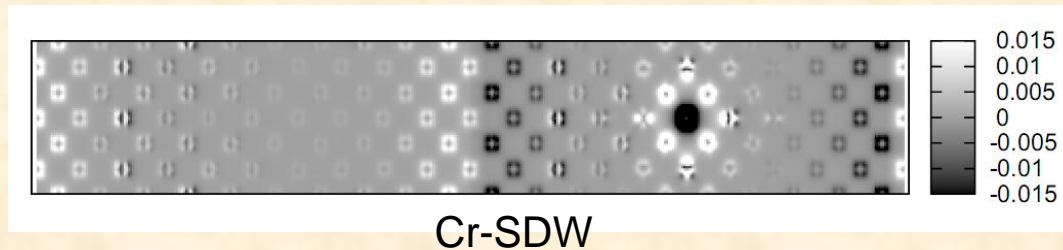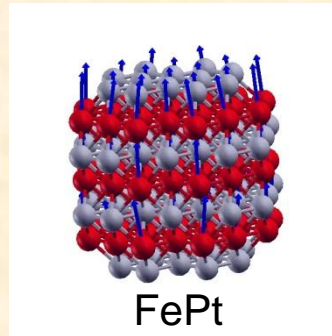# Correlation Between Magnetism and Structure in Fe alloys: the case of Fe-Cr and Fe-Pt
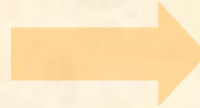
Cyrille Barreteau (SPCSI)
Chu Chun Fun (SRMP)
Romain Soulairol (SRMP)
Daniel Spanjaard (LPS)

FePt

Cr-SDW

Service de Physique et Chimie des Surfaces et Interfaces (**SPSCI**)
Service de Recherche sur la Métallurgie Physique (**SRMP**)
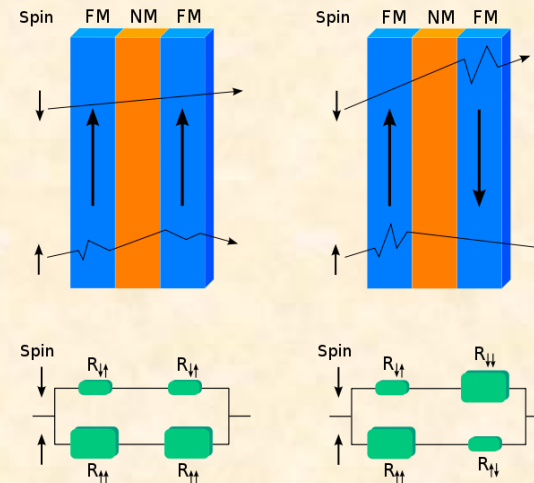Laboratoire de Physique des Solides (**LPS**)
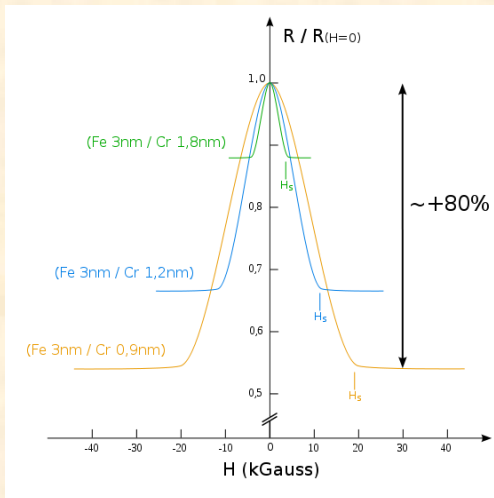
Why Fe-Cr

Material for nuclear industry
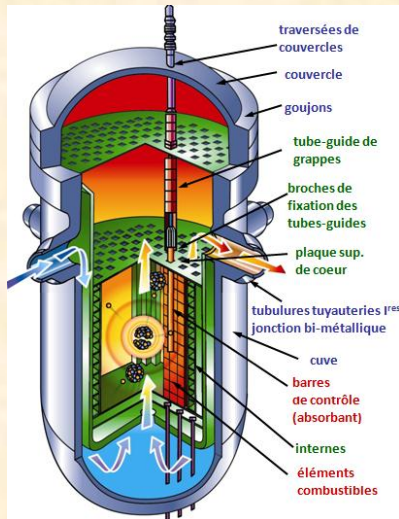
- **FeCr alloy: resistance to corrosion, and irradiation. Decrease of swelling**

- **Structure material for future nuclear reactors (fission, fusion).**

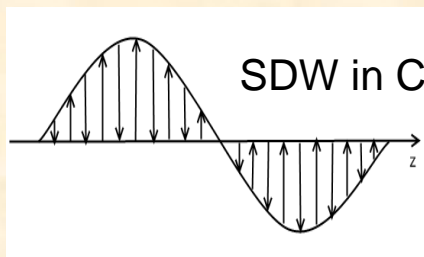**GMR in FeCr multilayers**
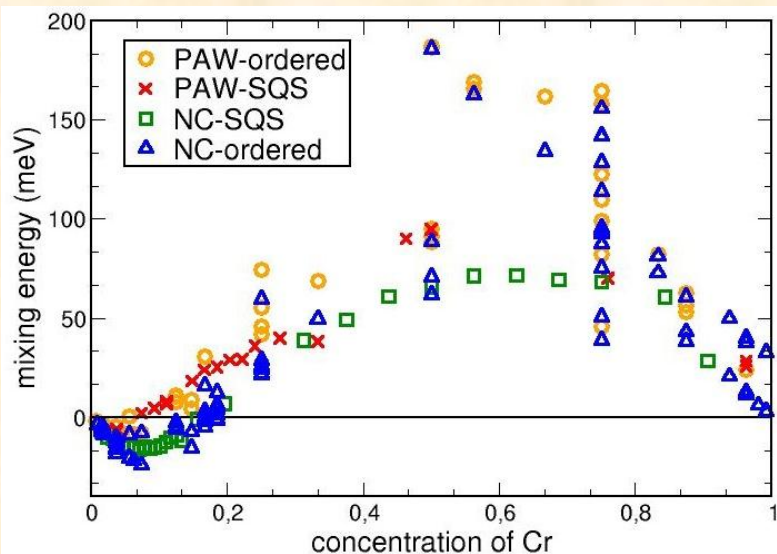
Why Fe-Cr

Complex magnetic order

Spin spiral in Fe fcc

SDW in Cr bcc

How magnetic order modifies the energetic of defects and vice versa..

Mixing energy

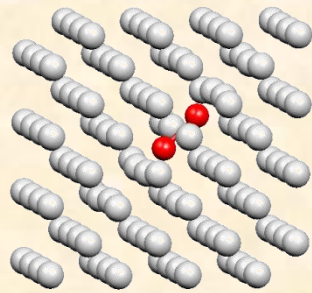Influence of magnetism on alloy properties
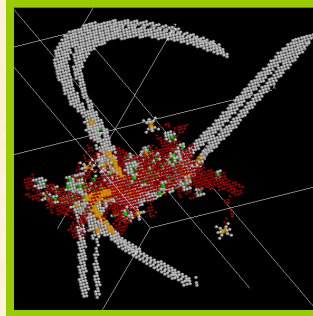
Methods

Simulated time

1h

1ns

0

DFT (SIESTA, PWSCF)   *Tight-Binding (TB)*

Molecular dynamics with semi-empirical potentials
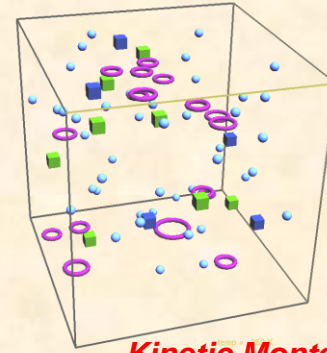
Kinetic Monte Carlo

Size of the system

100 at.   1000 at.   10nm   1μm

Code	DFT - PWscf	DFT - SIESTA	TB-Stoner
E_{XC}	GGA	GGA	-
Pseudopot.	NC, US, PAW	NC	-
Basis	Plane waves	Localized	Localized (spd)
Efficiency/precision	Very precise	Precise and efficient	Very efficient
Size of the system	< 500 at	< 1000 at	> 1000 at

Testing the methods

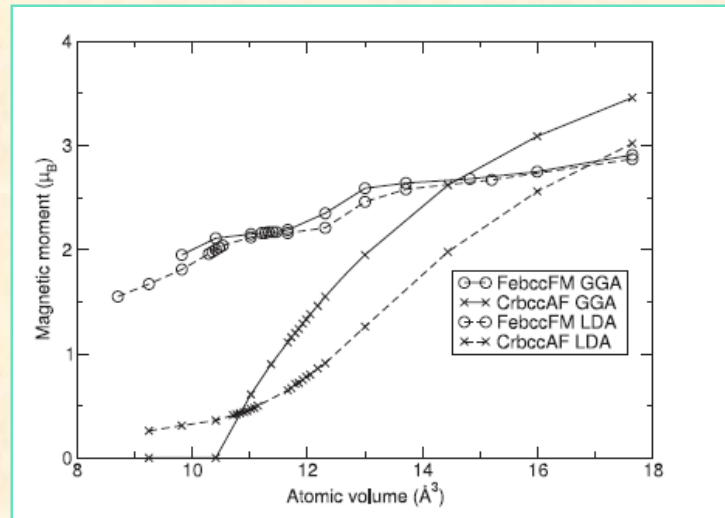## Functional Effect: LDA vs GGA (PWscf PAW)

E(d)
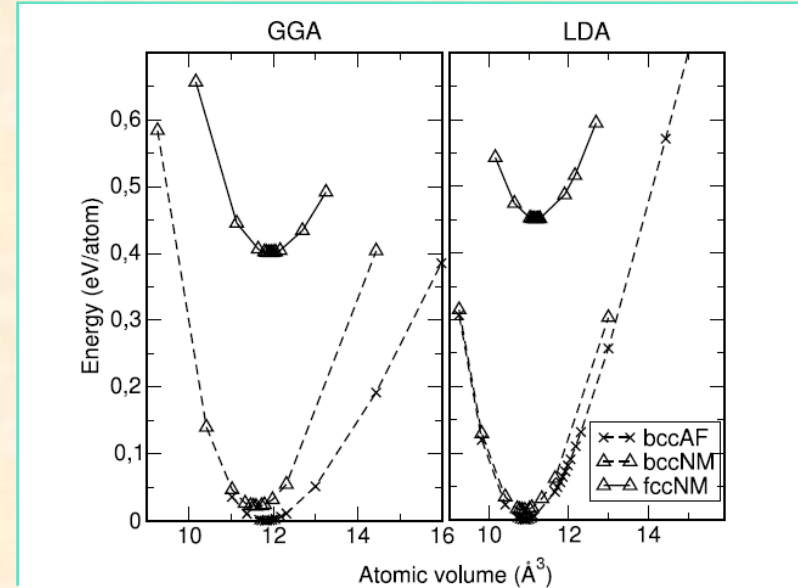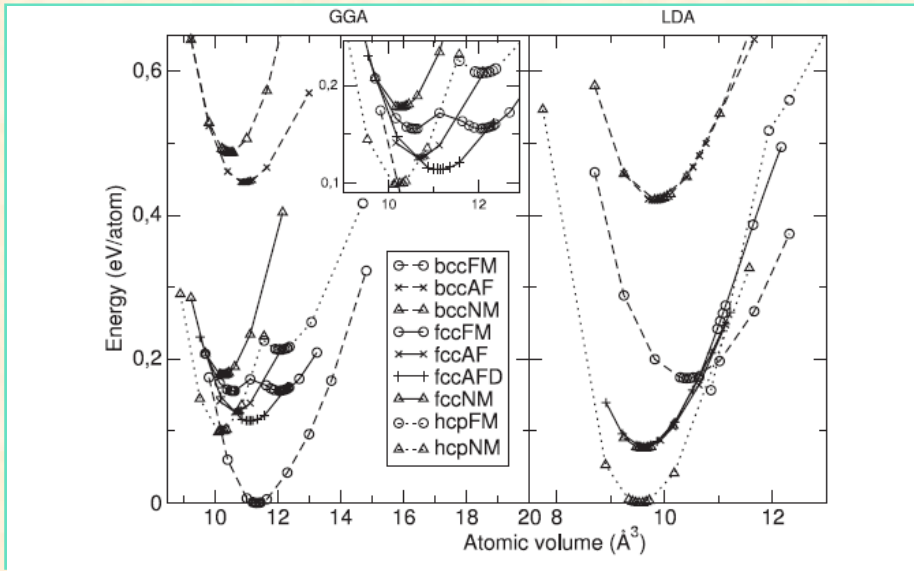
M(d)

Testing the methods

Pseudopotential Effect NC, US, PAW

ΔE(eV)

	GGA				LDA			
	NC/LCAO	PAW	US	NC	NC/LCAO	PAW	US	NC
FebccFM	0	0	0	0	0.13	0.17	0.13	0.16
FefccFM-HS	0.11	0.16	0.13	0.11	—	—	—	—
FefccFM-LS	0.20	0.16	0.18	0.22	—	—	—	—
FefccAF	0.15	0.13	0.14	0.17	0.07	—	—	—
FefccAFD	0.10	0.11	0.34	0.12	—	—	—	—
FehcpNM	0.17	0.10	0.11	0.19	0	0	0	0
CrbccAF	0	0	0	0	—	0	—	—
CrbccNM	0.03	0.02	0.02	0.04	0	0.01	0	0

$M(\mu_B)$

	GGA				LDA				
FebccFM	NC/LCAO	PAW	US	NC	NC/LCAO	PAW	US	NC	Exp. [16]
Exp. (2.86)	2.22	2.19	2.25	2.23	2.16	2.16	2.19	2.16	2.22
Calc.	2.25	2.17	2.23	2.27	2.08	2.00	2.12	2.06	2.22
(a)	(2.87)	(2.83)	(2.85)	(2.87)	(2.79)	(2.75)	(2.77)	(2.78)	

	GGA				LDA				
CrbccAF	NC/LCAO	PAW	US	NC	NC/LCAO	PAW	US	NC	Exp. [31]
Exp. (2.88)	1.39	1.29	1.25	1.66	0.59	0.75	0	0.78	0.5
Calc.	1.39	1.20	1.30	1.70	0	0.44	0	0	0.5
(a)	(2.88)	(2.87)	(2.88)	(2.89)	(—)	(2.79)	(—)	(—)	

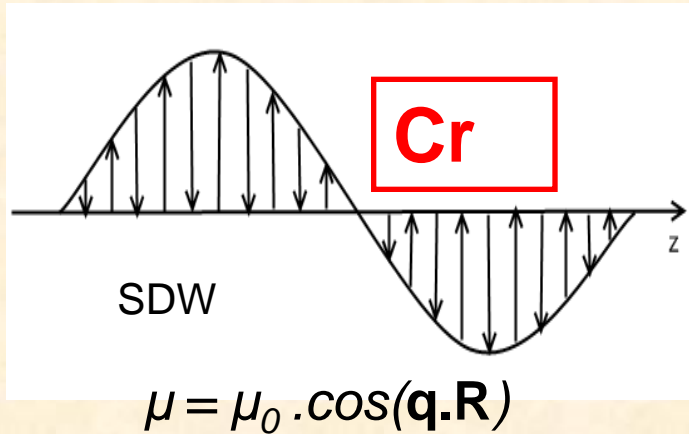# Testing the methods

Basis Effect

NC (PWscf)~NC(Siesta) if the localized basis is well optimized

Basis 1: DZ(2s), SZ(3p) SZ(5d)= 10 orbitals

Basis 2: DZ(2s), SZ(3p) SDZP(10d)= 15 orbitals
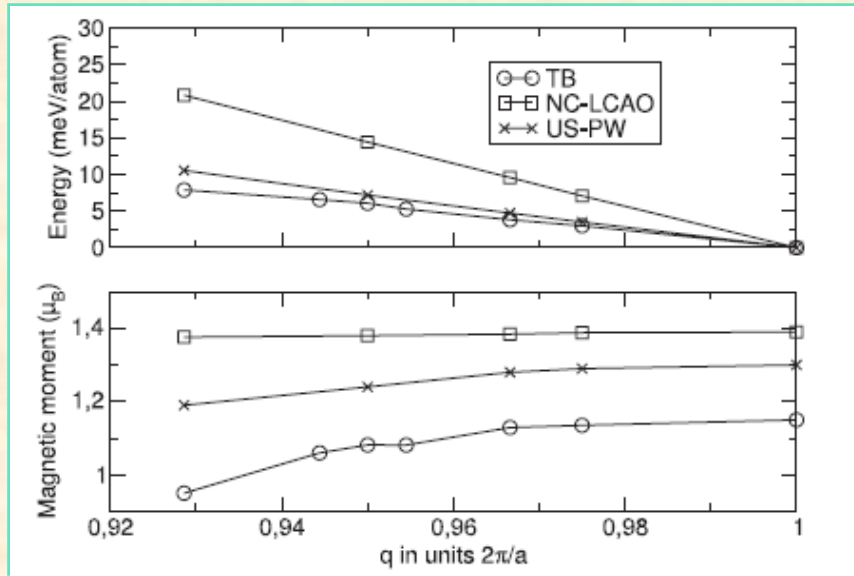
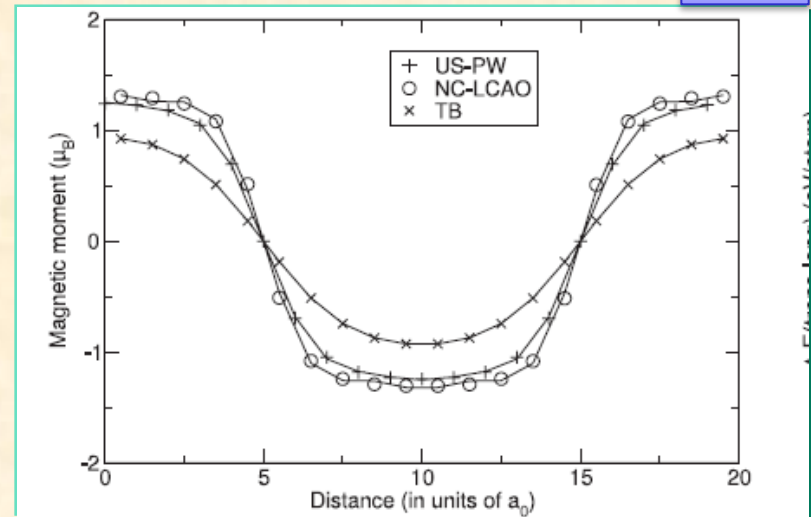Minimimal Basis seems accurate enough!

Ground state of Cr: SDW!!

SDW

Cr

$$\mu = \mu_0 . cos(\mathbf{q}.\mathbf{R})$$

Experimental observation by neutron scattering (Corliss, 1959) : direction (001) et q ≈ 0,953.

SDW is never stabilized

$\Delta E(q)$

$M(z)$

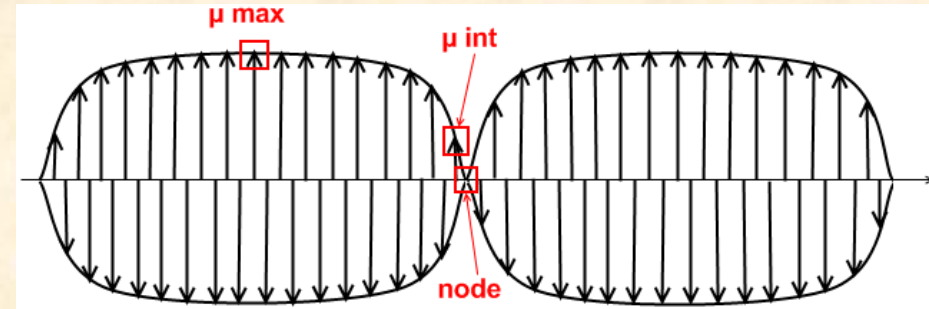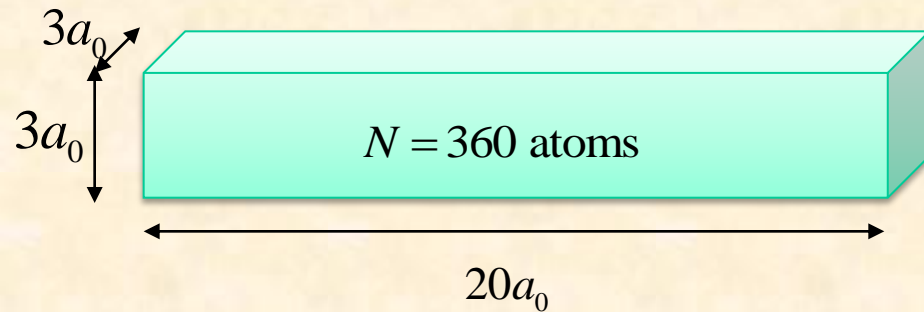# Vacancy formation energy in Cr SDW

$3a_0$

$3a_0$

$N = 360$ atoms

$20a_0$

$$E_V^f(Cr) = E\left((n-1)Cr, V\right) - \frac{(n-1)}{n} E(nCr)$$

Position V	AF	NM	SDW-nœud	SDW- site inter.	SDW-site max.	Exp.*
E^f_V (eV)	2.41	2.32	2.09	2.10	2.38	2.0

* Landolt-Börnstein, PAS experiments (1985)

SIESTA

Vacancy formation is easier in a SDW node

Vacancy migration energy in Cr SDW
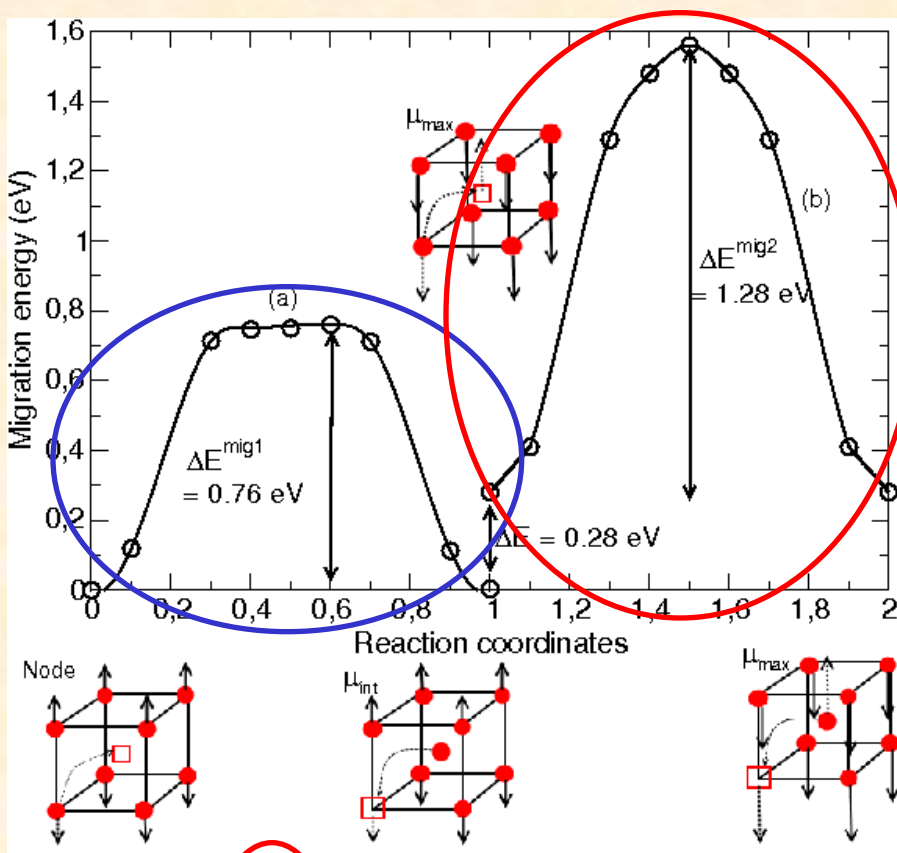
Cr	AF	NM	SDW-site μ_{max}	SDW-nœud
E^{mig}_{Vac} (eV)	1.32	0.82	1.28	0.76

- Migration energy lower in SDW :
  E^{mig}_{Vac}(SDW) < E^{mig}_{Vac}(AF, NM)

- Anisotropy of migration energy in SDW:
  E^{mig}_{Vac}(SDW node) < E^{mig}_{Vac}(SDW μ_{max})
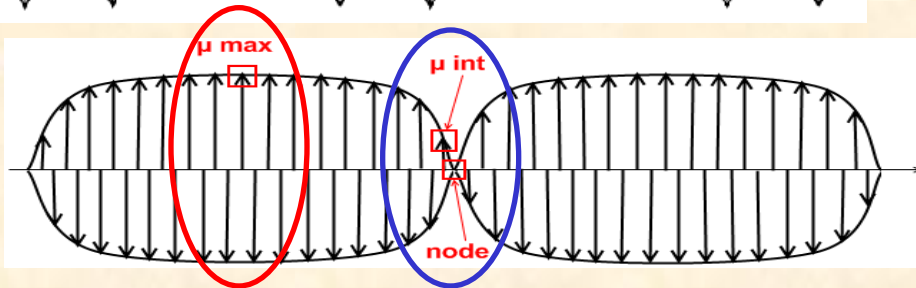
Soulairol, Fu and Barreteau, PRB 83, 214103 (2011)

# Solution energy of Fe in Cr SDW

Strongly magnetic impurity: Fe
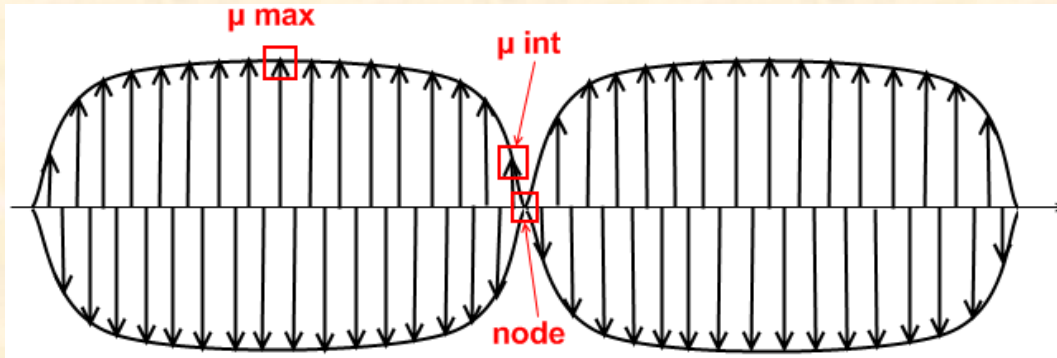
Position	AF	NM	SDW-nœud	SDW- site inter.	SDW-site max
E^{sol}_{Fe} (eV)	0.38	0.29	0.27	0.28	0.39

SIESTA

• The solution energies are lower in the SDW.

• But ΔE(AF-SDW) is rather low for Fe (< ΔE(AF-SDW) for Cu)

➔ Magnetic frustration of Fe in Cr : 2 possible spin states, μ_{Fe} = 0 ou 2 μ_B. Multiples metastable solution when %Fe ↑.

• SDW experimentally stable for %Fe < 1.6% ➔ understanding the destruction mechanism of the SDW

FeCr Interfaces

Interface energies
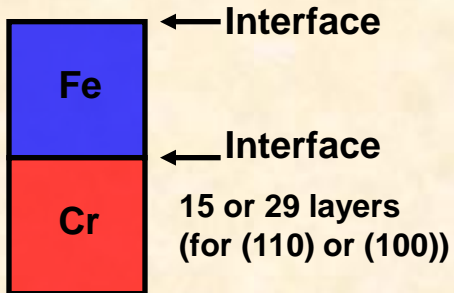
$E^f_{interface}$ (J/ m²)	AF Cr	NM Cr	NCol.	Cr (100) SDW
Fe/Cr (100)	0.108	0.135	0.171	0.102
Fe/Cr (110)	0.189	0.091	0.174	0.115
Fe/Cr (111)	0.134	0.123	0.194	-

SIESTA

Fe
← **Interface**

Cr
← **Interface**
15 or 29 layers
(for (110) or (100))

• **Fe/Cr (100) interface is stabilized by magnetic effect contrary to the (110) interface**

➔ **Magnetic frustration** **Fe-Fe** **Fe-Cr** **Cr-Cr**
↑ ↑ ↑ ↓ ↑ ↓

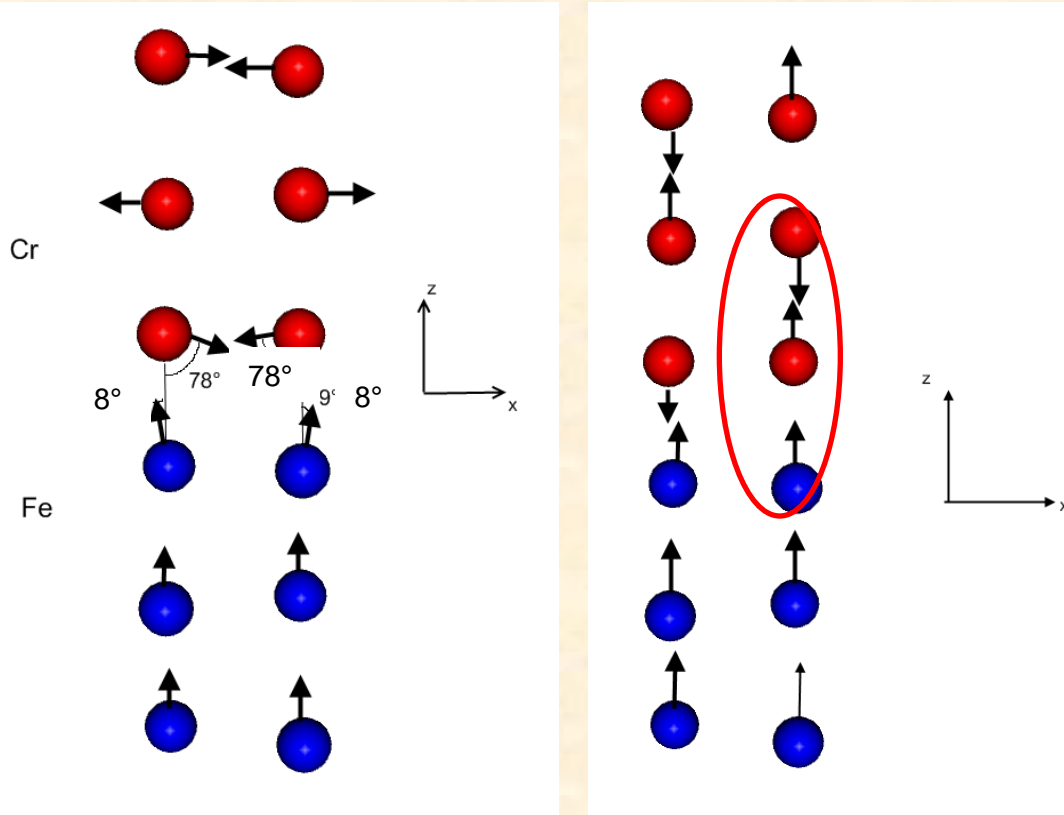• **Two possible ways of relaxing the magnetic frustration:**

➔ **SDW with NM nodes near the interface (exp. :** Bödeker *et al.* PRL, **81,** 914**)**

➔ **Non collinear configurations (exp. :** Fritzsche *et al.* PRB, **65,** 144408**)**

FeCr Interfaces

Interface magnetic configurations
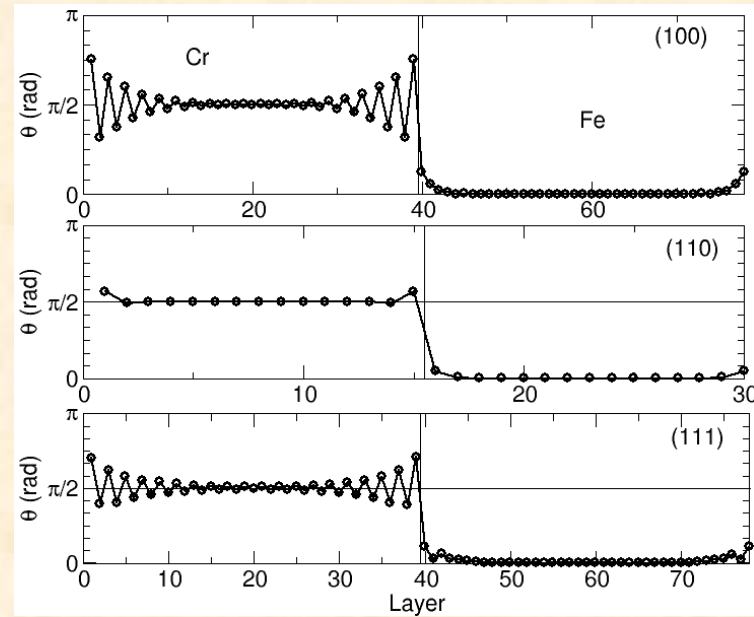
Non collinear

Collinear

E^f (NCol.)   < E^f (Col.)

0.174 J/m²   0.189 J/m²

• Non collinearity lowers interface energy in Fe/Cr (110).

• Perpendicular magnetic coupling between Fe and Cr

Cr clusters in Fe matrix

$Fe_X Cr_Y$	$Fe_{123}Cr_5$	$Fe_{121}Cr_7$	$Fe_{115}Cr_{13}$
ΔE(Col - NCol) (meV/Cr ou Fe)	0	0	7

SIESTA

• Collinear configurations for small Cr clusters in an Fe matrix (N_{Cr}= 5 and 7)

• Possible non collinear configurations of slightly lower energies for clusters of intermediate sizes (N_{Cr}=13) [Longo *et al.* PRB 77, 212406 (2008) and Robles *et al.* PRB 74, 094403 (2006)]

• Possible non collinear configurations of slightly lower energies for clusters with (110) facets


Cr
Fe

Z

$N_{Cr} = 5$ $N_{Cr} = 7$ $N_{Cr} = 13$

Fe clusters in Cr matrix
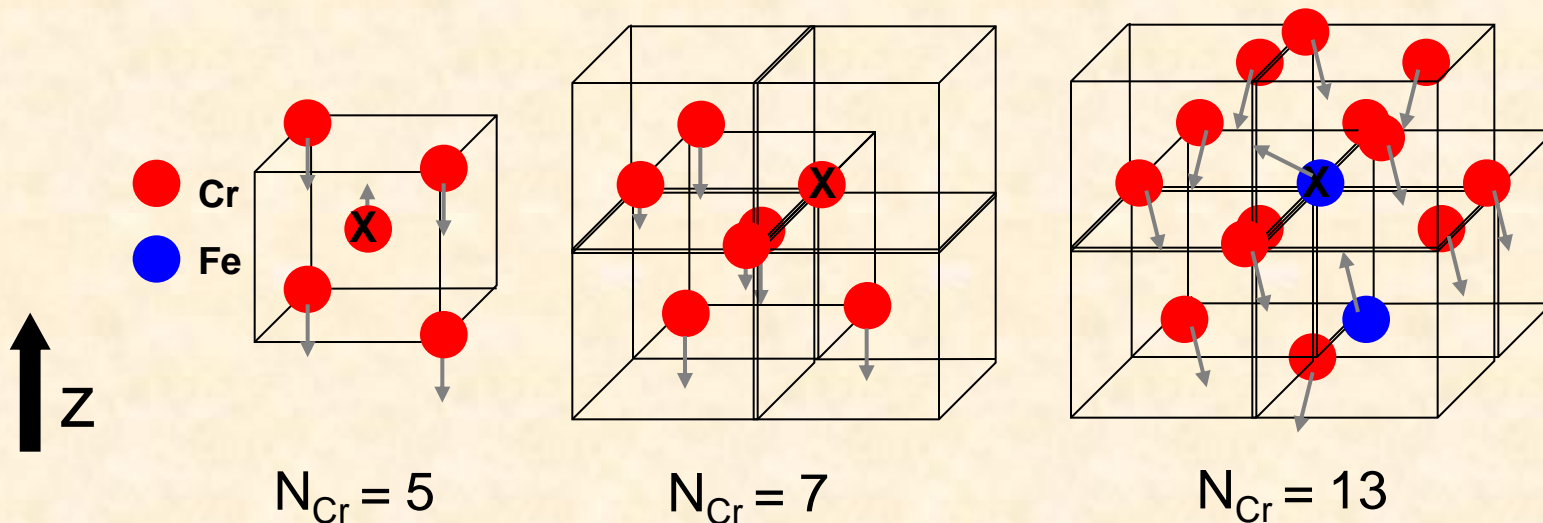
+ attraction
- répulsion

Fe-Fe interaction energy

Environnement Cr	AF	AF'	NCol.	SDW- node
E^b_{Fe-Fe} (eV)	- 0.01	- 0.04	+ 0.07	+ 0.12
μ_{Fe1} (μ_B)	2.26	0.07	1.89	2.06
μ_{Fe2} (μ_B)	0.67	0.06	1.88	2.04

- **Multiple magnetic states for Fe dimer in Cr.**
- **Precipitation of Fe is favored in Cr SDW.**
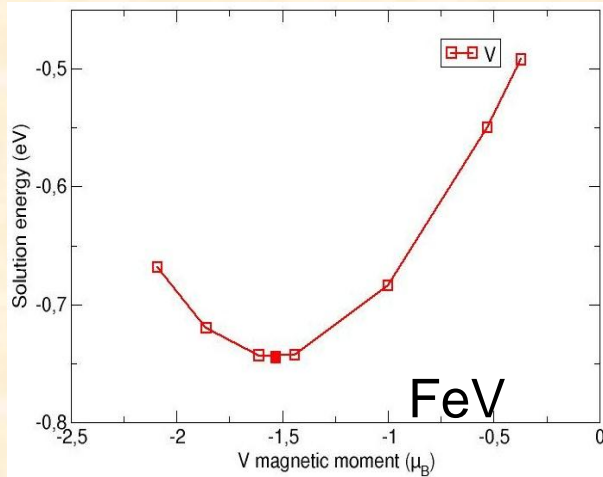- **Configurations non colinéaires de faible énergie pour les clusters avec facettes (110).**

[001]

AF   **AF'**   **NCol.**   **SDW node**

FeX alloys

M. Levesque PhD.
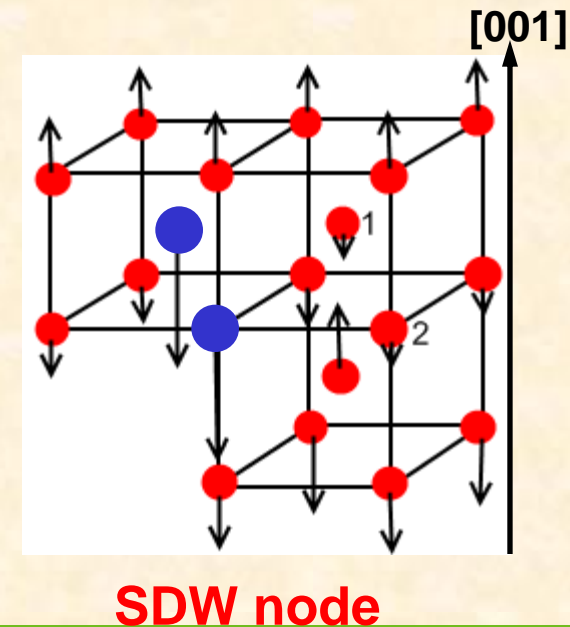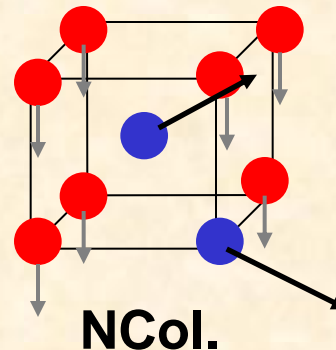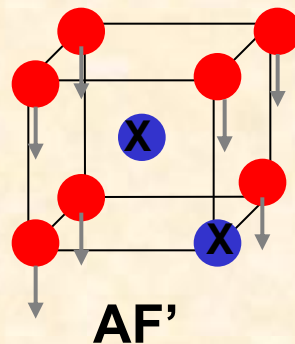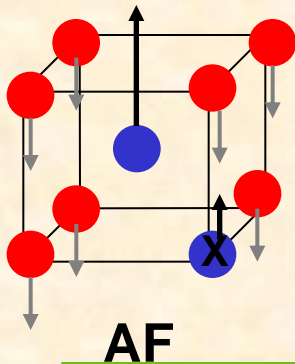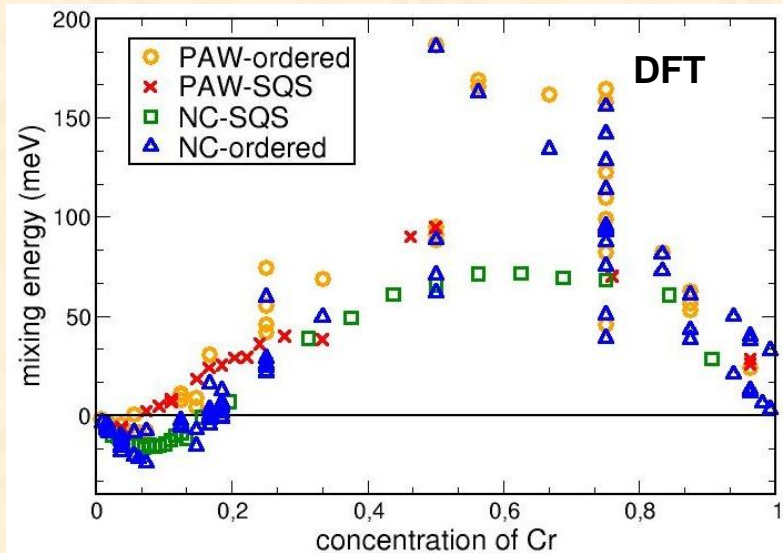
Mixing energy calculated at P=0

(Cr exp. [Mirebeau *et al.,* PRL 53, 687 (1984)])

Some trends in the periodic table

	FeV	**FeCr**	**FeMn**
ΔEsol	-	- puis +	+
$N^d_{Fe} - N^d_X$	3	2	1
$\Delta\mu = \mu_{sol} - \mu_{bulk}$ (μ_B)	1,53	1.00	0,85

FeX alloys

$$\Delta E_{sol} = E\left[(n-1)Fe, Cr\right] - (n-1)E(Fe) - E(Cr) \qquad V, Cr, Mn = 1.85\% at$$

FeV

FeCr

FeMn
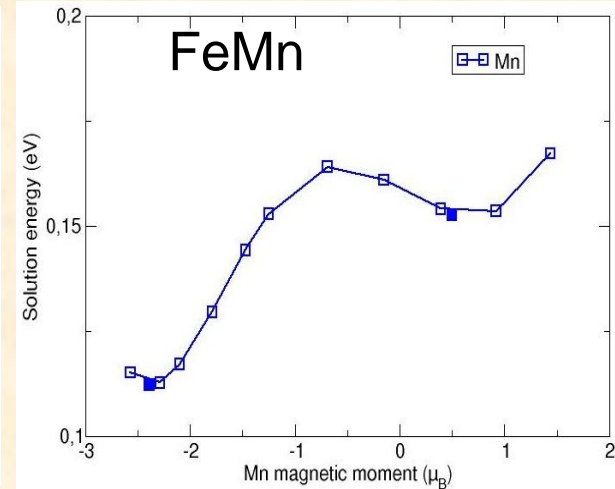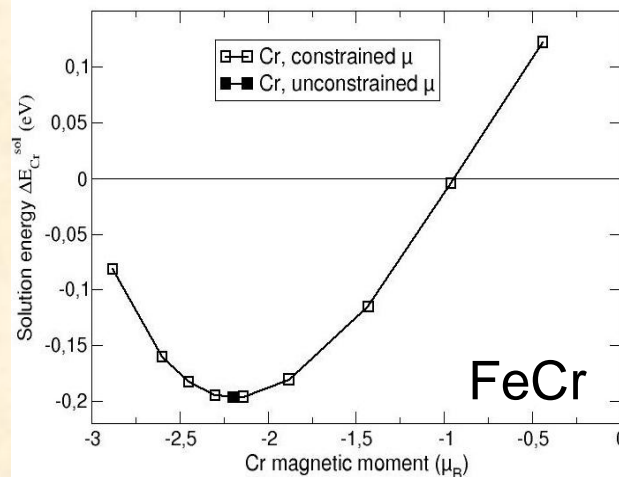
PWscf

- **Effet of d band filling on the solubility of V, Cr et Mn in Fe**

- **AF interaction between Fe and Cr, Mn or V favors AF solutions**

FeCr: intermédiate case : magnétisme is the driving force

$\mu_{Cr} < - 0.8\mu_B$ ➔ **mixing** $\mu_{Cr} > - 0.8\mu_B$ ➔ **demixing**

Partial Conclusion

•Fe-Cr is a particularly complex system where magnetism plays a crucial role
In the energetics.

Questions and Comments

• Can we stabilize the SDW (Fermi Surface Nesting?)

•   How could we introduce (spin and ion) temperature effects?

•   Need for simpler models?

FePt L10

FePt phase diagram

Calculated Fe-Pt phase diagram assessed by 2001 P.Fredriksson

NIMS
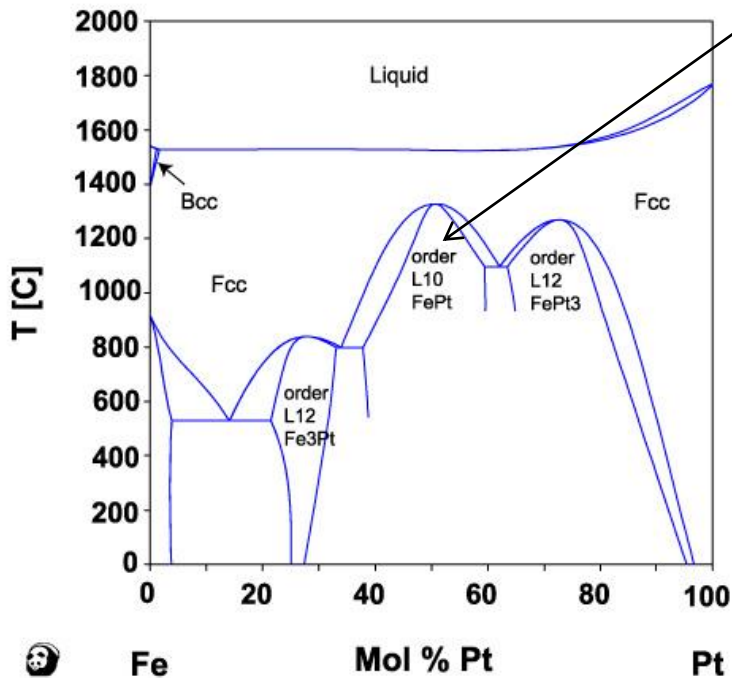
L10 structure
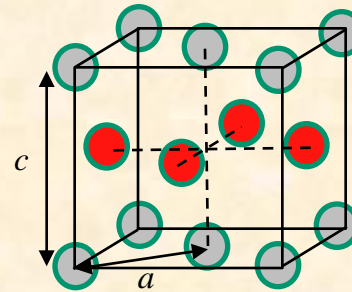
$$a_{exp} = \frac{3.86}{\sqrt{2}} = 2.73A$$

$$c_{exp} = 3.72A$$

$$\frac{c_{exp}}{a_{exp}} = 1.36$$

$$V_{exp} = 27.7A^3$$

very high magnetic uniaxial anisotropy

MAE=1.4meV/atom (exp.)

Good control of nanocrystal growth
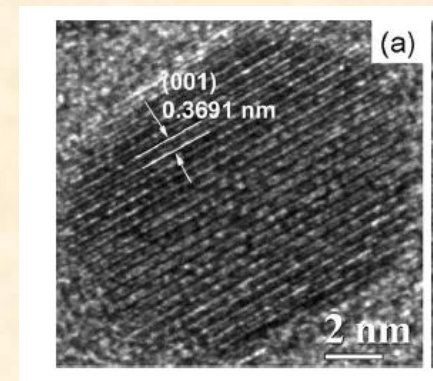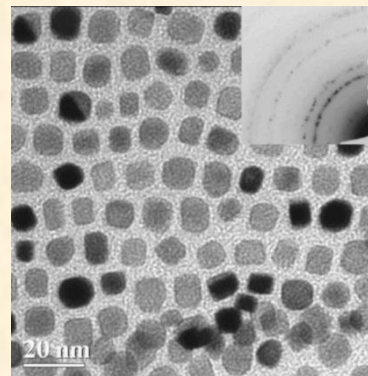
Magnetic TB model

$$H = H_0 + H_{mag} + H_{LCN} + H_{SOC}$$

• H_0: spd Tight-Binding (non magnetic)Hamiltonian

• H_{mag}: Stoner Hamiltonian

$$H_{mag} = -\frac{1}{2}\sum_{i\lambda} I_{i\lambda} \vec{m}_{i\lambda} . \vec{\sigma}$$

• H_{LCN}: local charge neutrality constraint

$$H_{LCN} = \sum_{i\lambda} U_{LCN}(n_i - n_i^0)|i\lambda\rangle\langle i\lambda| + \sum_{i\lambda \notin d} U_d(n_{i,d} - n_{i,d}^0)|i\lambda\rangle\langle i\lambda|$$
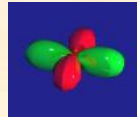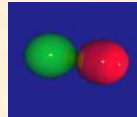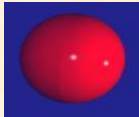
• H_{SOC}: Spin Orbit Coupling

$$H_{SOC} = \sum_i \xi_i(r - R_i)\vec{L}_i . \vec{S} \qquad \xi_{d,i} = \int_0^\infty R_{d,i}^2(r) r^2 dr$$

Determination of parameters

$$H_0 = \sum_{ij\lambda\mu} |i\lambda\rangle\langle i\lambda|H|j\mu\rangle\langle j\mu|$$

i=atom
λ=orbital
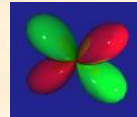
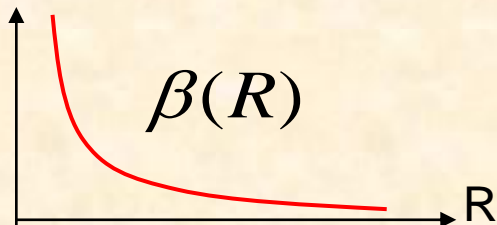| $\lambda =$ | s | p_x | p_y | p_z | d_{xy} | d_{xz} | d_{xz} | $d_{x^2-y^2}$ | $d_{3z^2-r^2}$ |

Hopping integral

Onsite term

$$\beta_{ij}^{\lambda\mu} = \langle i\lambda|H|j\mu\rangle$$

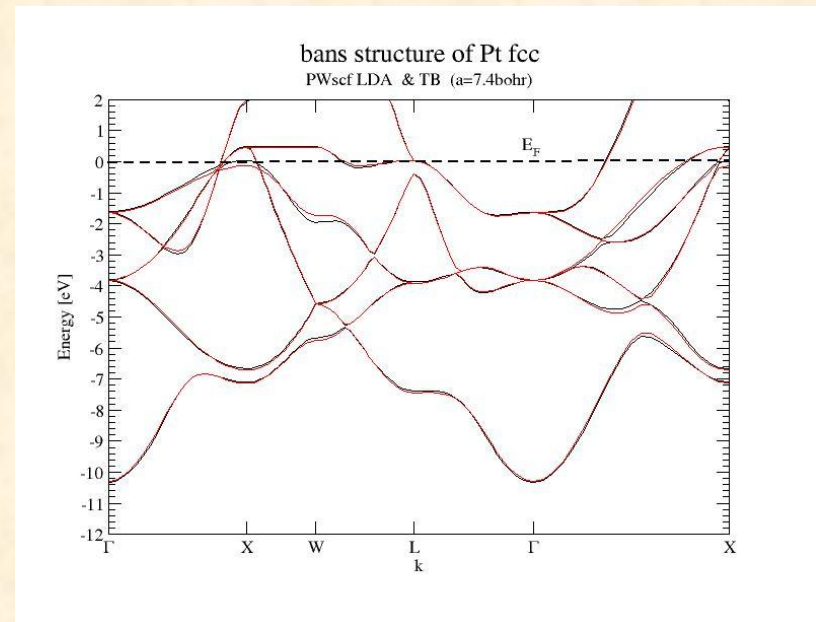$$\varepsilon_{i\lambda} = \langle i\lambda|H|i\lambda\rangle$$

$\beta(R)$

R

Determination of parameters

- H_0: Hopping integrals and onsite elements obtained from simultaneous fit of ab-initio **band structure** and **total energy** curves of **bulk non magnetic Fe and Pt**
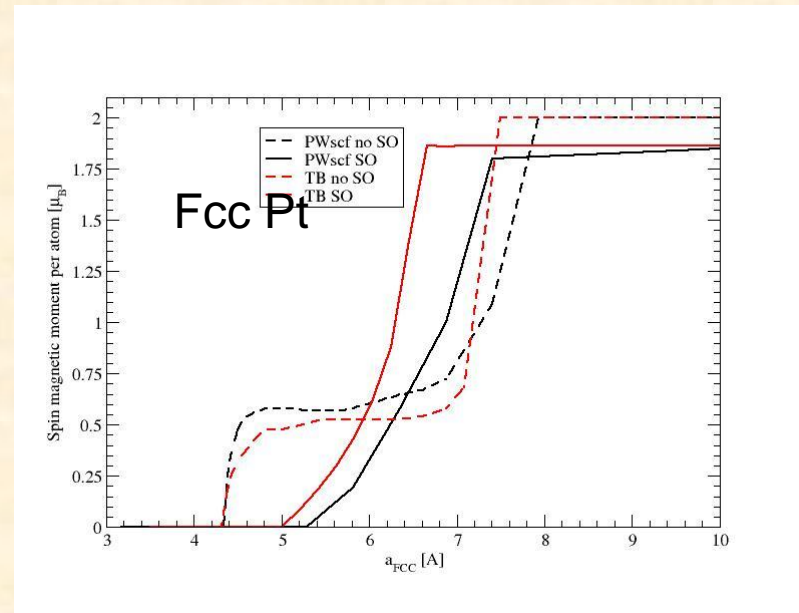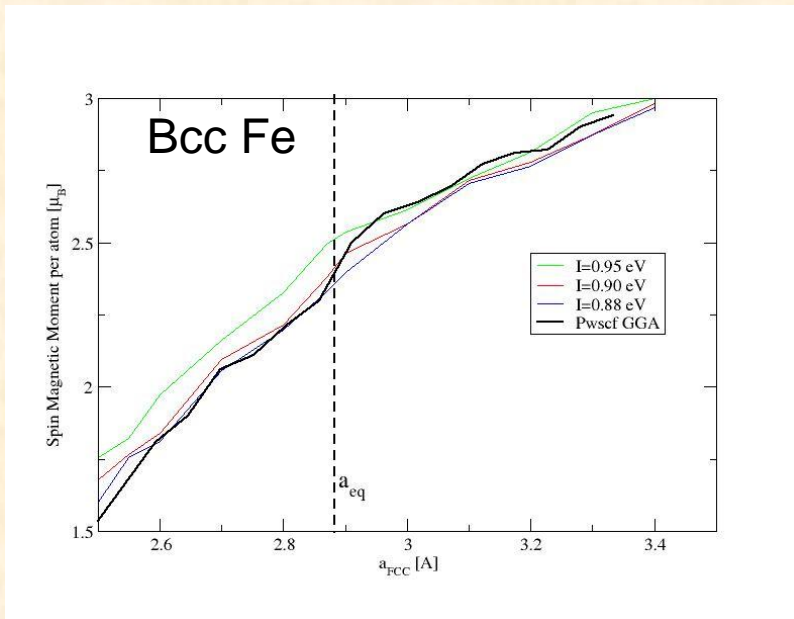
Total energy
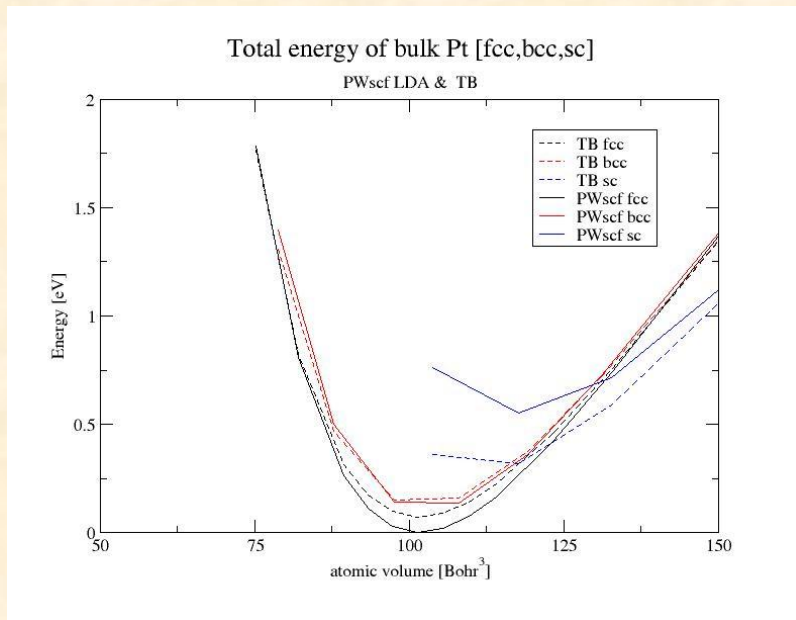
Band structure

Determination of parameters

- H$_{mag}$: Stoner parameter I adjusted to reproduce ab-initio M(d) of bulk Fe and Pt

$$H_{mag} = -\frac{1}{2}\sum_{i\lambda} I_{i\lambda}\,\vec{m}_{i\lambda}.\vec{\sigma}$$
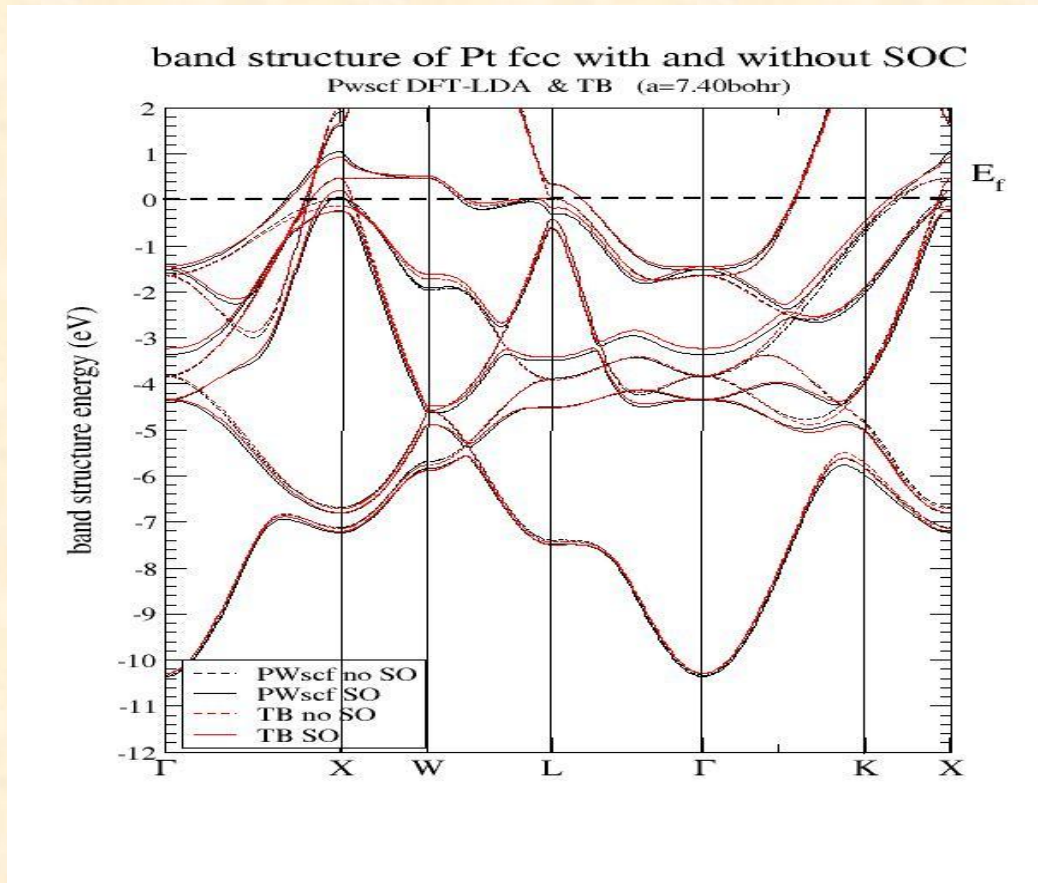
$$I_{Fe} \in [0.88, 0.95]\,eV$$

$$I_{Pt} = 0.60\,eV$$

Determination of parameters

• H_{SOC}: Spin Orbit Coupling adjusted to reproduce ab-initio band structure

$$H_{SOC} = \sum_i \xi_i(r - R_i)\vec{L}_i.\vec{S}$$

$$\xi_{d,i} = \int_0^\infty R_{d,i}^2(r)r^2 dr$$

band structure of Pt fcc with and without SOC
Pwscf DFT-LDA & TB (a=7.40bohr)

$$\xi_{Fe} = 0.06 eV$$

$$\xi_{Pt} = 0.57 eV$$

Determination of parameters

• H_{LCN}: local charge neutrality

$$H_{LCN} = \sum_{i\lambda} U_{LCN}(n_i - n_i^0)|i\lambda\rangle\langle i\lambda| + \sum_{i\lambda \notin d} U_d(n_{i,d} - n_{i,d}^0)|i\lambda\rangle\langle i\lambda|$$

Charge neutrality   "d" orbital filling

$$U = U_d = 20eV$$

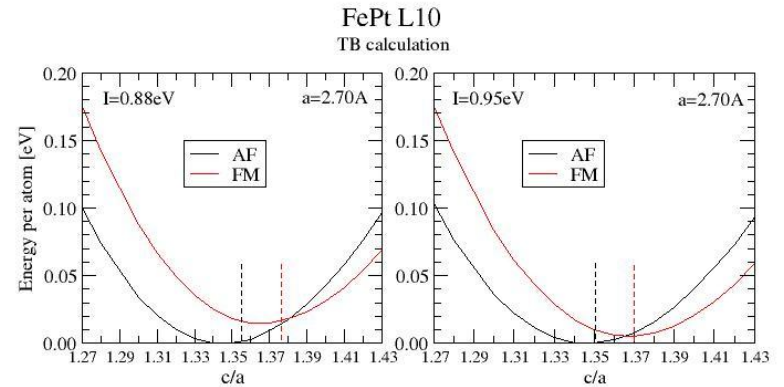$n_{i,d}^0$ adjusted to reproduce electronic and magnetic properties of FePt L10

$$n_{Fe,d}^0 = 6.6 \quad n_{Pt,d}^0 = 8.8 \quad \Longrightarrow \quad M_{Fe} \sim 3\mu_B \quad M_{Pt} \sim 0.35\mu_B$$

Magnetic and Structural properties of FePtL10

FM vs AF

Functionnal effect
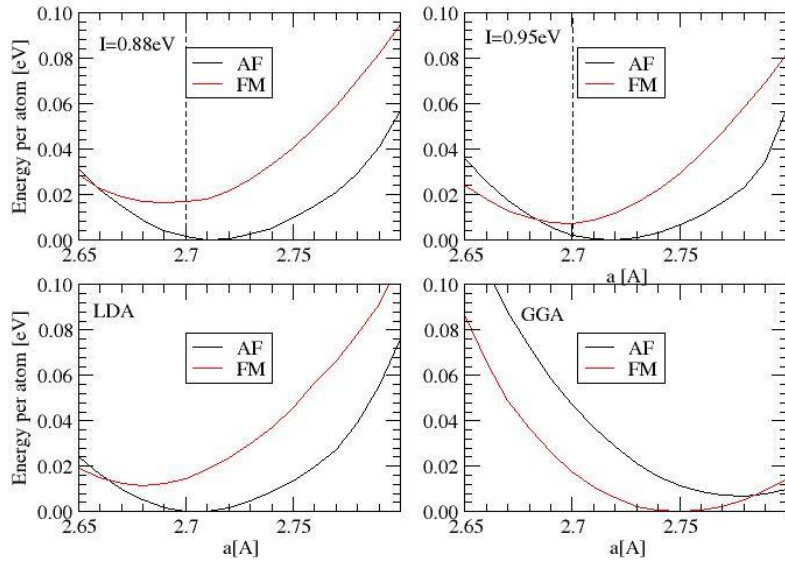
Structural effect

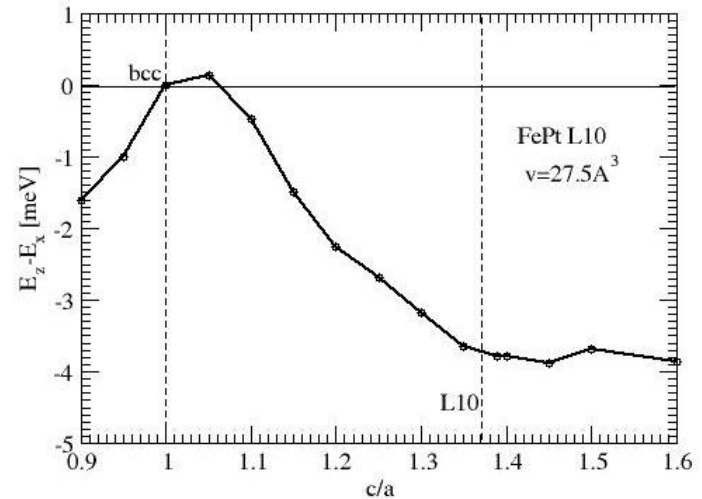# Magnetic and Structural properties of FePtL10

Magnetic Anisotropy Energy

J.Phys.: Condens. Matter 17 (2005) 4157
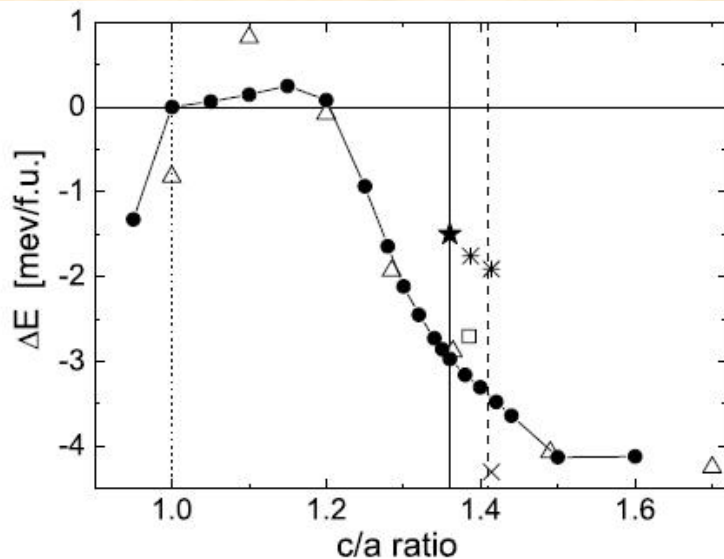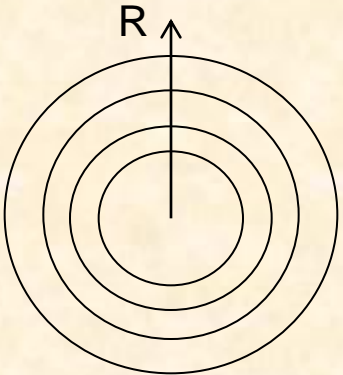
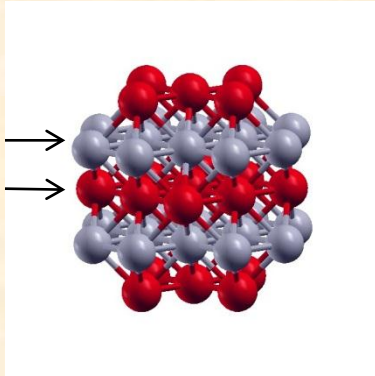Tight-Binding

Remark: MAE too large!

LSDA+U+SOC

Disorder?

FePt L10 clusters
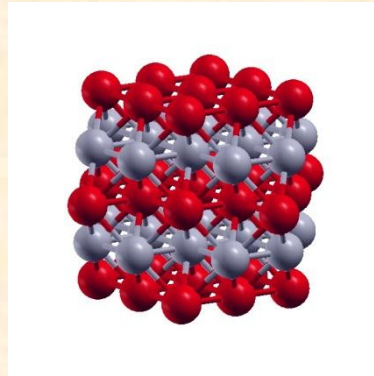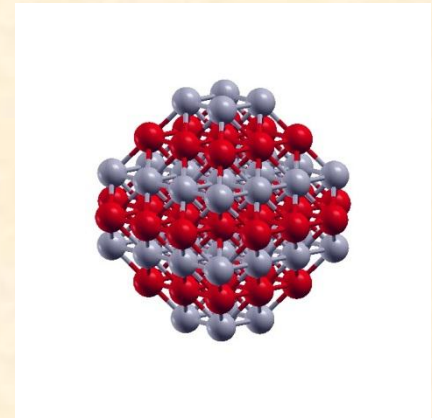
Clusters of increasing size

R

Pt →
Fe →

$N = 43$
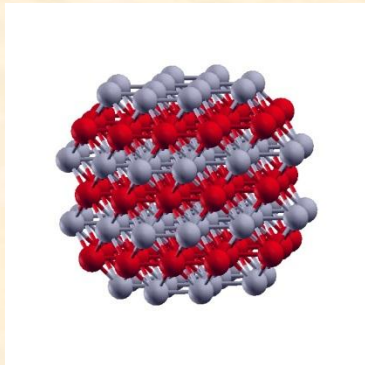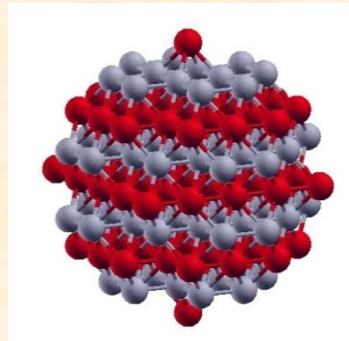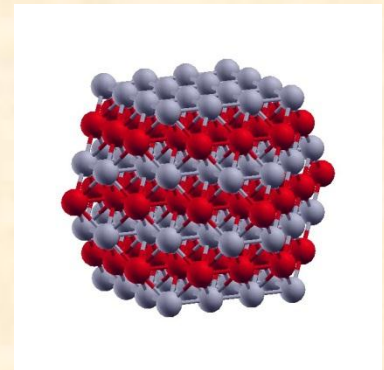

$N = 55$
cuboctahedron

$N = 79$

R   N

147
141
135
87
79
55
43
19
13
1

$N = 135$

$N = 141$

$N = 147$
cuboctahedron

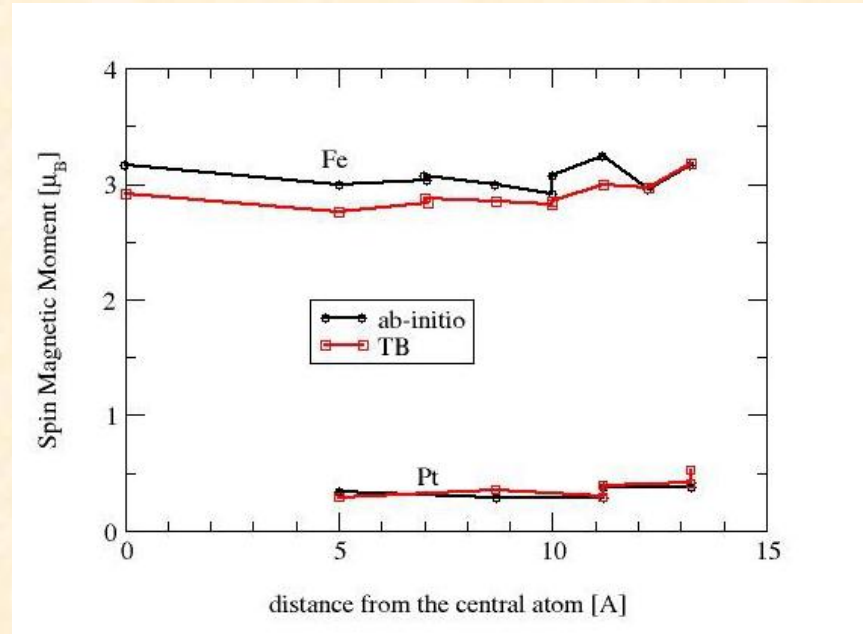Not a spherical shell

Magnetic properties of FePt L10 clusters

Repartition of spin magnetic moment in the cluster

FM // z
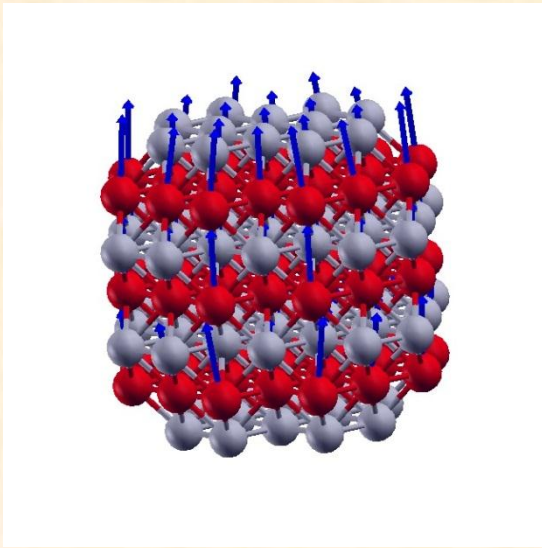
$$N = 135$$

Ab-initio= Comput. Matt. Sci. 35 (2006) 279

Magnetic properties of FePt L10 clusters

Repartition of spin magnetic moment in the cluster

AF // x

-0.4μ_B
-3μ_B
0μ_B
3μ_B
0μ_B
-3μ_B
-0.4μ_B
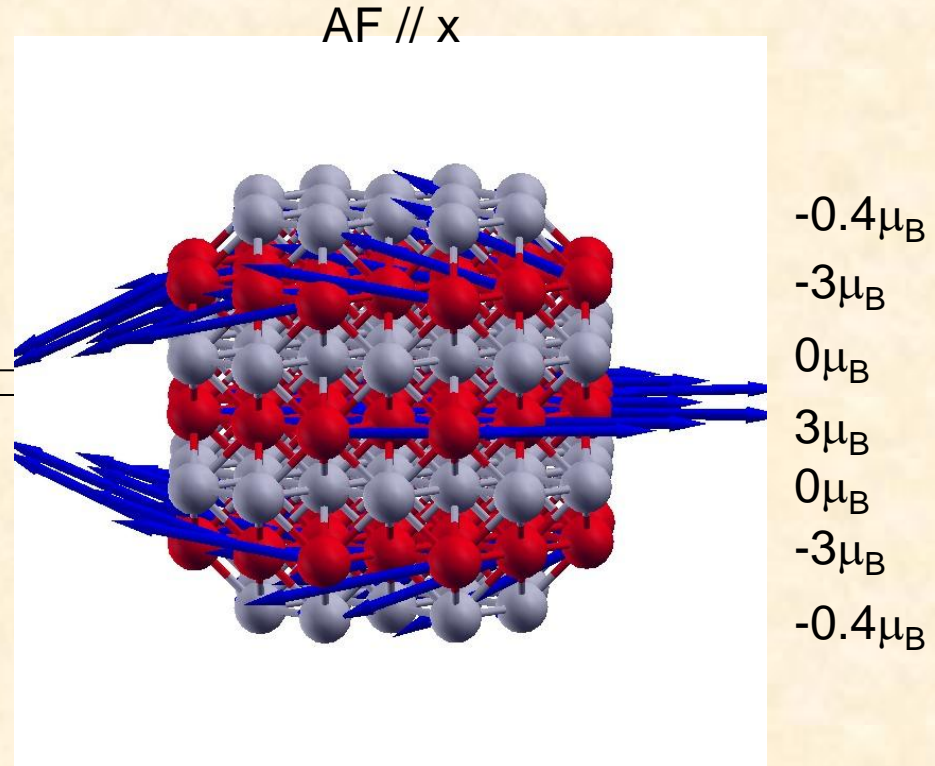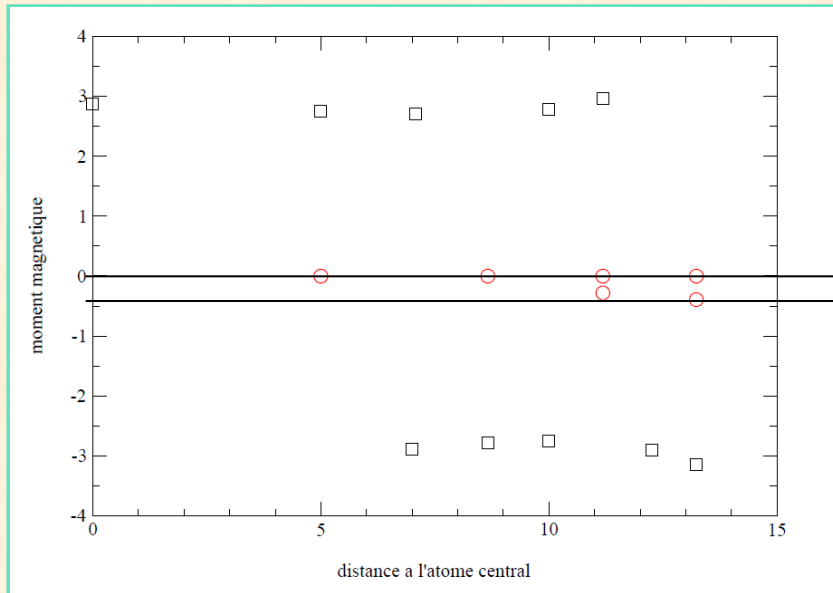
AF vs FM order in FePt clusters

FePt L10 clusters: FM vs AF
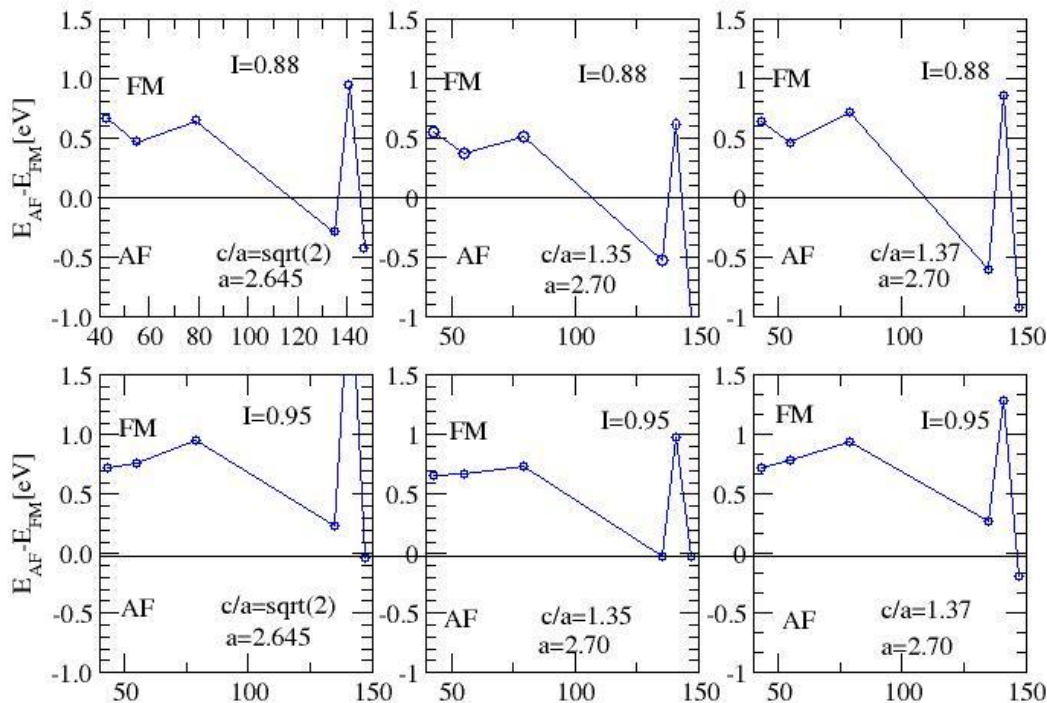
Pt termination favors AF

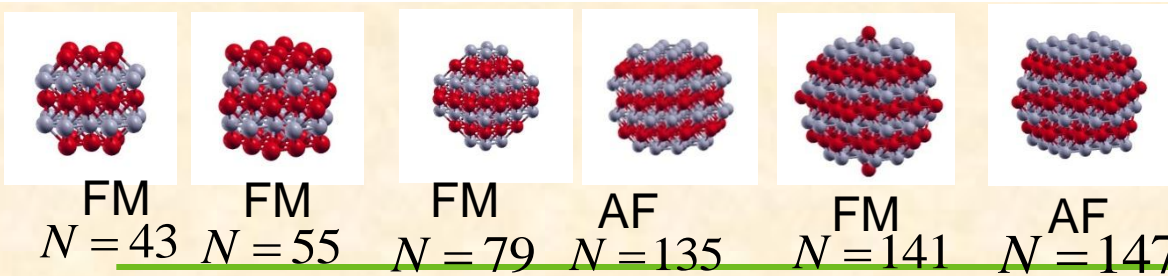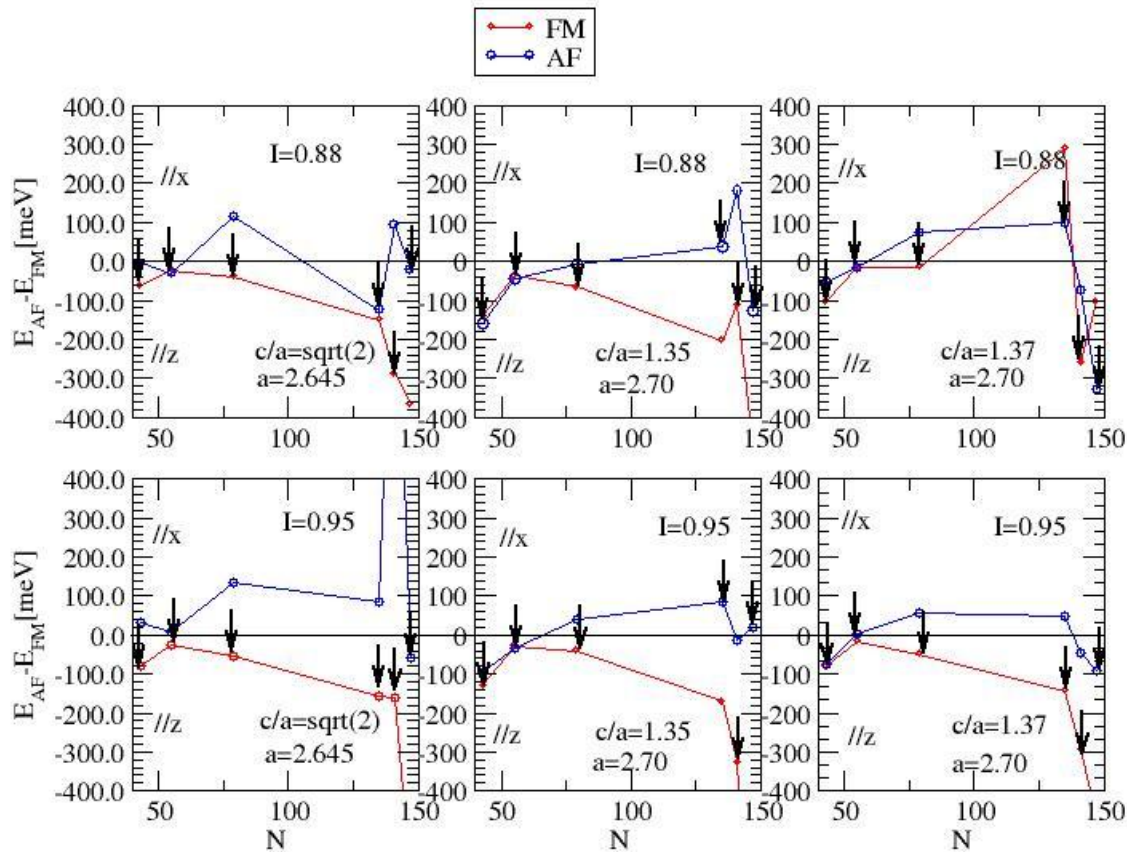Fe termination favors FM

Large Stoner parameter favors FM

Large c/a favors FM

FM $N = 43$ FM $N = 55$ FM $N = 79$ AF $N = 135$ FM $N = 141$ AF $N = 147$

MAE in FePt clusters

Easy axis along z

Except for N=135,147
 (AF ordering)

Partial Conclusion

- Efficient and quantitative TB method for electronic and magnetic properties of metals and their alloys.

- Complex magnetic behavior of FePt clusters: FM vs AF, oscillating MAE etc..
        influence of surface termination
        influence of c/a

Questions and Comments

Why is there no experimental evidence of AF order?

LSDA+U   Disorder?   Strain effect?

THANK YOU FOR YOUR ATTENTION