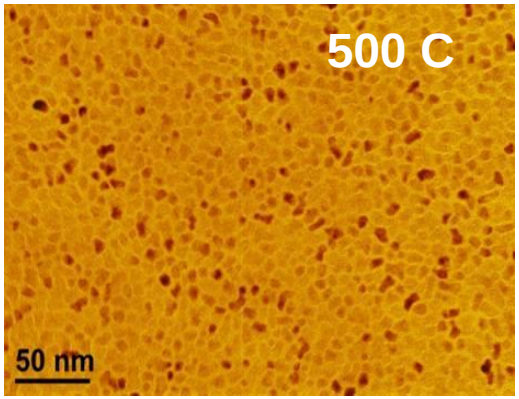
Capping layer : 5 nm Al_2O_3 **amorphous** film

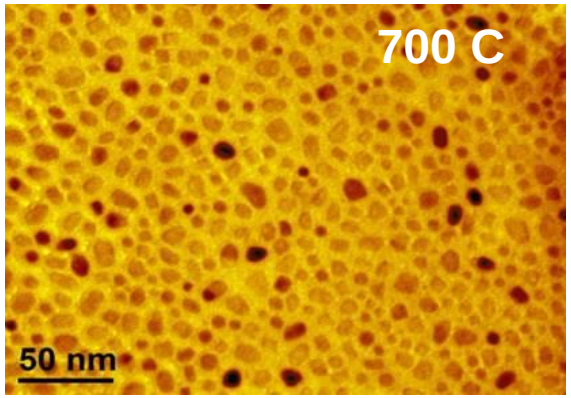


Au growth : avoid nucleation of pure Au particles ⇒ high T (optimized **800 C**)



Fe growth : 3D growth with neat facets requires a growth temperature **> 700 C**



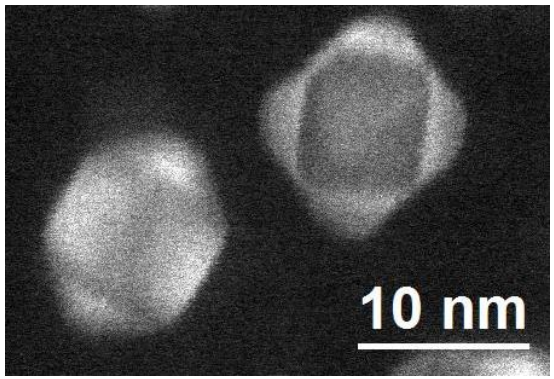


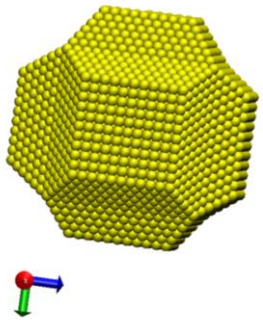
Fe : Deposited thickness 2 nm

Fe@Au : 2 nm @ 1nm

The Fe@Au Nanoparticles

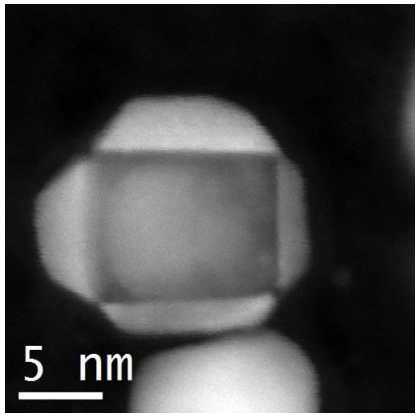
Iron nanocube size : 5- 10 nm



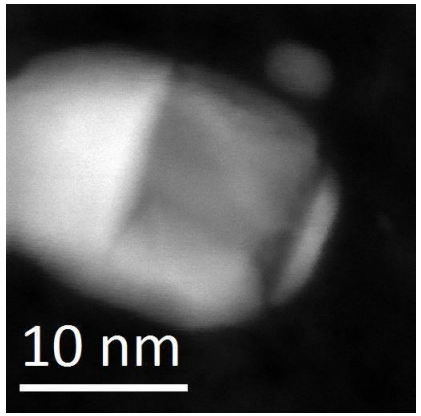


Regular

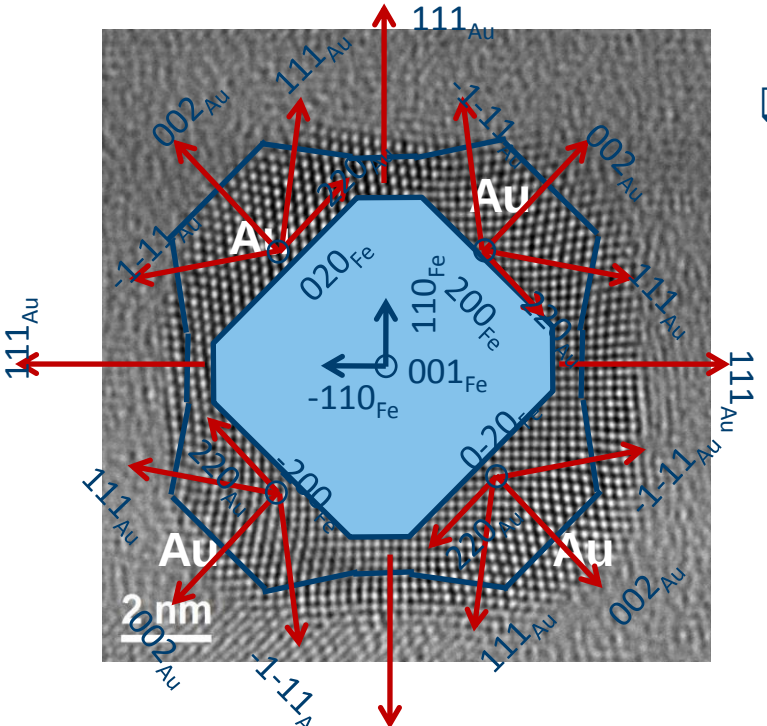
(Larger particles: grown directly on NaCl)



Irregular



Janus



- **{001} Fe facets** : $(001)_{Au}[100]_{Au}//(001)_{Fe}[110]_{Fe}$
- **{110} Fe facets** :$(111)_{Au}[1\text{-}10]_{Au}//(110)_{Fe}[001]_{Fe}$

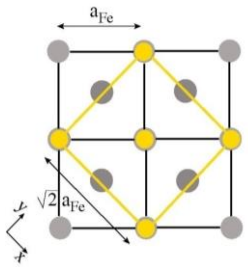
Equilibrium Morphology ?

Critical size?

What happens at the interface??

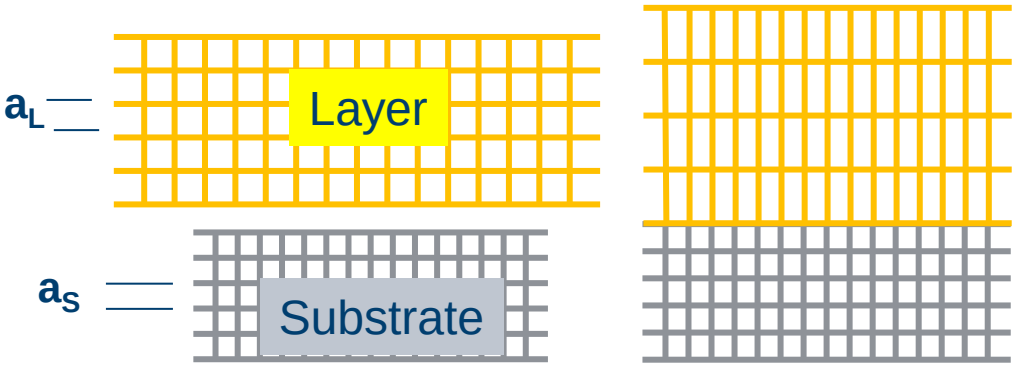
Growth under stress

Au grows on (100)Fe facets under compressive biaxial stress



In plane strain $\varepsilon_{//} = -\Delta a/a$

Out of plane strain $\varepsilon_{\perp} = -\frac{C_{11}}{2\,C_{12}}\,\varepsilon_{//}$

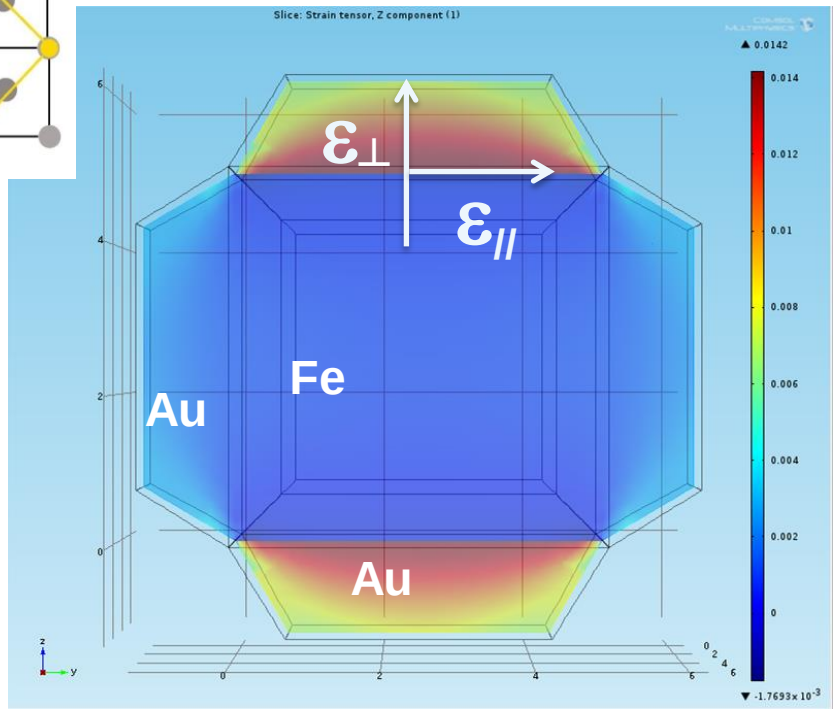


Misfit : $\Delta a/a = (a_L - a_S)/a_L = 0.60\ \%$

Au pyramides submitted to compressive biaxial stess $\varepsilon_{//}^{Au} = \mathbf{-\ 0.60\%}$

$\varepsilon_{\perp}^{Au} = \mathbf{1.02\%}$

Finite Elements



Simulated :

$\varepsilon_{//}^{Au} \sim -\ 0.5\%$

$\varepsilon_{\perp}^{Au} \sim 0.77\%$ at the interface

➔ Fe core- slightly expanded

Model of the Au(001)/Fe(001) interface

Spin-polarized DFT calculations* for Fe and the interface

Problem: what is good for Fe is bad for Au and vice-versa !!

➔Test of Exc functionals on the lattice constant, the bulk modulus, the (001) surface energy and the magnetic GS for Fe

	LDA	PBE	PW91	PBEsol	VdW-opt86b
Fe	✘	✓	✓	✘	✘
Au	✓	✘	✘	✓	✓

Choice of the good description of the substrate (Fe) but:

Lattice mismatch at the interface:

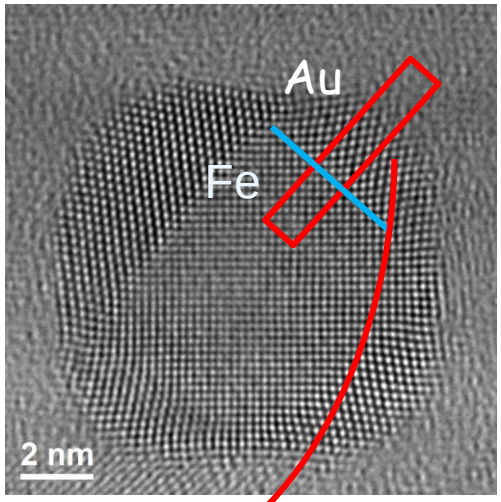
$$(a_{Au} - \sqrt{2}a_{Fe})/a_{Au}$$

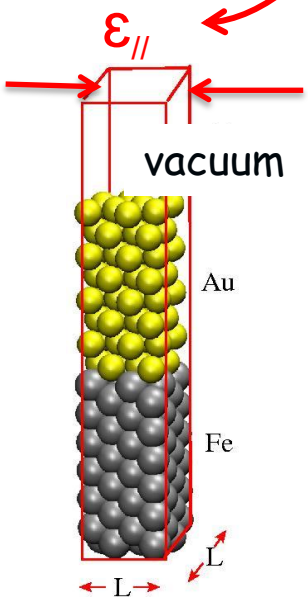
→ Exp = +0.60 %

→ PBE = +3.95 %

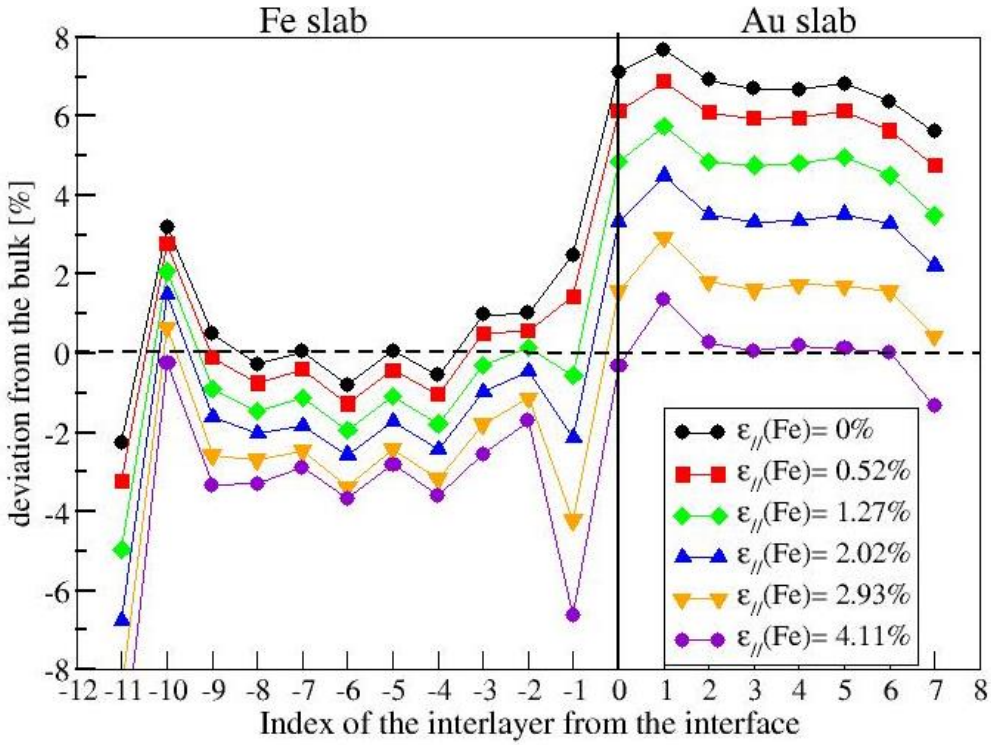
* VASP, PAW, Ecut = 600 eV, PBC, kpt 12x12x1 for slab calculations

The Au(001)/Fe(001) interface as a function of in-plane strain



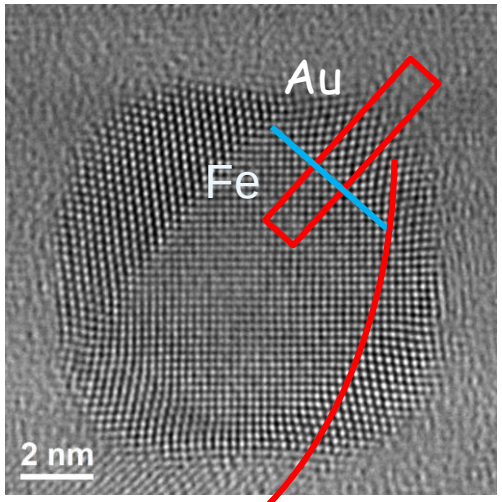


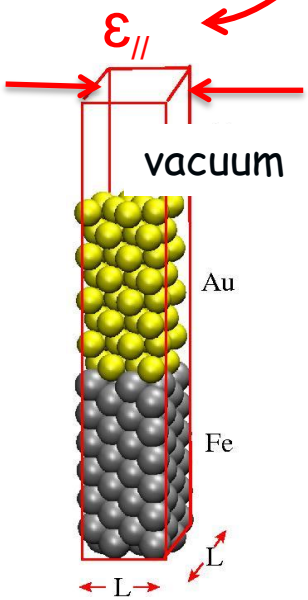
Interlayer distances



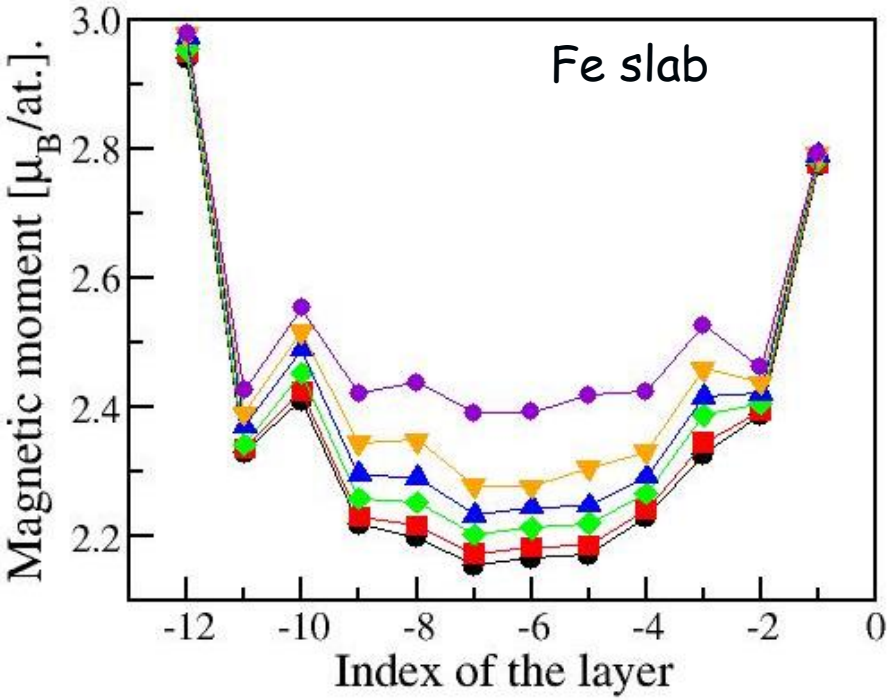
✓ Strong elastic effects due to the PBE misfit of +3.95%

The Au(001)/Fe(001) interface as a function of in-plane strain





Magnetic moments



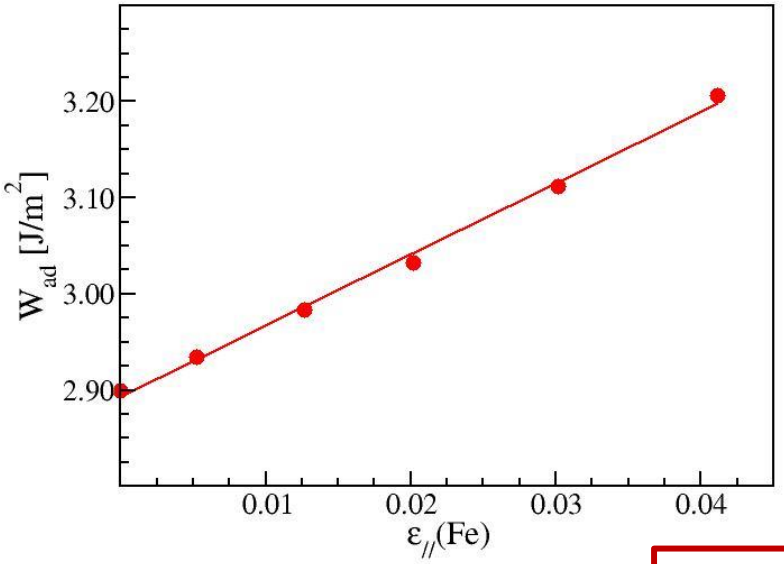
- ✓ Enhancement of the Fe magnetic moment at the interface
- ✓ Small magnetic moment of 0.6 μ_B/at. on Au atoms at the interface

The Au(001)/Fe(001) interface as a function of in-plane strain

The work of adhesion is the difference between the free slabs energies and the Au(001)/Fe(001) energy:

$$Wad = \left[E_{Fe(001)} + E_{Au(001)} - E_{Au(001)/Fe(001)}\right]/A$$
$$= \gamma_{001}(Fe) + \gamma_{001}(Au) + 2\,\sigma_{001}(Au)\varepsilon_{//}$$
$$+2\,\sigma_{001}(Fe)\varepsilon_{//} - \left(\gamma_{int} + 2\,\sigma_{int}\varepsilon_{//}\right)$$

W_{ad} as a function of in-plane strain $\varepsilon_{//}$ (for 8 Au planes)



➔Interface energy

- γ_{int}= 0.458 J/m^2 σ_{int} = - 0.532 J/m^2 (Fe as reference)

- γ_{int}= 0.389 J/m^2 σ_{int} = -0.401 J/m^2 (Au as reference)

➔Wetting parameter S >0

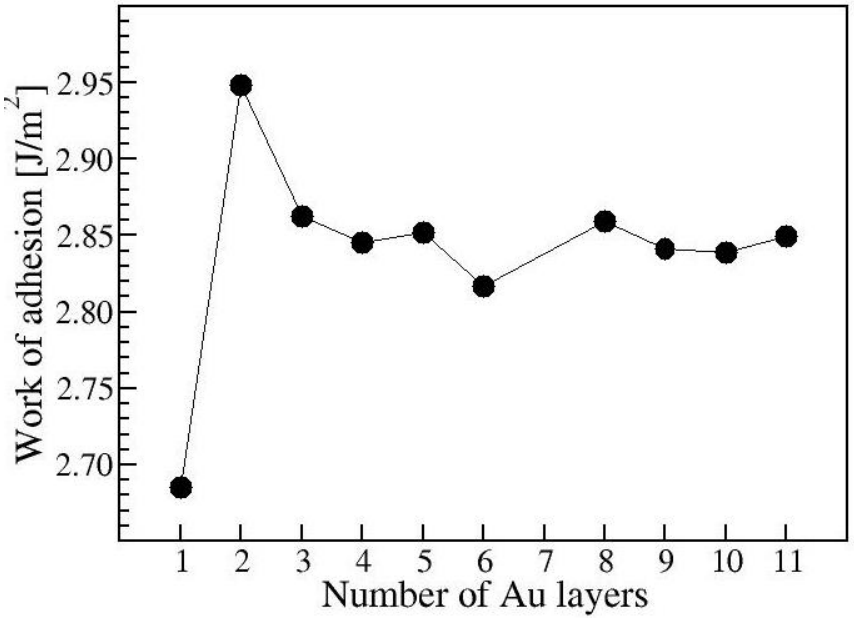
$$S = \gamma_{001}^{Fe} + 2\sigma_{001}^{Fe}\varepsilon_{//} - \gamma_{\text{int}} - 2\sigma_{\text{int}}\varepsilon_{//} - \gamma_{001}^{Au} - 2\sigma_{001}^{Au}\varepsilon_{//}$$

The (001)Au/(001)Fe interface as a function of the number of Au layers

The work of adhesion is the difference between the free slabs energies and the Au(001)/Fe(001) energy:

$$Wad = \left[E_{Fe(001)} + E_{Au(001)} - E_{Au(001)/Fe(001)}\right]/A$$
$$= \gamma_{001}(Fe) + \gamma_{001}(Au) + 2\,\sigma_{001}(Au)\varepsilon_{//}$$
$$+2\,\sigma_{001}(Fe)\varepsilon_{//} - \left(\gamma_{int} + 2\,\sigma_{int}\varepsilon_{//}\right)$$

W_{ad} as a function of the number of Au planes (for $\varepsilon_{//}$(Fe)= 0%)



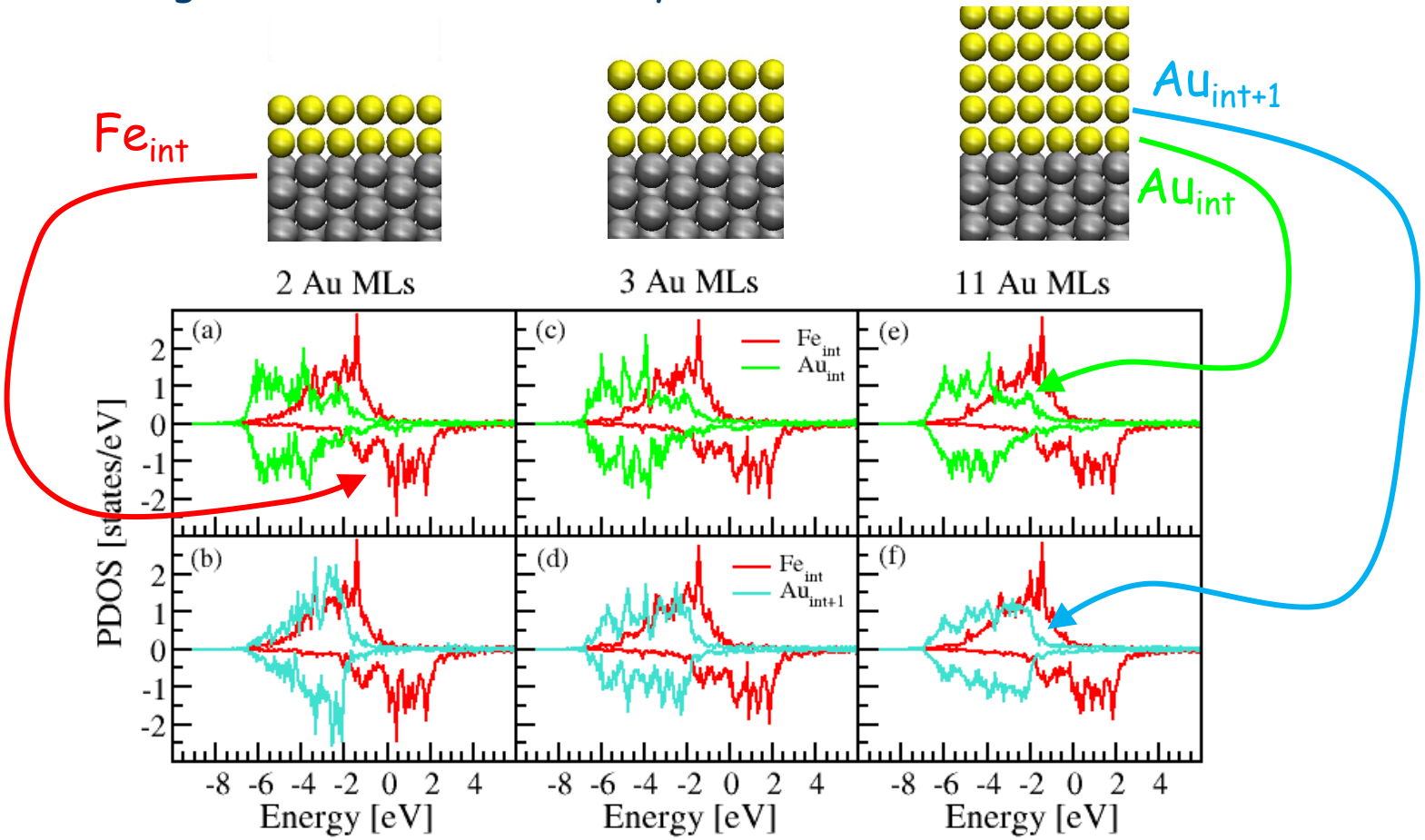
- ✓ W_{ad} is larger for 2 Au monolayers (MLs) → stronger interface bonding
- ✓ W_{ad} converges for 3-4 Au MLs:

$W_{ad} \approx 2.85$ J/m²

[VASP, PBE, Ecut = 600 eV, kpt=12x12x1]

The (001)Au/(001)Fe interface as a function of the number of Au layers

Projected densities of the *d* states onto selected atoms as a function of the Au coating (number of Au monolayers, MLs)



Stronger overlap between Fe_{int} and Au_{int+1} for 2 Au MLs

➔ maximum work of adhesion for this coating ➔ particle reactivity ?

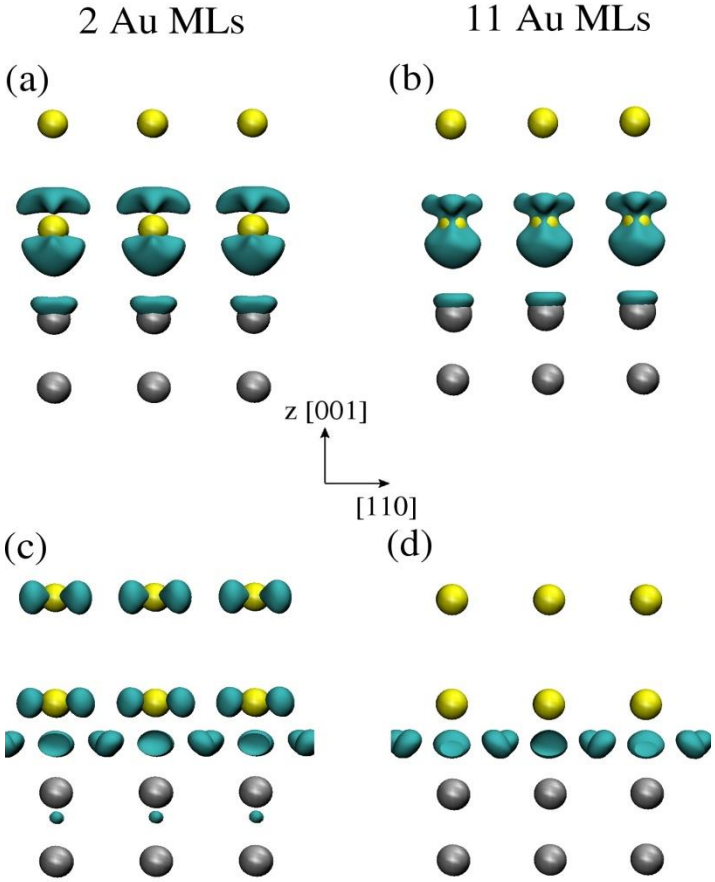
The (001)Au/(001)Fe interface as a function of the number of Au layers

Charge density difference:

ρ^*_{Au} and ρ^*_{Fe} are the charge densities of Au and Fe slabs with atoms fixed at their positions in the Au(001)/Fe(001) interface

$\Delta\rho > 0 \Rightarrow$ deficit of electrons due to the interface

$\Delta\rho < 0 \Rightarrow$ excess of electrons due to the interface



For a coating of 2 Au MLs:

- excess of electrons on the surface atoms
- stronger overlap between the Fe_{int} and the Au_{int+1} atoms

Conclusion and work in progress

Core@shell nanostructures synthesized through PVD techniques:

- cristalline nanoparticles with neat facets
- original morphologies – "growth on a nanosubstrate"

- DFT interface energy in agreement with particle morphology
- Strong enhancement of the Fe magnetic moment at the interface
- Stronger adhesion for 2 Au MLs, whatever the in-plane strain

➔ Implication for the nanoparticle reactivity ?

Perspectives:

- ✓ Simulating the whole nanoparticle (EAM pot., DFTB ?)
- ✓ Look at the Au(2 ML)/Fe reactivity

- DFT: M. Benoit et al., Phys. Rev. B **86**, 075460 (2012)
- Exp: M.-J. Casanove et al., in preparation

CEMES, Toulouse, France

Synthesis conditions

Sequential procedure by dc magnetron sputtering

Substrate : 5 nm Al_2O_3 **amorphous** film on NaCl substrate

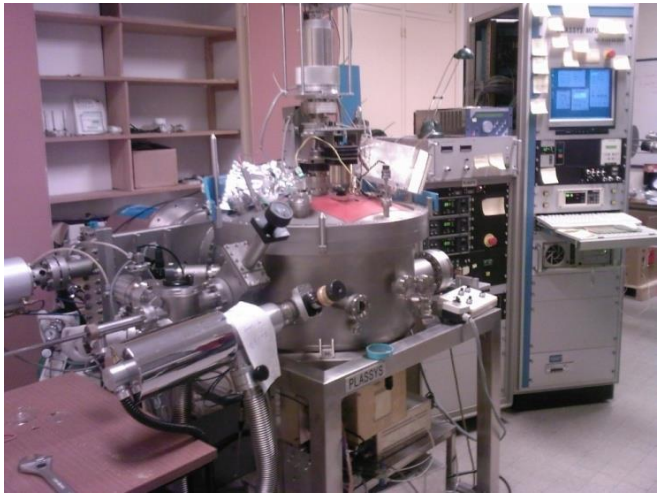
Capping layer : 5 nm Al_2O_3 **amorphous** film

1st step : Al_2O_3 substrate preparation (RT)

2nd step : Fe deposition

3rd step : Au deposition

4th step : Al_2O_3 capping layer (RT)



RF and DC Magnetron Sputtering