Des cristaux aux quasicristaux
Quelques exemples de modélisation

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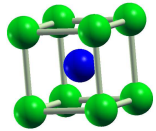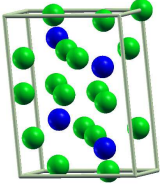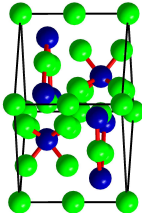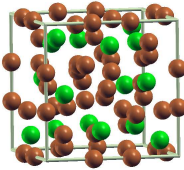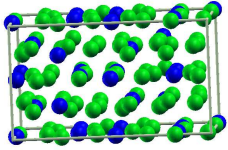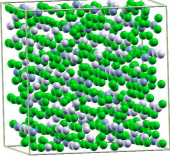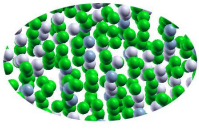$\simeq$ 500 personnes

4 départements:

- Physique de la Matière et des Matériaux
- Chimie et Physique des Solides et des Surfaces
- Science et Ingénierie des Matériaux et Métallurgie
- Nanomatériaux, électronique et vivant

Complex Intermetallic Compounds (CIMs)

$N=2$	22	28	52	102	544	∞
B2 AlCo	Al_9Co_2	Al_5Co_2	Al_4Cu_9	$Al_{13}Co_4$	2/1 approx.	i-AlPdMn
	Periodic Complex Intermetallic Compounds					

Al=green, Co=blue, Cu=brown

- Complex intermetallics (CIMs) are intermetallic compounds character-ized by large unit cells and the presence of well-defined atomic clusters.
- N (atoms nb per unit cell) is generally used to quantify the complexity

22	52	102	infinity
Al_9Co_2	Al_4Cu_9	$Al_{13}Co_4$	Quasicrystal
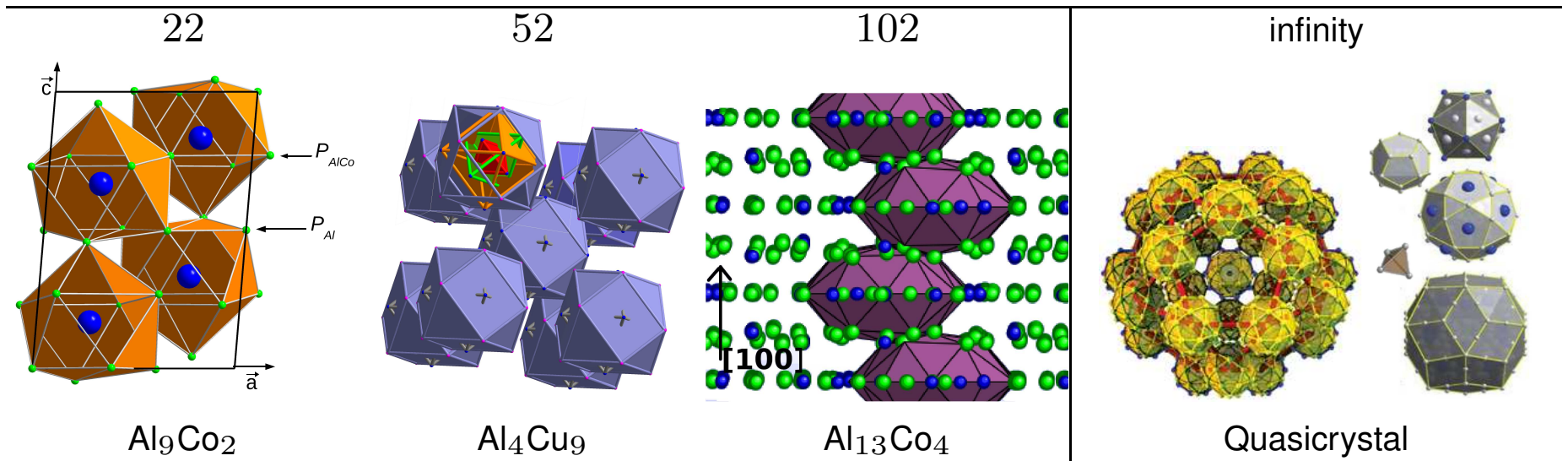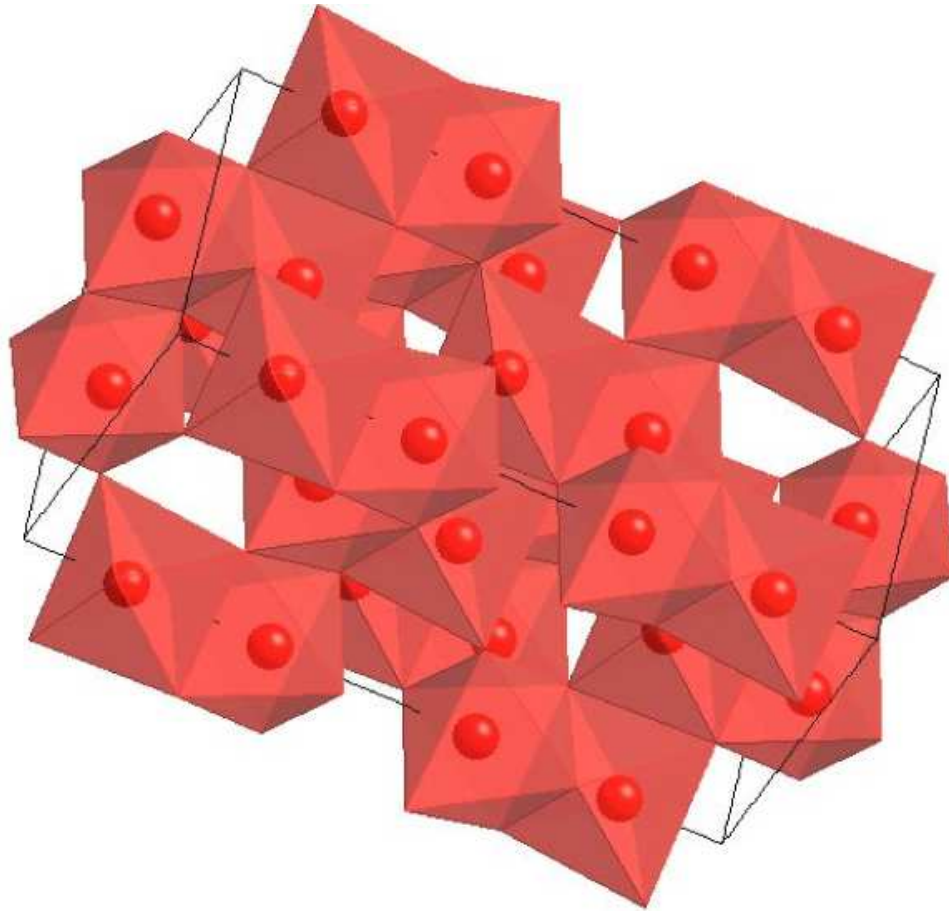
What is a crystal?

Al$_2$O$_3$ crystal ($R\bar{3}c$, 167)

$$a = b = c = 5.178 \text{ Å}, \alpha = \beta = \gamma = 55.29^0$$

What is a crystal?

Order, periodicity, rotational symmetries (rotations et roto-inversions).
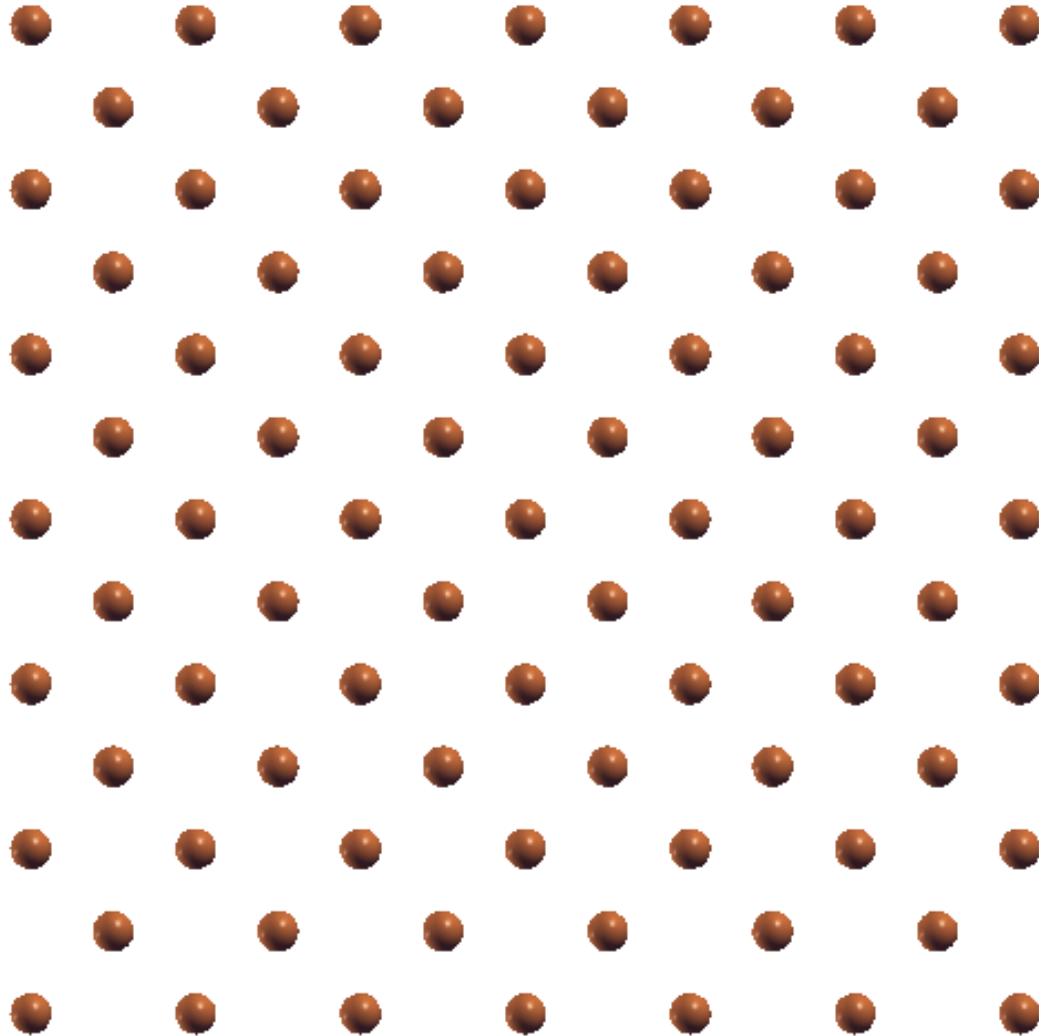
Few symmetry operations:

Rotational operations n: $1, 2, 3$, etc

Rotational symmetry: angle $\frac{2\pi}{n}$

Roto-inversion symmetries $\bar{n}$: $\bar{1}, \bar{2}, \bar{3}$, etc

Rotational symmetry (angle $\frac{2\pi}{n}$) and then

inversion symmetry

X-ray Diffraction: crystal

A diffraction pattern from a periodic crystal is characterized by:

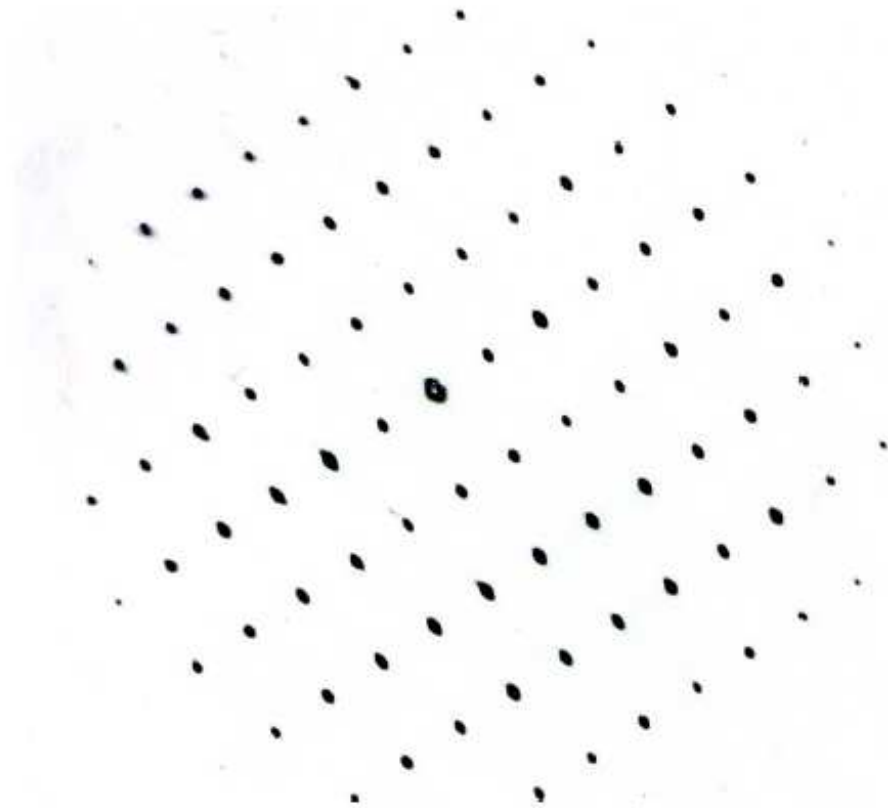♣ Periodicity of diffraction peaks in the reciprocal Space

♣ Rotational symmetries: 1,2,3,4 and 6-fold

♣ No 5-fold rotational symmetry and nothing beyond 6-fold

From D. Shechtman

Definition: crystal (before 1992)

- A solid composed of atoms arranged in a pattern periodic in three dimensions

  "X-ray Diffraction", Culity 1959

- Atoms in a crystal are arranged in a pattern that repeats itself in three dimensions throughout the interior of the crystal

  "Structure of Metals" Barrett and Massalski, 1966

Due to their three-dimensional periodicity, crystals can have only the following rotational symmetries: $1, 2, 3, 4, 6$

From Kittel *Introduction to solid state physics*

We can make a crystal from molecules which individually have a five-fold rotation axis, but we should not expect a lattice to have a five-fold rotation axis.
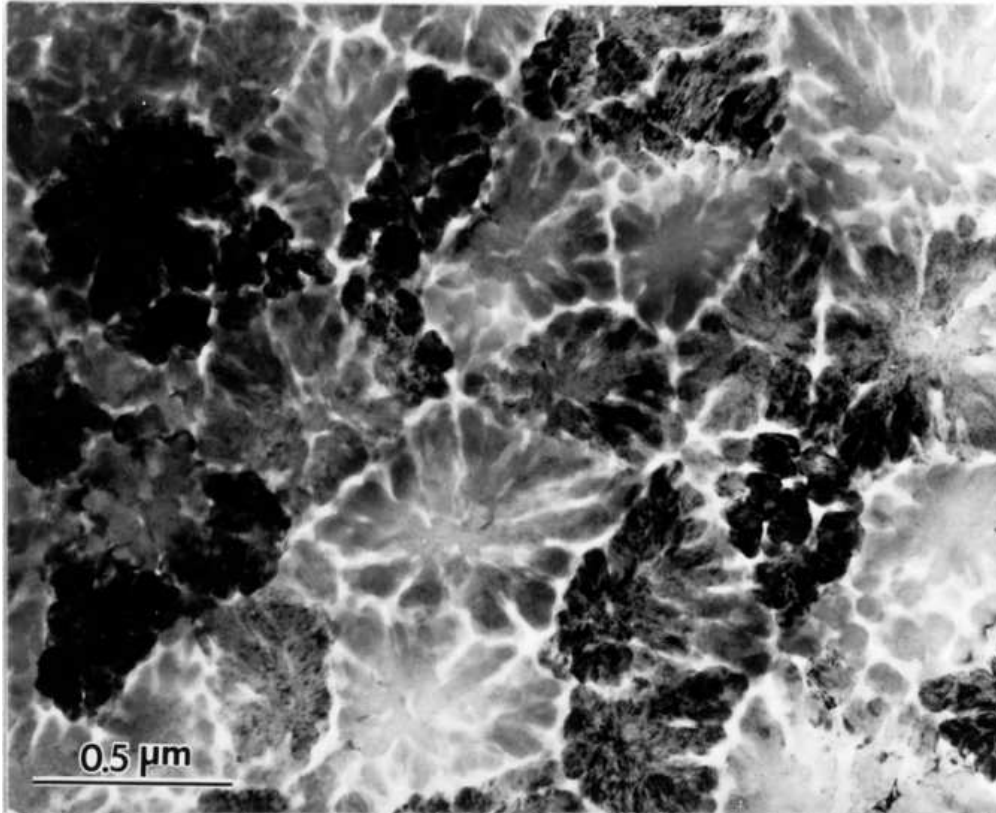
Discovery
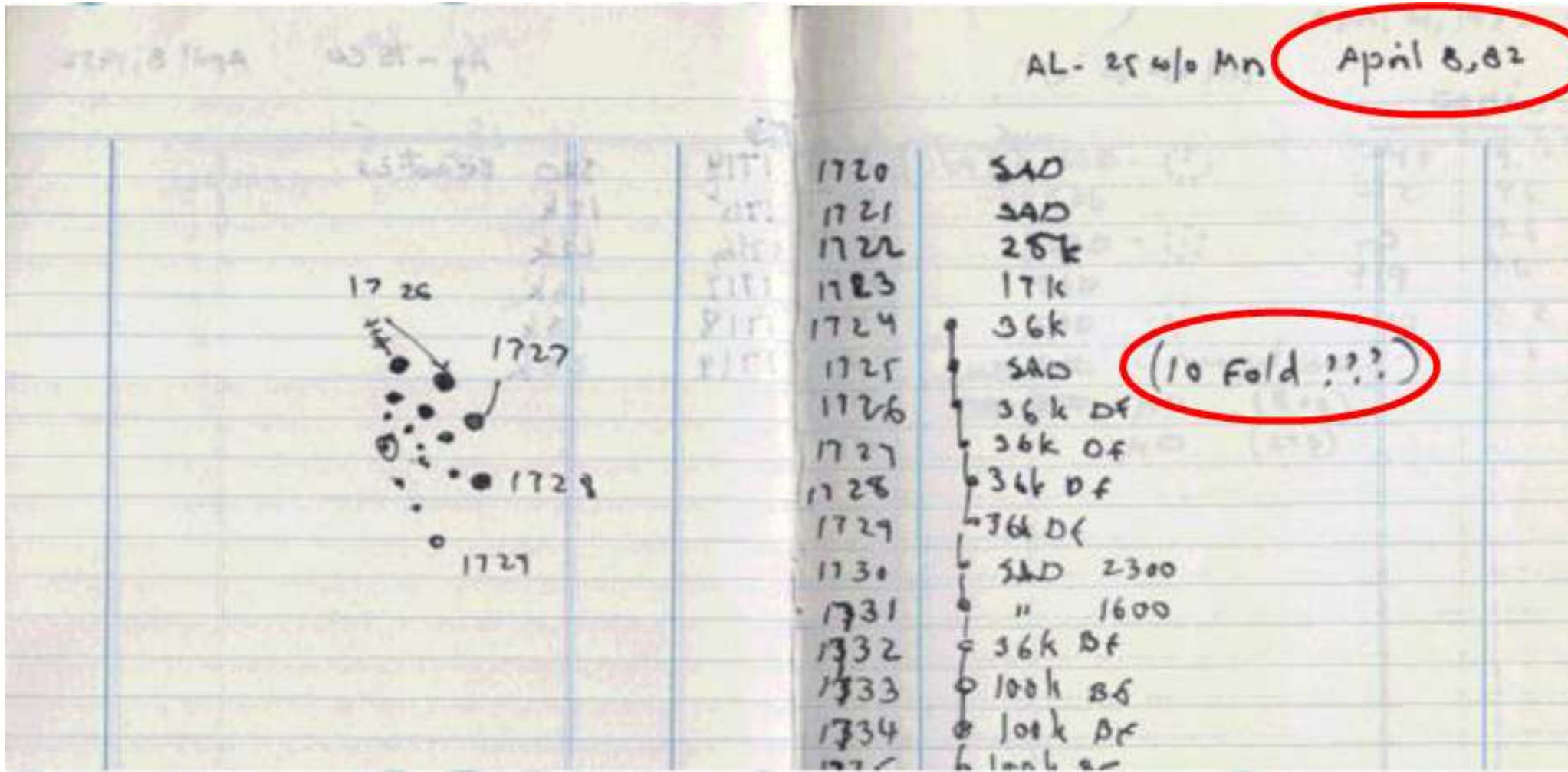
From D. Shechtman

Discovery

Electron diffraction from the Icosahedral Phase has five-fold rotational axes

It is not periodic.

From D. Shechtman

After 1992, a new definition for crystals
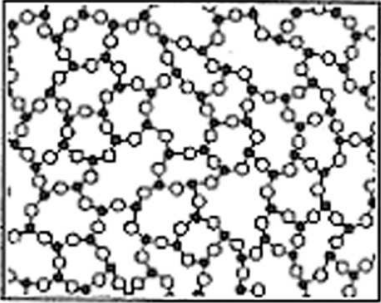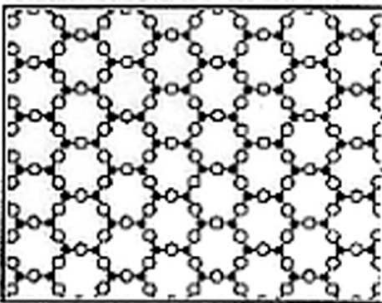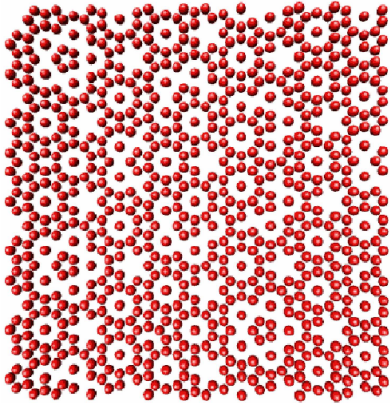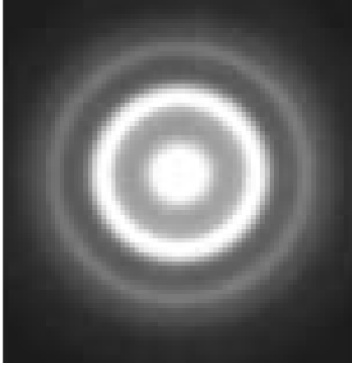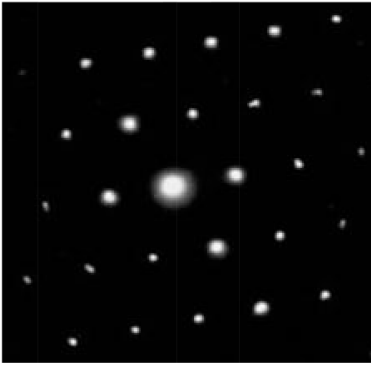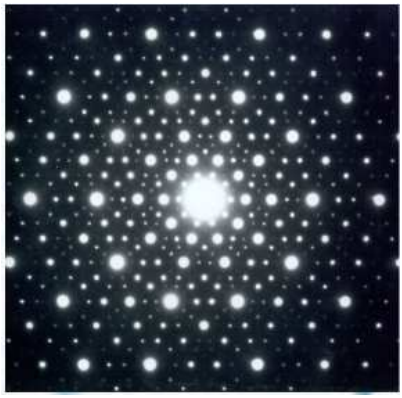
"By crystal we mean any solid having an essentially discrete diffraction diagram, and by aperiodic crystal we mean any crystal in which three dimensional lattice periodicity can be considered to be absent." Ref.: International Union of Crystallography, "Report of the executive Committee for 1991", Acta Cryst. A48 (1992) 922-946
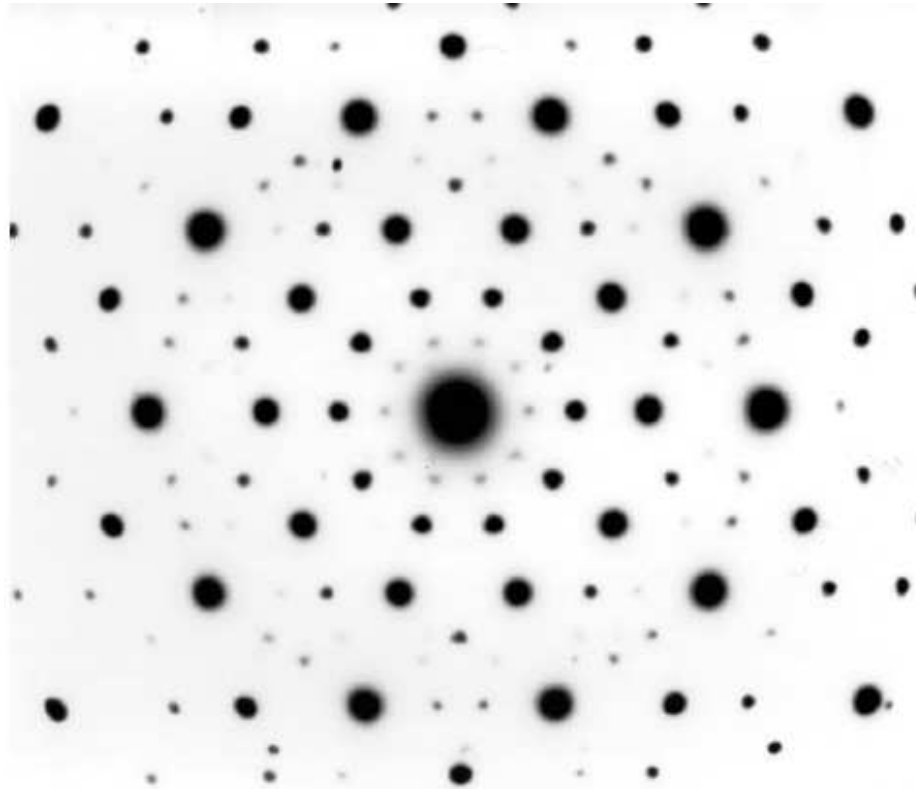
Sharp diffraction peaks: long-range ordered structure

Exhibit crystallographically forbidden symmetries (5-fold for example)

Solids: order and disorder

glass	crystal	
disorder	order	
no periodicity	periodicity	quasiperiodicity
	n-dimensional periodicity	
glass	quartz	
diffraction pattern		

- Diffraction is not an exclusive property of periodicity

- The long-range order does not necessarily lead to diffraction phenomena

QCs and the gold number

Why QC were never discovered before 1982?

- Are they rare?

- Are they stable?

- Are they easy to synthesize?

- Do natural QC exist?

Are QCs rare?

Number of Qcs are known:

- Al-based

- but also: TM-Mg-Zn, Ag-In-Yb, etc

Al-Cr-Ge	Al-Cr-Si	Al-Cr-Mn-Si	Al-Cr-Zr-Mn
Al-Fe-Mn	Al-Fe-Si	Al-Fe-Mn-Si	
Al-B-Mn	Al-Ge-Mn	Al-Ni-Mn	Al-Ru-Mn

Al-Cu-Li	Al-Cu-Mn	Al-Cu-Mn-Zn	Al-Cu-V
Al-Cu-Fe			

Al-Ag-Mg	Al-Au-Li	Al-Zn-Li	Al-Mg-Zn
Ga-Mg-Zn			

Are they stable?
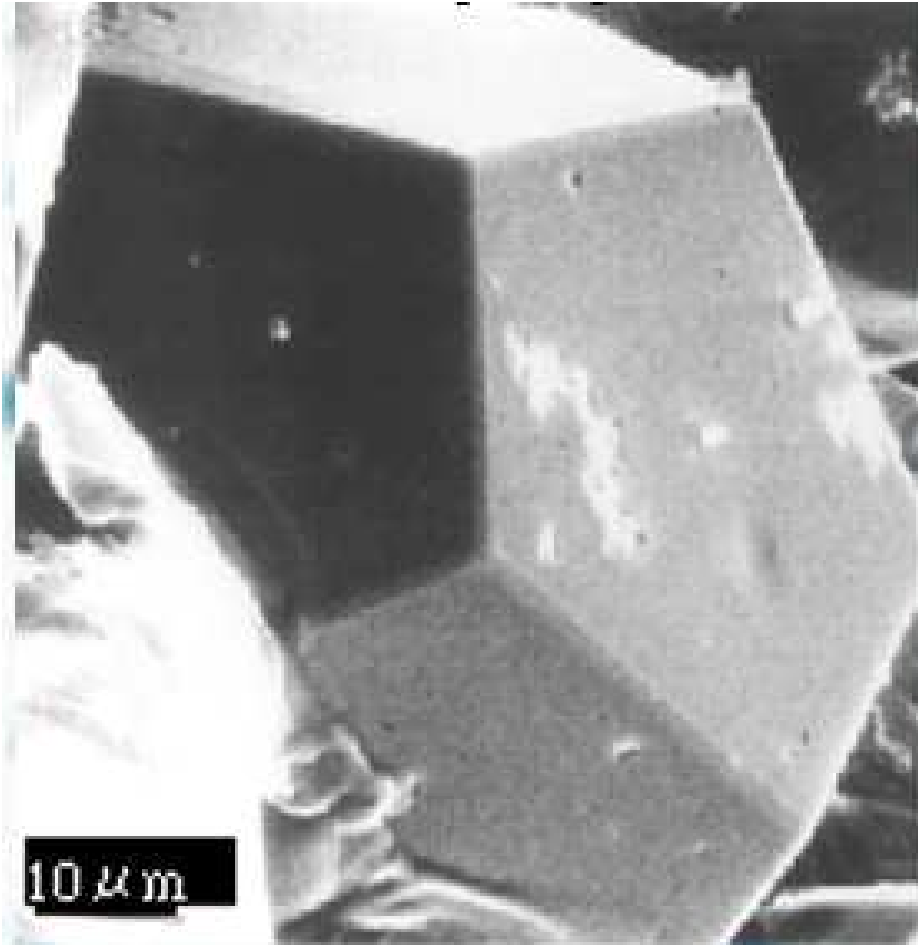
From H. Trebin, *Quasicrystals: Structure and Physical properties*, Wiley (2003)
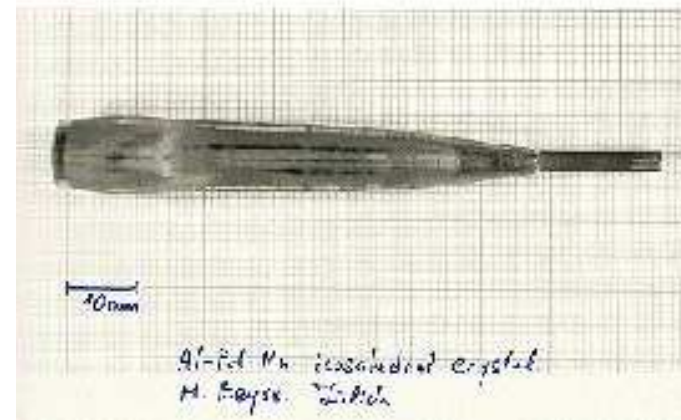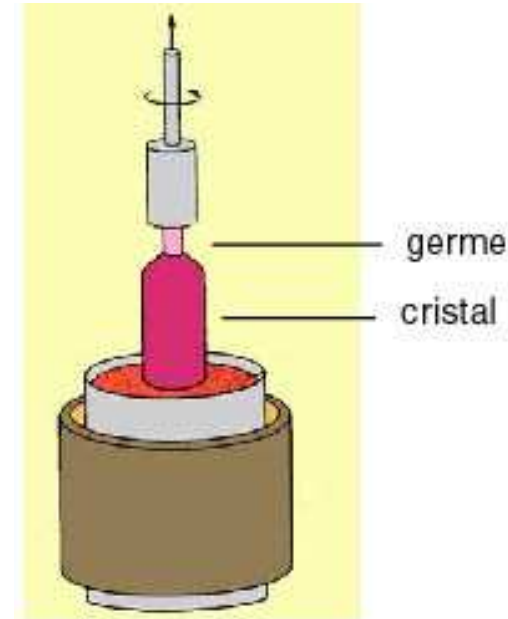
germe

cristal

Do natural QC exist?

Various methods to synthesize QCs: single crystal growth, rapid solidif., PVD, CVD, etc

Natural QCs do exist: Steinhardtite ($Al_{0.38}Ni_{0.32}Fe_{0.30}$), (Am. Min. **99** (2014) 2433; Science **324** (2009))

Figure 5. A picture of the original khatyrkite-bearing sample belonging to the collections of the Museo di Storia Naturale of the Università degli Studi di Firenze (catalog number 46407/G). The lighter-colored material on the exterior contains a mixture of spinel, clinopyroxene and olivine. The dark material consists predominantly of khatyrkite ($CuAl_2$) and cupalite ($CuAl$), but also includes granules of icosahedrite with composition $Al_{63}Cu_{24}Fe_{13}$.

Do natural QC exist?

Various methods to synthesize QCs: single crystal growth, rapid solidif., PVD, CVD, etc

Natural QCs do exist: Steinhardtite ($Al_{0.38}Ni_{0.32}Fe_{0.30}$), (Am. Min. **99** (2014) 2433; Science **324** (2009))

Figure 13. Members of the Koryak expedition team (left to right): Bogdan Makovskii (driver), Glenn MacPherson (Smithsonian Institution, USA), Will Steinhardt (Harvard, USA), Christopher Andronicos (Cornell, USA), Marina Yudovskaya (IGEM, Russia), Luca Bindi (University of Firenze, Italy), Victor Komelkov (driver), Olga Komelkova (cook), Paul Steinhardt (Princeton, USA), Alexander Kostin (BHP Billiton, USA), Valery Kryachko (Voronezh, IGEM), Michael Eddy (MIT, USA) and Vadim Distler (IGEM, Russia). Photo by W M Steinhardt.

Figure 15. Field operations at the Listvenitovyi stream (clockwise): mapping the structural geology, examining mineral samples, extracting clay from areas along the stream, and panning the clay down to mineral separates.
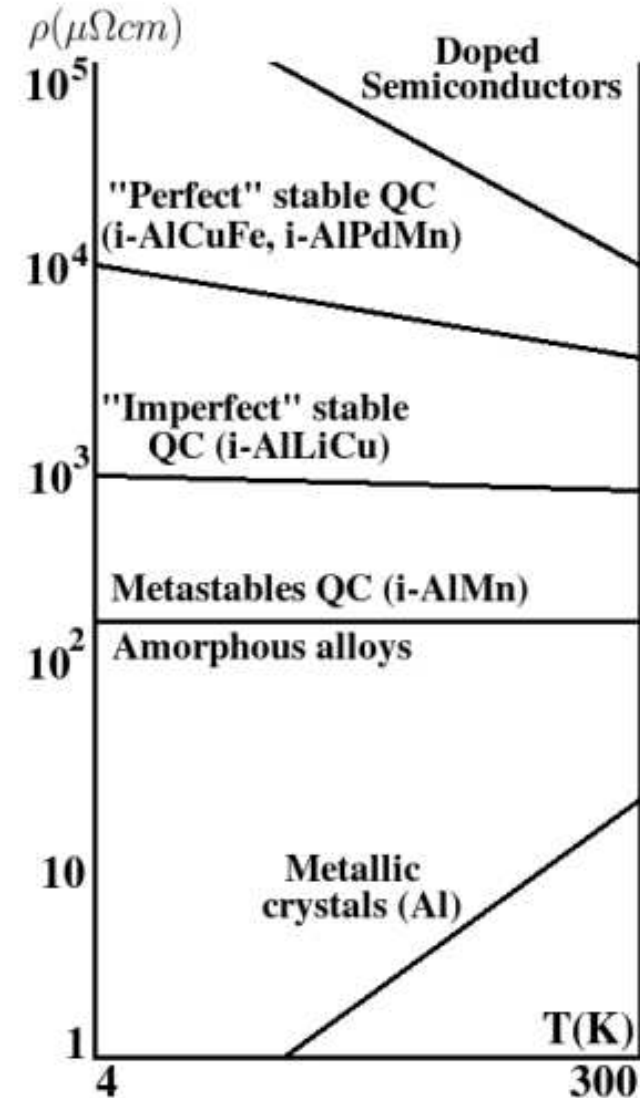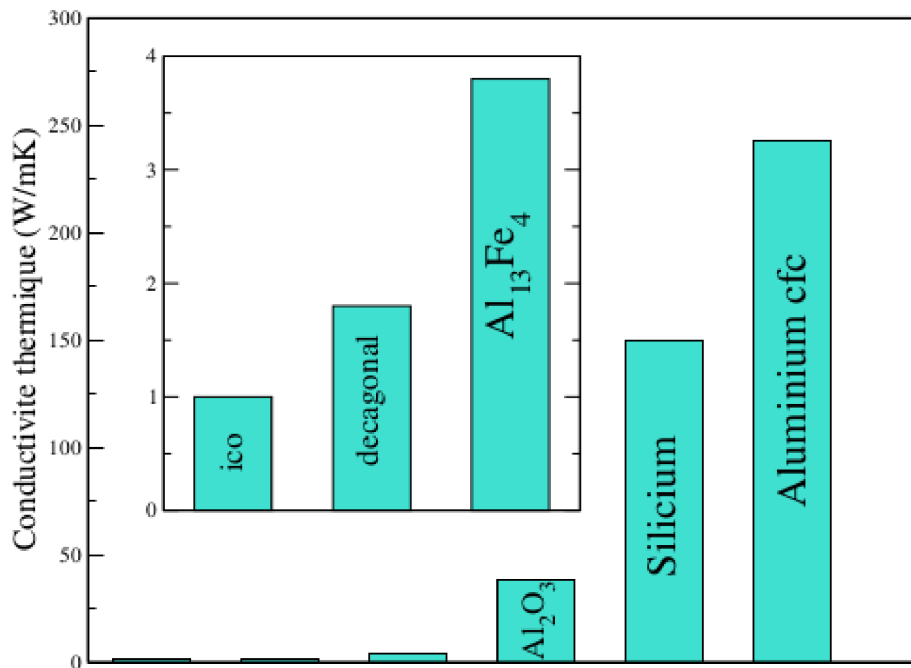
Few interesting properties

- Transport properties

  - Electronic (transport) properties

  - Thermal conductivity

- Mechanical properties

- Chemical properties

  - corrosion resistant surfaces

  - low cost catalysts

  - hydrogen storage media

Electronic and Thermal Conductivity

material	resistivity 300 K ($\Omega.m$)
metal (Cu)	1.7×10^{-8}
doped Si	10^{2} to 10^{-4}
i-AlPdRe	10^{-4}

E. Belin-Ferré, C. Berger, M. Quiquandon and A. Sadoc *Quasicrystals: Current Topics,* World Scientific Publishing, Singapore (2000).
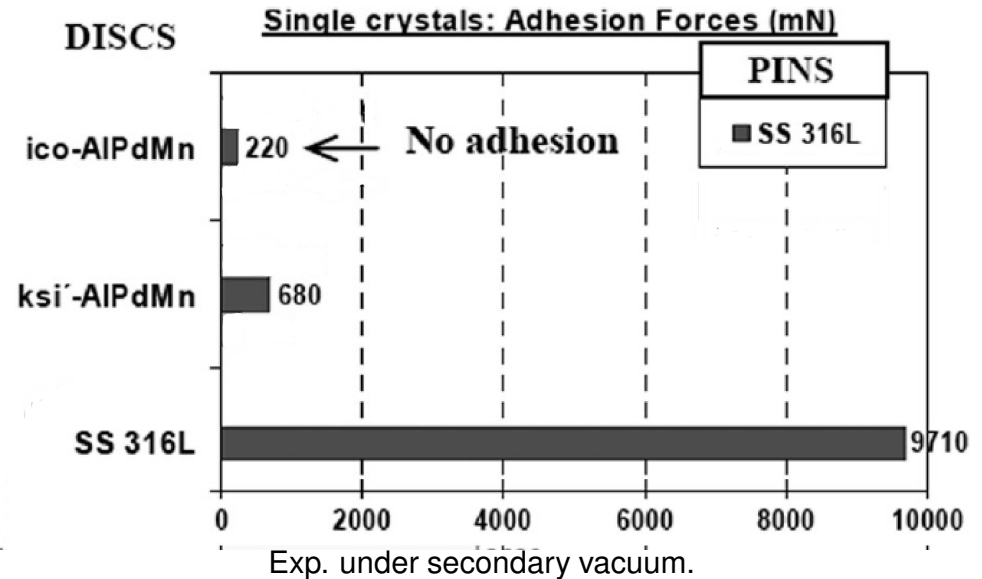
Mechanical properties

● **Hardness**:

Quasicrystals are hard, but fragile

material	Al fcc	Si	i-Al-Pd-Mn
H (GPa)	0.5	10	7

These mechanical properties are still valid at high temperature (600^0C)

DISCS — Single crystals: Adhesion Forces (mN)

PINS — ■ SS 316L

ico-AlPdMn | 220 ← No adhesion

ksi´-AlPdMn | 680

SS 316L | 9710

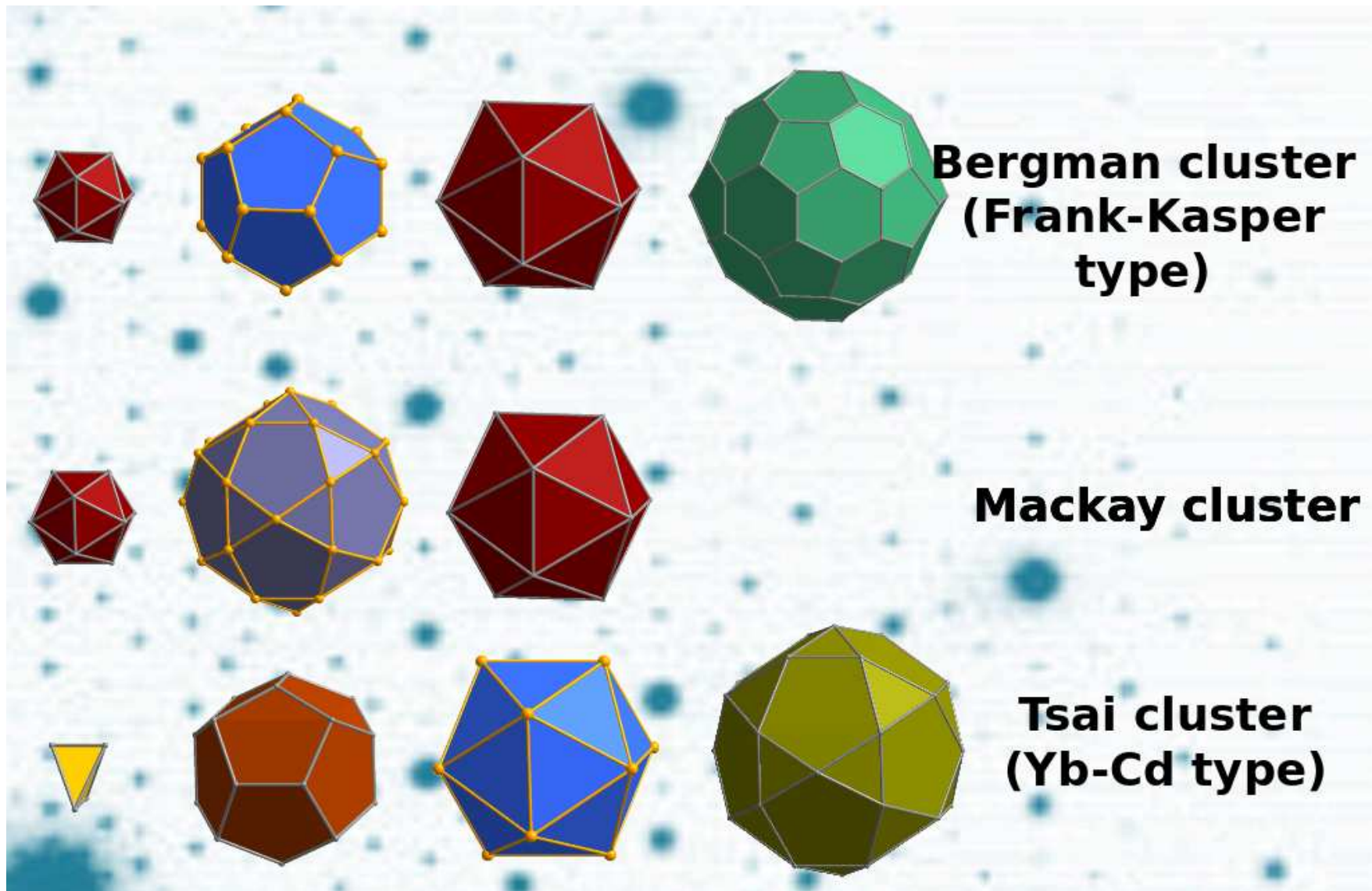0   2000   4000   6000   8000   10000

Exp. under secondary vacuum.

J.-M. Dubois, $Chem.\ Soc.\ Rev.$, **41**, 6760-6777 (2012)

● **Adhesion and friction**

material	steal on diamond	i-Al-Pd-Mn on diamond
friction coeff.	$\simeq 0.1$	0.05
material	steal on Al_2O_3	i-Al-Pd-Mn on Al_2O_3
friction coeff.	$\simeq 0.5$	0.15

Cluster substructure

Bergman cluster (Frank-Kasper type)

Mackay cluster

Tsai cluster (Yb-Cd type)

Cluster substructure

1/1 approximant $YbCd_6$

2/1 approximant $Yb_{13}Cd_{76}$

From Cesar Pay Gomez
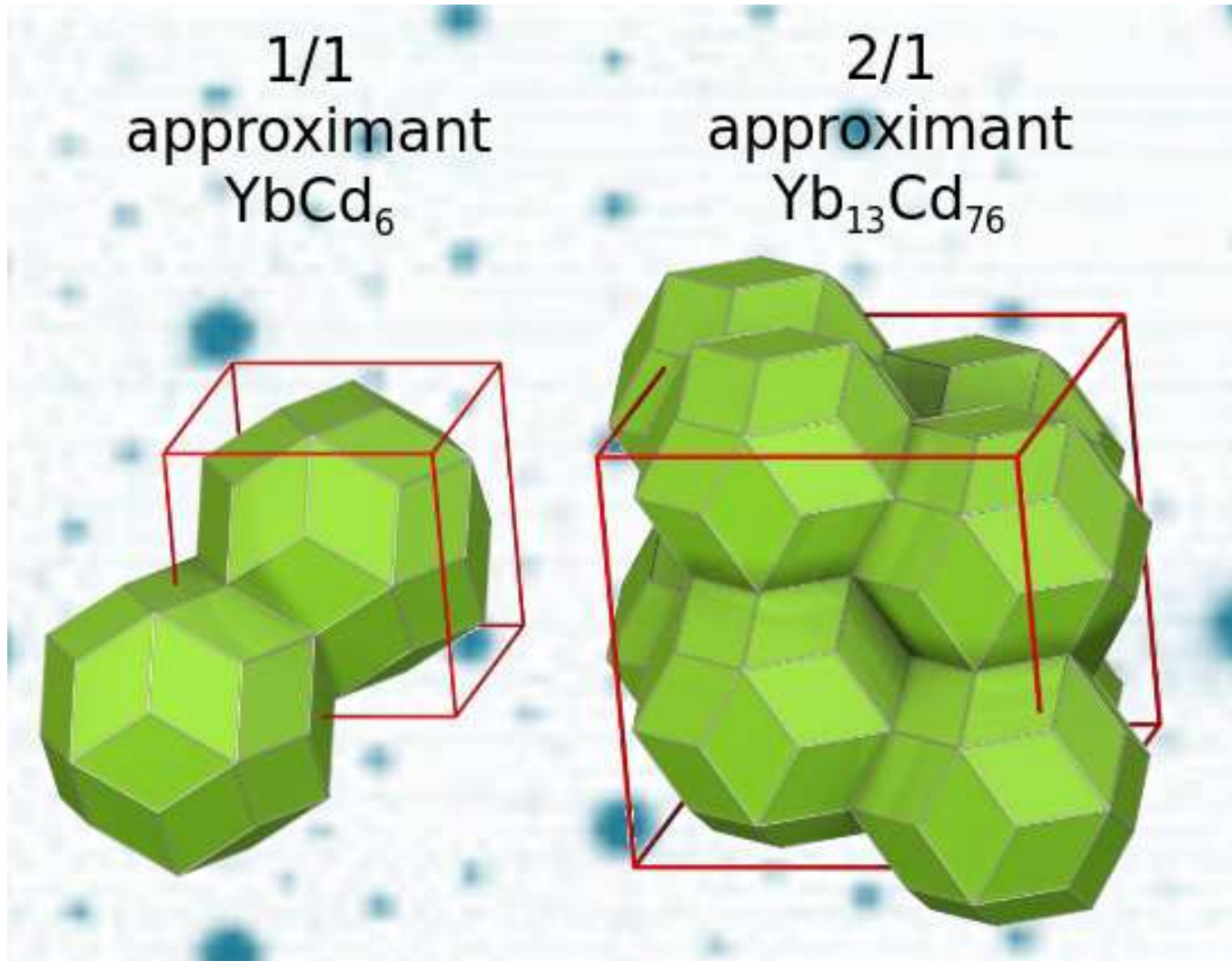
Chemical properties

● Al-based QCs are covered by Al_2O_3, leading to corrosion resistant materials

● Catalysis

| Before leaching | Initial stage of leaching | After leaching |

Homogeneous layer
(Cu,Fe,Al and their oxides)

QC-AlCuFe

Quasicrystalline alloy ($Al_{63}Cu_{25}Fe_{12}$)

Quasicrystalline alloy

~500nm

Low dissolution rate

● Hydrogen storage

From A. P. Tsai et al.
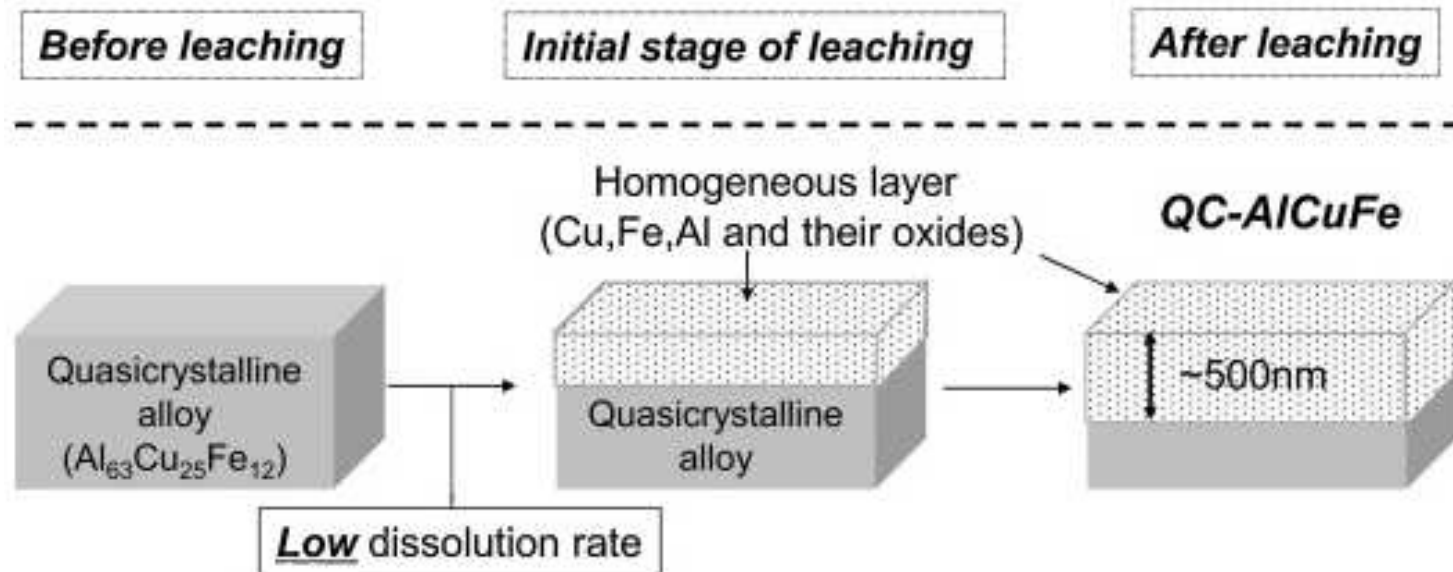
When crystals become quasi

Beautiful picture of an historic quasicrystalline tiling.

Darb-i Imam, Isfahan, Iran (1600s)

Some issues linked with QCs

- Can modeling help understanding the stability of quasicrystalline phases? What are the factors governing the stability of QCs phases?

  $\rightarrow$ bulk properties

- Some properties are linked to the surface. Then, the determination of the surface structure is essential. Can modeling help determining complex intermetallic surface structures?

  $\rightarrow$ surface structure

- Can modeling predict properties?

  $\rightarrow$ surface reactivity

Which method would you choose?

Method

- Step 1: Specify the physical/chemical problem

- Step 2: Choose a method adapted to the physical/chemical problem (time and space scales)

  - ab initio or (semi)-empirical method

  - static or dynamic method

  - choose the approximations (basis set, functional, set of parameters linked with the calculation)

- Step 3:

- Step 4:

- Step 5:

Modeling of solids $\rightarrow$ (generally) periodic boundary conditions

How to model (quasiperiodic $\neq$ periodic) QCs,

using codes based on periodic conditions?
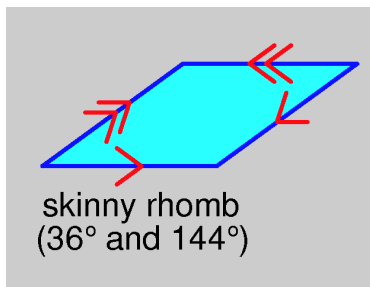
How to build a quasicrystalline tiling (1)

How to build a quasicrystalline tiling (1)

- Method 1: stacking of elemental building blocks

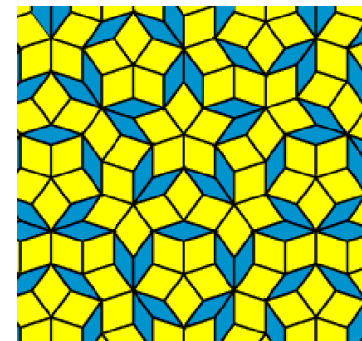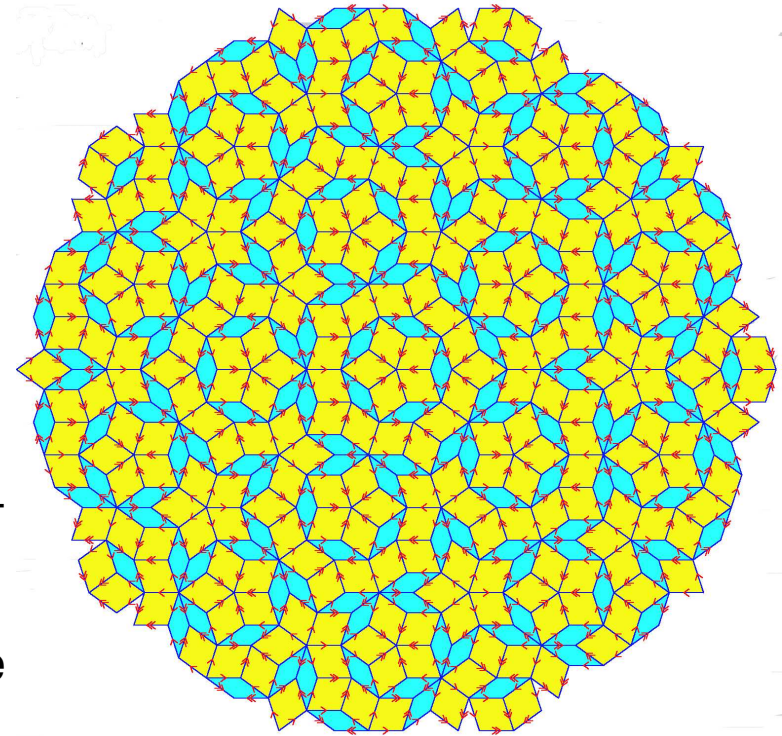 (Penrose tiling, 1972)

  - Two types of builing blocks

    skinny rhomb
    (36° and 144°)

    fat rhomb
    (72° and 108°)

  - Rule: match the type and direction of the arrows on common diamond edges.
  - Non periodic tiling, but few assembly units are repeated
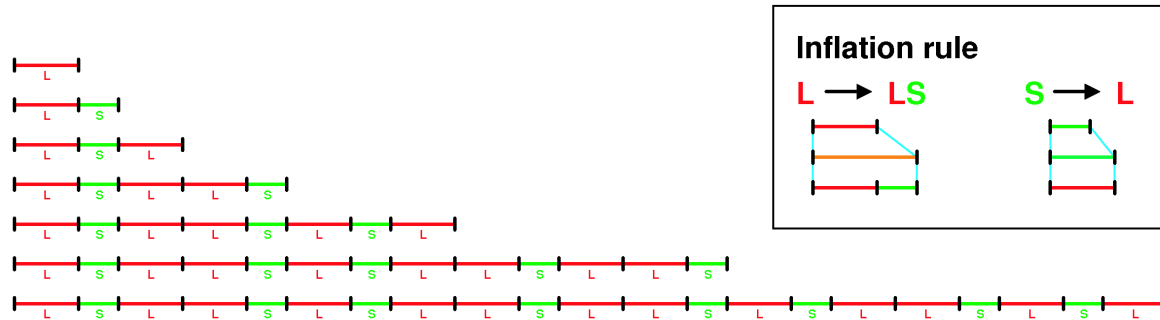 - Surface Ratio of two types of building blocks = gold number ($\frac{1+\sqrt{5}}{2}$)
  - each diamond appears in five different orientations

How to build a quasicrystalline tiling (2)

● Method 2: Fibonacci sequence

Example: Inflation for the Fibonacci chain, a one-dimensional example with two intervals as 'tiles'.

From the Royal Society Summer Science Exhibition 2004

● Number of long (L) and short (S) segments are numbers of the Fibonacci sequence

● The ratio $\frac{\text{Number of L}}{\text{Number of C}}$ tends towards the golden number $\tau = \frac{1+\sqrt{5}}{2}$

● Consequences for real QCs

● Concept of approximant

$$\begin{pmatrix} L \\ S \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} L \\ S \end{pmatrix} = \begin{pmatrix} LS \\ L \end{pmatrix}$$

How to build a quasicrystalline tiling (3)

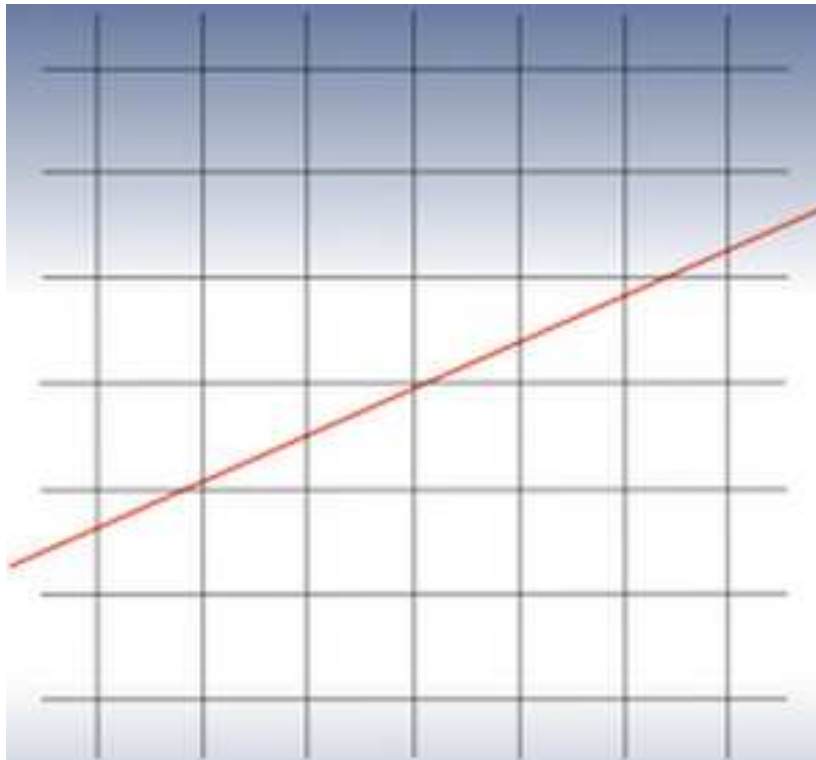Example: Periodic function with two variables x and y (period 1 and $\frac{1}{\sqrt{2}}$)

$$f(x, y) = \cos(2\pi x) + \cos(2\sqrt{2}\pi y)$$

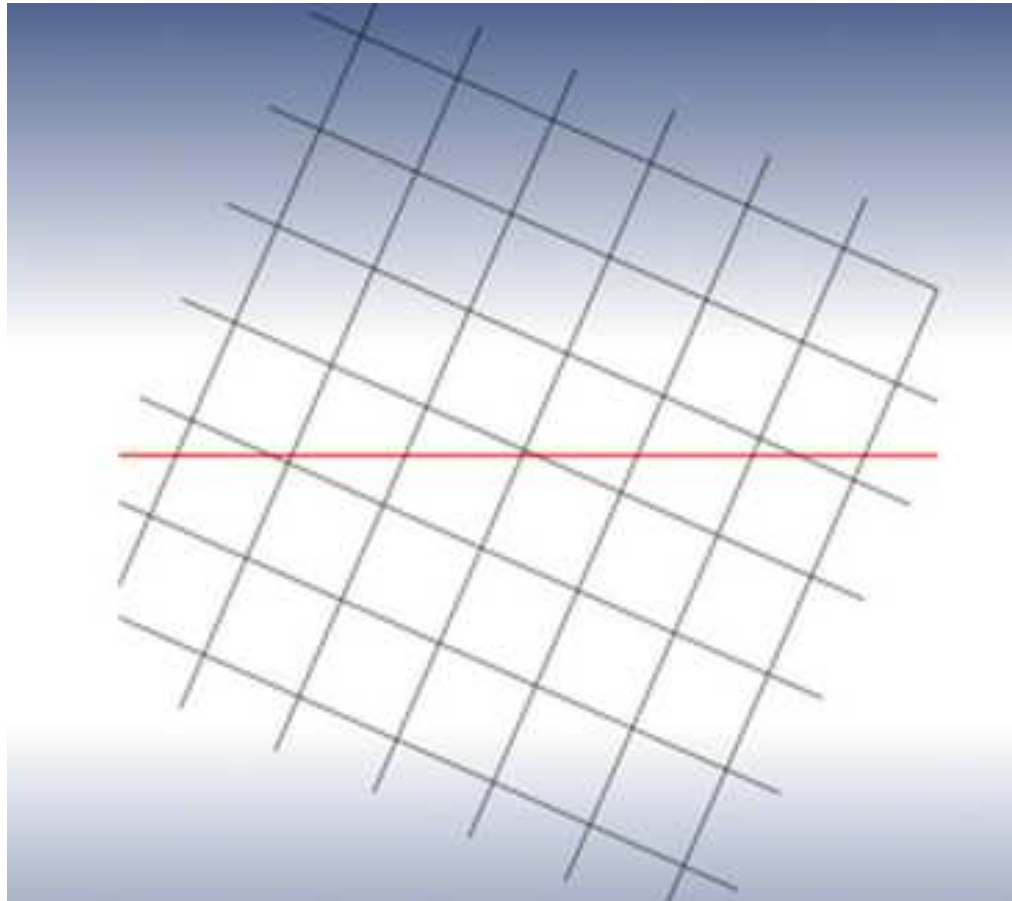Example: Quasi-periodic function with one variable x (cut along $y = x$)

$$f(x, y) = \cos(2\pi x) + \cos(2\sqrt{2}\pi x)$$

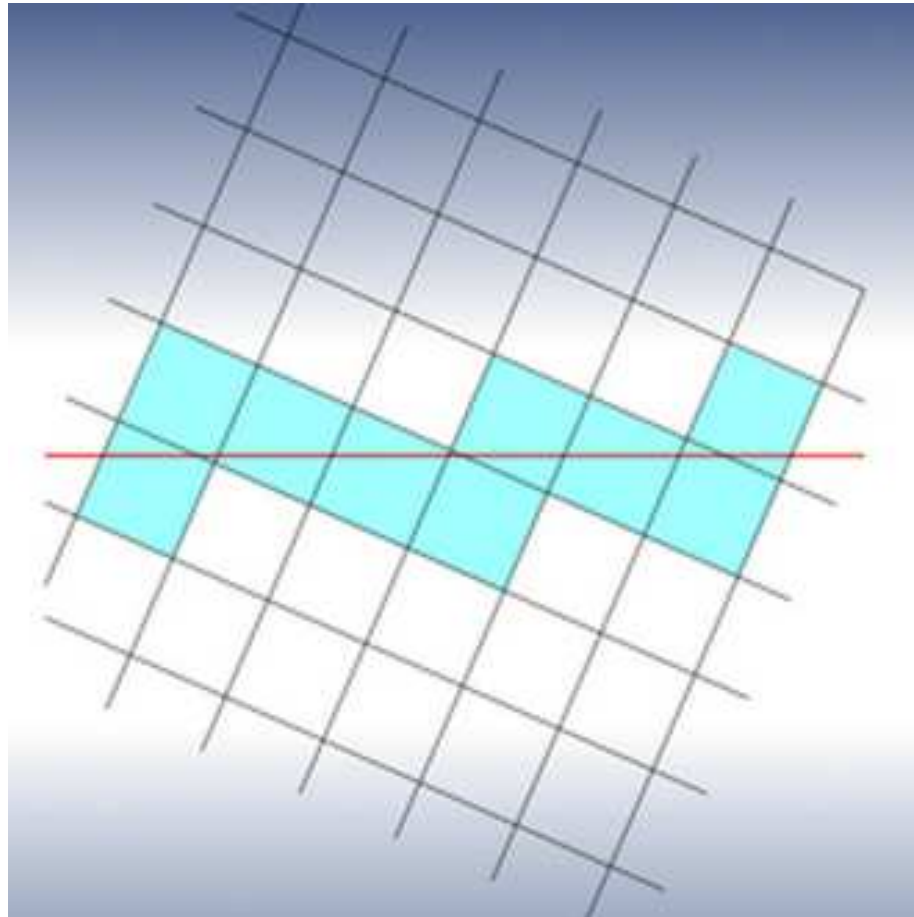3-dimensional periodicity is not compatible with 5-fold rotational symmetry.

However, it is possible to build a 3-dimensional crystal with the "cut and projection" method from a higher dimensional space.
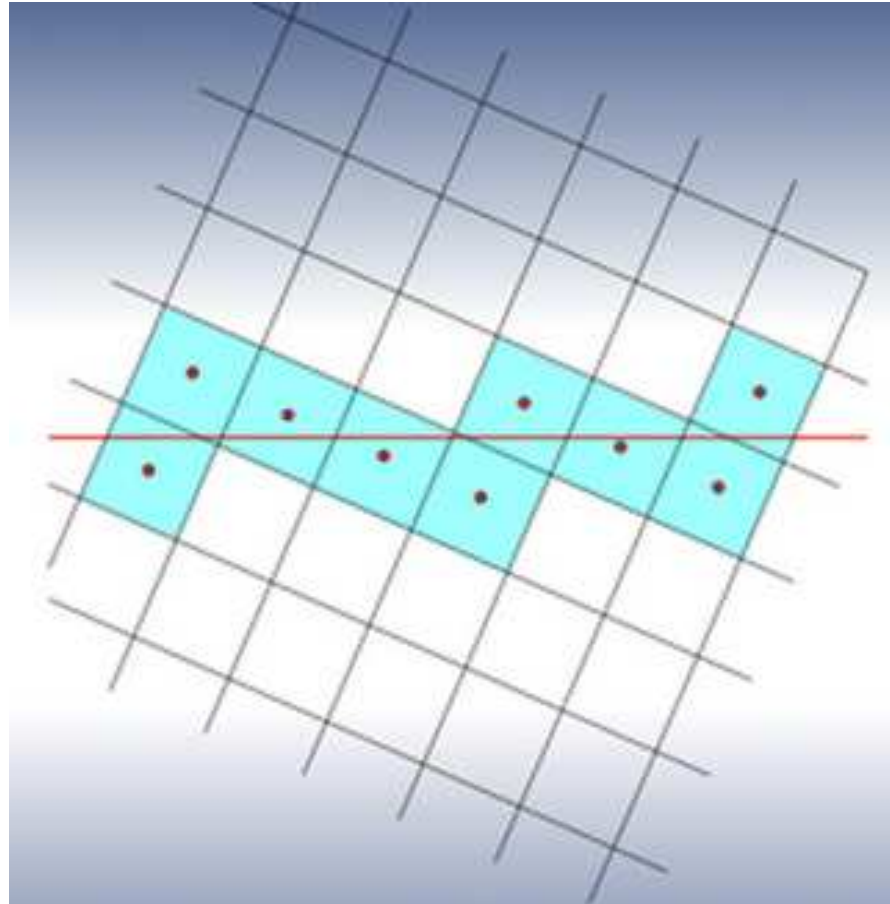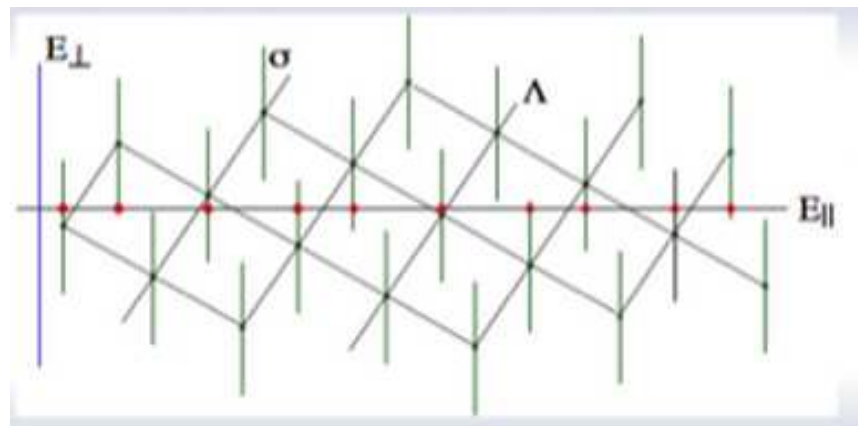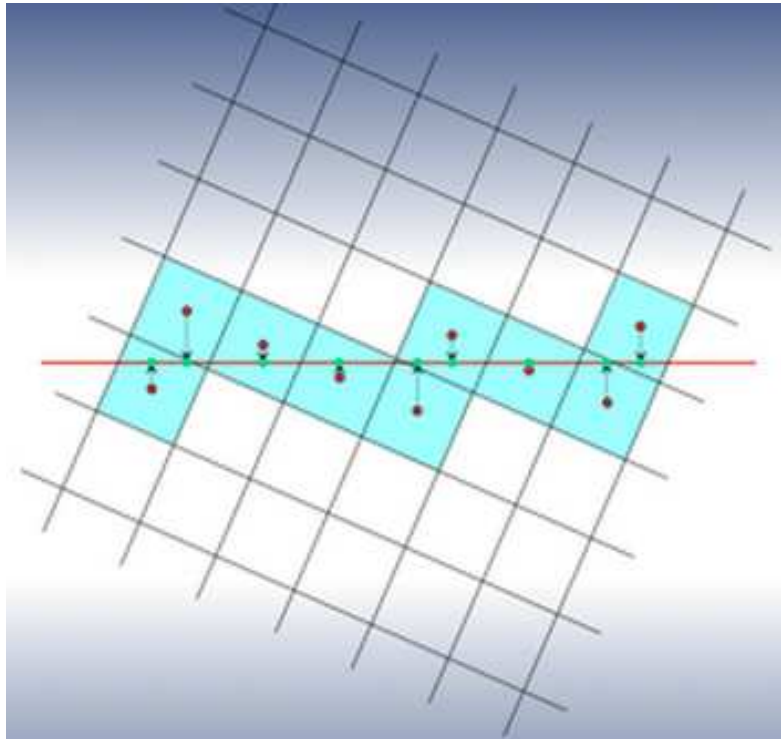
D. Gratias, UDPPC-2014, http://culturesciencesphysique.ens-lyon.fr/

D. Gratias, UDPPC-2014, http://culturesciencesphysique.ens-lyon.fr/

D. Gratias, UDPPC-2014, http://culturesciencesphysique.ens-lyon.fr/
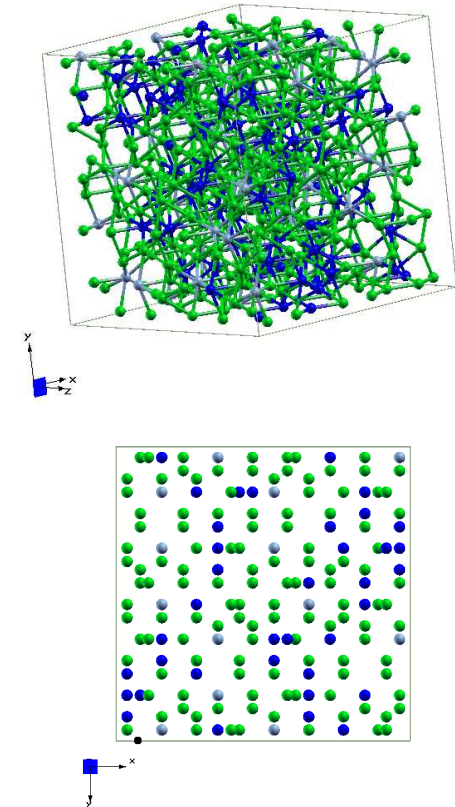
D. Gratias, UDPPC-2014, http://culturesciencesphysique.ens-lyon.fr/
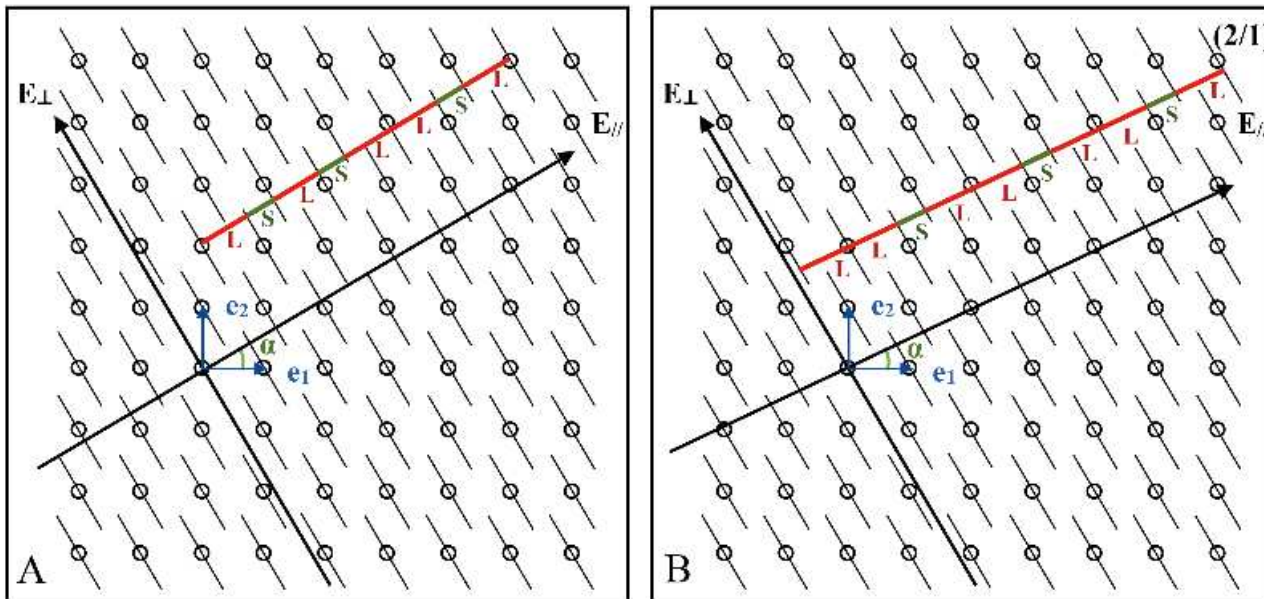
Model for i-AlPdMn

Concept of approximants to model QCs with codes based on periodic boundaries conditions

Modèle	Nb atomes	N_{Al}	N_{Pd}	N_{Mn}	Composition
2/1	544	372	124	48	$Al_{68}Pd_{23}Mn_9$
3/2	2292	1612	472	208	$Al_{70}Pd_{21}Mn_9$
5/3	9700	6844	2012	844	$Al_{70}Pd_{21}Mn_9$

M. Krajci *et al.*, PRB **71**, 054202 (2005)

Example 1: stability of QCs

- How to evaluate the stability of a given complex intermetallic?

- The stablity is generally attributed to ... How to check the influence of some of these parameters using calculations?

Example 1: stability of QCs and related phases

- How to evaluate the stability of a given complex intermetallic?

- The stablity is generally attributed to electronic band structure and geometrical factors.
  How to check the influence of the some of electronic parameters using calculations?
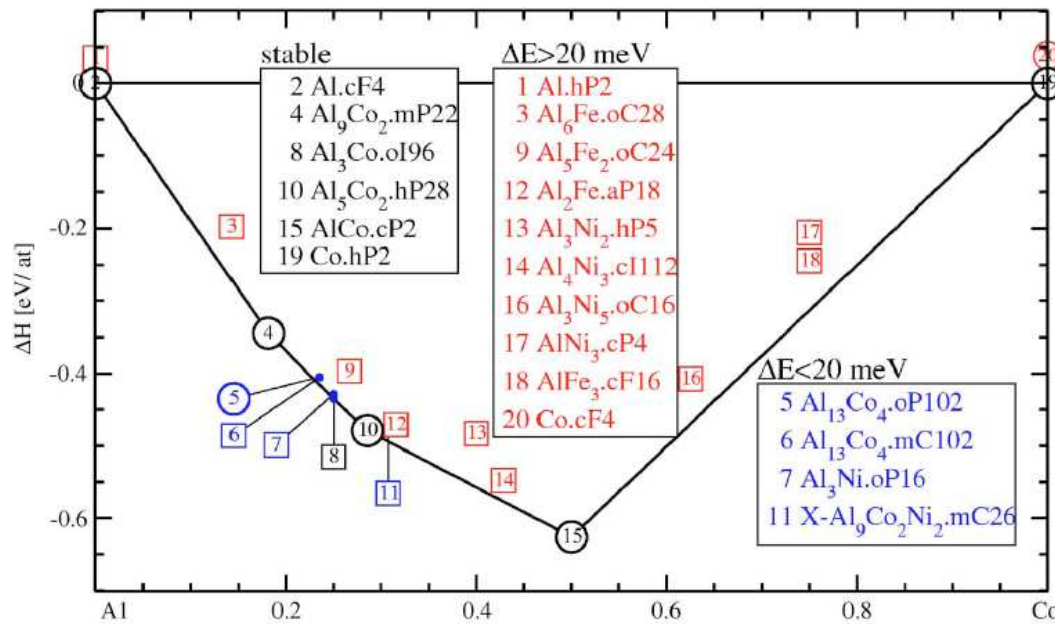
Example of the Al-Co system

Related QC: d-AlNiCo

Stable compounds in the Al-Co system

The structure or coexistence of two structures that minimizes the enthalpy is the thermodynamically stable structure for a given composition at low temperature.

$$\Delta H_f(\text{Co}_x\text{Al}_{1-x}) = H_{tot}(\text{Co}_x\text{Al}_{1-x}) - x H_{tot}(\text{Co}) - (1-x) H_{tot}(\text{Al})$$
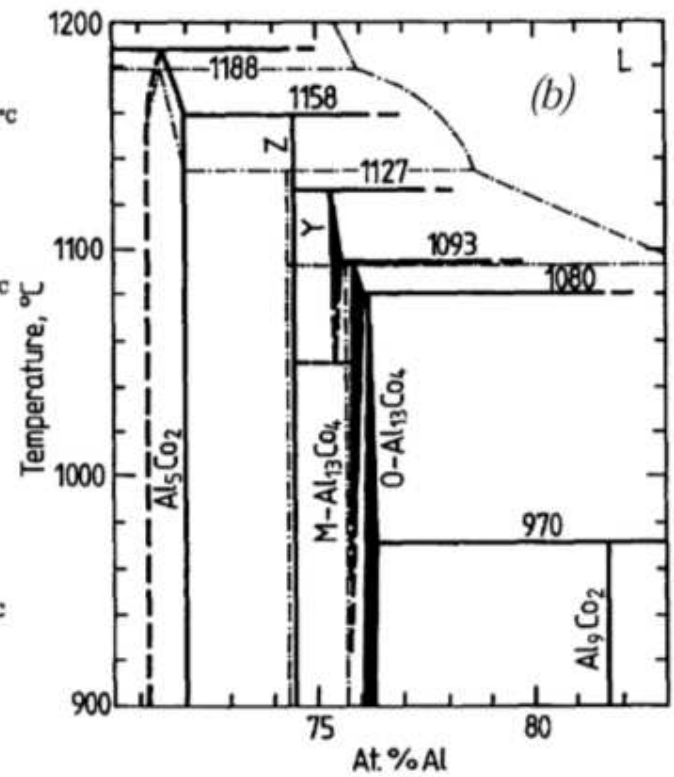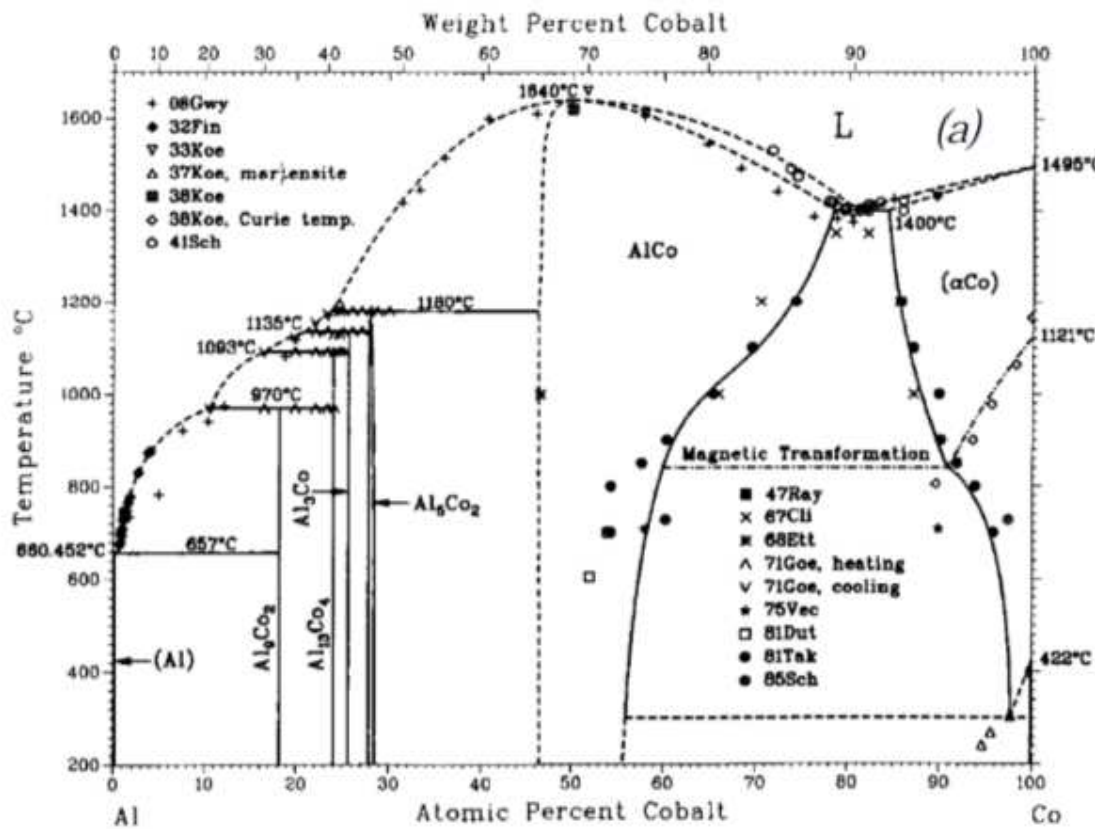
($T = 0$ K, solid $\rightarrow$ use E)

Mihalkovic and Widom,

PRB **75** 014207 (2007)

Structures for study are selected from established exp. phase diagrams, collections of intermetallic struct., etc.

Nearly perfect agreement with the exp. phase diagram. With the exception of the $Al_{13}Co_4$ structures, all known low temperature phases lie on the convex hull.
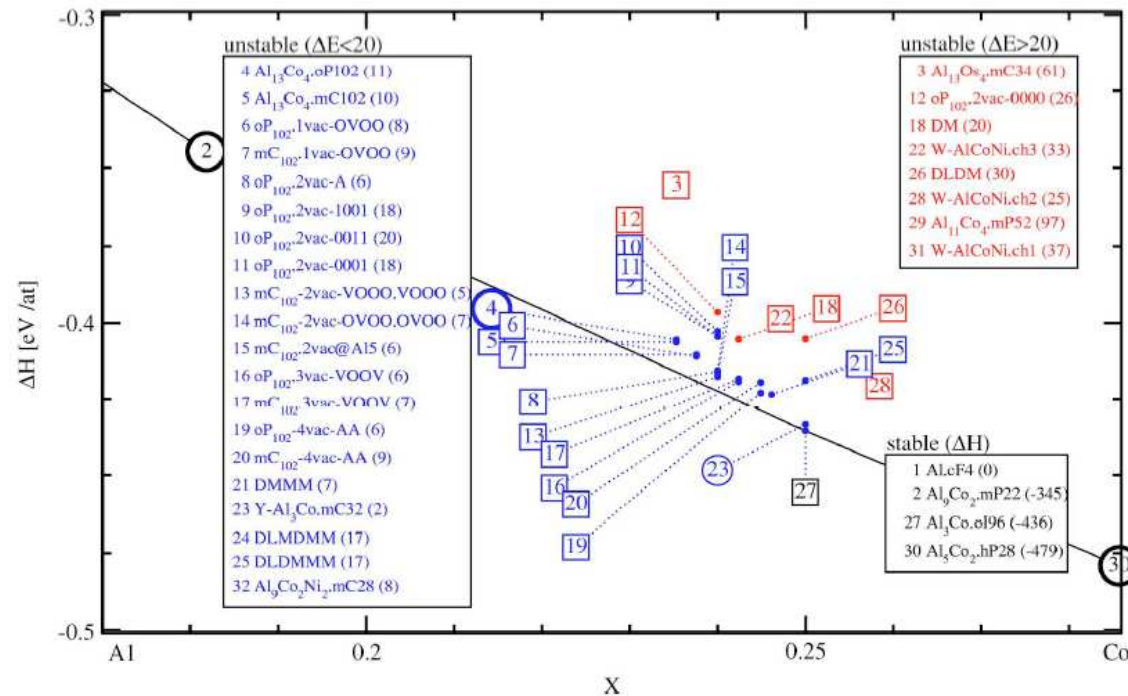
Weight Percent Cobalt

A.J. McAlister, *Bulletin of Alloy Phase Diagrams*, **10**, number 6 (1989)

B. Grushko, R. Wittenberg, K. Bickmann, C. Freibourg, *J. Alloys Compd.*, **233** (1996) 279

Stable compounds in the Al-Co system: $Al_{13}Co_4$

Gibbs Free Energy $G = H - TS$

- Disorder can generate entropy

$Al_{13}Co_4$: vacancy disorder [1] and/or positional disorder [2]

Vacancy disorder in o-$Al_{13}Co_4$: the config. entropy is evaluated by statistical mechanics

- Vibrations can generate entropy

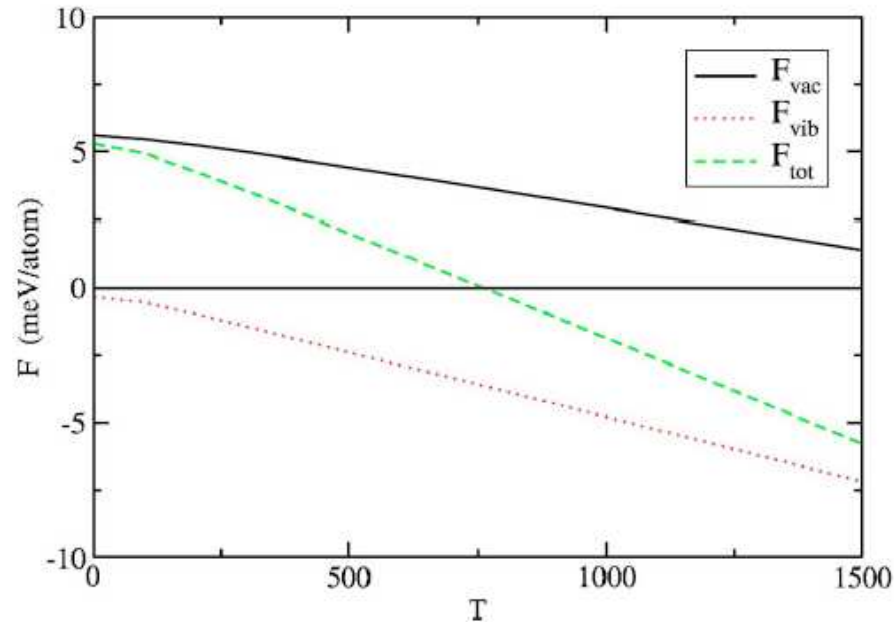The vib. contrib. is $\int g(\omega)k_B T \ln\left(2\sinh\frac{\hbar\omega}{2k_B T}\right)$ with $g(\omega)$ phonon DOS (Debye model).

[1] Hudd and Taylor, *Acta Crystallogr.* **15** 441 (1962). Freiburg *et al. Mater. Sci. Forum* **583** 228-231 (1996).

[2] J. Grin *et al. J. Alloys Comp.* **206** 243-247 (1994).

Stable compounds in the Al-Co system: $Al_{13}Co_4$

Gibbs Free Energy $G = H - TS$

- Disorder can generate entropy
- Vibrations can generate entropy

Combining vacancy and vibrational entropy, the free energy of $Al_{13}Co_4$ falls below the tie-line of coexisting phases at nearby compositions when temperature exceeds T=750 K.

[1] Hudd and Taylor, *Acta Crystallogr.* **15** 441 (1962). Freiburg *et al.* *Mater. Sci. Forum* **583** 228-231 (1996).
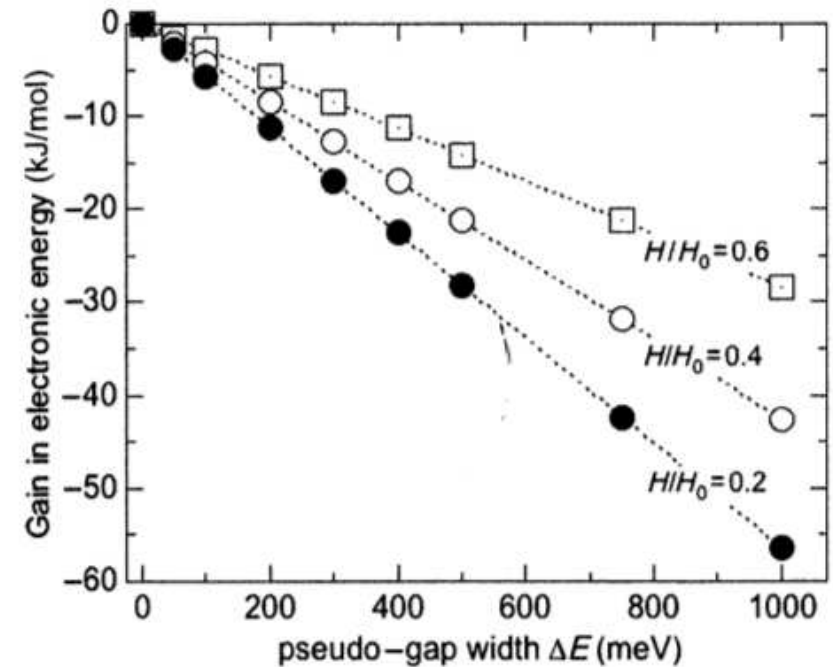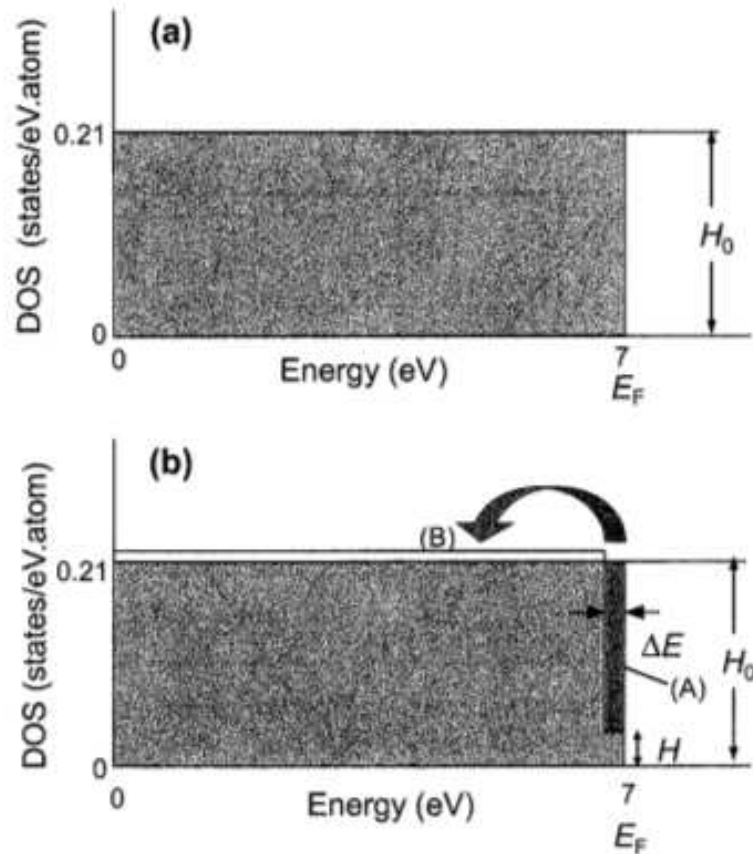[2] J. Grin *et al.* *J. Alloys Comp.* **206** 243-247 (1994).
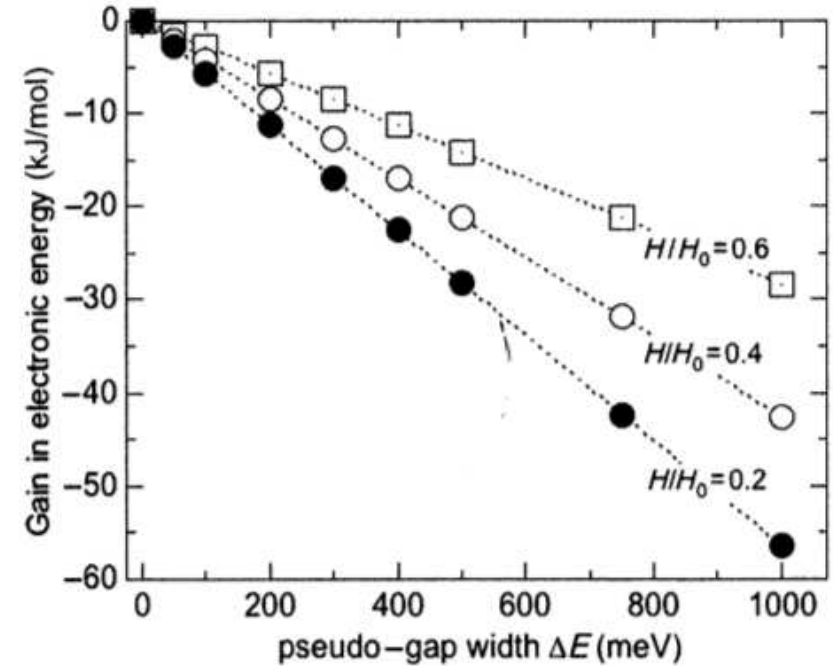
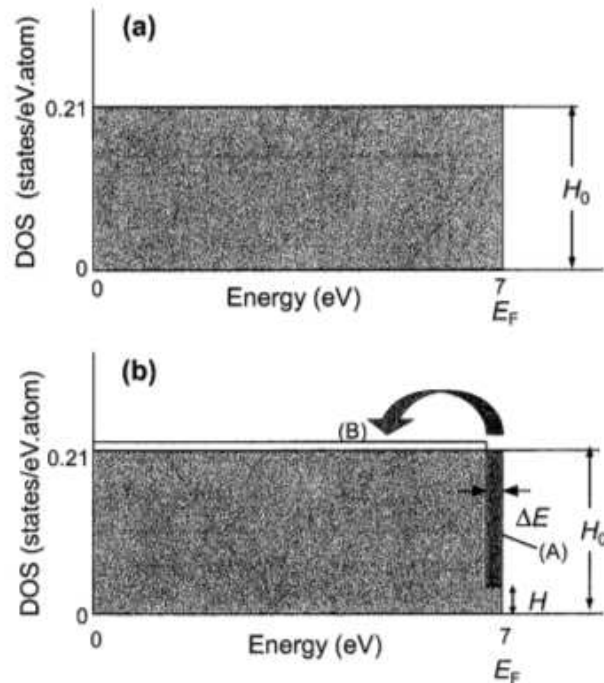Example 1: stability of QCs and related phases

🔴 How to evaluate the stability of a given complex intermetallic? $\rightarrow$ convex hull

🔴 The stablity is generally attributed to electronic band structure and geometrical factors.

Kinetic energy of electrons and the role of the pseudo-gap

Origin of the pseudogap: ???

Kinetic energy of electrons and the role of the pseudo-gap

U. Mizutani et al, Physical metallurgy, Elsevier (2014)
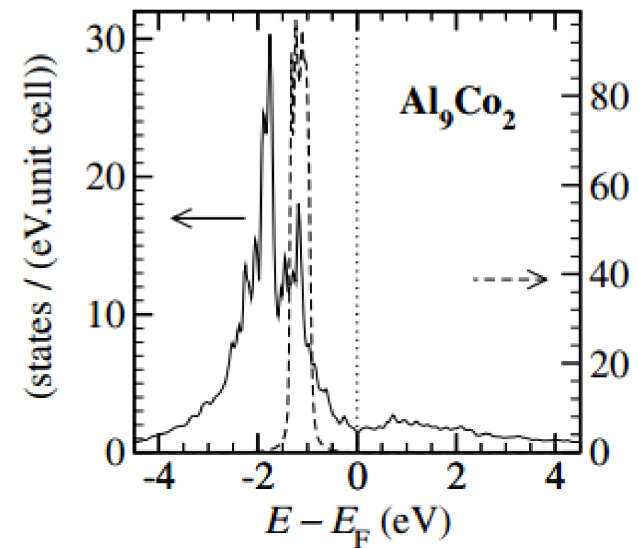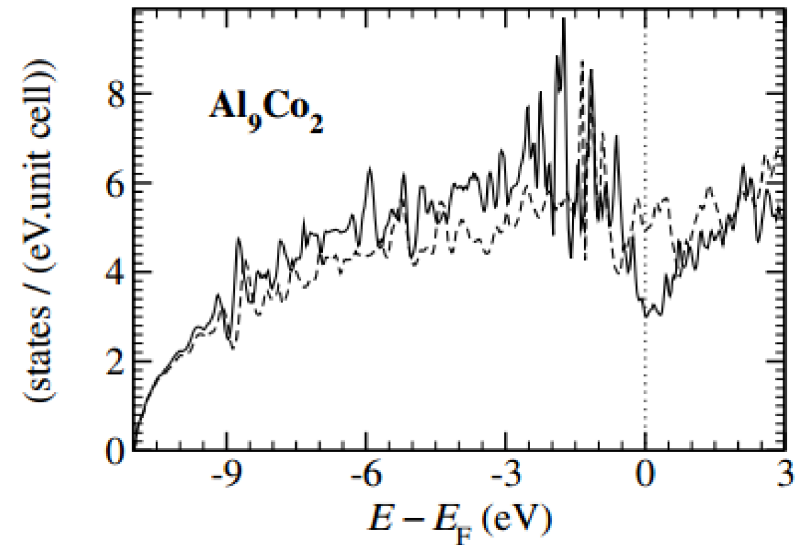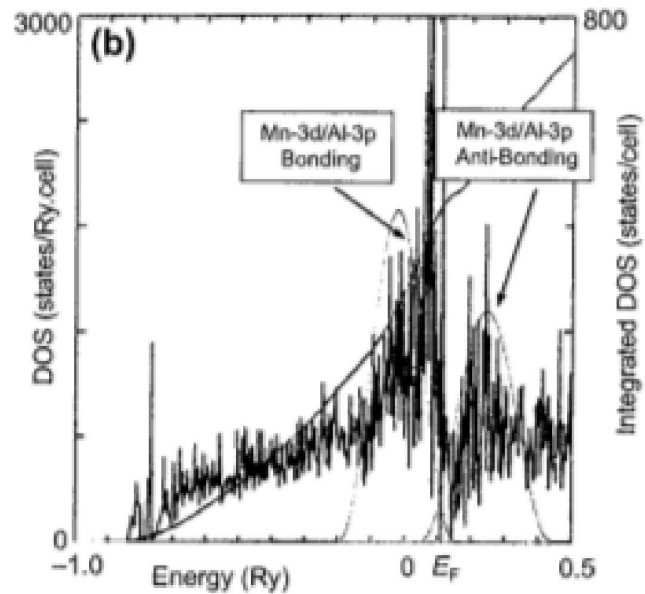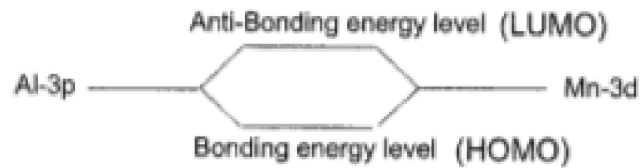
Origin of the pseudogap:

🔴 orbital hybridization

🔴 FsBz interaction

How to investigate the mecanisms at the origin of the pseudo-gap formation?

Hybridization

Al-Mn approx (138 at/cell)

Anti-Bonding energy level (LUMO)

Al-3p ——— Mn-3d

Bonding energy level (HOMO)

(b) Mn-3d/Al-3p Bonding, Mn-3d/Al-3p Anti-Bonding

DOS (states/Ry.cell) — Integrated DOS (states/cell)

Energy (Ry), E_F

Al_9Co_2

(states / (eV.unit cell))

$E - E_F$ (eV)

Al_9Co_2

(states / (eV.unit cell))

$E - E_F$ (eV)

— without sp-d hybridization

Hume-Rothery stabilization mechanism: Al-Cu system

The Al_xCu_{1-x} alloys present thermodynamically stable structural forms that differ, depending on the concentration x

α phase

β phase

γ1 phase
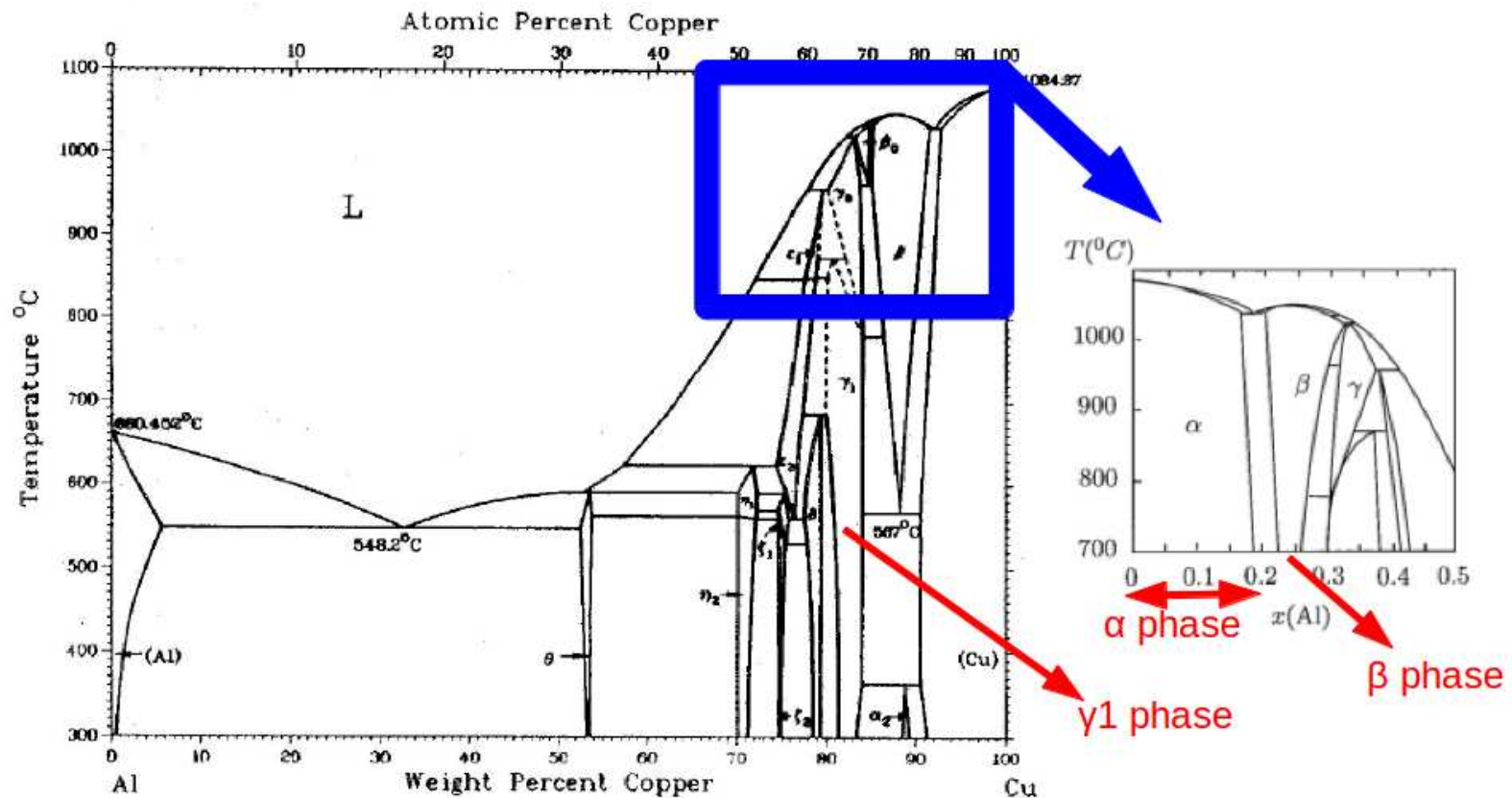
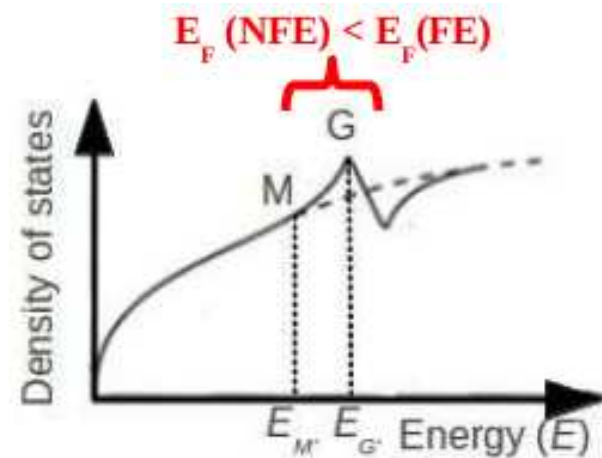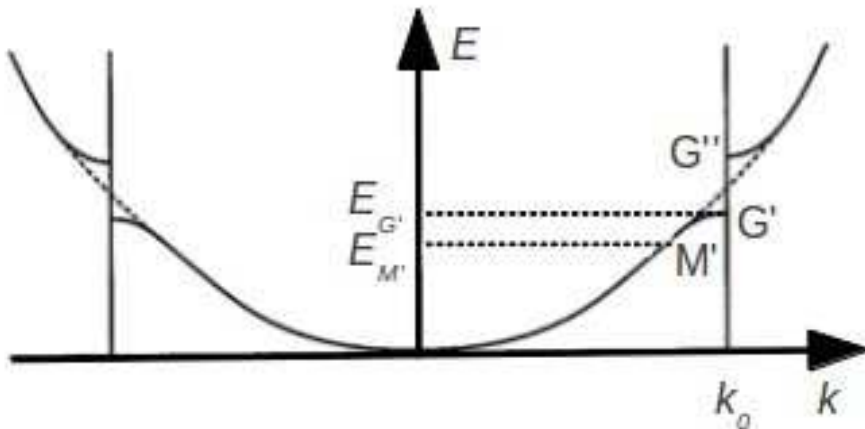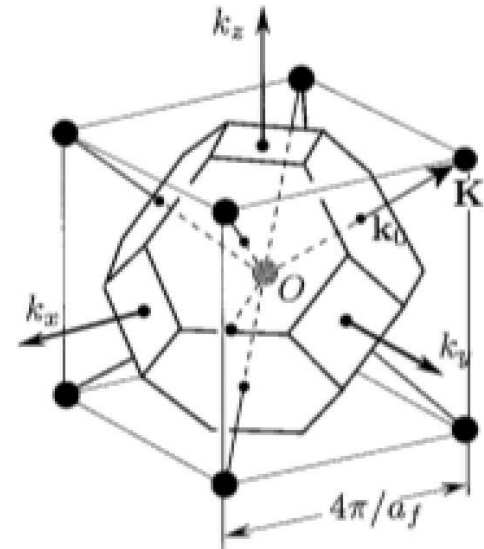# Hume-Rothery stabilization mechanism: Al-Cu system

● <u>Case study: α (fcc)</u>

Within the free elec. model, the DOS presents a parabolic shape and the the Fermi wave-vector k_F is given by:

$$k_F = \left(3\pi^2 n\right)^{\frac{1}{3}} = \left(3\pi^2 \frac{\nu}{\Omega}\right)^{\frac{1}{3}} = \frac{2\pi}{a_f}\left(\frac{3\nu}{2\pi}\right)^{\frac{1}{3}}$$

where n is theelectronic density, ν the number of valence electrons and Ω the mean atomic volume ($\Omega = \frac{a_{fcc}^3}{4} = \frac{a_{cc}^3}{2}$).

If we consider now the nearly free electron model, the elec. structure along a direction that corresponds to the vector (called $\vec{k}_0$) going from the origin to the point of the first Brillouin Zone the closest to the origin, is modified.

Hume-Rothery stabilization mechanism: Al-Cu system

Point G corresponds to a contact between the Fermi sphere and the first Brillouin Zone.

fcc: $d = \dfrac{4\pi}{a_f}\dfrac{\sqrt{3}}{2}$
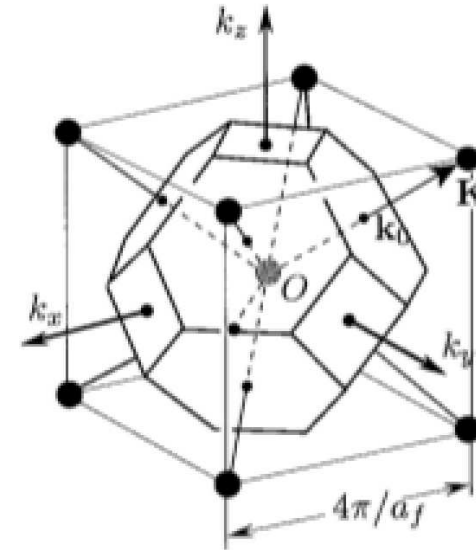
The previous stabilization mechanism implies that alloys of a given structure will only form at a specific chemical composition. According to the Hume-Rothery stabilization rule, the electronic energy is lowered when $2k_F = K_p$ where $2k_F$ is the Fermi diameter and K_p is the magnitude of the relevant reciprocal lattice vector (Fermi sphere - first Brillouin zone interaction).

This condition ($2k_F = K_p$) can be rewritten as $\boxed{[\dfrac{3}{\pi}(e/a)N]^{\frac{2}{3}} = h^2 + k^2 + \ell^2}$
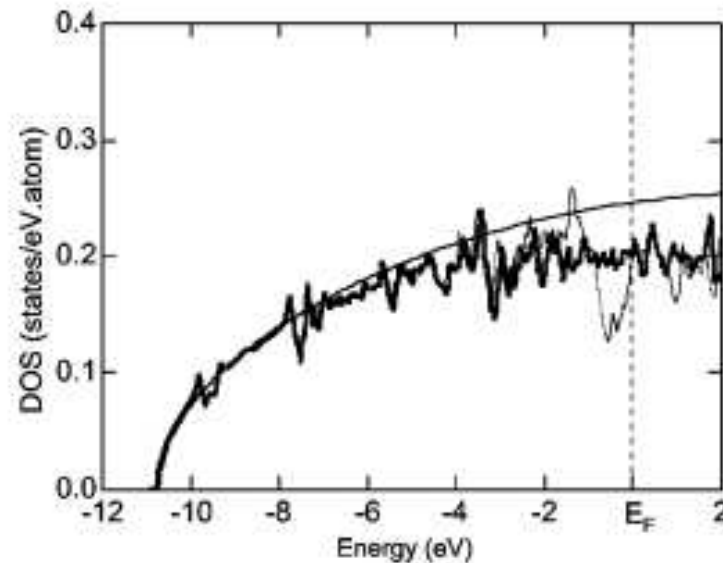
N is the nb. of at. in the unit cell and (h, k, ℓ) is the set of Miller index of the relevant zone.

Hume-Rothery stabilization mechanism: Al-Cu system

$2k_F = K_p$ corresp. to $[\frac{3}{\pi}\nu N]^{\frac{2}{3}} = h^2 + k^2 + \ell^2$

N is the nb. of at. in the unit cell and (h, k, ℓ) is the set of Miller index of the relevant zone.

- Cu_5Zn_8 Intermetallic compound : $(e/a) \simeq 1.61; [(3/\pi)(e/a)N]^{\frac{2}{3}} \simeq 18.5$

Asahi et $al.$ performed the FLAPW band calculations for Cu_5Zn_8.

By analyzing states near the Fermi level, Asahi et $al.$ show that {330} and {411} zone planes are responsible for the formation of a sizable pseudo-gap in Cu_5Zn_8.

Example 1: stability of QCs and related phases

🔴 How to evaluate the stability of a given complex intermetallic? $\rightarrow$ convex hull

🔴 The stablity is generally attributed to electronic band structure and geometrical factors.
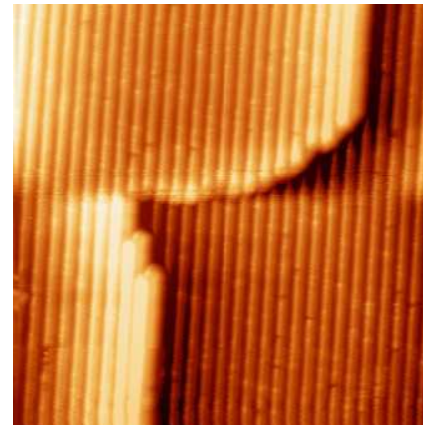
$\rightarrow$ role of the electronic structure

Example 2: surface structures (and properties)

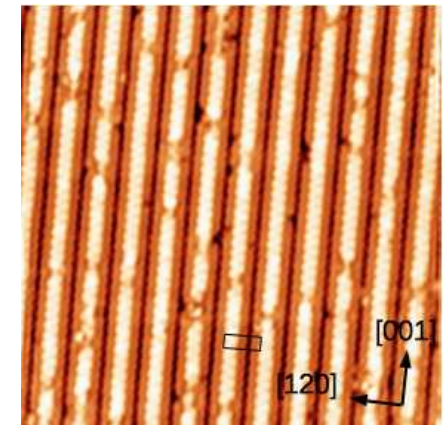Metallic surfaces are usually investigated experimentally under ultra-high vacuum.
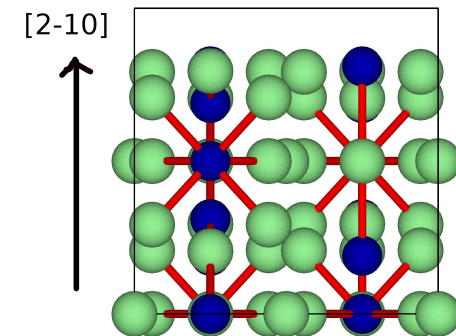
$Al_5Co_2(001)$ surface
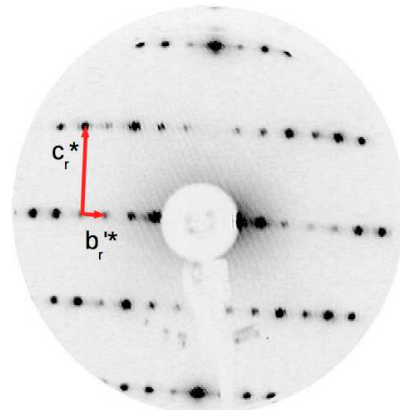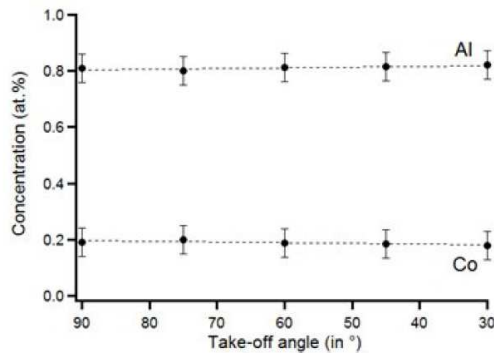
20 eV

75×75 nm^2
$V_b = -2$V; $I_t = 0.1$nA

20×20 nm^2
$V_b = -1$V; $I_t = 0.2$nA

[001]

[120]

- No surface segregation (angle dependent XPS)

- Surface plane selection: Step heights $\simeq a/2$ (3.8 $\pm$ 0.2 Å)
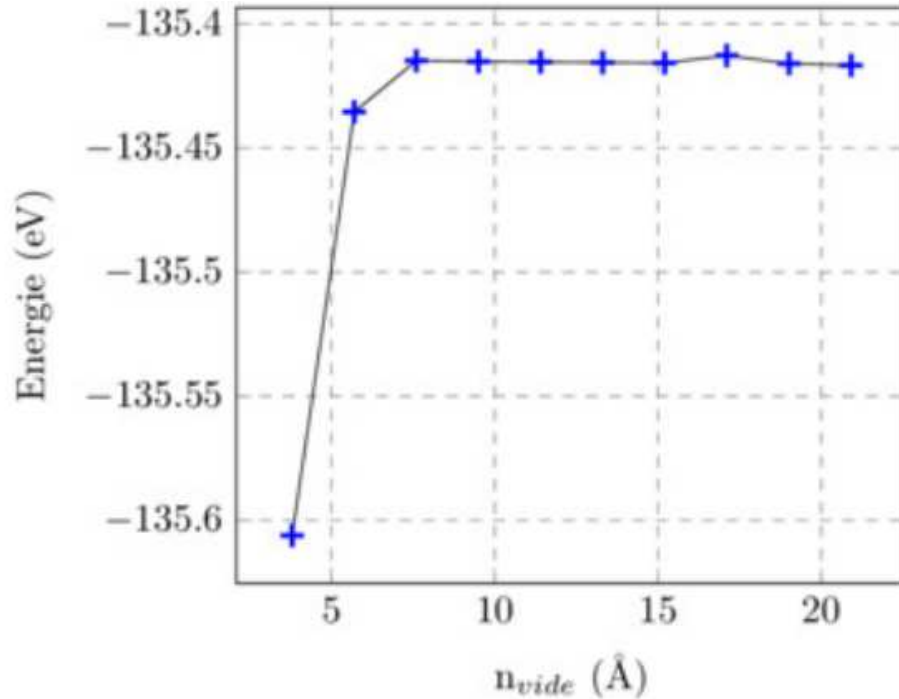
- a surface reconstruction (LEED): (2$\times$ 1)
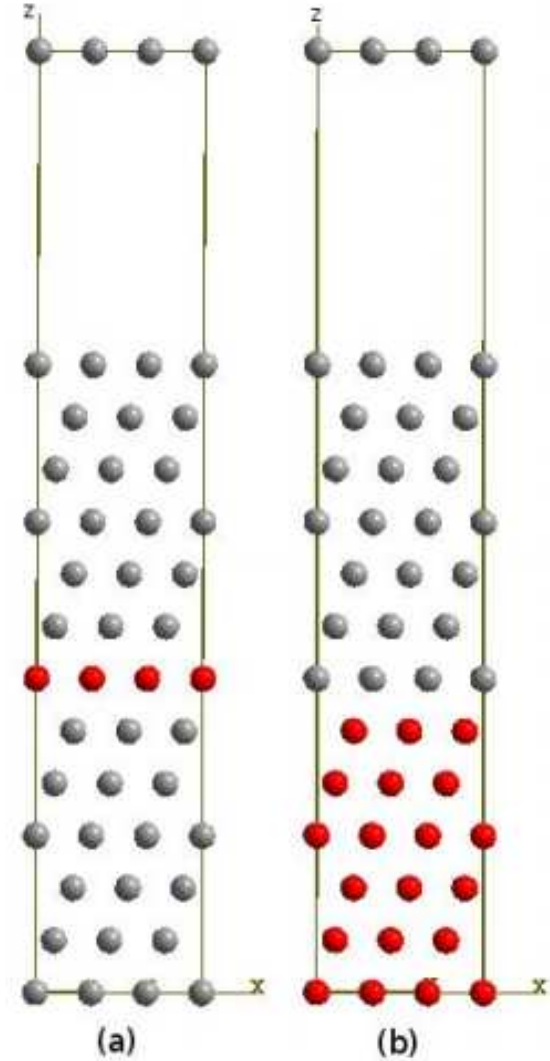
[2-10]

Example 2: surface structures
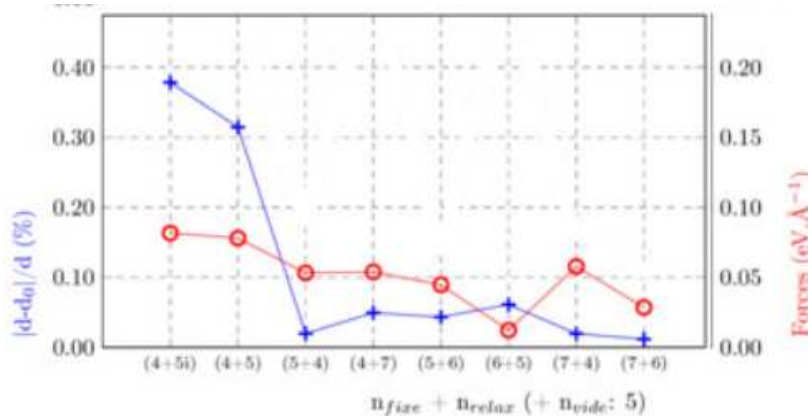
- How to model a non periodic system (surface) with a code using periodic boundary conditions?

- How to identify stable surface structures?

- How to check the relevance of the proposed structural model?

First principles surface studies

Convergence of the void thickness ($Al_5Co_2(001)$)

Convergence of the slab thickness ($Al_5Co_2(001)$)
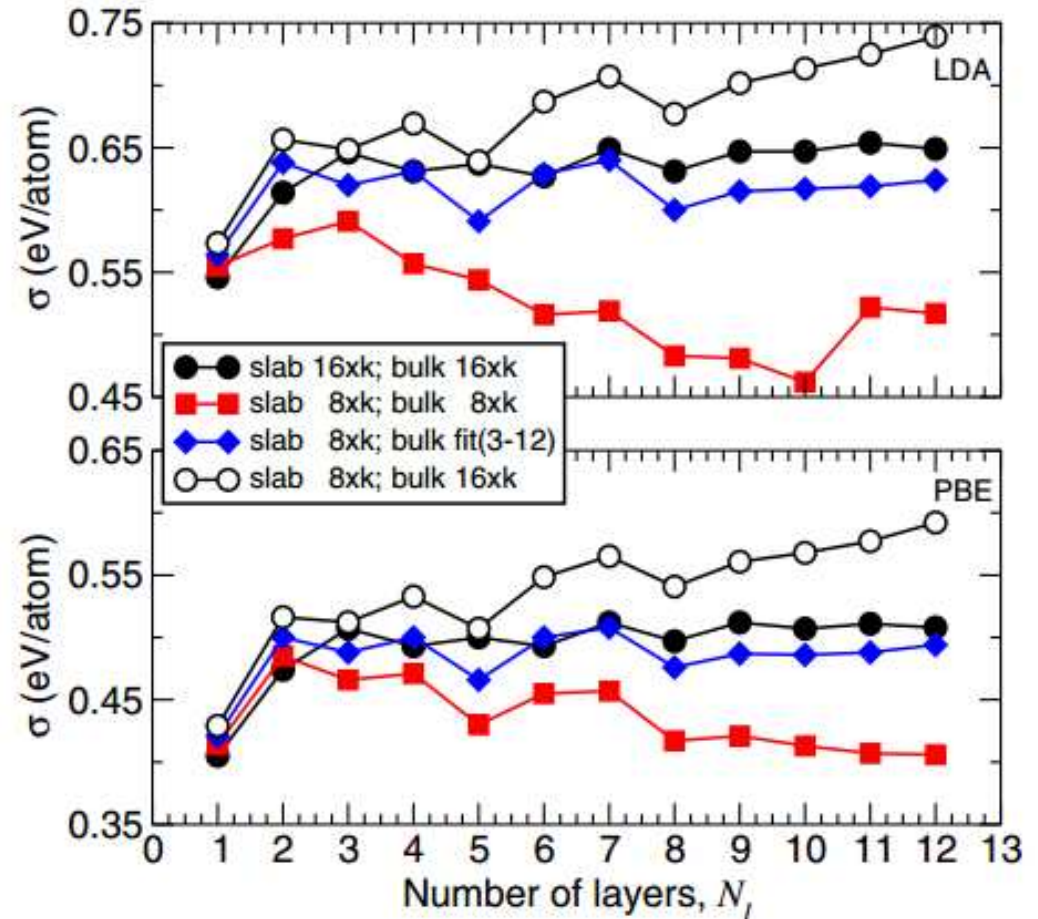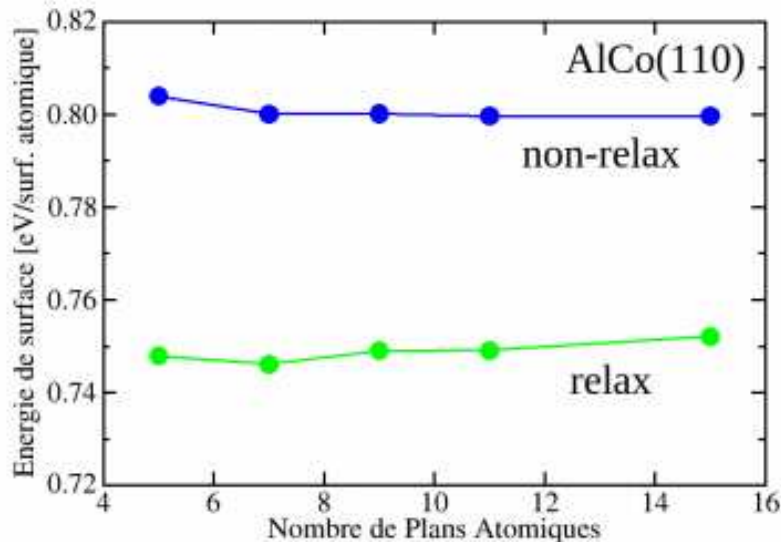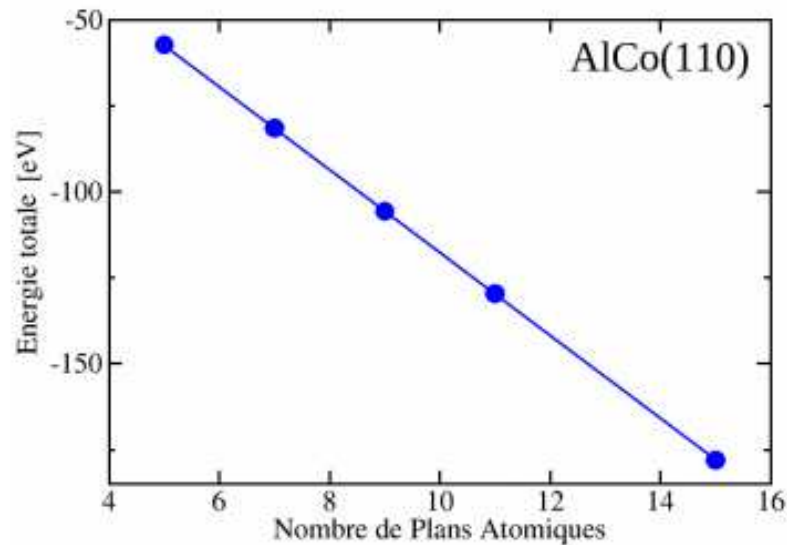

(a)   (b)

From M. Meier, PhD thesis

First principles surface studies

Surface energy calculation

<u>Simple metals</u> $\gamma = \frac{1}{2}(E_{slab} - nE_{bulk})$

PhD thesis, S. Alarcon, 2011

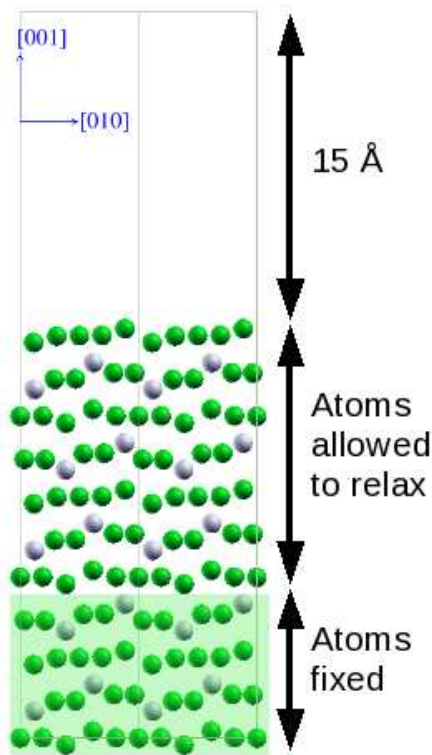Da Silva *et al.*, *Surf. Sci.*, **600** (2006) 703.

$Al_9Co_2(001)$ surface: surf. energy calc. (T = 0 K)

The most stable surface comp. and geom. is the one that minimizes the surface energy:

$$A \quad \times \quad (\gamma^{top} + \gamma^{bottom}) \quad = \quad [E_{slab}(N_{Al}, N_{Co})] - N_{Al}\mu_{Al} - N_{Co}\mu_{Co}$$

area   Sum of surf. energies   Difference between slab energy and corresp. cohesive energy

Chemical potentials

[001]

[010]

15 Å

Atoms allowed to relax

Atoms fixed

- For the crystalline phases consisting of only one species i:

  μ_i^{bulk} = total energy per atom calculated at $T = 0K$

- For the Al_9Co_2 intermetallic compound:

  $\mu_{Al_9Co_2}^{bulk} = 9\mu_{Al}^{bulk} + 2\mu_{Co}^{bulk} - \Delta H_f^{Al_9Co_2}$

  $\mu_{Al_9Co_2}^{bulk} = 9\mu_{Al} + 2\mu_{Co}$

- The chem. potentials depend on samples, off-stoichiometric effects, surf. preparation conditions [Bechstedt, 2003] These variations may be represented by deviations $\Delta\mu_{Al} = \mu_{Al} - \mu_{Al}^{bulk}$

The surface is in equilibrium with its surroundings

$$\Rightarrow \quad \boxed{\frac{-\Delta H_f^{Al_9Co_2}}{9} \leq \Delta\mu_{Al} \leq 0}$$

$\mathbf{Al_5Co_2(2\bar{1}0)}$: theoretical results
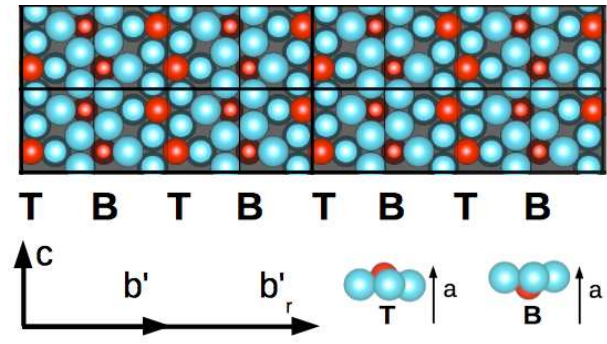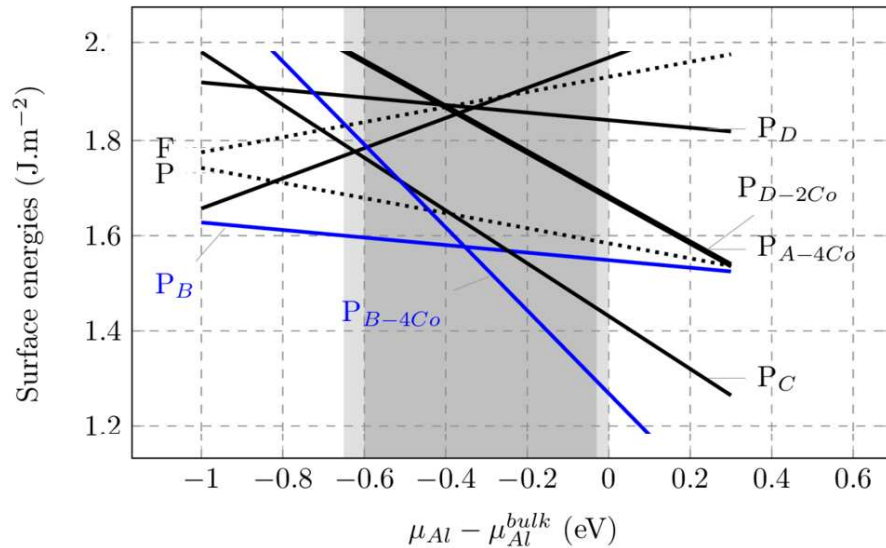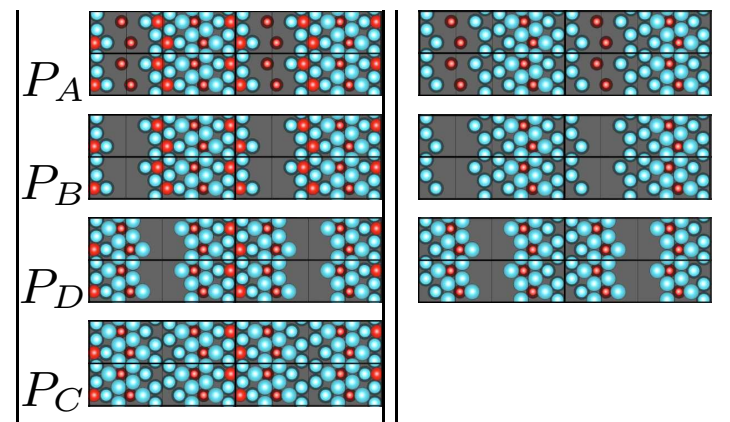
M. Meier *et al.*, submitted

Best agreement with P_B-type models

Al$_5$Co$_2$(2$\bar{1}$0): theoretical results
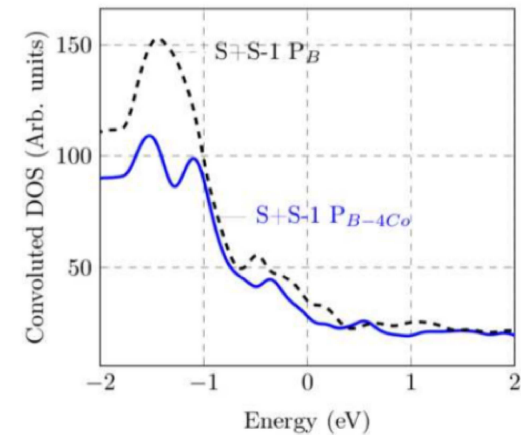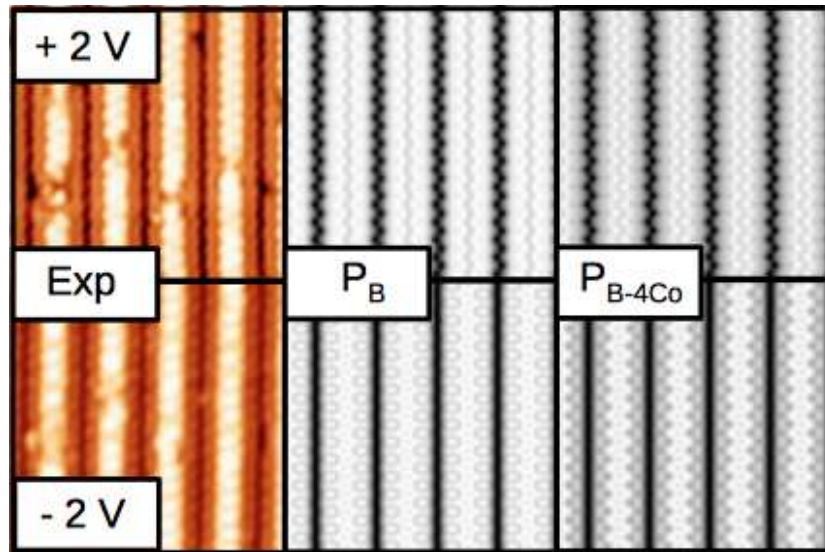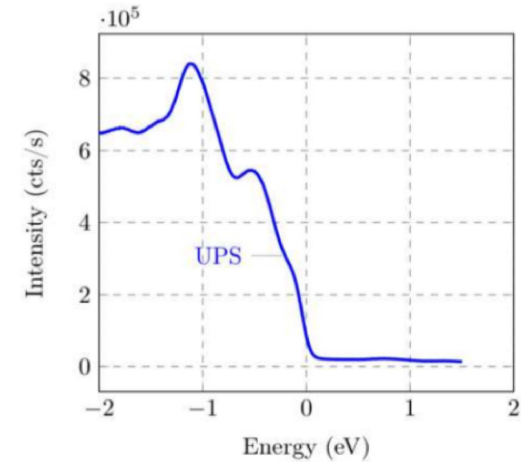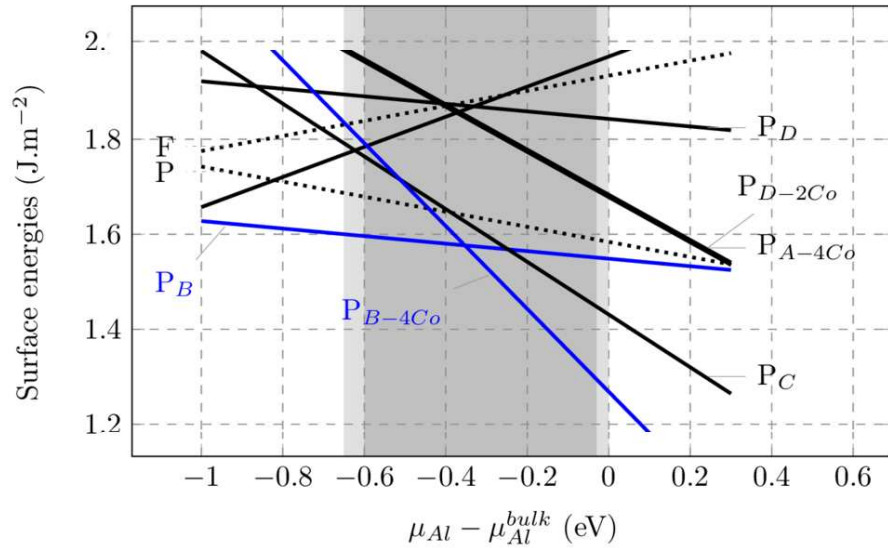
M. Meier et $al.$, submitted

Best agreement with P_B-type models

Example 2: surface structures

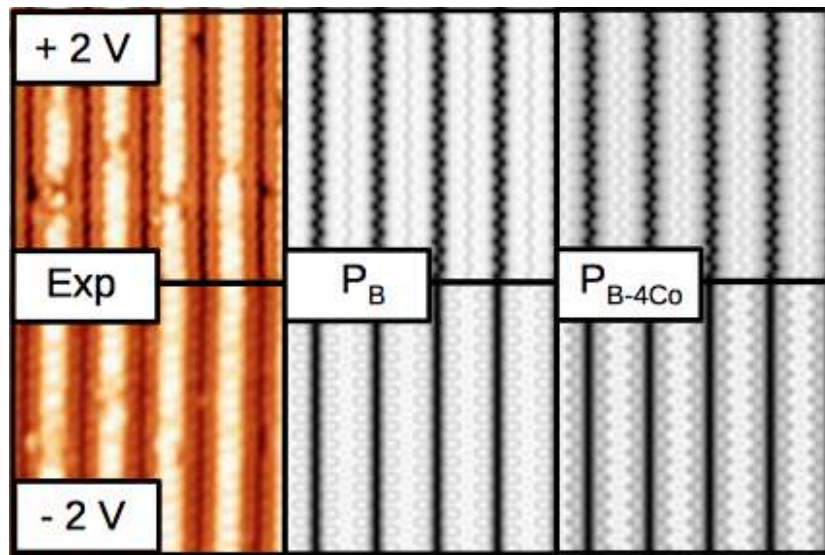- How to model a non periodic system (surface) with a code using periodic boundary conditions? $\rightarrow$ slab calculations (void and thickness, symmetric slab or not, etc)

- How to identify stable surface structures?

  $\rightarrow$ surface energy calculations

- How to check the relevance of the proposed structural model?

  $\rightarrow$ comparison with exp. data

Example 3: adsorption properties on a surface

C_{60} on a quasicristalline surface

- How to identify the favorable adsorption sites?

- How to check the relevance of the proposed adsorption scheme?

  $\rightarrow$ comparison with exp. data

- What about the origin of adsorption properties?

C$_{60}$ on metallic surfaces

- the relationship between the size of the molecule and the surface cell parameter
- the relationship between the symmetries of the molecule and of the substrate
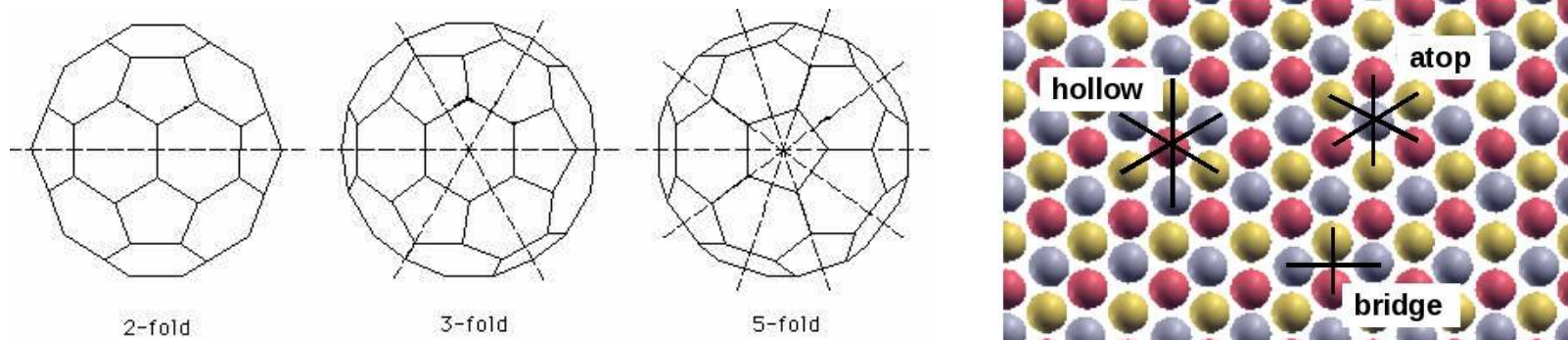
A large number of surface reconstructions are observed experimentally, often linked with the formation of a vacancy or a group of several vacancies

Simple metals offer a limited number of possible adsorption sites

Quasicrystalline surfaces

Sites with 5-fold symmetry, complexity of the surface

C_{60} molecular film on a quasicristalline surface

Well-known sites on the surface:

- 🔴 "Dark Stars"

- 🔴 "White flowers"
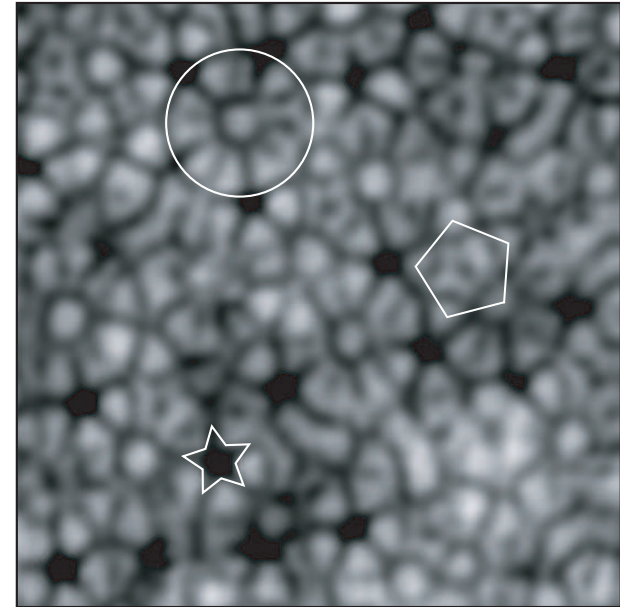
First attempts: C_{60}/i-AlPdMn

- No molecular film

- Disordered Adsorption

J. Ledieu et $al.$, $Surf.$ $Sci.$ **472** (2001) 89

E. Cox et $al.$, $Surf.$ $Sci.$ **566-568** (2004) 1200
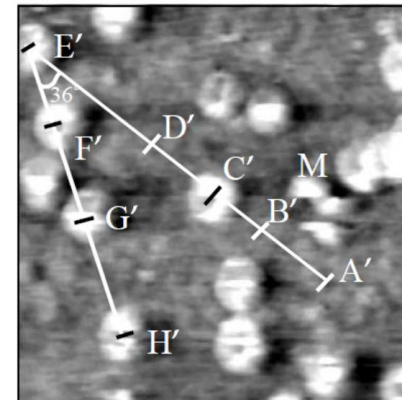
Résultats expérimentaux - 1

Expériences subtiles: dépôt à haute température (623 K à 673 K)

Compromis diffusion-fragmentation C_{60} sur la surface 5-fold de i-AlCuFe
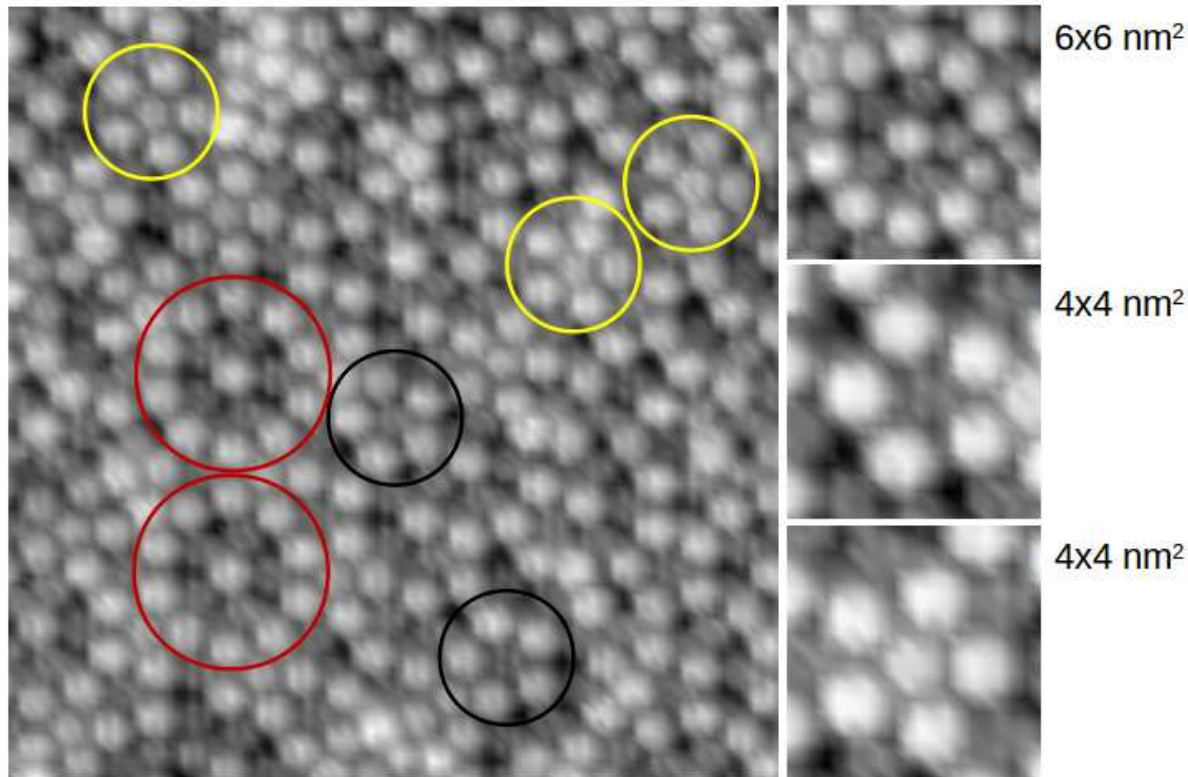
Arête des motifs pentagonaux = 1.2 nm

Plus petite distance C_{60}-C_{60} = 1.0 nm ($\simeq$ cristal de C_{60})

Plus petite distance C_{60}-C_{60} = 1.0 nm ($\simeq$ cristal de C_{60})

From V. Fournée

V. Fournée *et al.*, ACS Nano, 8(4), 3646-3653 (2014)

Résultats expérimentaux - 2

C$_{60}$ sur la surface 5-fold de i-AlCuFe
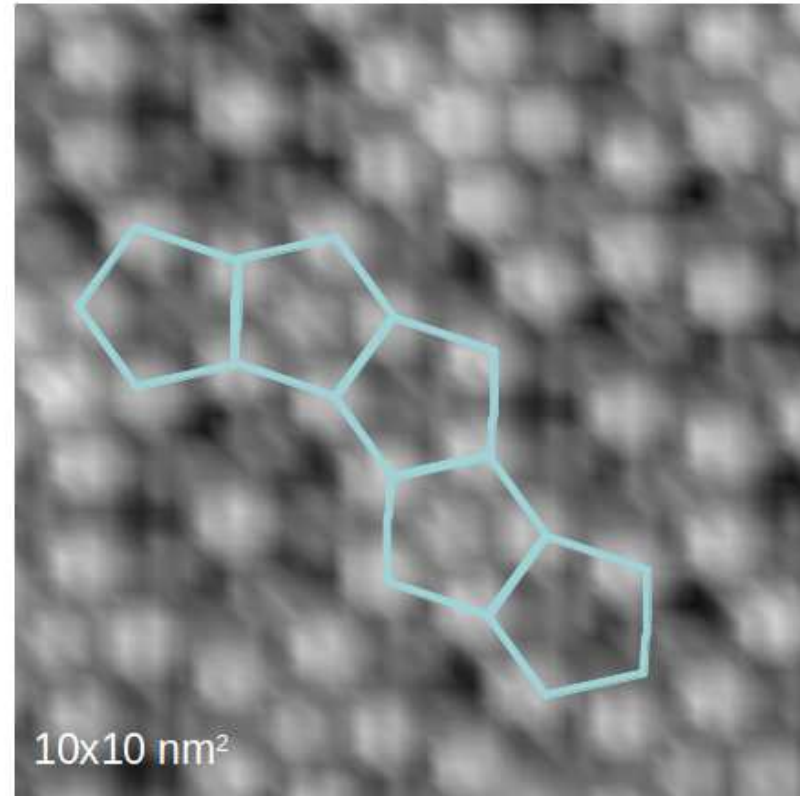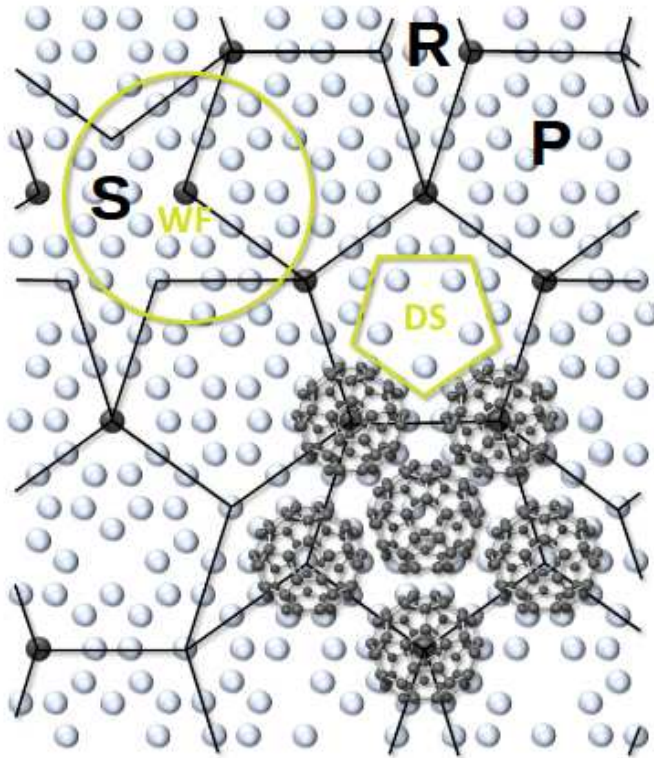
La structure quasi-périodique de la surface peut être décrite par le pavage de penrose $P1$.

Le pavage "dilaté" d'un facteur τ ($\tau P1$), en noir, présente des arêtes de longueur $\simeq$ 1.2 nm correspondant à des distances WF-WF

Taille des motifs pentagonaux formés par les C$_{60}$ $\simeq$ Longueur des arêtes du pavage $\tau P1$

Résultats expérimentaux - 3

C$_{60}$ sur la surface 5-fold de i-AlPdMn
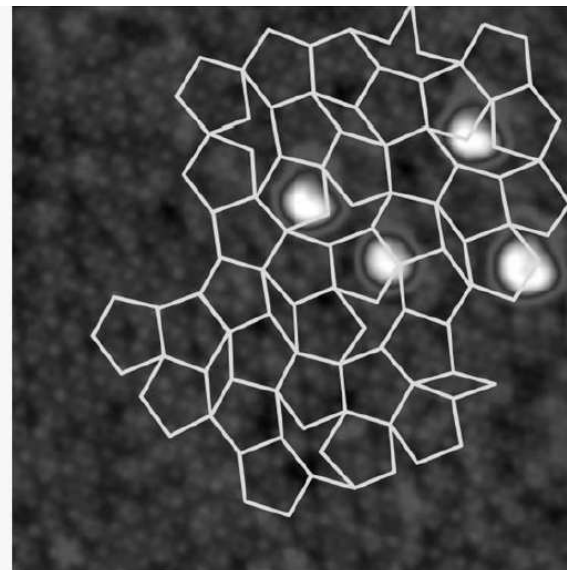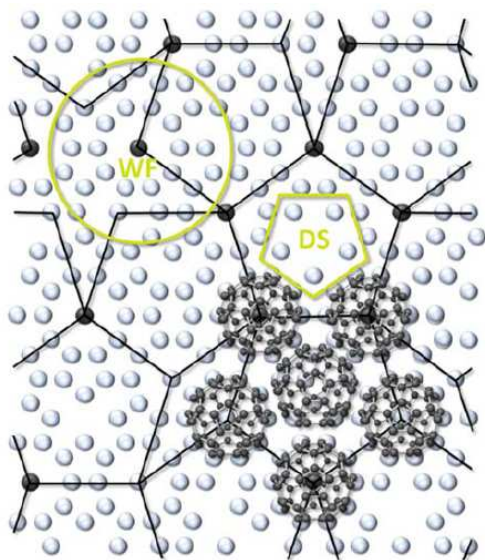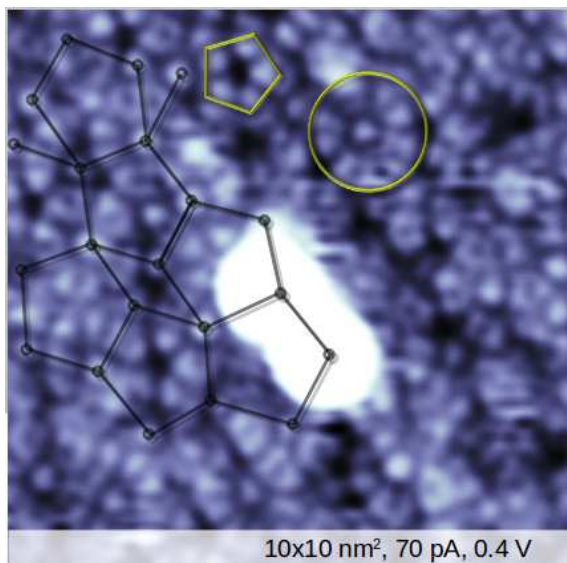
Les sites d'adsorption sont identifiés comme étant les noeuds ou les centres du pavage quasipériodique.

Sites d'adsorption: WF et DS

Configuration de la molécule de C$_{60}$ à la surface?

Nature de la liaison C$_{60}$-substrat?

V. Fournée *et al.*, ACS Nano, 8(4), 3646-3653 (2014)

Method

- Step 1: Specify the physical/chemical problem $\rightarrow$ done

- Step 2: Choose a method adapted to the physical/chemical problem $\rightarrow$ to do

- Step 3: Model the system, consistently with the method chosen $\rightarrow$ to do

- Step 4: Do the calculations $\rightarrow$ to do

- Step 5: Discuss the results $\rightarrow$ to do

Modèle atomique de la surface - 2
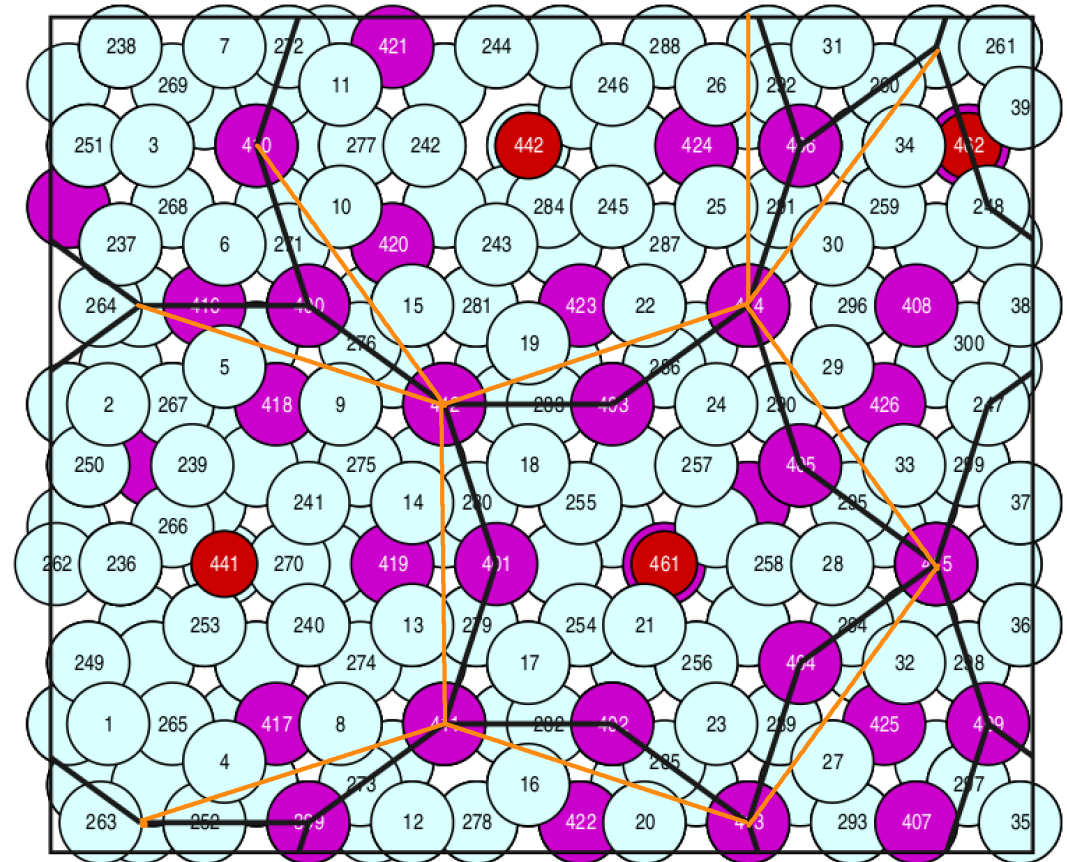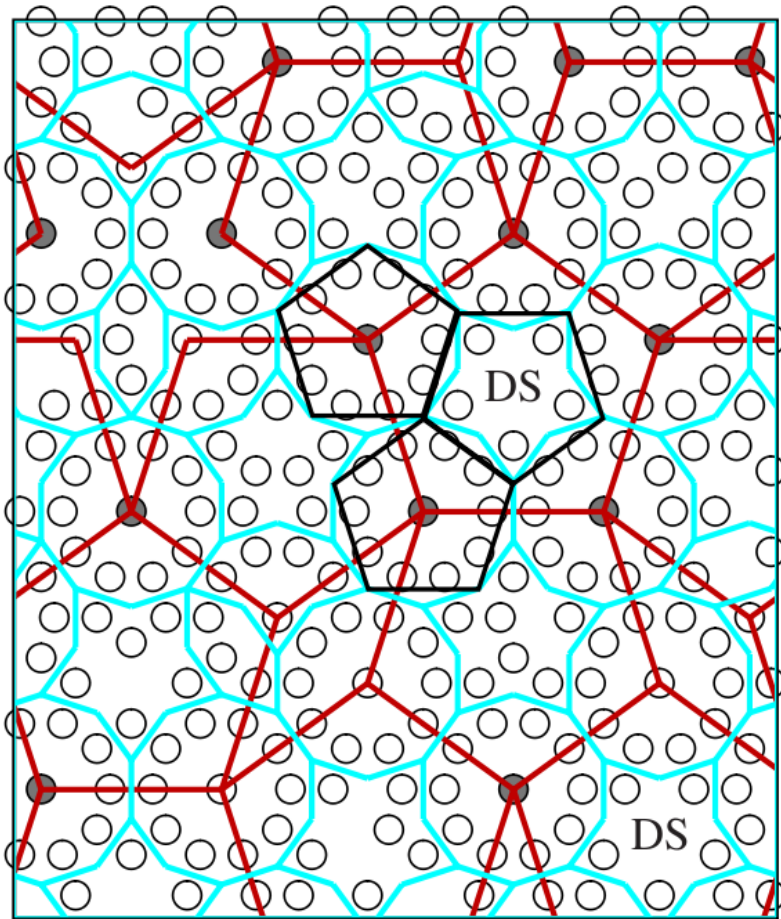
5/3 approximant

bleu = pavage DHBS

noir = pavage P1

rouge = pavage τP1

2/1 approximant

noir = pavage DHBS

orange = pavage P1

DHBS=Decagon-Hexagon-Boat-Star   Images from. M. Krajci

Modèle atomique de la surface - 3

Surface construite à partir de l'approximant 2/1

- 204 at = 148 Al + 44 Pd + 12 Mn

dimensions latérales 23.87×20.31 Å^2

épaisseur du slab $\simeq 6.60$ Å

- densité atomique de surface 0.134 at./Å^2 (exp. 0.136 at./Å^2)

- L'image STM simulée reproduit les motifs caractéristiques des images expérimentales
(Dark Stars DS et White Flowers WF)

Prise en compte de la dispersion

Méthode 1: Grimme DFT-D2 S.Grimme, *J. Comput. Chem.* (2006) **27**, 1787-1799

Ajout d'une contribution due à la dispersion aux énergies DFT de Kohn-Sham

$$E_{DFT-D2} = E_{KS-DFT} + E_{disp} \text{ avec } E_{disp} = -s_6 \sum_{i;j>i}^{N_{at}} \frac{C_6^{ij}}{(R^{ij})^6} f_{damp}(R^{ij})$$

$$f_{damp}(R^{ij}) = \frac{1}{1+e^{-d(R^{ij}/R_0^{ij}-1)}}$$

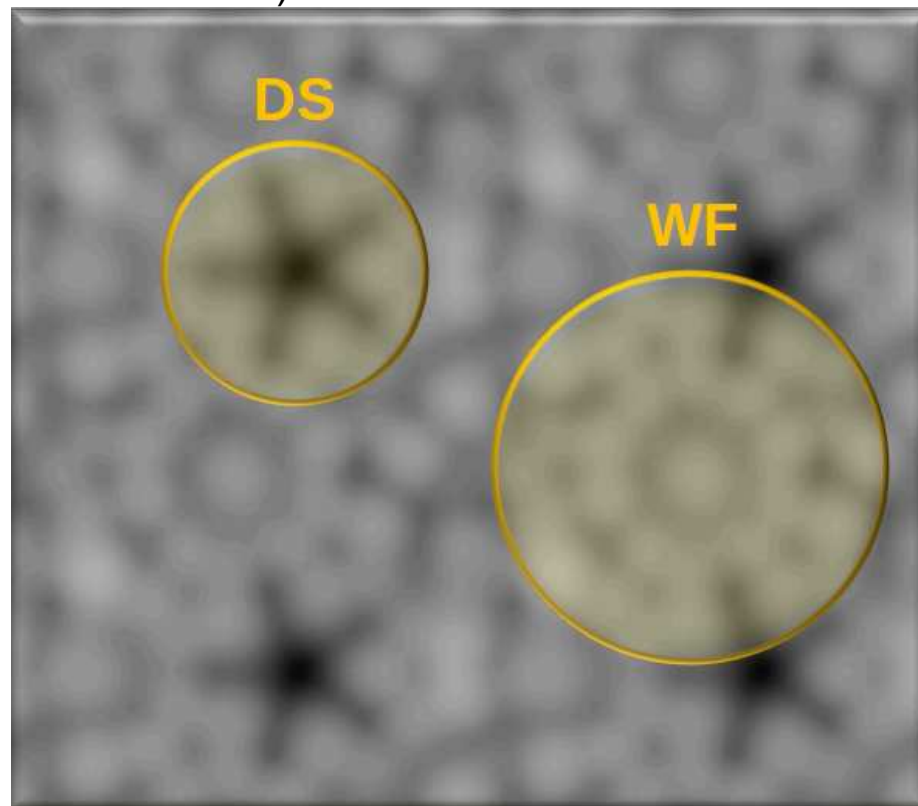$R_0^{ij} = R_0^i + R_0^j$ Somme des rayons de Van der Waals des atomes i et j

$C_6^{ij} = \sqrt{C_6^i C_6^j}$ avec C_6^i coefficient de dispersion atomique de l'atome i

	Al	Pd	Mn	C
C_6 (J nm^6 mol^{-1})	10.79	24.67	10.80	1.75
R_0 (Å)	1.716	1.639	1.562	1.452

d est un facteur d'amortissement $\rightarrow d = 20$

s_6 est un facteur d'échelle qui dépend de la fonctionnelle utilisée $\rightarrow s_6 = 0.75$ (PBE) La portée maximale des interactions de dispersion est limitée à 30 Å

Prise en compte de la dispersion

Méthode 2: classe des fonctionnelles vdW-DF

Méthode proposée initialement par Dion $et\ al.$ (PRL $\mathbf{92}$:246401, 2004).

Ici, choix de la fonctionnelle "opt-B88" pour laquelle la fonctionnelle d'échange a été optimisé pour la partie corrélation:

$E_{xc} = E_x^{GGA} + E_c^0 + E_c^{nl}$ (où $E_x^{GGA} + E_c^0 + E_c^{GGA}$ est l'énergie standart d'échange et corrélation GGA)

Le terme E_c^{nl} prend en compte les effets de corrélation électroniques à grande distance, responsables des interactions de Van der Waals:

$E_c^{nl} = \frac{1}{2} \int \int \rho(\vec{r})\Phi(\vec{r},\vec{r'})\rho(\vec{r'})d^3r\,d^3r'$ où $\Phi(\vec{r},\vec{r'})$ est une fonction qui dépend de $\vec{r} - \vec{r'}$ et des densités électroniques au voisinage de $\vec{r}$ et $\vec{r'}$.

Dans Vasp, implémentée par Klimeš $et\ al.$ (PRB $\mathbf{83}$:195131, 2011) avec l'algorithme de Roman-Perez and Soler (PRL $\mathbf{103}$:096102, 2009).

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Énergies et géométries d'adsorption - 1

Ads. sites	Top view	Side view	DFT-D2	opt-B88
Vac1			-3.20 eV	-2.74 eV
Vac2			-1.57 eV	-1.58 eV
VacHex			-1.61 eV	-1.81 eV
VacHex2			-1.82 eV	-1.81 eV
WF1			-2.90 eV	-2.81 eV
WF2			-2.97 eV	-2.74 eV
WFHex			-2.29 eV	-2.41 eV
WFHex2			-2.34 eV	-2.41 eV

DS site

WF site

Les sites les plus stables sont ceux avec la face pentagonale de C_{60} sur la surface:

- le pentagone de C_{60} aligné avec le pentagone Al_5 de la surface pour WF
- les pos. relat. des pent. de C_{60} et de Al_5 (surf.) n'ont pas une grande influence sur E_{ads}

Énergies & géométries d'adsorption - 2

Distance entre le centre de gravité des 5 atomes de carbone du pentagone (C_{60}) et

- le centre de gravité des 5 atomes d'aluminium de la surface
- l'atome de Mn de surface

Ads. sites	Top view	Side view	DFT-D2	opt-B88	
Vac1			1.09 Å	1.12 Å	
Vac2			1.43 Å	1.81 Å	DS site
VacHex			1.61 Å	1.80 Å	
VacHex2			1.52 Å	1.79 Å	
WF1			1.77 Å	1.85 Å	
WF2			1.73 Å	1.80 Å	WF site
WFHex			2.00 Å	2.11 Å	
WFHex2			1.93 Å	2.04 Å	

	DFT-D2	opt-B88
C-Al (Vac1)	2.13 Å	2.14 Å
C-Mn (WF2)	2.13 Å	2.19 Å

Quelques informations sur la liaison chimique

DS   WF
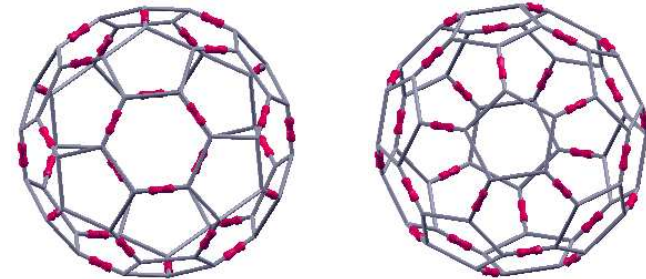

Isosurfaces $\pm 4 \times 10^{-6}$ e/Å^3
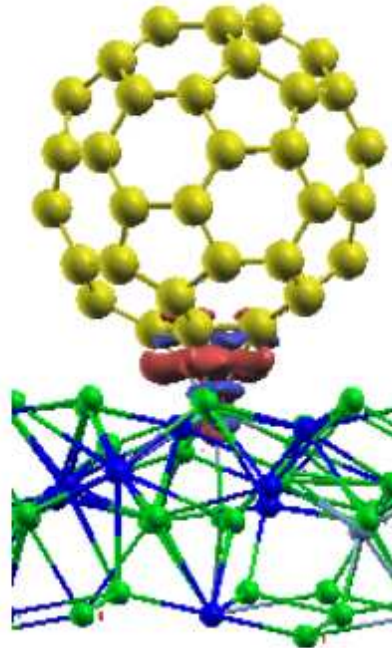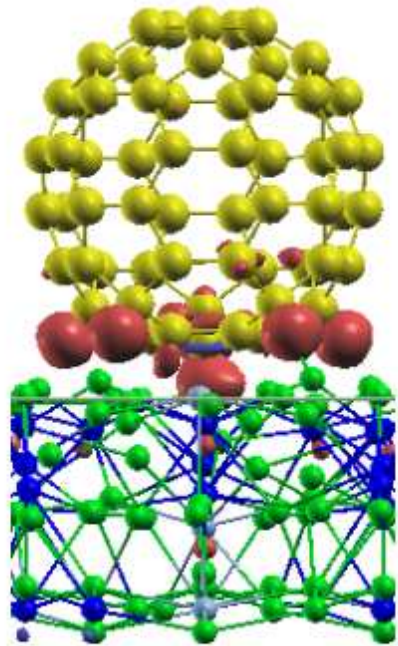
$$\Delta\rho = \rho_{C_{60}+surface} - \rho_{C_{60}} - \rho_{surface}$$

$\Delta\rho > 0 \Rightarrow$ Rouge $\Delta\rho < 0 \Rightarrow$ Bleu

- Sur les sites DS,
  $\Delta\rho$ est directionnel selon la direction Al-C
- Sur les sites WF,
  $\Delta\rho$ est entre Mn et le pentagone du C_{60}

Isodensité: molécule C_{60} seule
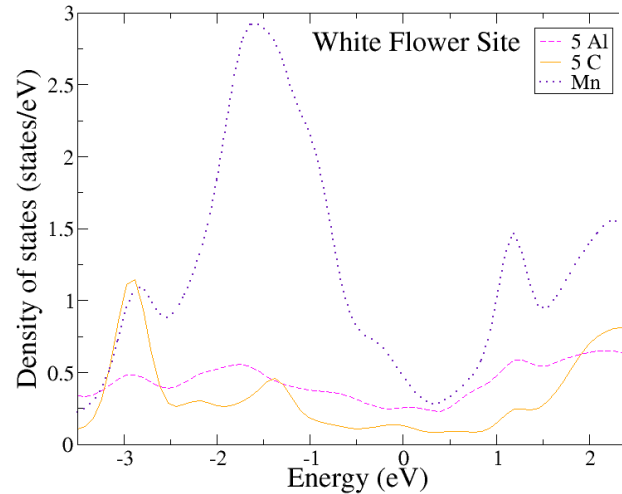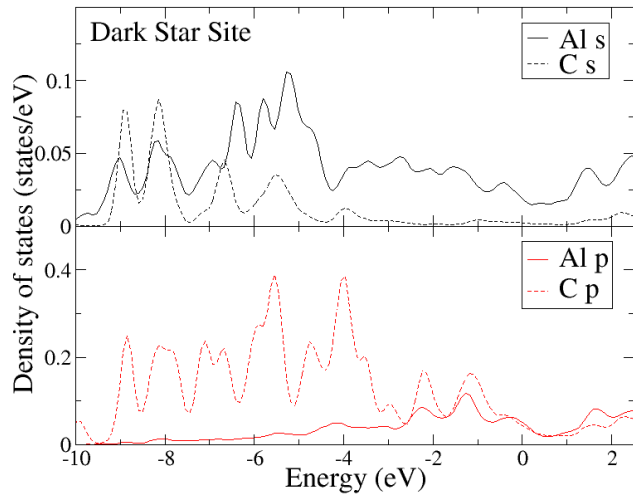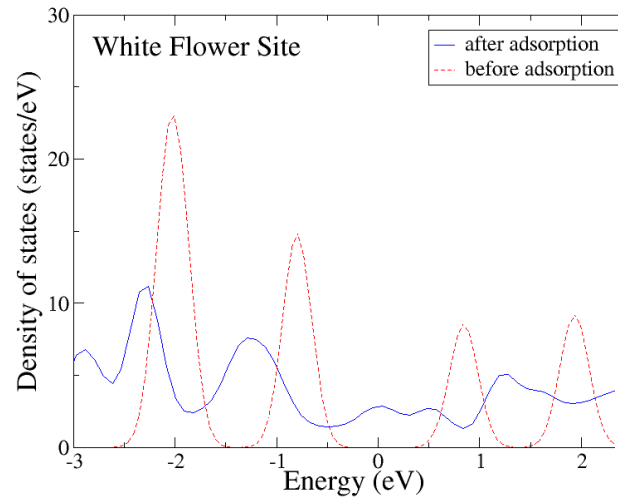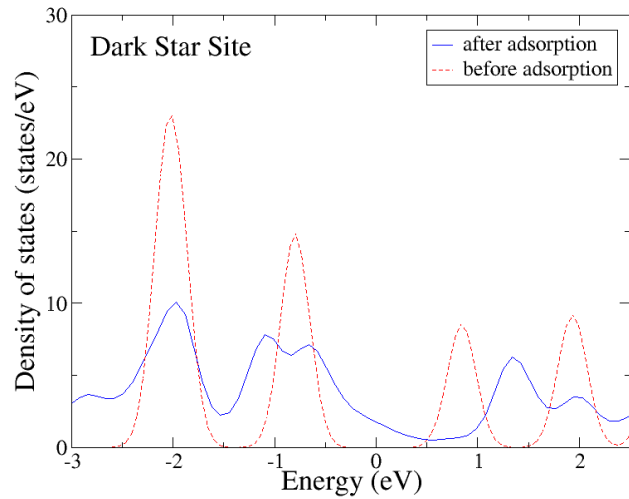

30 liaisons [6,6] avec un caractère "C=C" fort

60 liaisons [5,6] avec un carac. "C=C" moins marqué

$$d_{C-C}^{[6,6]} = 1.40 \text{ et } d_{C-C}^{[5,6]} = 1.45$$

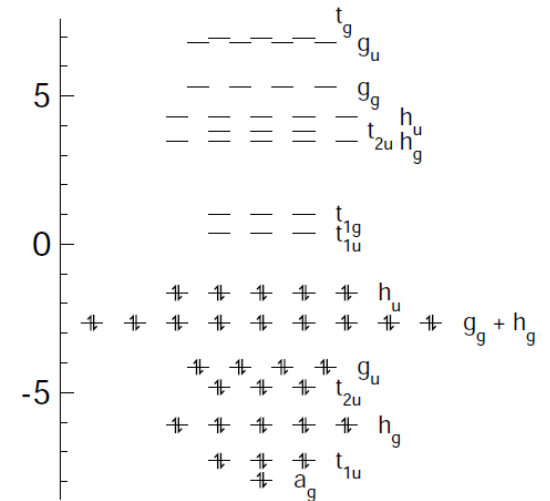Tous les atomes C sont conjugués... mais C_{60} n'est pas un composé aromatique parfait.

Quelques informations sur la liaison chimique

HOMO et LUMO modifiées par l'adsorption (états au niveau de Fermi)

- <u>Sites DS</u>: hybridisation sp Al-C

- <u>Sites WF</u>: hybridisation spd C-Mn

Conclusion and perspectives

Density Functional theory for CIM structures and properties

DFT is presently the most successful approach to compute the electronic structure of complex intermetallic compounds (and more generally materials)

DFT predicts a great variety of complex intermetallic properties: structures, vibrational frequencies, electric and magnetic properties, reaction paths, chemical bonding, surface structures, etc.

However

Basic DFT is not so good when dealing with large electronic correlations (ex: NiO), Van der Waals interactions, excited states $\rightarrow$ DFT+U, GW, etc.

DFT is limited to quite "simple systems" ($\simeq 10^2 - 10^3$ atoms)

DFT can be used to built parameters for simulations at a larger size scale

$\rightarrow$ Towards multiscale modeling