ATOMISTIC SIMULATIONS IN PHYSICAL METALLURGY: THE ROLE OF *AB INITIO* ELECTRONIC STRUCTURE CALCULATIONS

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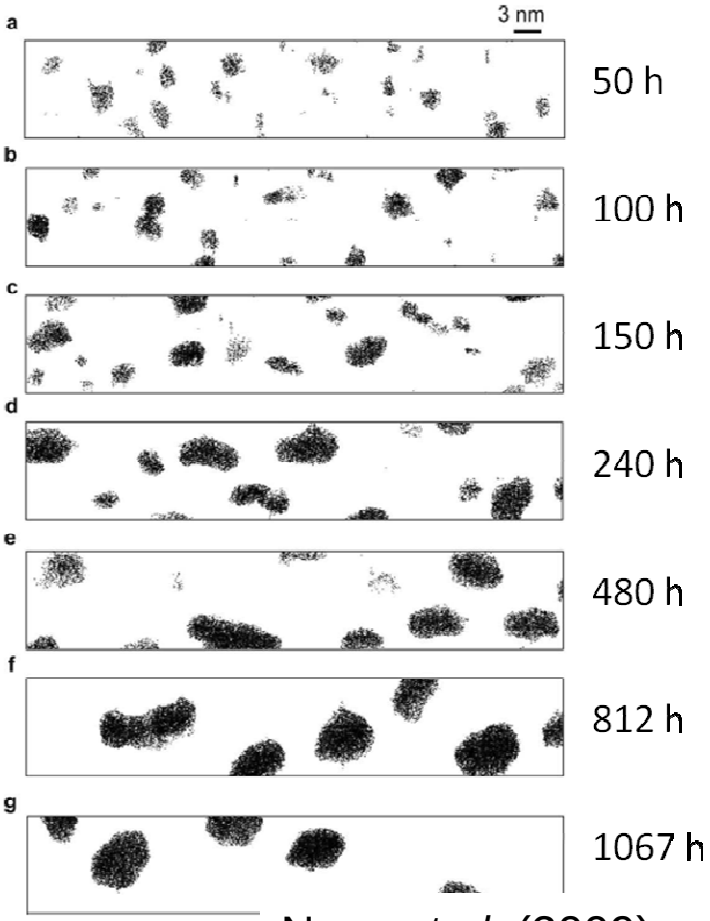
PHYSICAL METALLURGY AT THE ATOMIC SCALE

Decomposition kinetics of Fe-20%Cr during thermal aging at 500℃

Experiment

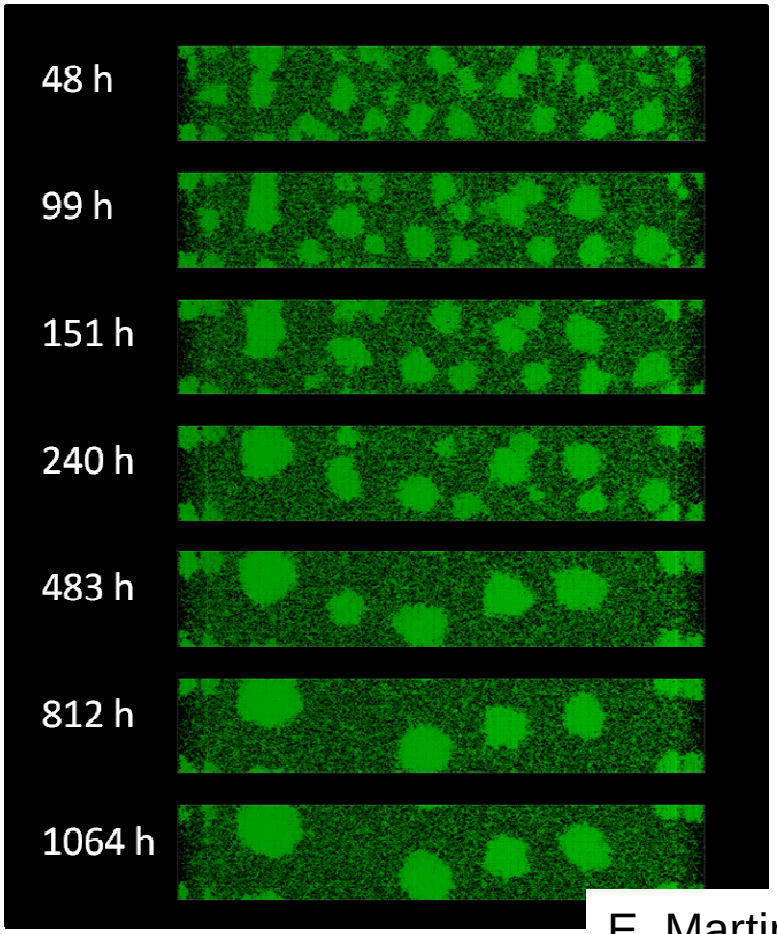
3D atom probe

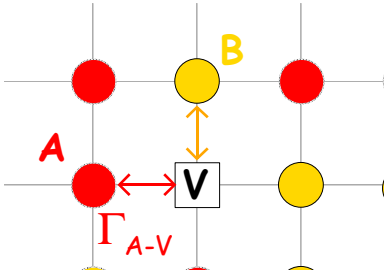


Novy *et al.* (2009)

Simulation

Kinetic Monte Carlo with *ab initio* inputs





E. Martinez *et al.* (2011)

OUTLINE

I. Introduction

II. Hierarchy of interatomic interaction models

- *Ab initio* electronic structure calculations (Density Functional Theory framework)
- Brief introduction toTight-binding models and semi-empirical potentials

III. Different types of calculations

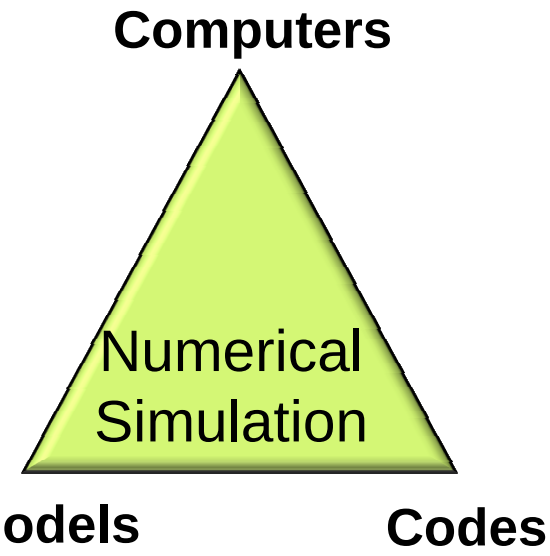
- Static calculations
- Structure optimization
- Energy barriers
- Quasi-harmonic calculations
- Molecular dynamics (not shown)

IV. A few examples

INCREASING WEIGHT OF *AB INITIO* SIMULATIONS IN MATERIALS SCIENCE

In this talk: *Ab Initio* = Density Functional Theory (DFT)

Curie, CCRT, 2 Pflops, 100 000 cores



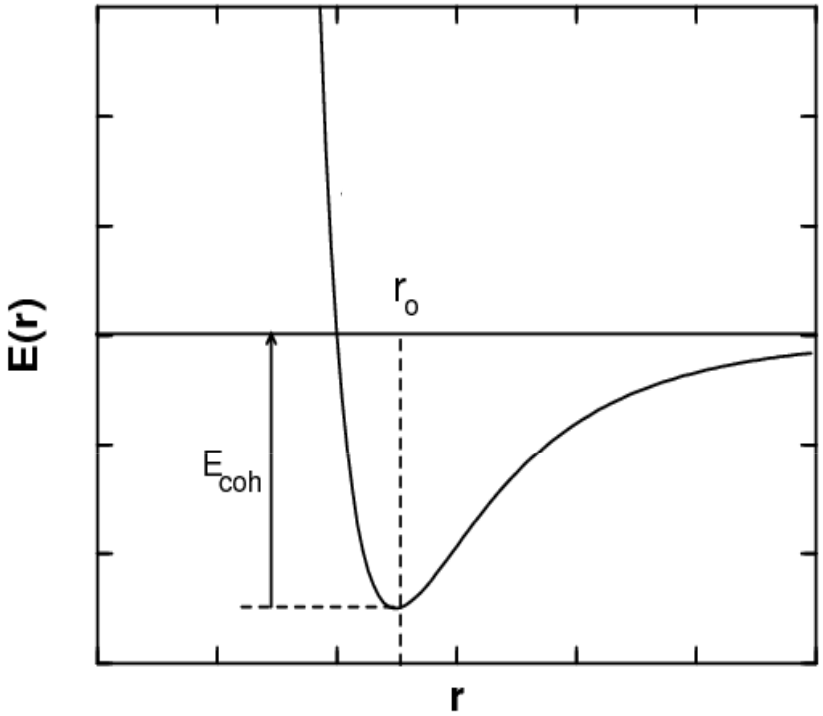
- Continuous increase of computer power (Moore's law)
- Large part of supercomputer time dedicated to materials science (in particular DFT)

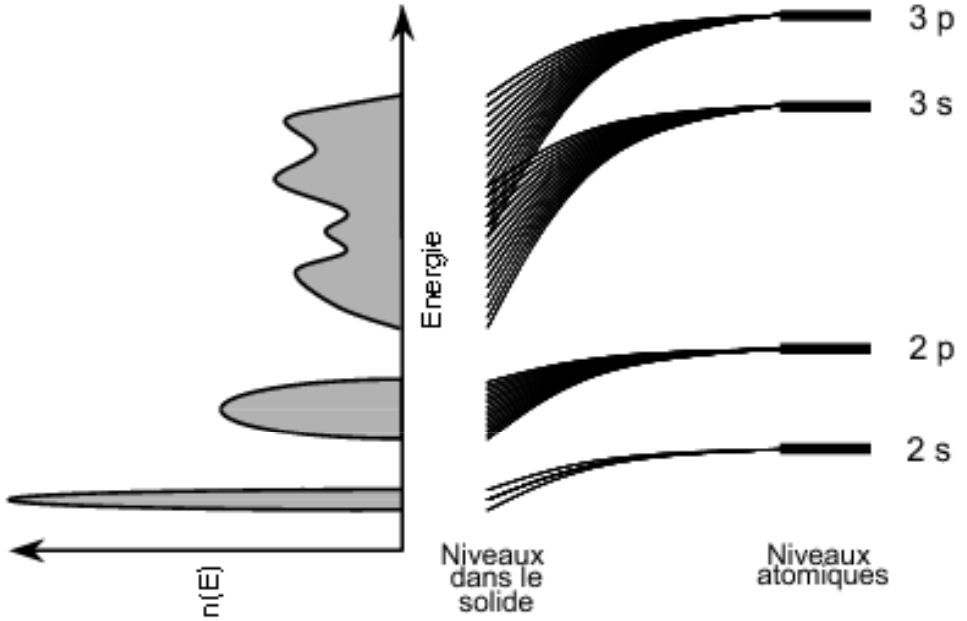
- **Efficiency of DFT** for computing quantities relevant to materials studies

- DFT codes well adapted to **massively parallel** supercomputers

CONTEXT

- Simulation of metals and alloys at the atomic scale
- $E(\{r_i\})$ needed
- Electronic structure origin of the binding energy
- Required accuracy in metallurgy: < 1 meV /atom

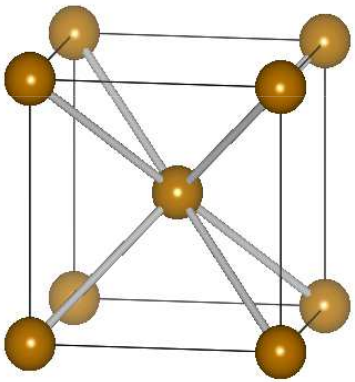




Cohesive energy: 3 to 9 eV/atom (metals)
Interatomic distance : 2 to 5 Å

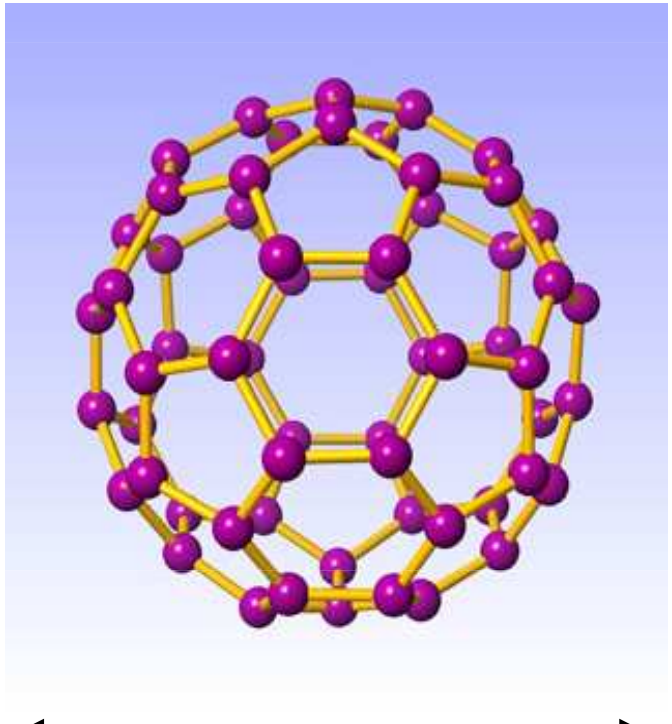
Leads to non pairwise interactions in metals $E_{pot} \neq \frac{1}{2}\sum_i \sum_{j \neq i} V(r_{ij})$ otherwise $E_{fv}=E_{coh}$ instead of ~ $E_{coh}/3$

LENGTH SCALES IN ATOMISTIC SIMULATIONS



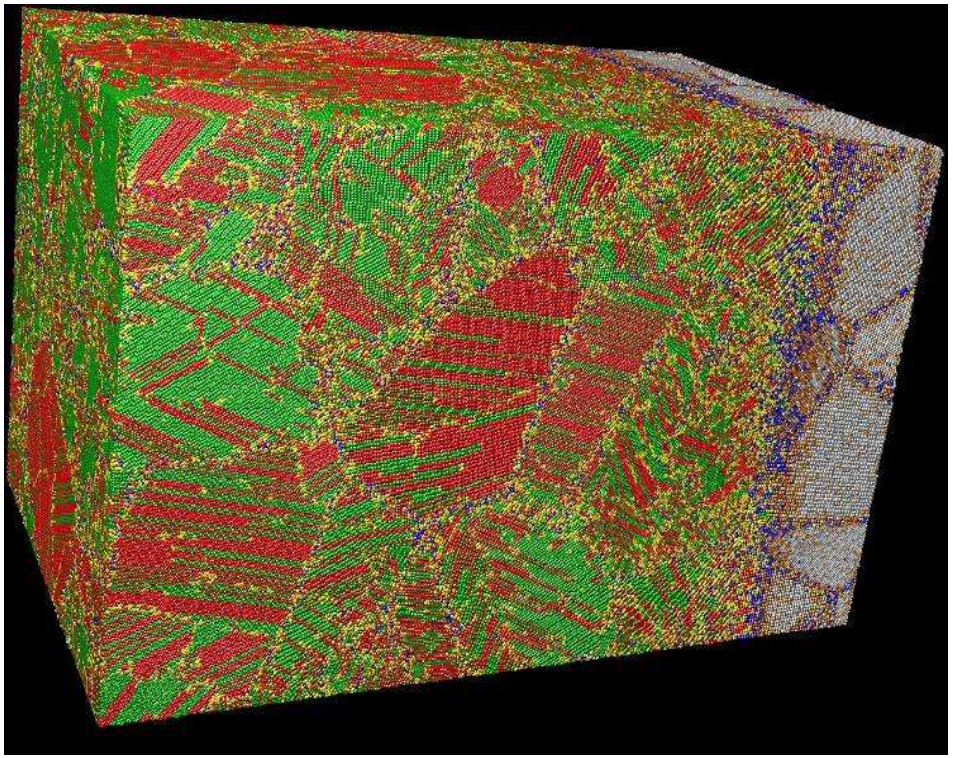
0.3 nm

1 atom (per unit cell)



1 nm

60 atoms

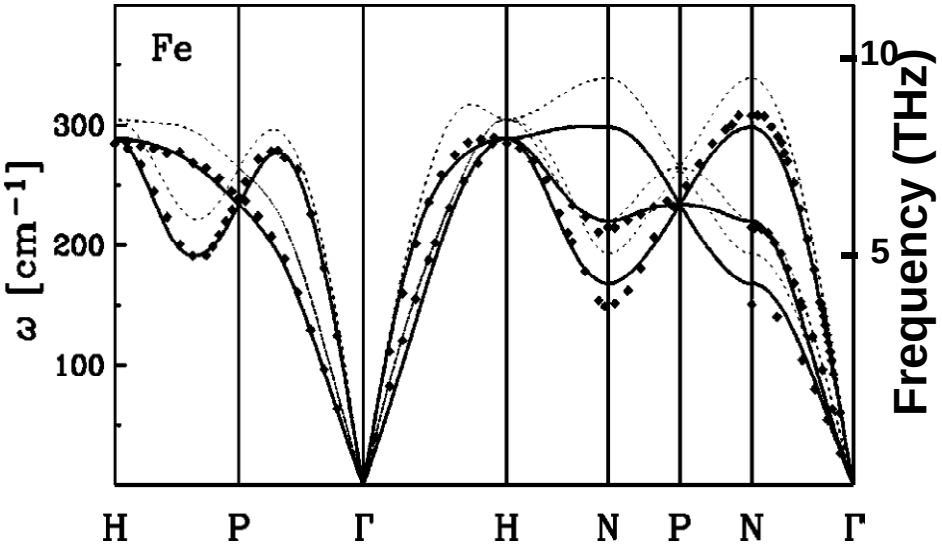


100 nm

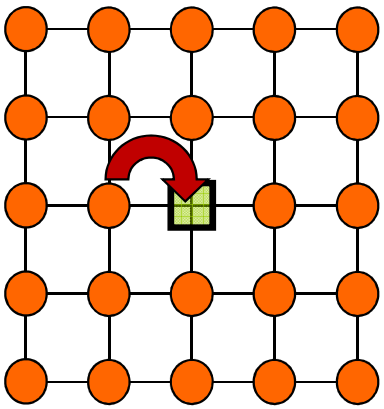
- Example : 30 10^6 atoms (K. Kadau, LANL, 2007)

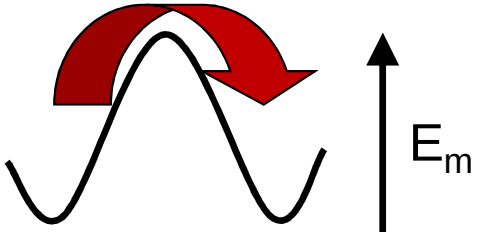
TIME SCALES IN ATOMISTIC SIMULATIONS

Lattice vibrations — Picosecond (10^{-12} sec)



Atomic jump — Nanosecond (10^{-9} sec)

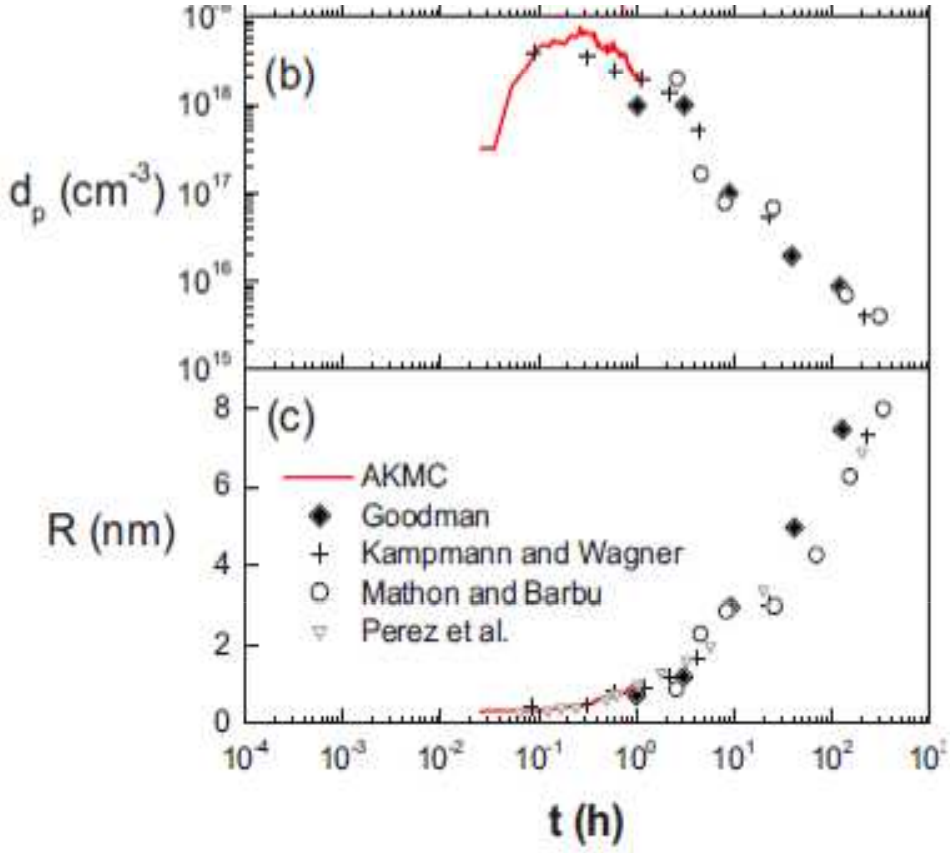




$$\nu = \nu_0 \exp(-E_m / k_B T)$$

$$\nu_0 = 5\ THz\ ; E_m = 0.5\ eV$$
$$T = 300\ K$$

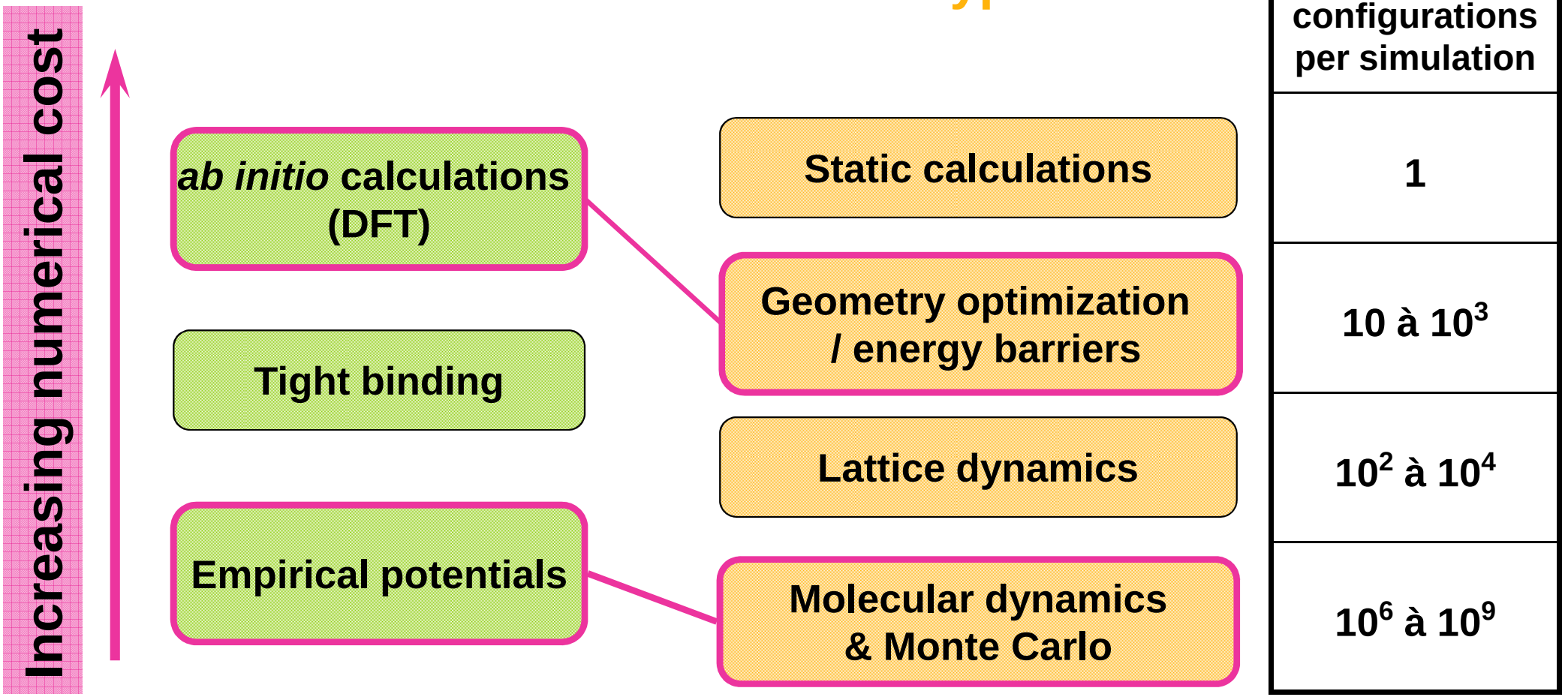
Long range diffusion — Second / hour



Cu precipitation in Fe
Lattice kinetic Monte Carlo

(F. Soisson, CEA, 2007)

VARIOUS TYPES OF ATOMISTIC SIMULATIONS



AB INITIO ELECTRONIC STRUCTURE CALCULATIONS (DFT)

- **Quantum solution of a single particule approximation of Schrödinger's equation**
- **No adjustable parameter**

- **Density Functional Theory (DFT)**

$$E=\min E[\rho]$$ Hohenberg & Kohn (1964)

- **Kohn-Sham Theory (1965)**

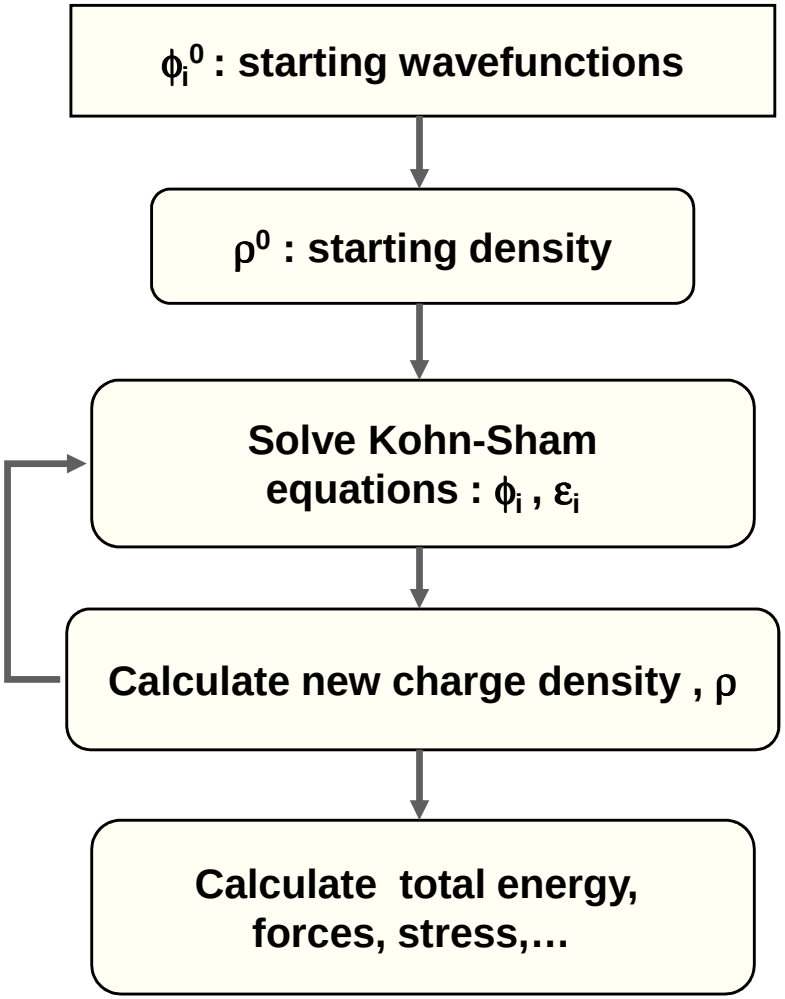
$$E[\rho] = E_{I\text{-}I} + E_{e\text{-}I} + E_H + T + E_{xc}$$

- Parametrize the particle density in terms of a set of one-electron orbitals representing a non-interacting reference system

$$\left(-\frac{1}{2}\nabla^2 + v(r) + \int \frac{\rho(r')}{|r-r'|}dr' + \mu_{xc}(\rho(r))\right)\varphi_i = \varepsilon_i\varphi_i$$

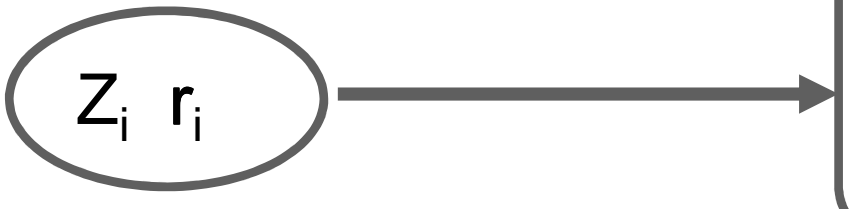
- **Local Density Approximation (LDA)**

- exchange-correlation energy of a homogeneous electron gas with the local density $\rho(r)$



AB INITIO ELECRONIC STRUCTURE CALCULATIONS (DFT-LDA/GGA)

"no adjustable parameter"



Most properties of most materials can be predicted with an accuracy of a few %:
a, B, C_{ij}, $\omega(k)$, ΔE (structures, surfaces), $E_{defects}$

Approximation: exchange correlation functional (LDA, GGA, …), difference gives error bar

Compromises (speed / accuracy)

- Valence electrons ; pseudopotential
- Basis set size
- Spin polarization
- Brillouin zone integration
- Convergence criteria (electronic structure, atomic relaxation)

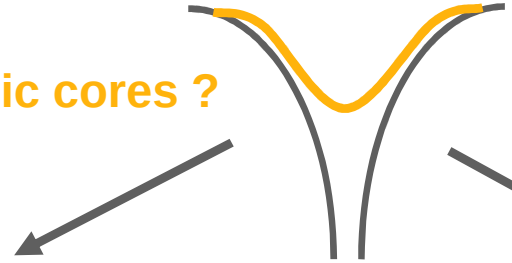
Limitations

- Exceptions: gap, strongly correlated electrons
- Cell size (max 100 to 1000 atoms)
- Finite temperature effects

Standard = pseudopotentials or PAW and plane waves (implemented in VASP, QuantumEspresso, ABINIT)

FAMILIES OF METHODS FOR SOLVING KOHN-SHAM EQUATIONS

How to deal with ionic cores ?



All-electron methods

- **Muffin-tin geometry : spheres around atoms + interstitial region**
- **various choices of basis sets in both regions**

FP-LMTO
Augmented Hankel Fonctions

FLAPW
Augmented Plane waves

Pseudopotential approximation

Plane waves

Mixed basis

Real space grids

Local orbital

Norm Conserving pseudopotentials (NCPP)

PAW
Projector Augmented Wave
P. Blöchl (1994)

Ultrasoft pseudopotentials (**USPP**)
- D. Vanderbilt (1990)
- Smaller basis sets
- more transferable (multiple projectors)

DFT CODES (NON EXHAUSTIVE LIST)

Plane wave and related (real space, wavelet, etc.) methods

- **VASP**
- **CASTEP and CETEP**
- **CPMD**
- **ABINIT** - GPL
- **BigDFT** - wavelets
- **Quantum-Espresso (formerly PWscf)** - GPL
- **PEtot** - GPL
- **DACAPO** - GPL
- **Socorro** - GPL
- **DFT++** - GPL
- **Octopus** - GPL
- **Paratec**
- **DoD Planewave**
- **ACRES**
- **PARSEC** - GPL - real space, pseudopotential
- **CP2K** - GPL (mixed basis DFT)
- **GPAW** - GPL - real-space multigrid PAW

Local orbital basis codes

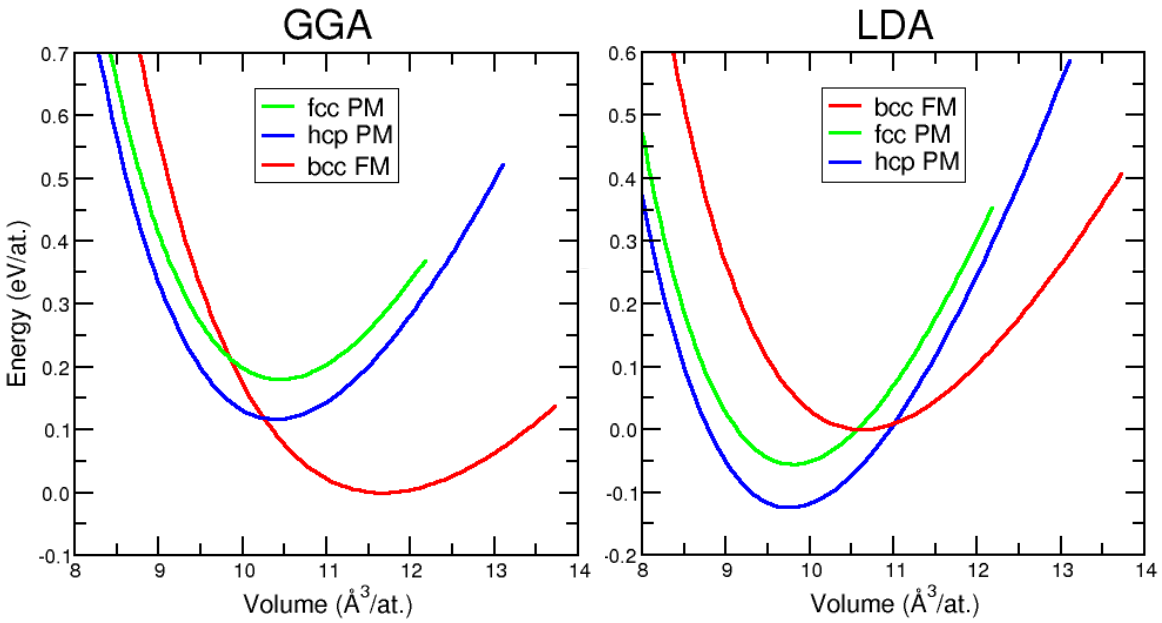
- **QUEST: SeqQuest** - gaussian basis pseudopotential
- **SIESTA** - numerical atom-centered basis pseudopotential
- **CRYSTAL - CSE -** gaussian basis all-electron
- **AIMPRO**
- **FPLO**
- **OpenMX** - GPL - numerical atom-centered basis PP code (Ozaki group)

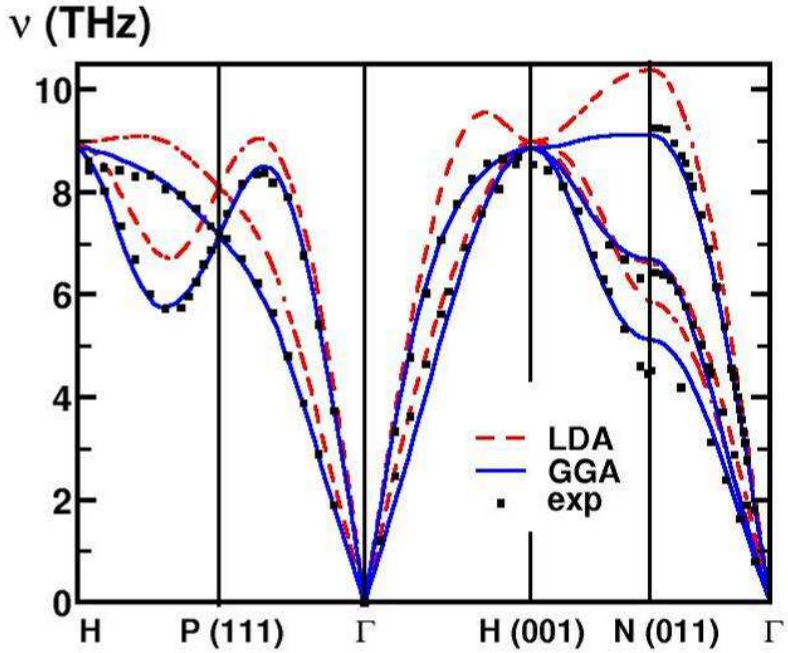
All-electron (augmented methods) codes

- **EXCITING** - GPL code for FP-LAPW
- **WIEN 2k**
- **FLAPW**
- **RSPt -** FP-LMTO

source : http://dft.sandia.gov/Quest/DFT_codes.html

LDA vs GGA in iron



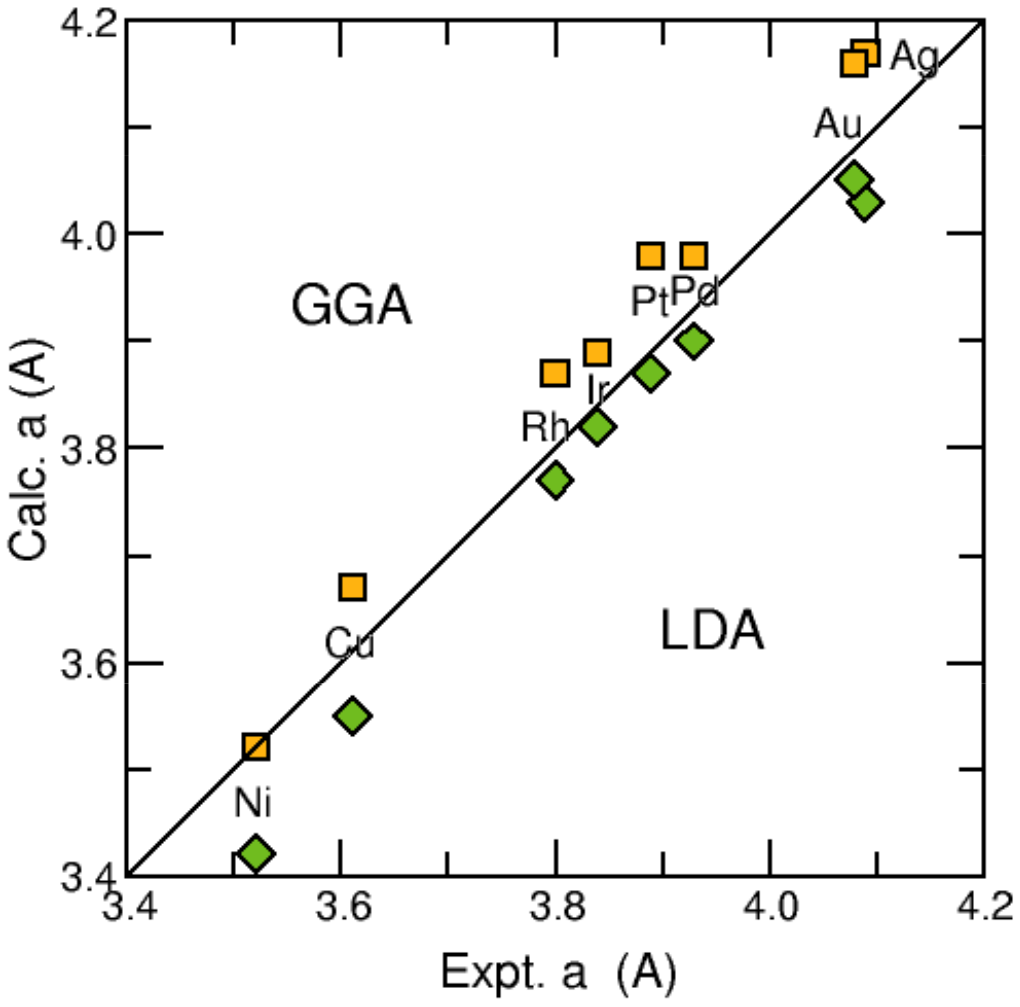


	Bulk			Vacancy	
	a (Å)	**B (Mbar)**	**μ (μ_B)**	**Formation (eV)**	**Migration (eV)**
GGA (various pseudos)	2.86	1.67 (1.52 - 1.67)	2.27 (2.26-2.38)	2.09 (1.93 - 2.09)	0.67 (0.59 - 0.67)
LDA	2.77	2.41	2.10	2.40	0.68
Exp.	2.87	1.68	2.22	2.35 ± 0.2	0.55 ± 0.05

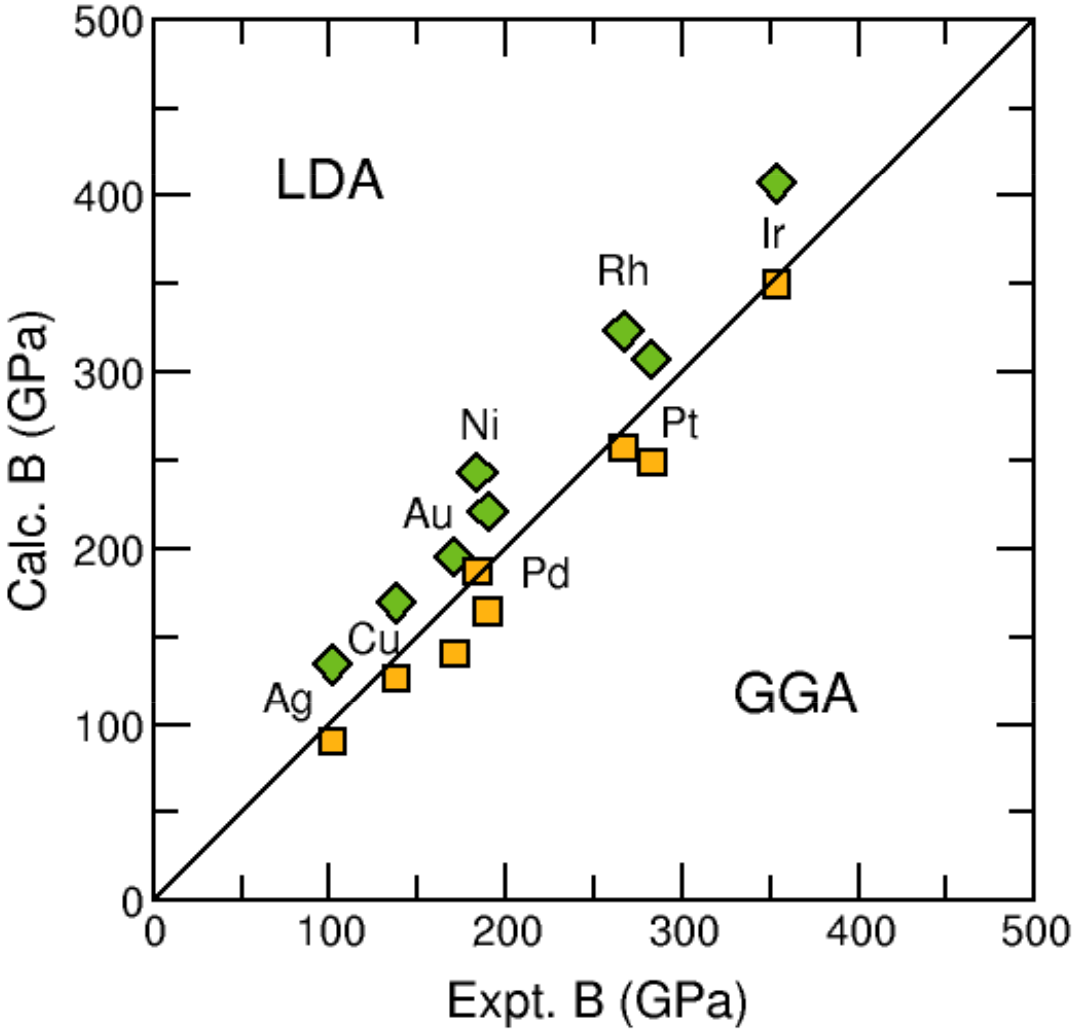
GGA better **LDA better**

LDA vs GGA: bulk properties of FCC metals

Lattice parameter



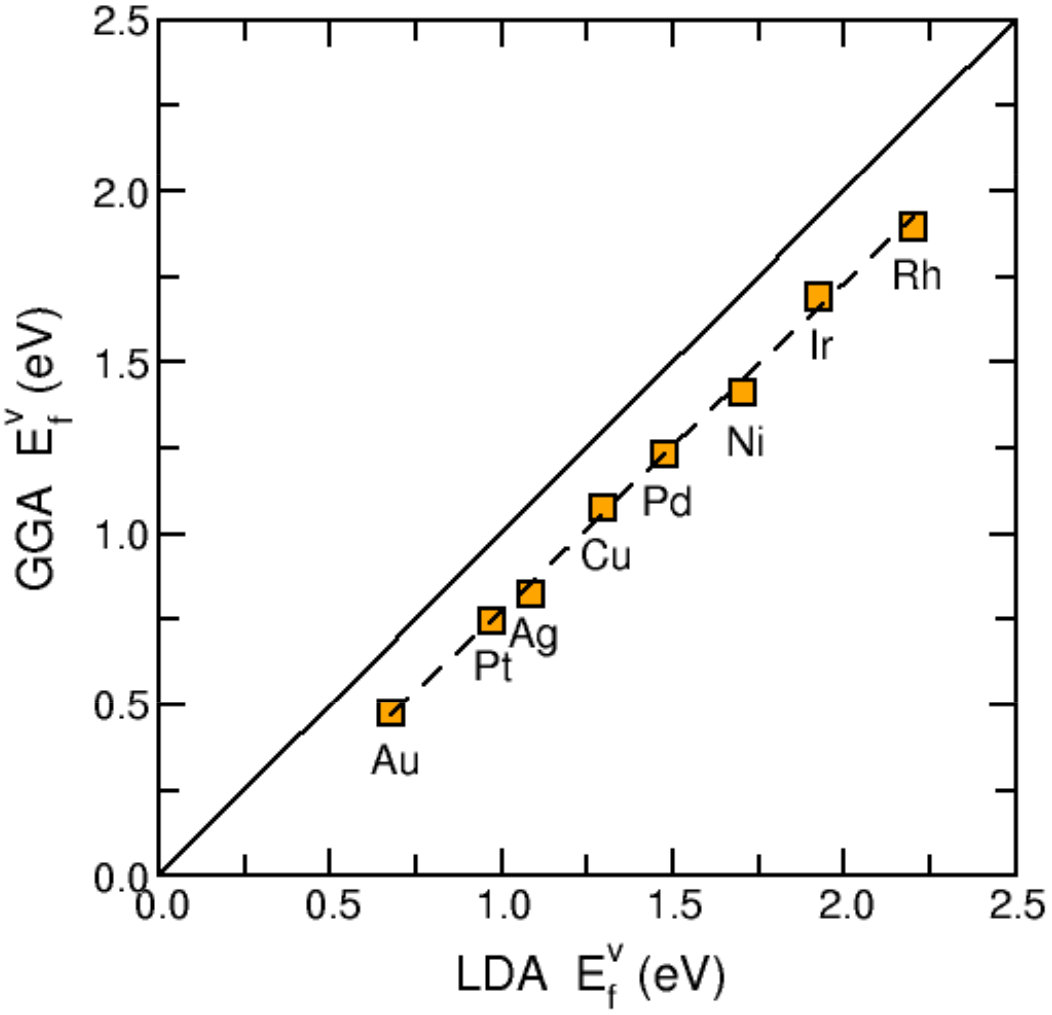
Bulk modulus



LDA underestimates a and overestimates B
GGA improves in particular for 3d metals

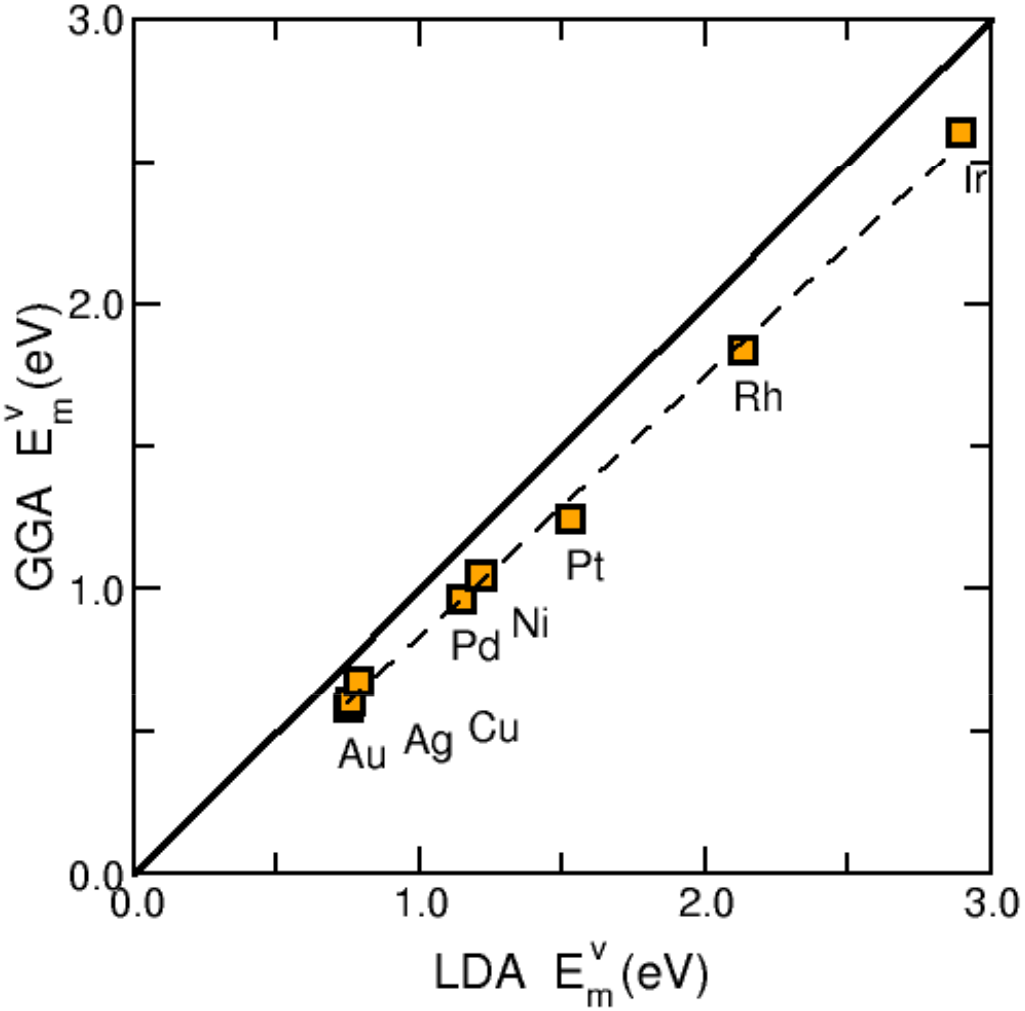
LDA vs GGA: vacancy properties of FCC metals (1/2)

Vacancy <u>formation</u> energy



GGA values lower than LDA
by 0.25±0.05 eV

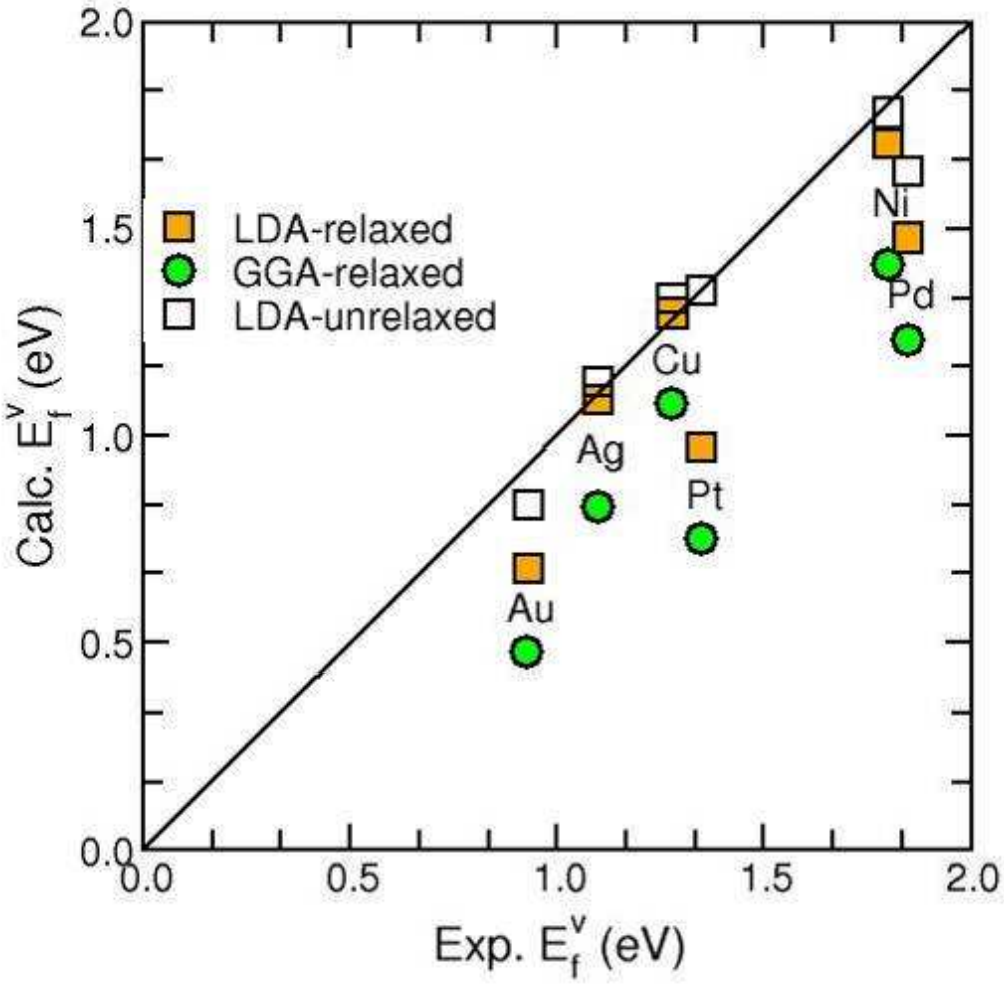
Vacancy <u>migration</u> energy



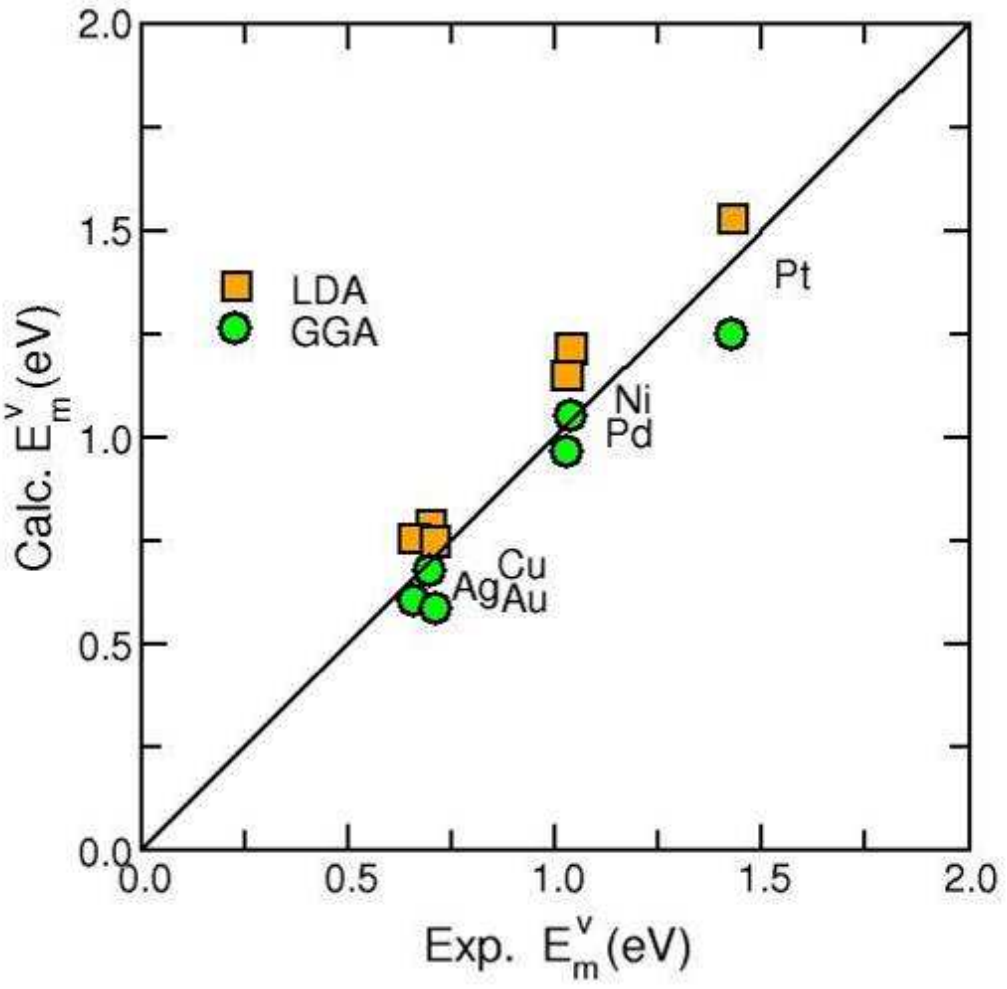
GGA values lower than LDA
by ~ 10%

LDA vs GGA: vacancy properties of FCC metals (2/2)

Vacancy formation energy



Vacancy migration energy



- LDA in better agreement with exp.
- GGA underestimates vac. form. energy

GGA < Expt. < LDA

MODÈLES DE LIAISONS FORTES

$$E_{tot} = E_{bande} + E_{rep}$$

Terme de bande :

- $$E_{bande} = \sum_{n}^{occupés} \langle \psi_n | H(\{r_{ij}\}) | \psi_n \rangle$$
- pour construire la matrice 5Nx5N $H_{i\alpha,j\beta}$ (métaux de transition) ; 2 sortes de paramètres
- pour les termes *non-diagonaux*, les paramètres de Slater-Koster pour les intégrales de saut :

  $V_{dd\sigma}(r)$, $V_{dd\pi}(r)$, $V_{dd\delta}(r)$

  de type V_0*fonction décroissante de r
- pour les termes *diagonaux*, les énergies de site : $e_{s,i}$, $e_{p,i}$, constantes, ou dépendantes de l'environnement i.e. $\{r_{ij}\}$

Terme répulsif :

- potentiel de paires : $E_{rep} = \sum_{i,j} \phi(r_{ij})$
- ou plus général : $E_{rep} = \sum_{i} f\left(\sum_{j} \phi(r_{ij}) \right)$

<u>En pratique</u> :

- 4 à 100 paramètres ajustables
- ajustement sur l'expérience ou les calculs ab initio

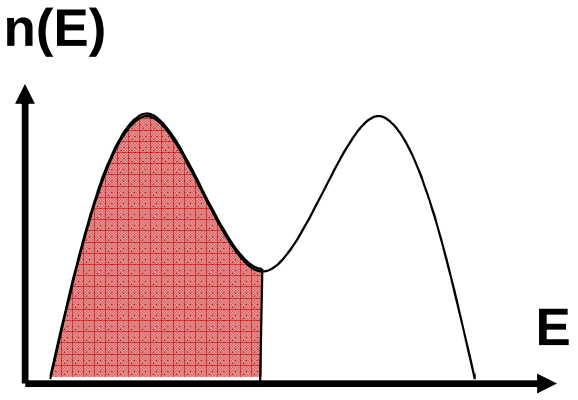
(structure de bande, courbes énergie/volume)

<u>Remarque</u> :

- c'est la forme la plus simple : orthogonale à 2 centres
- il existe de formes plus compliquées : non orthogonales et à plusieurs centres

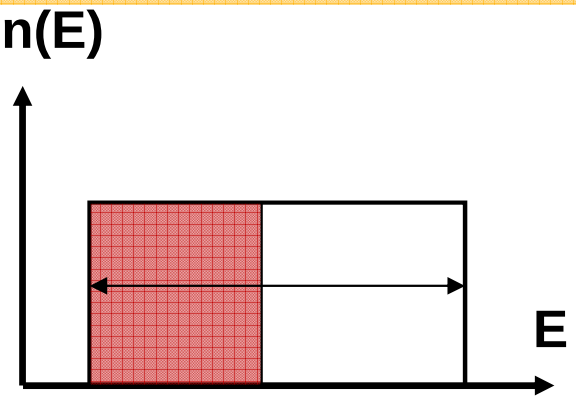
POTENTIELS EMPIRIQUES POUR LES MÉTAUX DE TRANSITION

Liaisons Fortes



- **Forces angulaires**
- **Propriétés dépendent du remplissage de la bande d**

Approximation du Second moment



$$E^i = E^i_{paire} + E^i_{bande}$$

$$E^i_{bande} = \sqrt{\rho_i}$$

- **Propriétés normalisées indépendantes du remplissage**
- **Pas de forces angulaires**
- **4 paramètres ajustés sur données expérimentales (E_{coh}, C_{ij}, a)**

Potentiel EAM

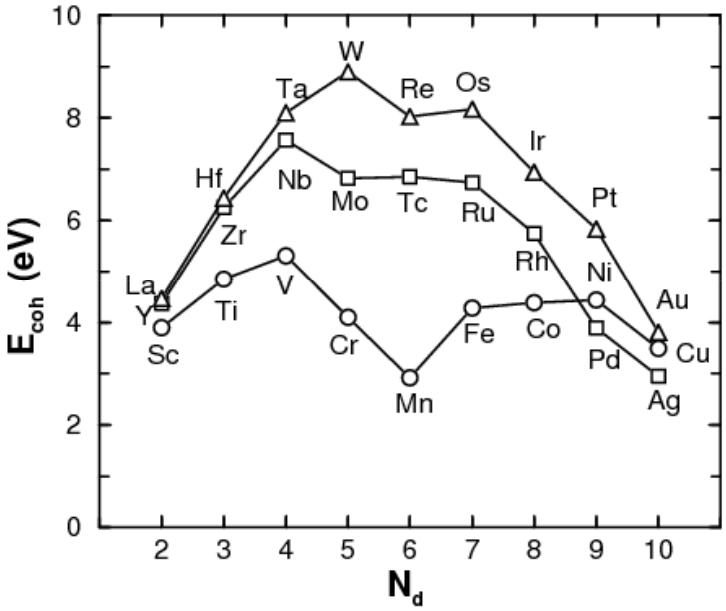
$$E^i = E^i_{paire} + F(\rho_i)$$

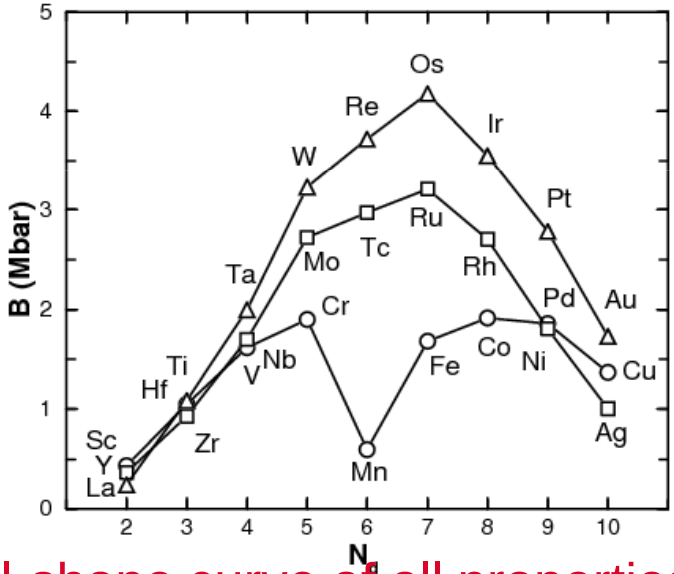
Mendelev et al. (2003):

$$F(\rho_i) = \sqrt{\rho_i} + a\rho_i^2$$

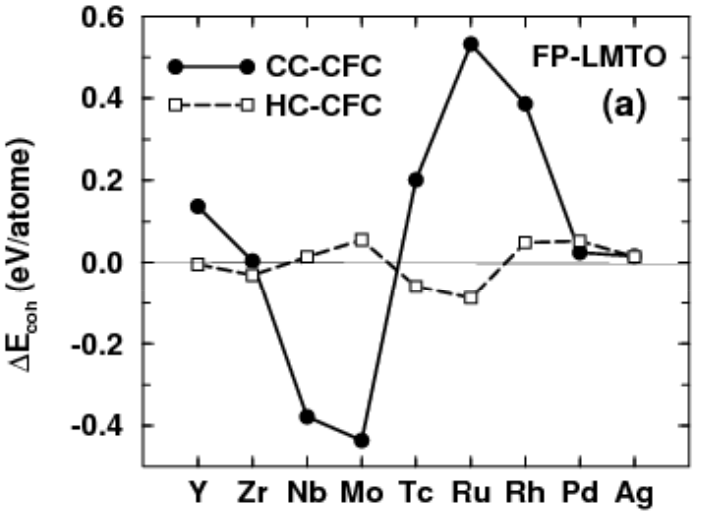
- **= généralisation empirique du second-moment**
- **+ de flexibilité dans dépendance en distance**
- **Ajustement des paramètres (10-15) sur résultats DFT (défauts, "liquide")**

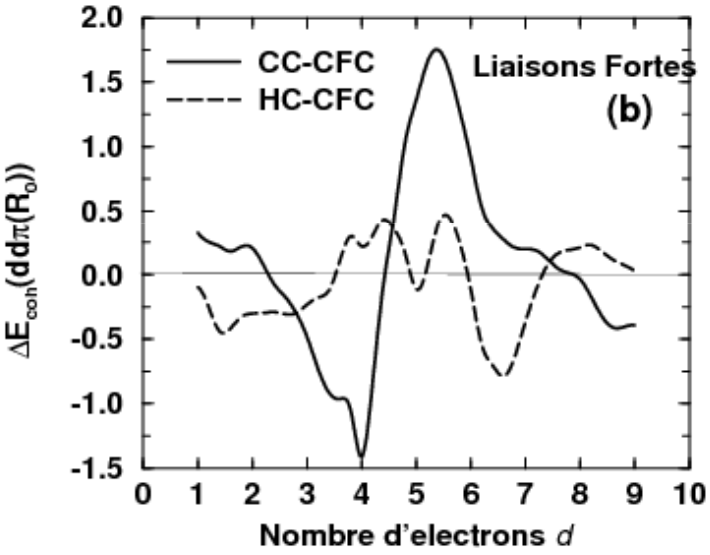
VARIATIONS ALONG TRANSITION METAL SERIES





Bell-shape curve of all properties: second-moment or band filling effect





Relative stabilities are senstive to details of the density of states: well reproduced by TB d-band model

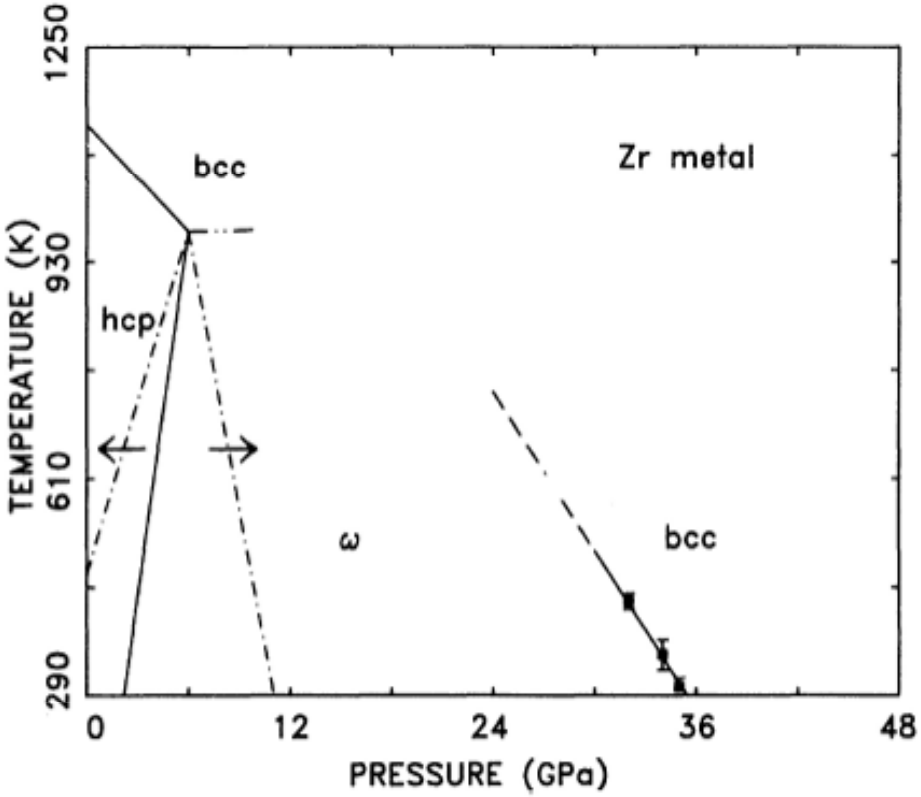
Ordre de grandeur des temps de calcul – cas du fer

	Temps CPU 250 atomes 1 configuration	Variation avec le nombre d'atomes (N)	Avantages et domaine de validité	Inconvénients et limitations
Potentiel empirique	10^{-3} sec	N	• études génériques • Valide près du domaine d'ajustement	• paramètres à ajuster • alliages très difficiles • ΔE approximatif
Liaisons Fortes	10 mn	N (récursion) à N^3 (diagonalisation)	• contient toute la physique • Très bon pour les tendances • Propriétés électroniques • Energies par atome	• paramètres à ajuster • alliages difficiles
DFT bases localisées (SIESTA)	6 heures	N^3	• Énergies quantitatives • Alliages	• Bases à développer
DFT ondes planes	15 jours	N^3	• très robuste	• temps de calcul

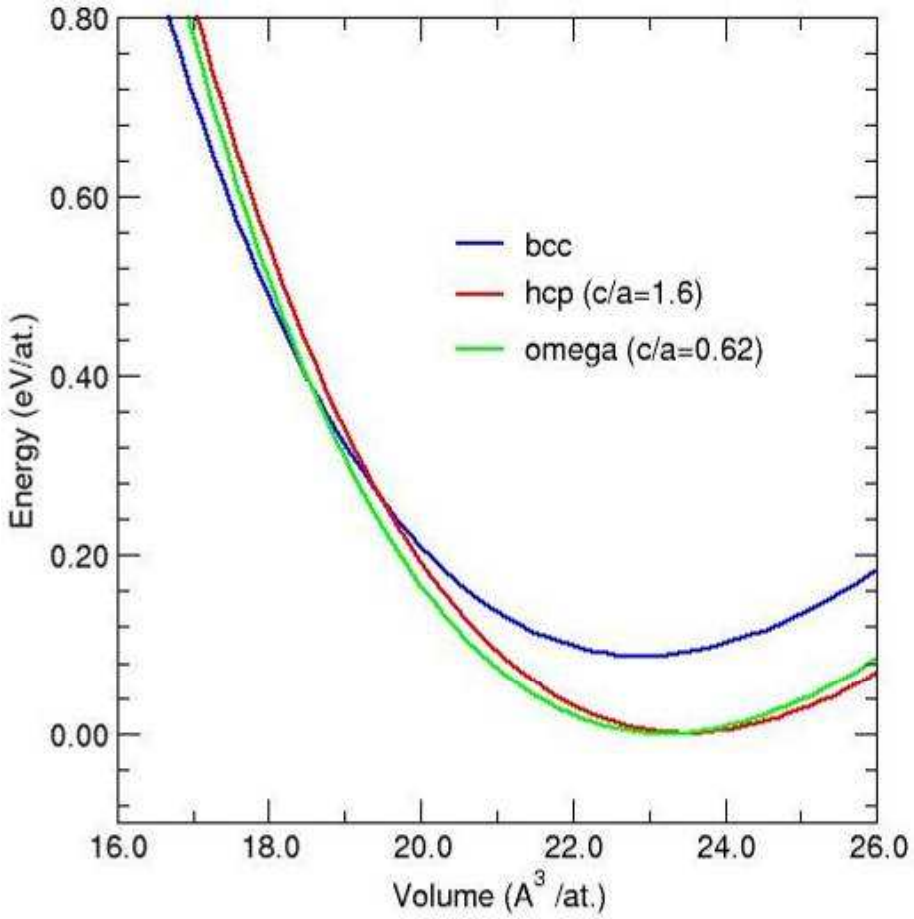
EXAMPLES OF DFT CALCULATIONS OF BASIC QUANTITIES

ENERGY-VOLUME CURVES

Experimental phase diagram



Relative stability at T=0
DFT-GGA



- Predicts successive phases under pressure: hcp-ω-bcc
- $P_{\omega\text{-bcc}}$= 30 GPa

ELASTIC CONSTANT CALCULATIONS – DFT

$$\begin{pmatrix} 1+\alpha & 0 & 0 \\ 0 & 1+\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} 1+\alpha & 0 & 0 \\ 0 & 1-\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1+\alpha \end{pmatrix}$$

$$\begin{pmatrix} 1 & 0 & \alpha \\ 0 & 1 & 0 \\ \alpha & 0 & 1 \end{pmatrix}$$

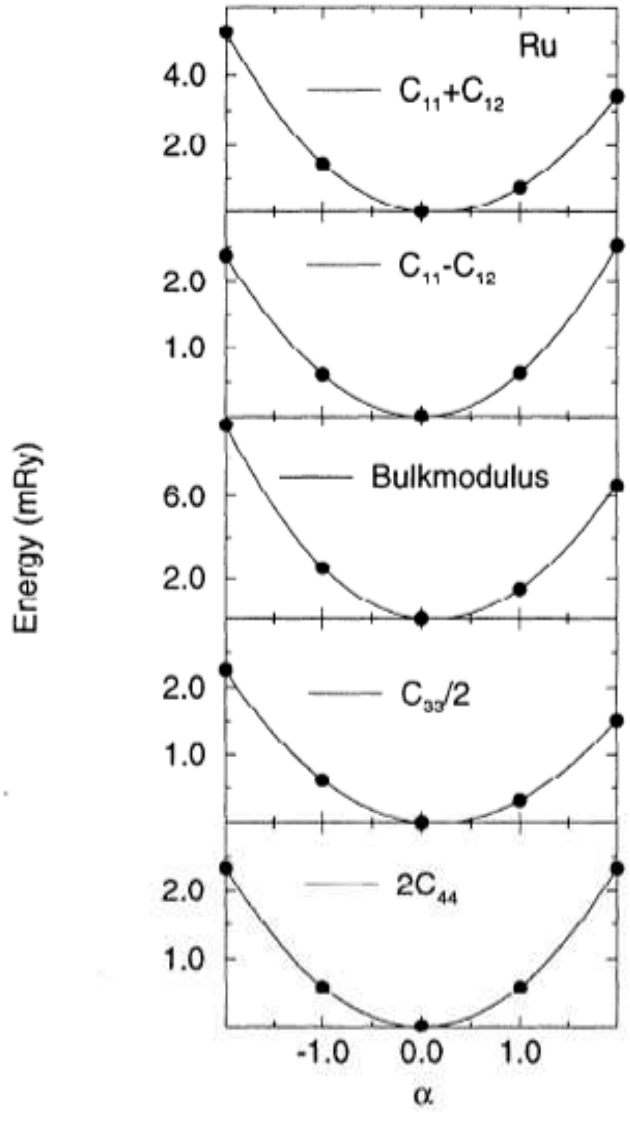


FIG. 1. Total energy of Ru as function of the lattice distortion parameter α, for the five different strains defined in the text. From the top panel to the bottom panel, the strains correspond to the distortions given in Eq. (5), Eq. (7), Eq. (14), Eq. (9), and Eq. (11), respectively.

hcp Ru

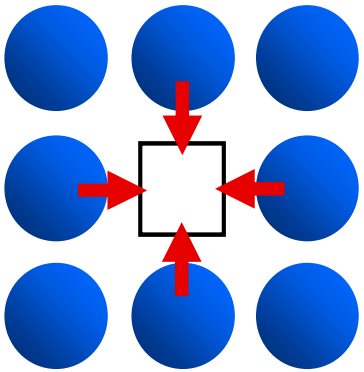
Accord avec l'expérience des calculs DFT : 10 à 20%

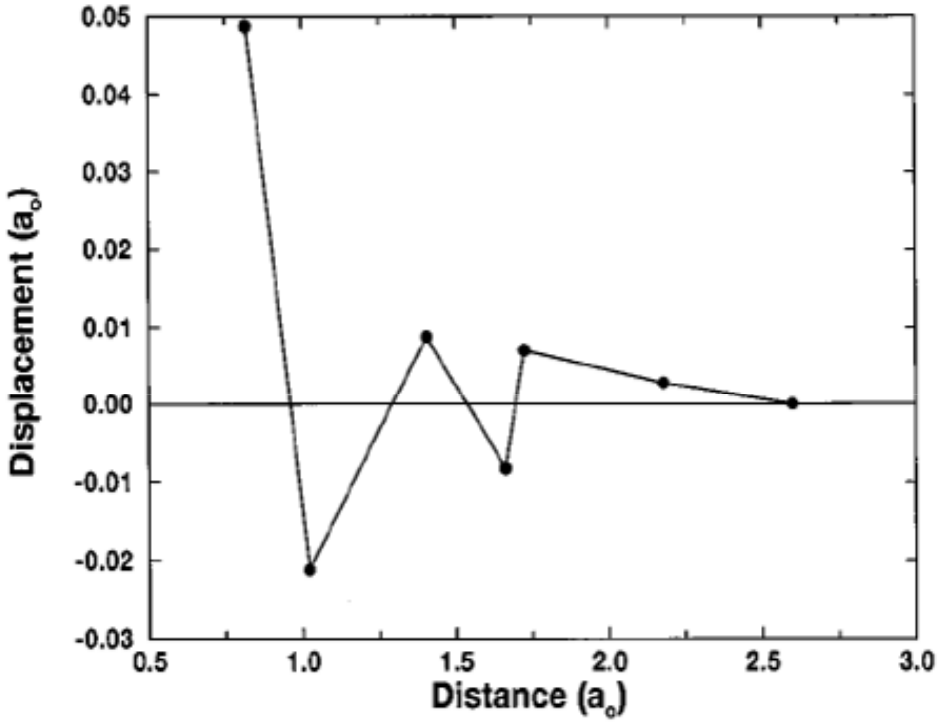
L. Fast et al. (1995)

RELAXATION CALCULATIONS

« Relaxation » or geometry optimisation = minimization of the energy, $E(\{\mathbf{r}_i\})$, wrt atomic positions, $\{\mathbf{r}_i\}$.

Example : arround a vacancy



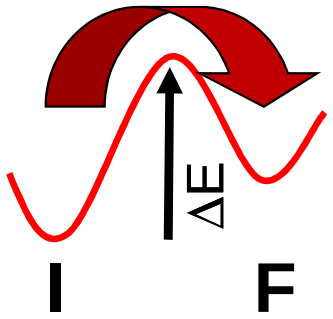


In Ta, relaxation reduces the DFT value of vacancy formation energy from 3.5 eV to 3.0 eV (Expt. = 3.1 eV)

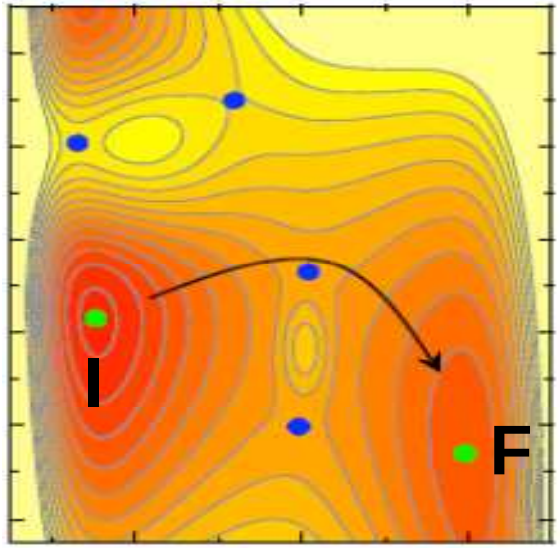
A. Satta et al.
Phys. Rev.B (1999)

SADDLE POINT CALCULATIONS

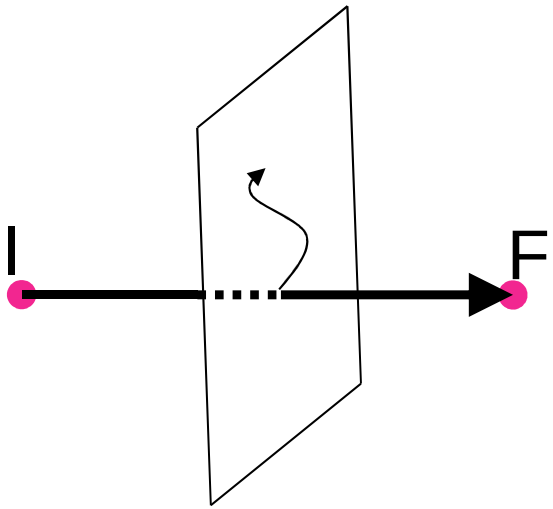
- Key ingredient for thermaly activated processes:



$$\Gamma(T) = \Gamma_0 \exp -(\Delta E / k_B T)$$



- reaction coordinate method:



- Minimization with a constrain, e.g.:

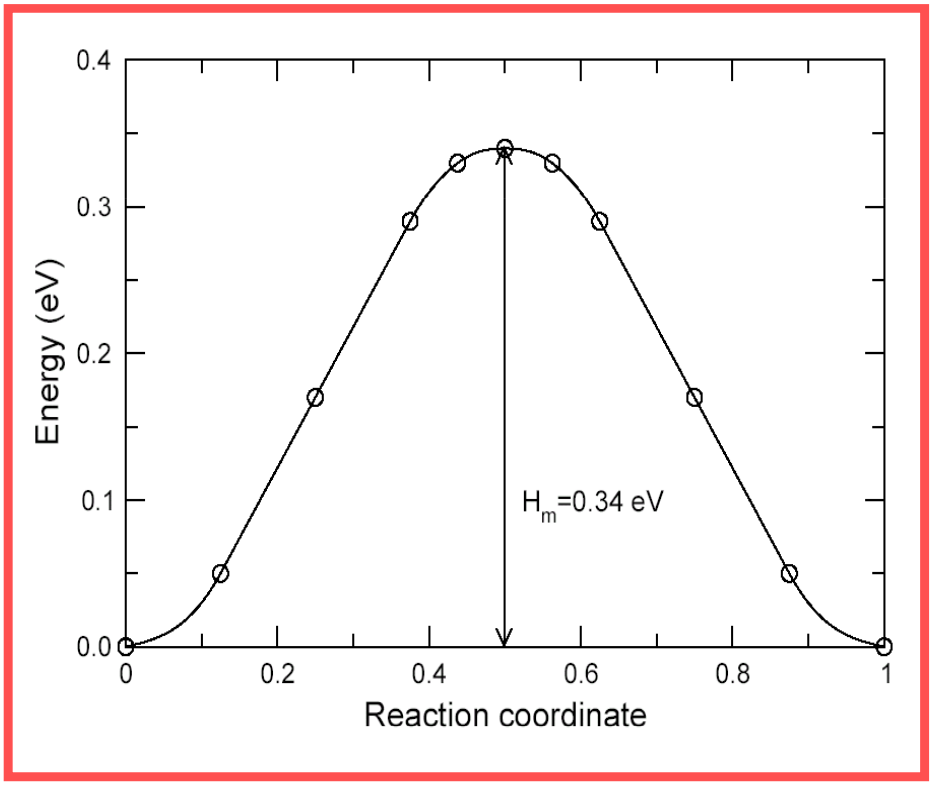
$$\xi(R) = \frac{(R - R_{CM})(R_F - R_I)}{|R_F - R_I|^2}$$

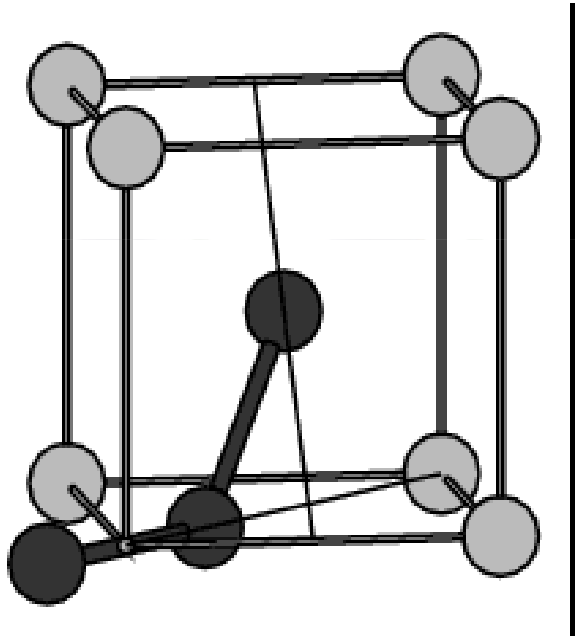
relaxation in the hyperplan perpendicular to the direct path

- Other method: Nudged Elastic Band (NEB)

EXAMPLE OF SADDLE POINT CALCULATION

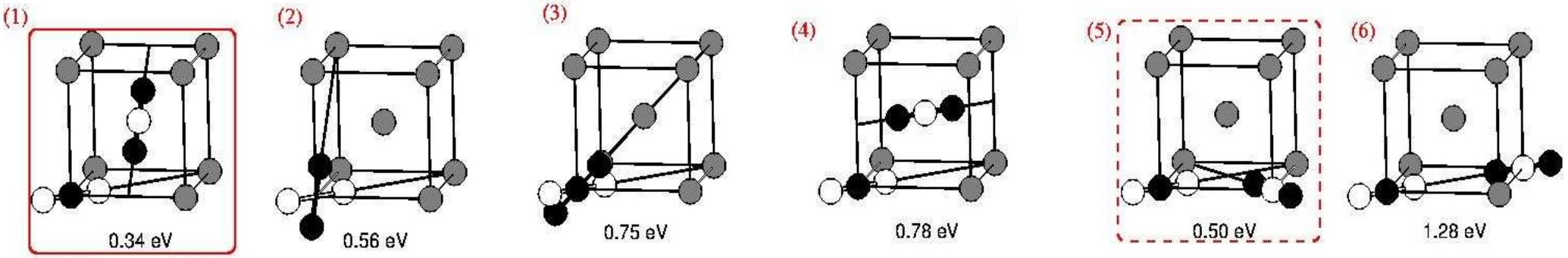
Self-interstitial in Fe (DFT)





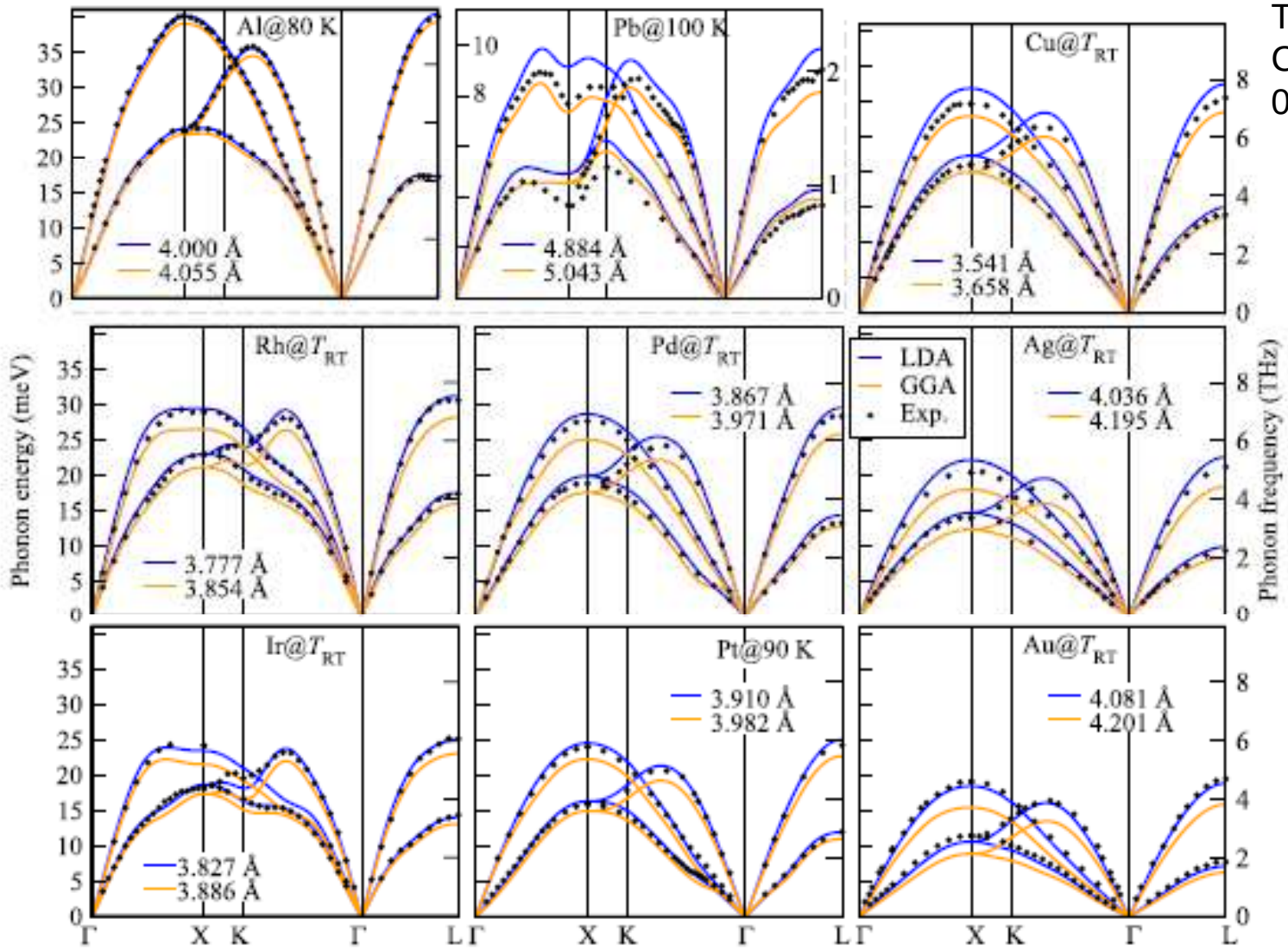
- Excellent agreement with exp. : H_M=0.3 eV

C.C. Fu et al. Phys. Rev. Lett (2002)



LATTICE DYNAMICS

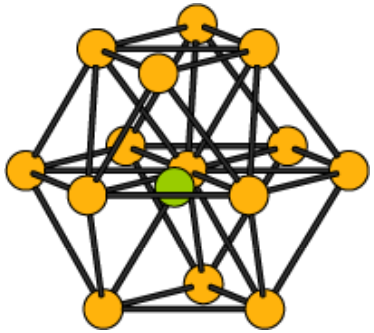
- Bulk phonons:



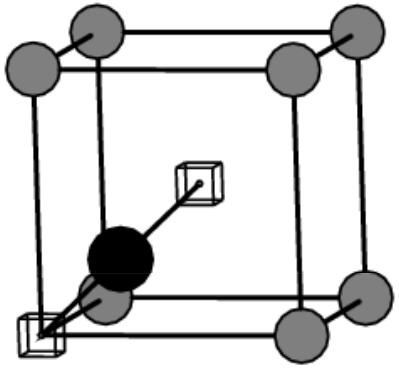
T. Hickel, et al. J. Phys.: Condens. Matter 24 (2012) 053202

- Can be used to compute defect attempt jump frequencies (Transition state theory)

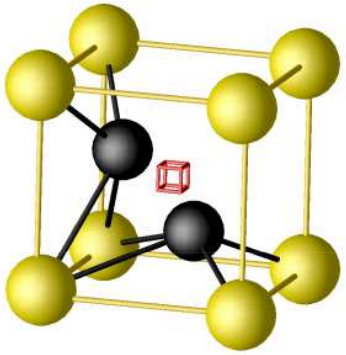
EXAMPLES OF RECENT DFT STUDIES



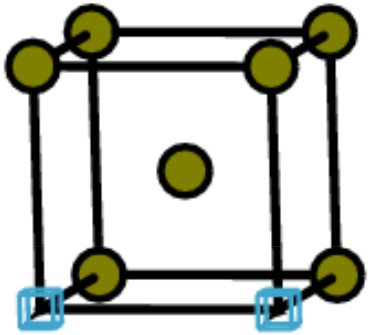
Self-interstitials in hcp metals
Vérité (2007)
Gasca (2010)



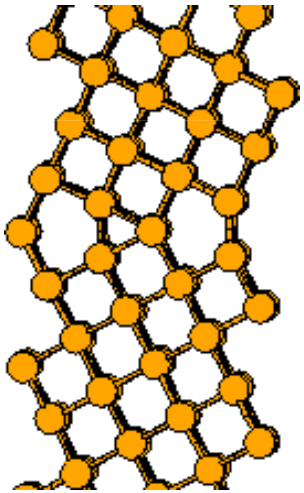
Helium-vacancy complexes in Fe
Fu (2005)



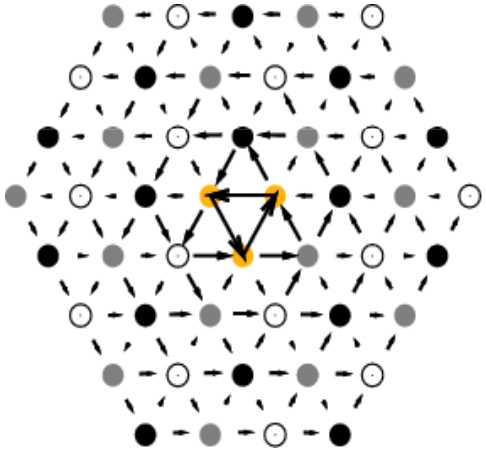
Vacancy-carbon complexes in Fe
Domain (2004)
Fu (2007)



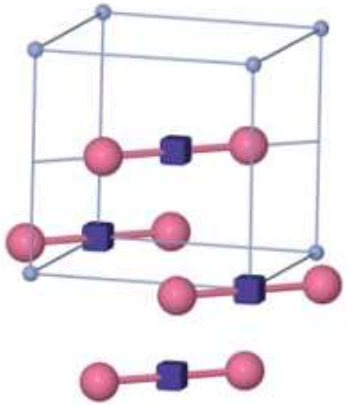
Di-vacancies in bcc metals
Ventelon (2012)



Grain boundary in Fe
Fu (2011)



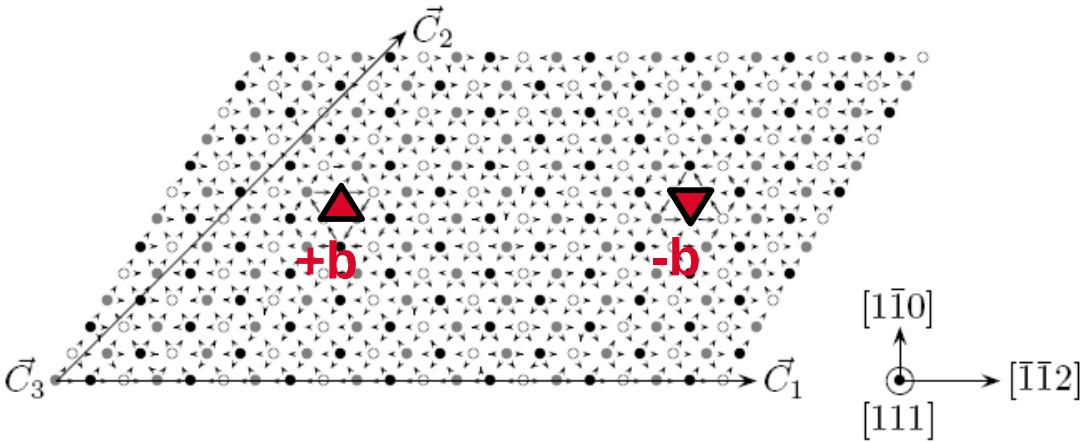
Dislocation cores in bcc metals
Ventelon (2012)



Self-interstitial clusters in Fe
Marinica (2012)

CORE OF <111> SCREW DISLOCATIONS IN BCC METALS (DFT)

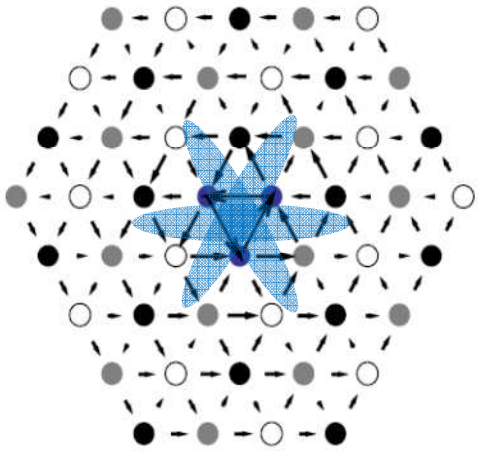
Simulation cell: 273 atom cell



Core structure

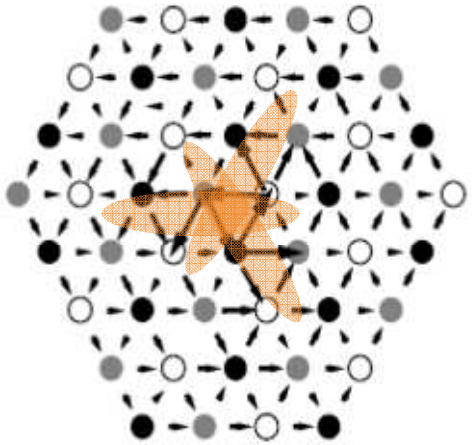
- Vitek representation
- Most empirical potentials predict degenerate cores

Fe, Mo, Ta, W



Non degenerate core

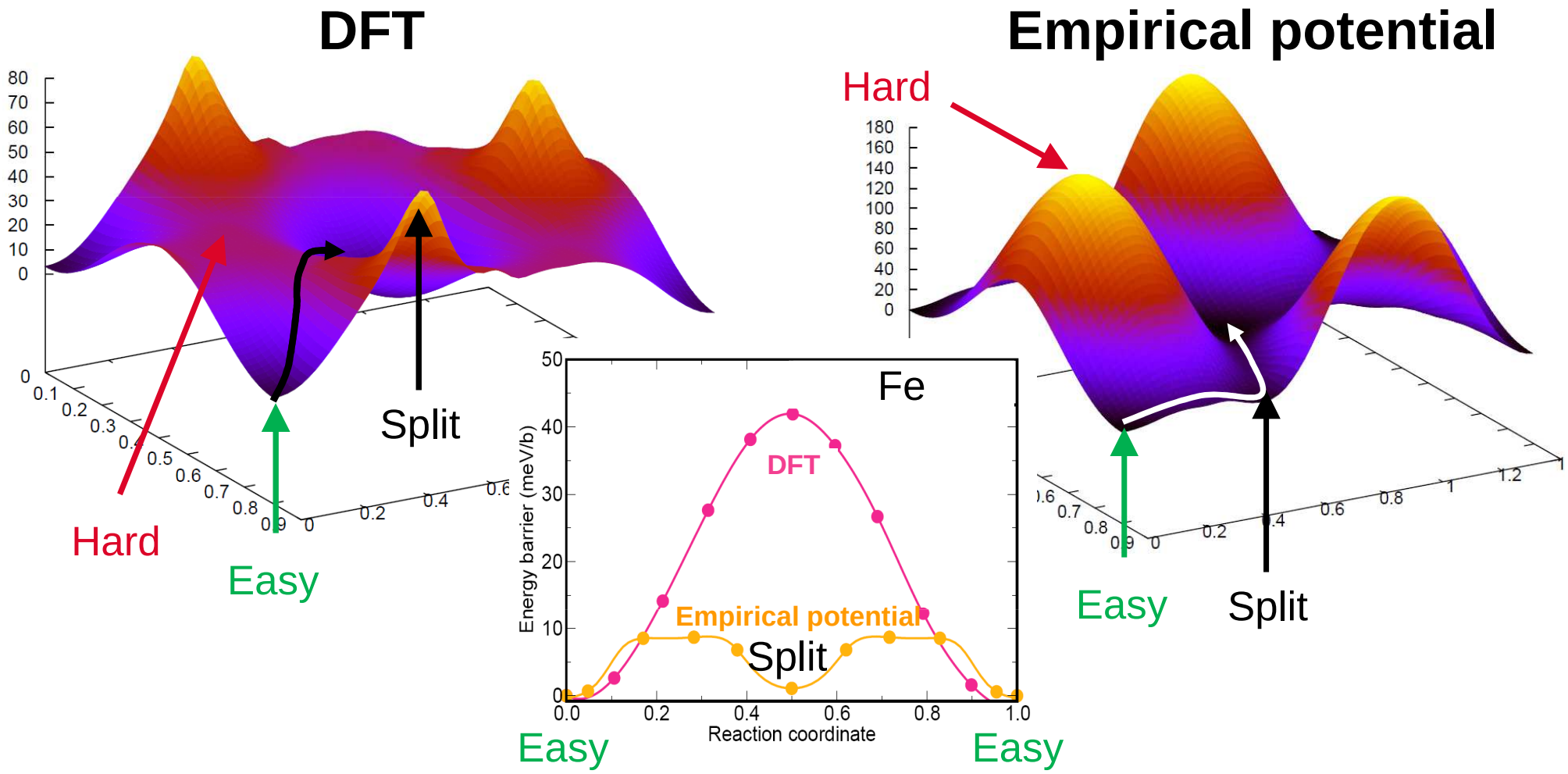
W-25%Re



Degenerate core

Romaner (2010)
Ventelon (2011)

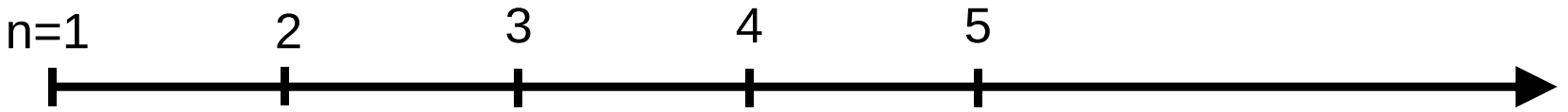
2D PEIERLS POTENTIAL OF <111> SCREW DISLOCATIONS IN BCC FE

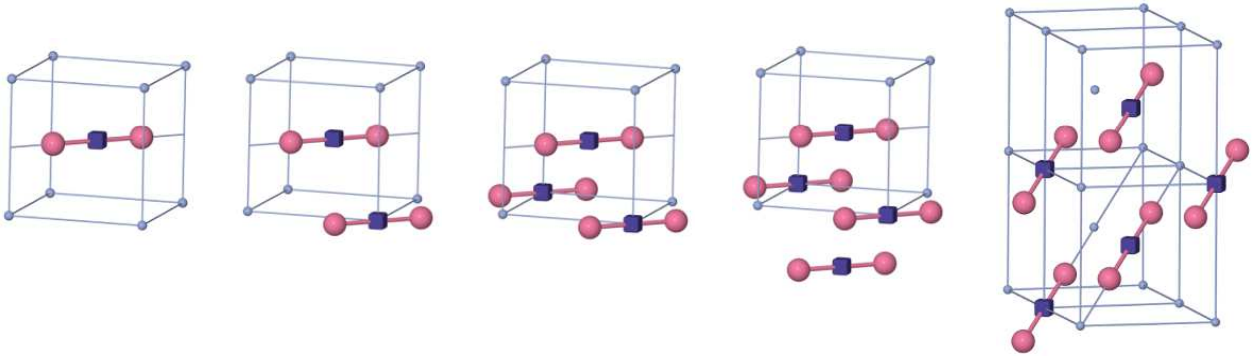


Compatible with absence of asymmetry in the crystal orientation dependence of the critical flow stress observed experimentally in iron at low temperature

L. Ventelon, L. Dezérald, FW, E. Clouet, D. Rodney

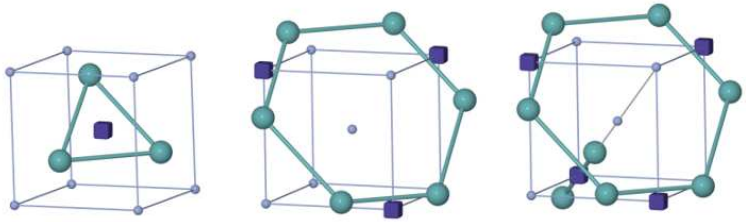
SELF INTERSTITIAL CLUSTERS IN BCC FE





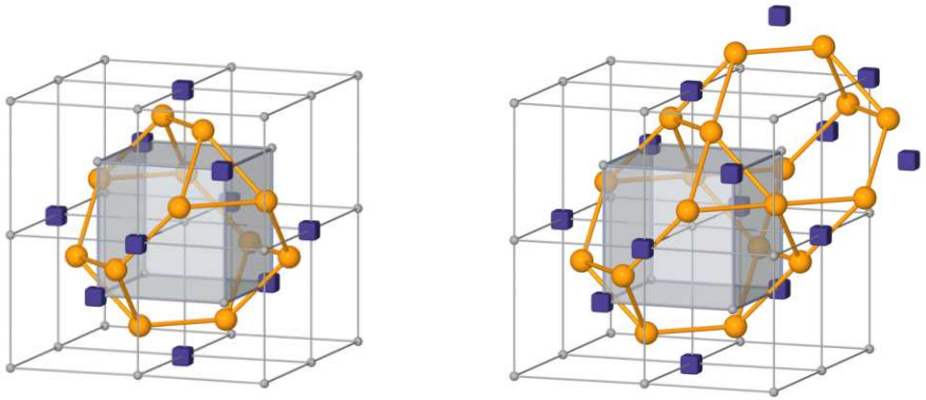
Parallel dumbbells

FW et al.; NIMB 228 (2005) 92



Triangle and rings

D.A. Terentyev et al.
PRL 100 (2008) 145503

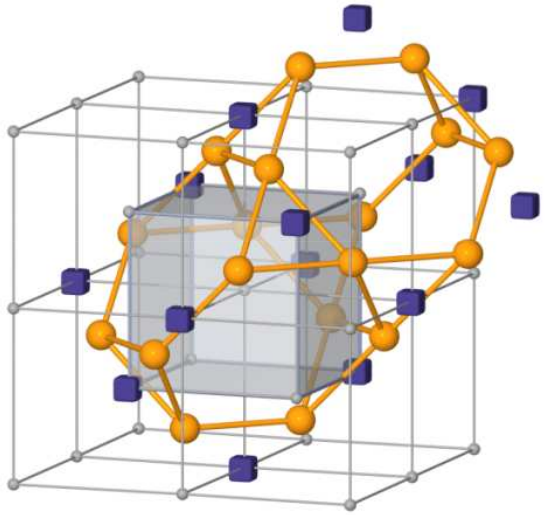


3D structure
C15 nanocrystals

M. C. Marinica, FW, J-P Crocombette
Phys. Rev. Lett.108 (2012) 025501

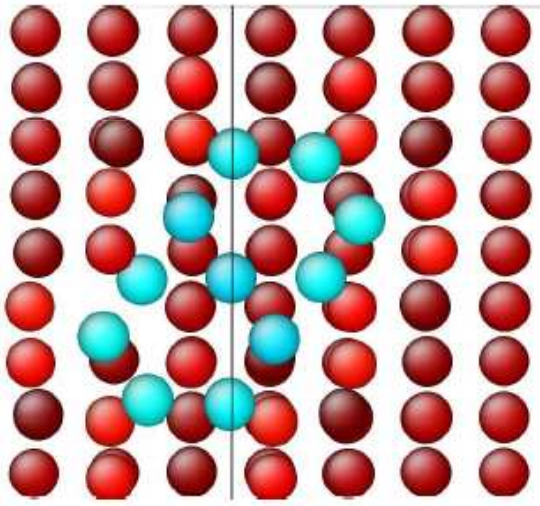
PROPERTIES OF C15 SELF-INTERSTITIAL CLUSTERS IN FE

3D crystalline structure predicted for self-interstitial clusters in bcc metals



DFT results:

- Very low energy structures in Fe, and to a lesser extend in Ta (DFT)
- They have large antiferromagnetic moments



Empirical potential (fitted to DFT):

- They are formed in cascades
- They can grow by capturing <110> dumbbells
- They are immobile

PERSPECTIVES AND CHALLENGES

DFT

- exchange-correlation functionals
- parallelization beyond 1000 cores
- finite temperature effects in DFT
- toolkits (phase diagrams, Onsager coefficients, etc.)
- automatic sampling of energy landscapes (ART, dimer)
- dislocation kinks

Other atomistic methods

- Empirical potentials for alloys and tight-binding models (eg Fe-C)
- Slow dynamics codes (CRESCENDO CD code)

Coupling with experiments

REFERENCES

- Electronic Structure: Basic Theory and Practical Methods, R. M. Martin (Cambridge University Press, 2004)
- Handbook of Materials Modeling, Ed. S. Yip (Springer, 2005)
- Comprehensive Nuclear Materials, Vol. 1: Basic Aspects of Radiation Effects in Solids/Basic Aspects of Multi-Scale Modeling, Ed. R. J.M. Konings (Elsevier, 2012)