Quasicrystals Investigated Using DFT: Bulk, Surface and Adsorbates

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Introduction

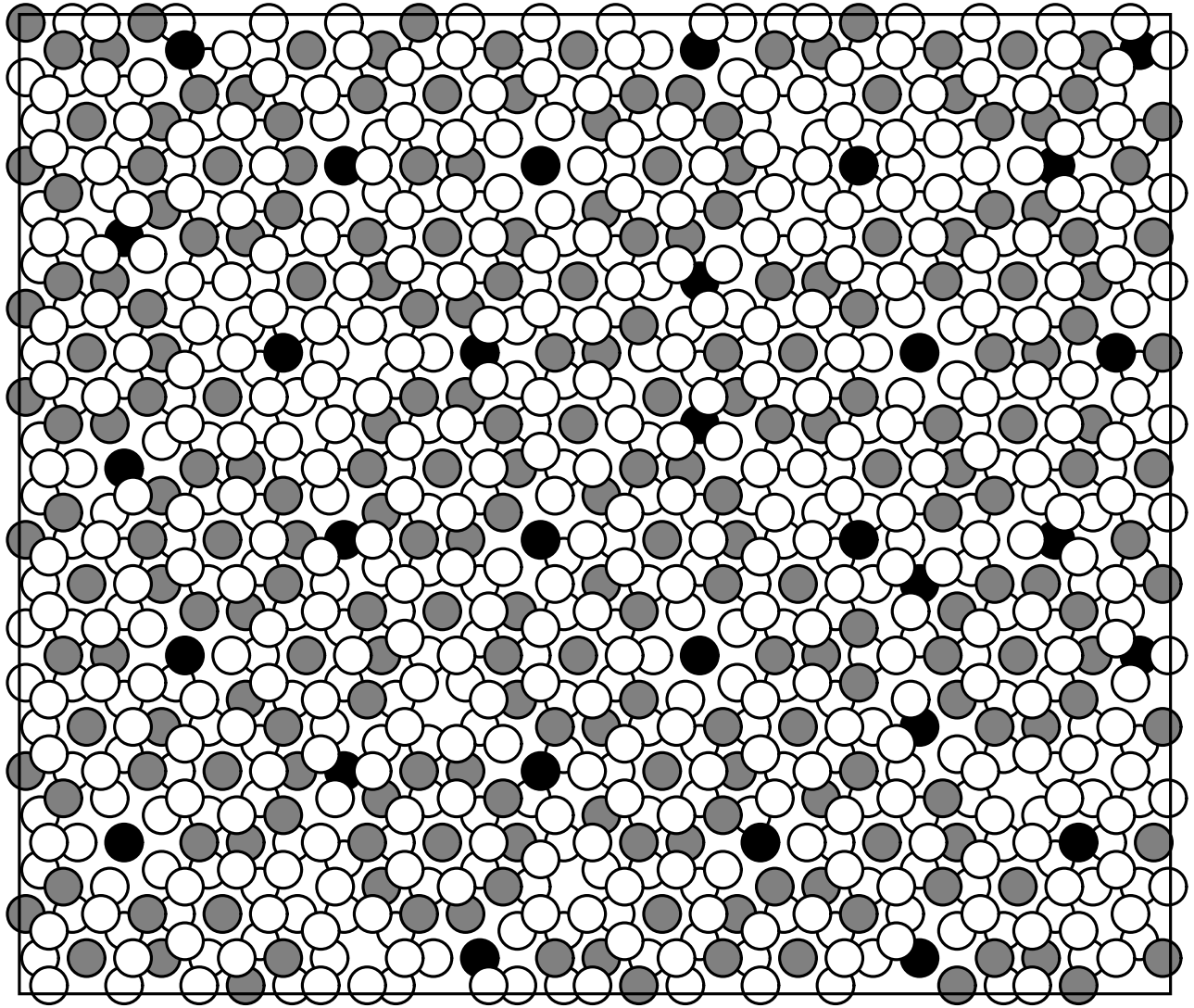
Quasicrystals

Discovered by Shechtmanom in 1982 at study of AlMn alloys

Basic characteristics

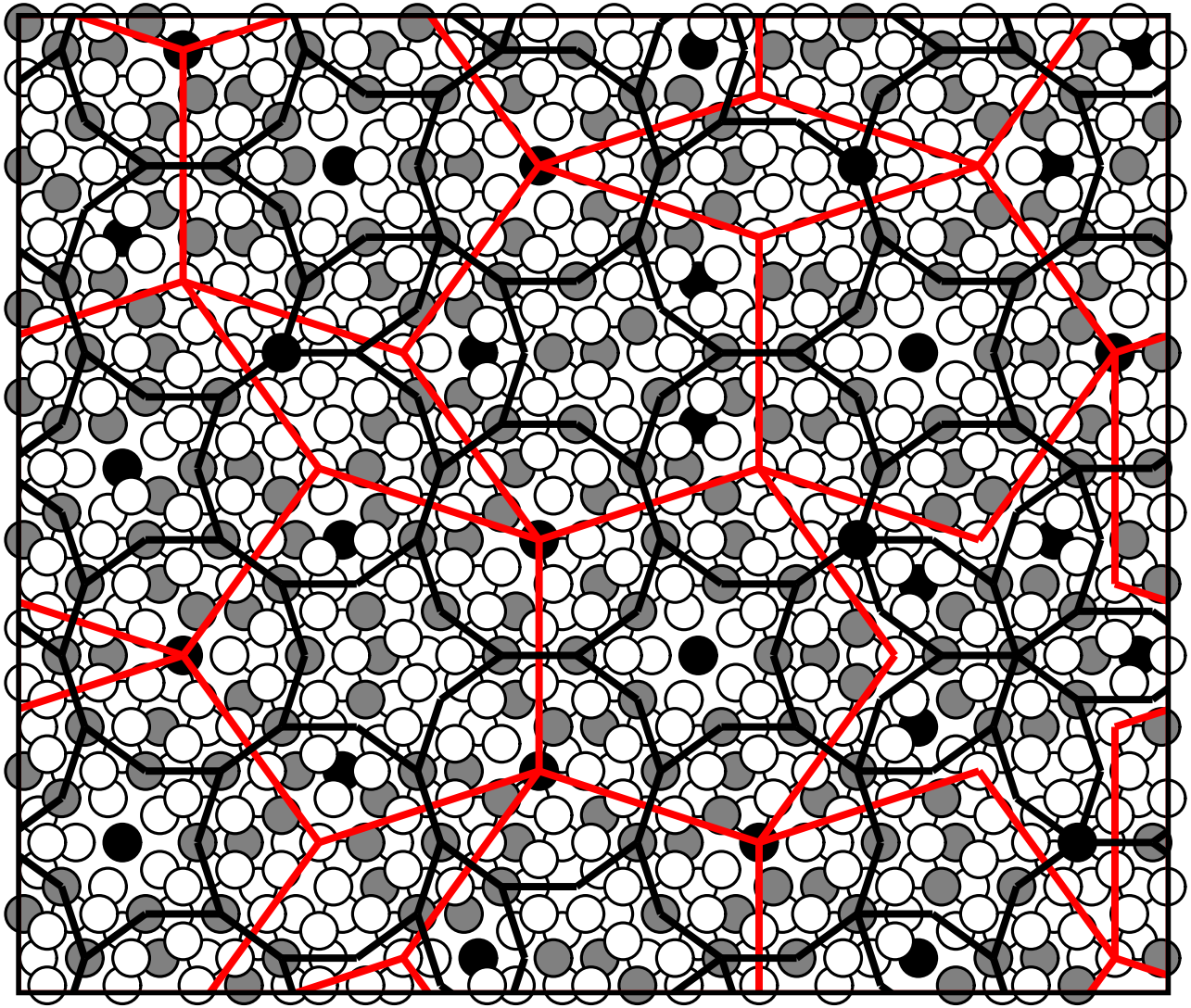
- Regular but not periodic - quasiperiodic arrangement of atoms
- „Forbidden“ symetries of diffraction patterns
- Structure described in high-dimensional space
- Metallic phases
- Anomalous physical properties

Quasiperiodic arrangement of atoms



5-fold surface of icosahedral AlPdMn quasicrystal

Quasiperiodic arrangement of atoms



5-fold surface of icosahedral AlPdMn quasicrystal

Classes of quasicrystals

- Icosahedral
- Decagonal
- Dodecagonal
- Octagonal
- .....

Quasicrystals as intermetallic phases

- Al-Mg (AlZnMg, AlCuLi, AlMgLi, …) - Frank-Kasper
- Al-Mn (AlMn, AlPdMn, AlPdRe, …) - Mackay
- Zn-Mg-RE (RE=Y, Dy, Gd, Ho, …)
- Ti-Zr-Ni
- Cd-Yb
- .....

Quasicrystals - (Al-based) complex metallic phases

Quasicrystals

Basic notions

Geometry of icosedral and decagonal quasicrystals is related to properties of the Golden Mean

$$\tau=(1+\sqrt{5})/2 \quad = 1.61803398\ldots$$

and the Fibonacci numbers F_n, n= 0, 1, 2, …

$$F_0=0,\ F_1=1,\ \ F_{n+1}=F_n+F_{n-1}$$

$$F_n = 0,1,1,2,3,5,8,13,21,\ldots.$$

$$\lim_{n\to\infty} F_{n+1}/F_n = \tau$$

F_{n+1}/F_n - rational approximant to τ

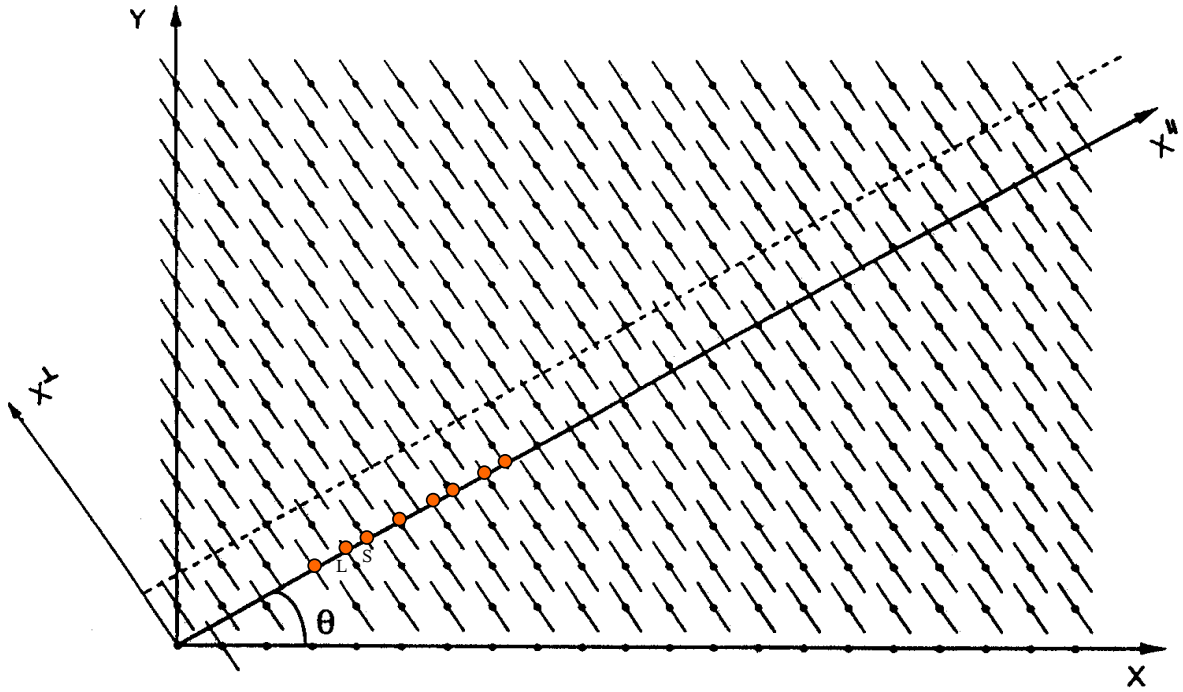
1/1, 2/1, 3/2, 5/3, 8/5, ... – approximants to a quasicrystal

Approximants to a quasicrystal $\longrightarrow$ crystals with large unit cells

Structural models of quasicrystals

Projection method

Construction of a 1D (quasi)periodic sequence

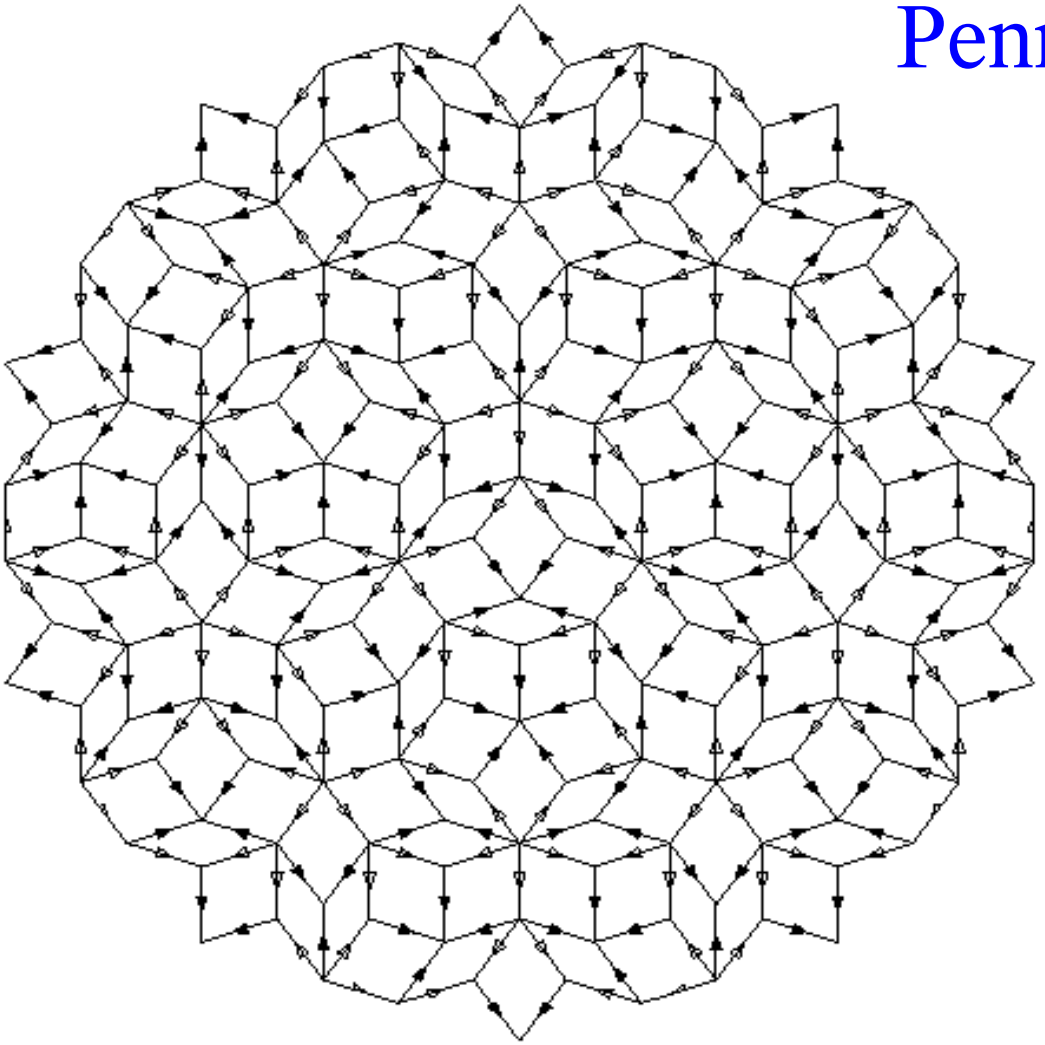


2D (square) lattice decorated by 1D acceptance domains (AD)

Intersections of parallel space with AD define a (quasi)periodic sequence

LSLLSLSL....

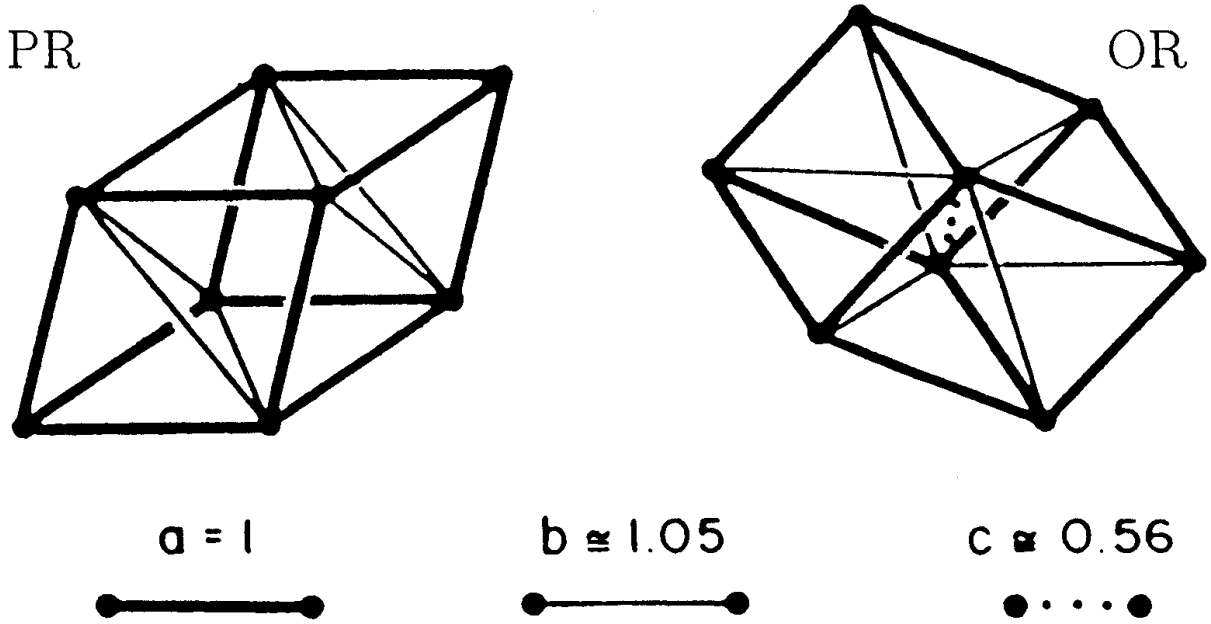
Penrose tiling



- two types of tiles:
  - fat rhombus
  - skinny rhombus

- matching rules

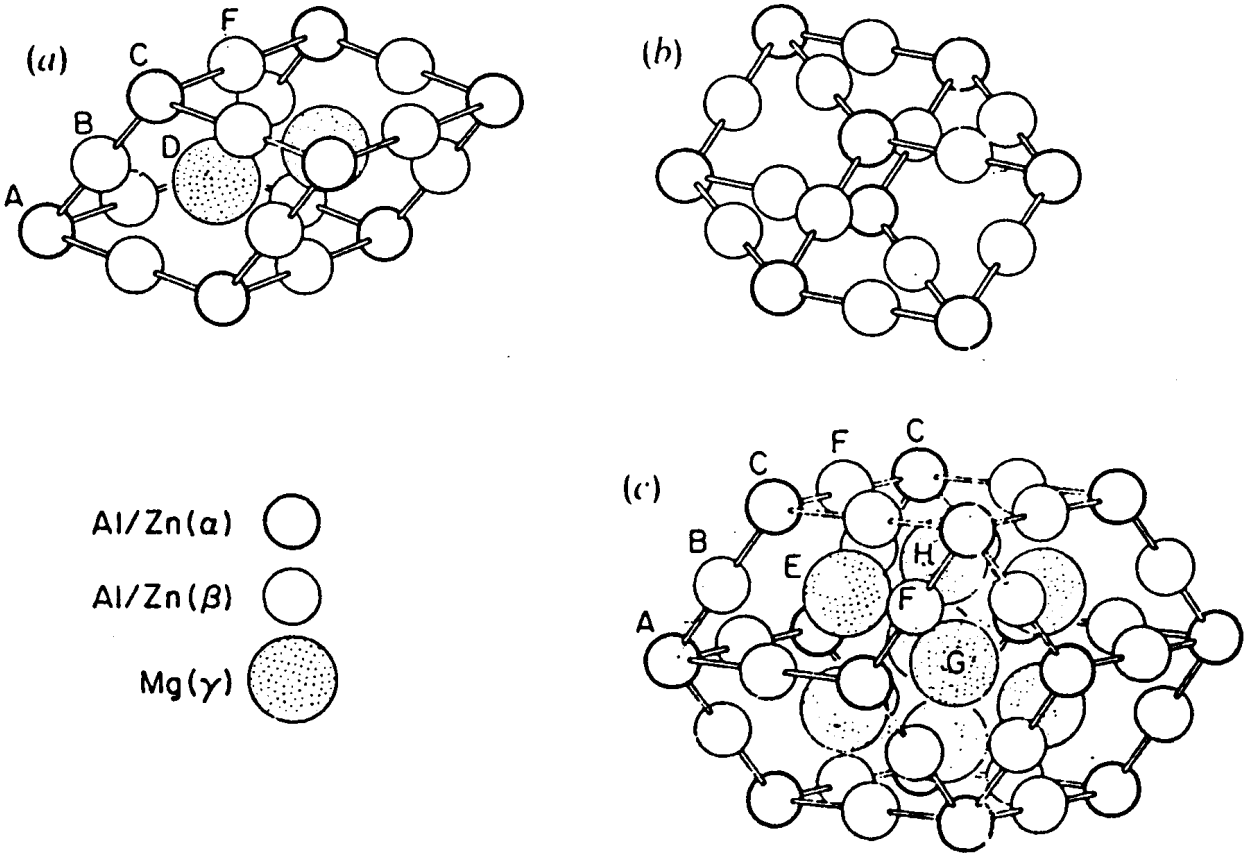
3D Penrose (Ammann) tiling



PR – prolate rhombohedron

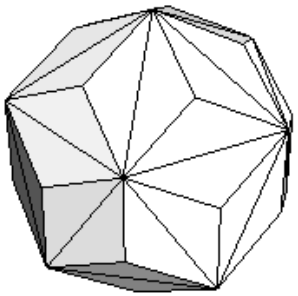
OR - oblate rhombohedron

Structural model AlZnMg – decoration of PR a OR by atoms

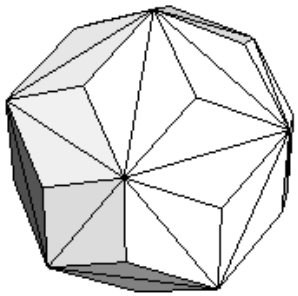


6D model of icosahedral AlPdMn

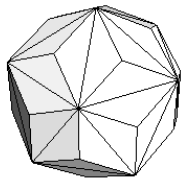
Acceptance domains (AD) – 3 polyhedra - triacontaheders



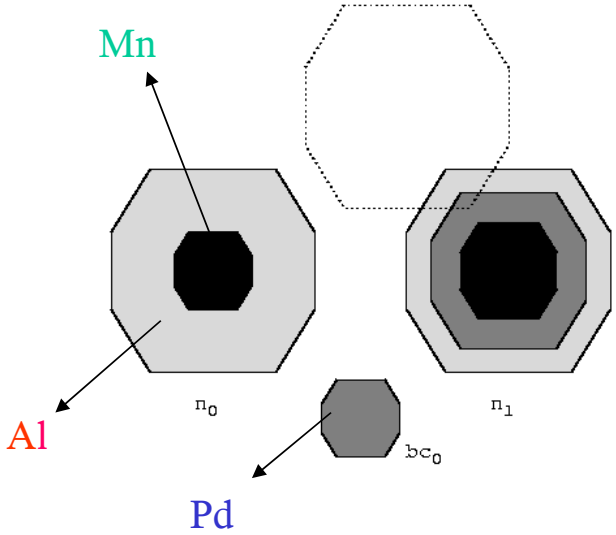
n_0



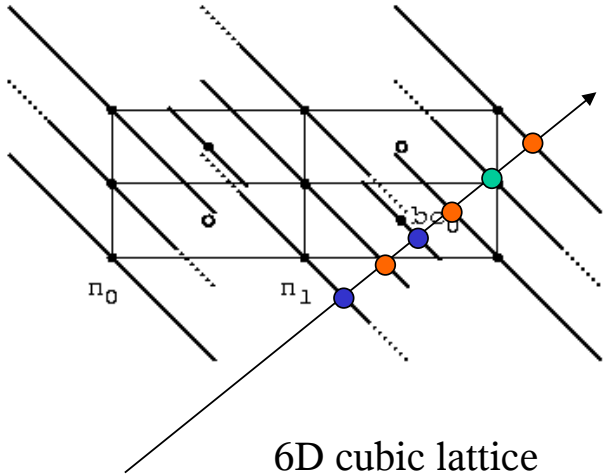
n_1



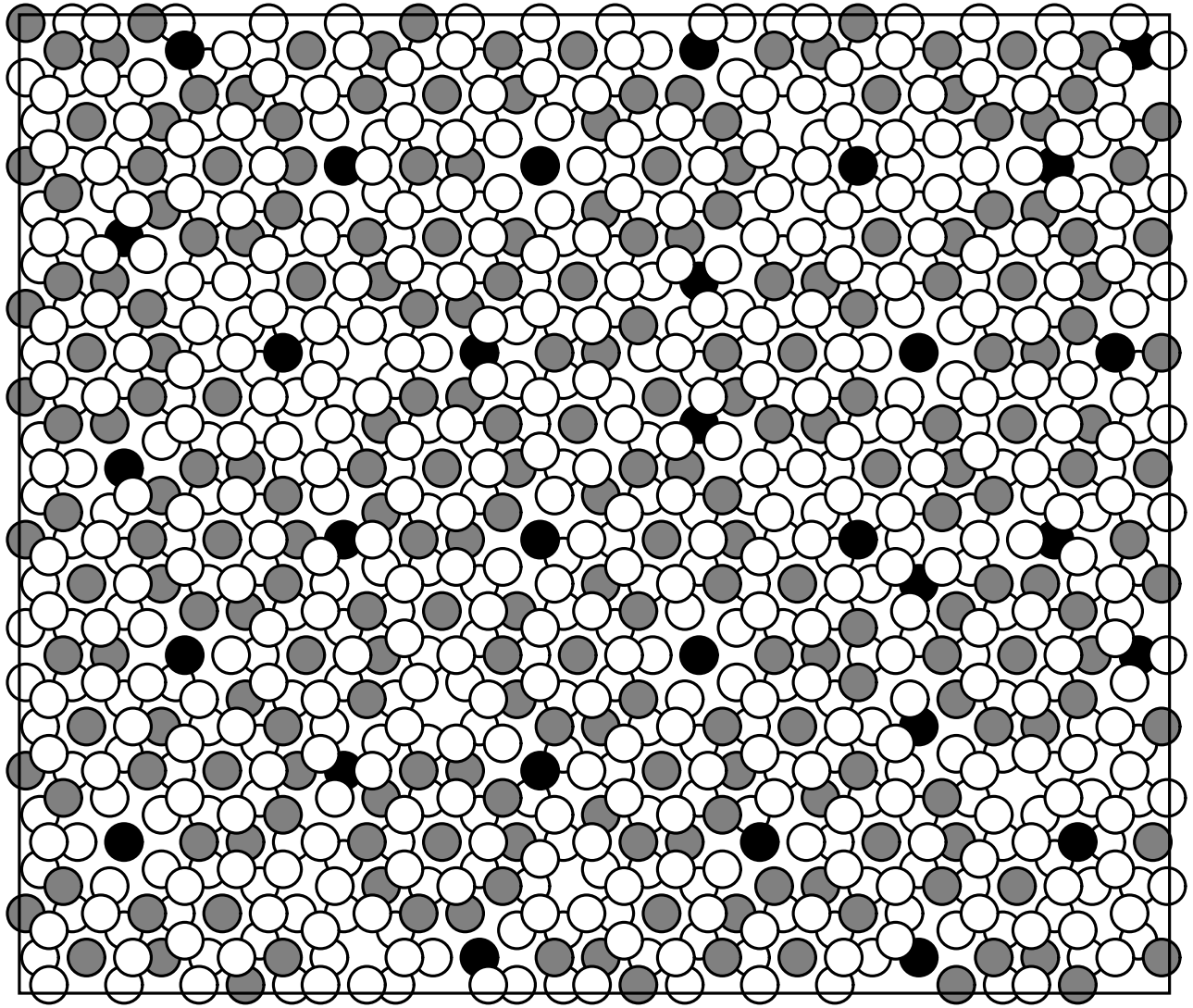
bc_0



Internal structure of AD define chemical ordering of atoms



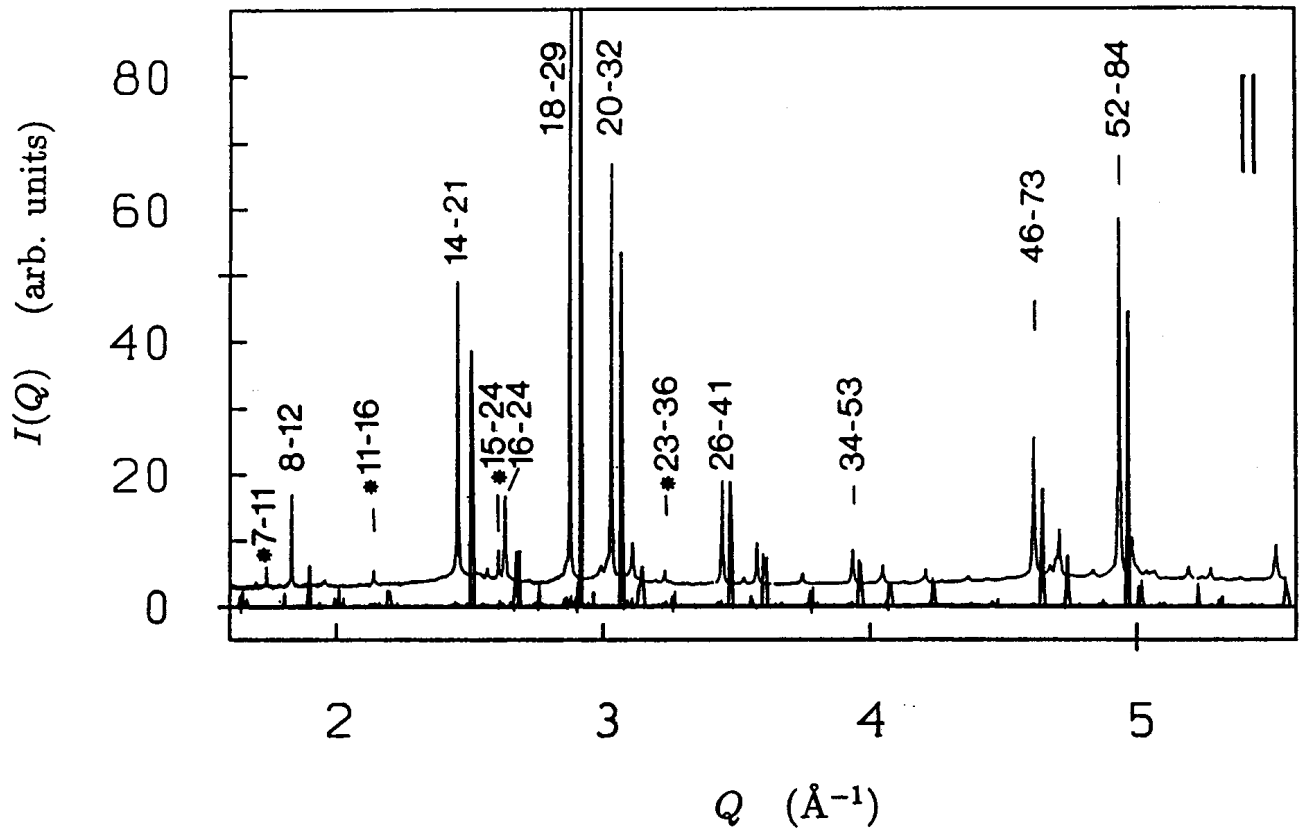
6D cubic lattice
decorated by AD



6D model of icosahedral AlPdMn quasicrystal

i-AlPdMn

Comparison of diffraction pattern from 6D model with experimentom



M.K., J. H., et al.: PRB **51**, 17355 (1995)

i-AlPdMn

Comparison of a PES from 6D model with experiment

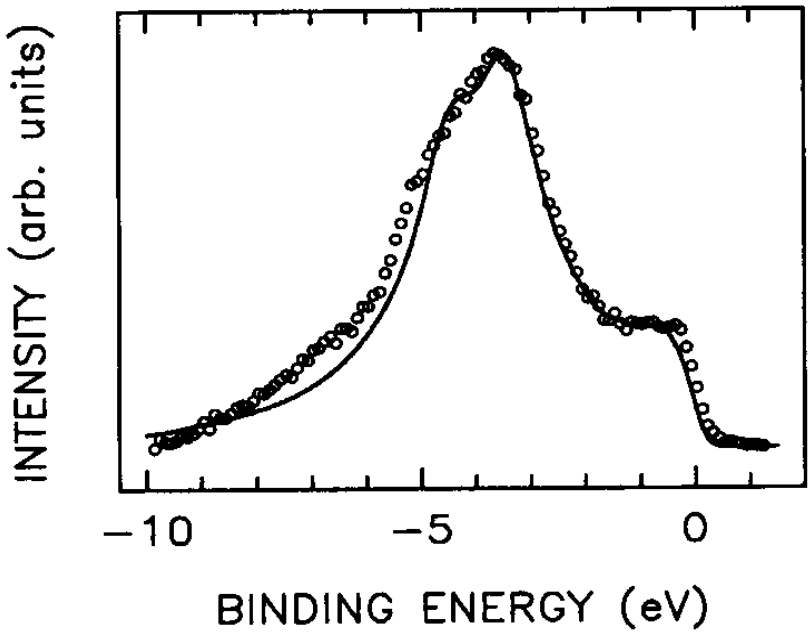
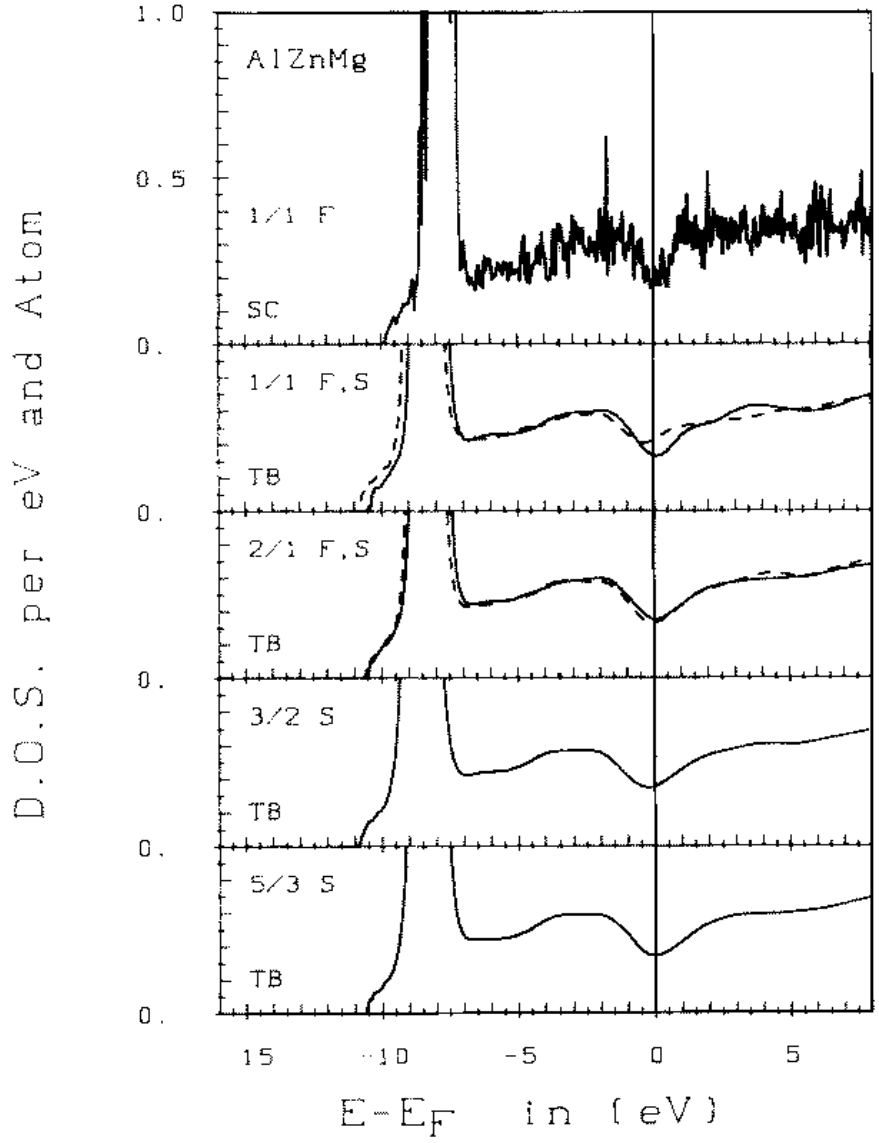


Fig. 8.11. Comparison of the valence band of i-$Al_{70}Pd_{20}Mn_{10}$ measured at $h\nu = 100$ eV (open circles, Zhang et al. 1994) with the broadened theoretical DOS for the 8/5 approximant to the i phase (solid line, Krajčí et al. 1995). After Zhang and Stadnik (1995).

Electronic structure of quasicrystals



DOS of quasicrystalline appproximants

AlZnMg

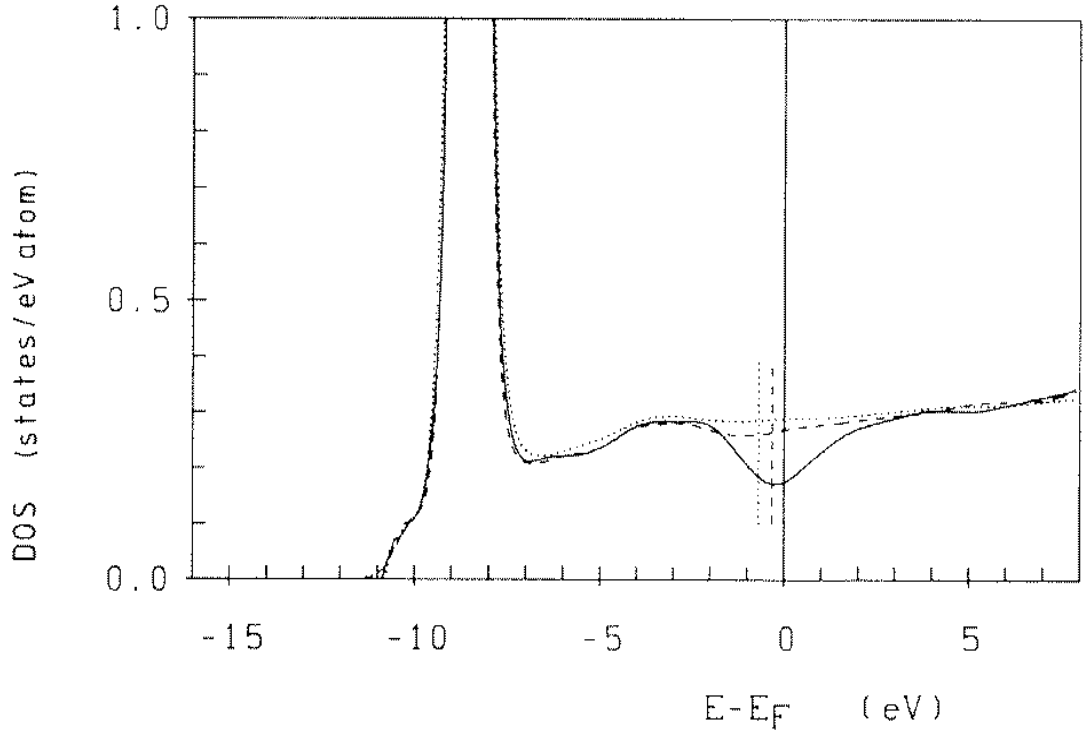
- 1/1 - 162 atoms
- 2/1 - 680 atoms
- 3/2 - 2920 atoms
- 5/3 - 12560 atoms

- „spiky“ character
- pseudogap at E_F
- fast convergence

J. H. and M. K.: PRB **47**, 11795 (1993)

DOS of quasicrystalline, amorphous and liquid system

3/2 – approximant i-AlZnMg
- 2920 atoms
- MD -> liquid state
- relaxed to amorphous state



QC

Amorf.

Liquid

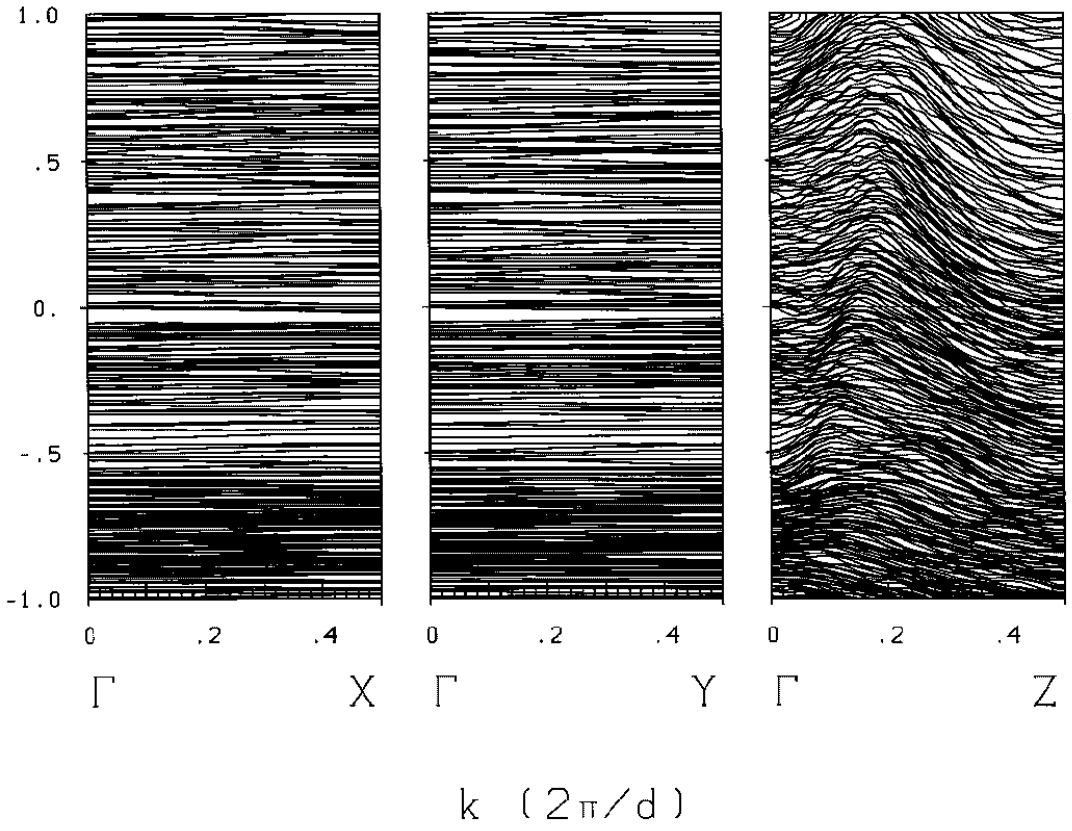
Hume-Rothery mechanizmus

$2k_F = Q_p$

J. H. and M. K.: PRB **47**, 11795 (1993)

Band structure of a d-AlCuCo approximant

x, y – quasiperiodic plane
z - decagonal axis



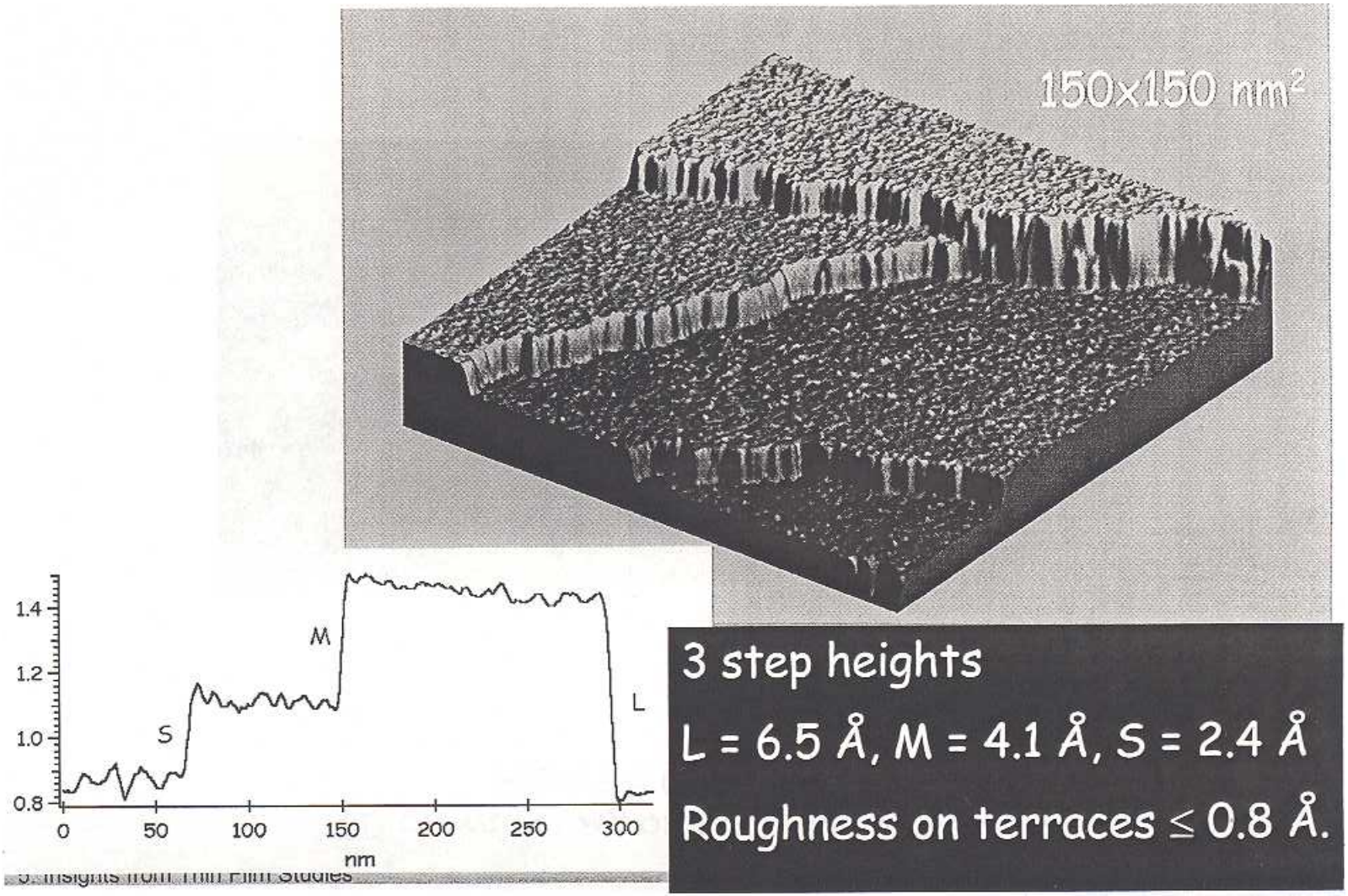
37.7 Å × 32.07 Å × 4.18 Å, 352 atoms

Quasicrystalline surfaces

Surfaces of quasicrystals

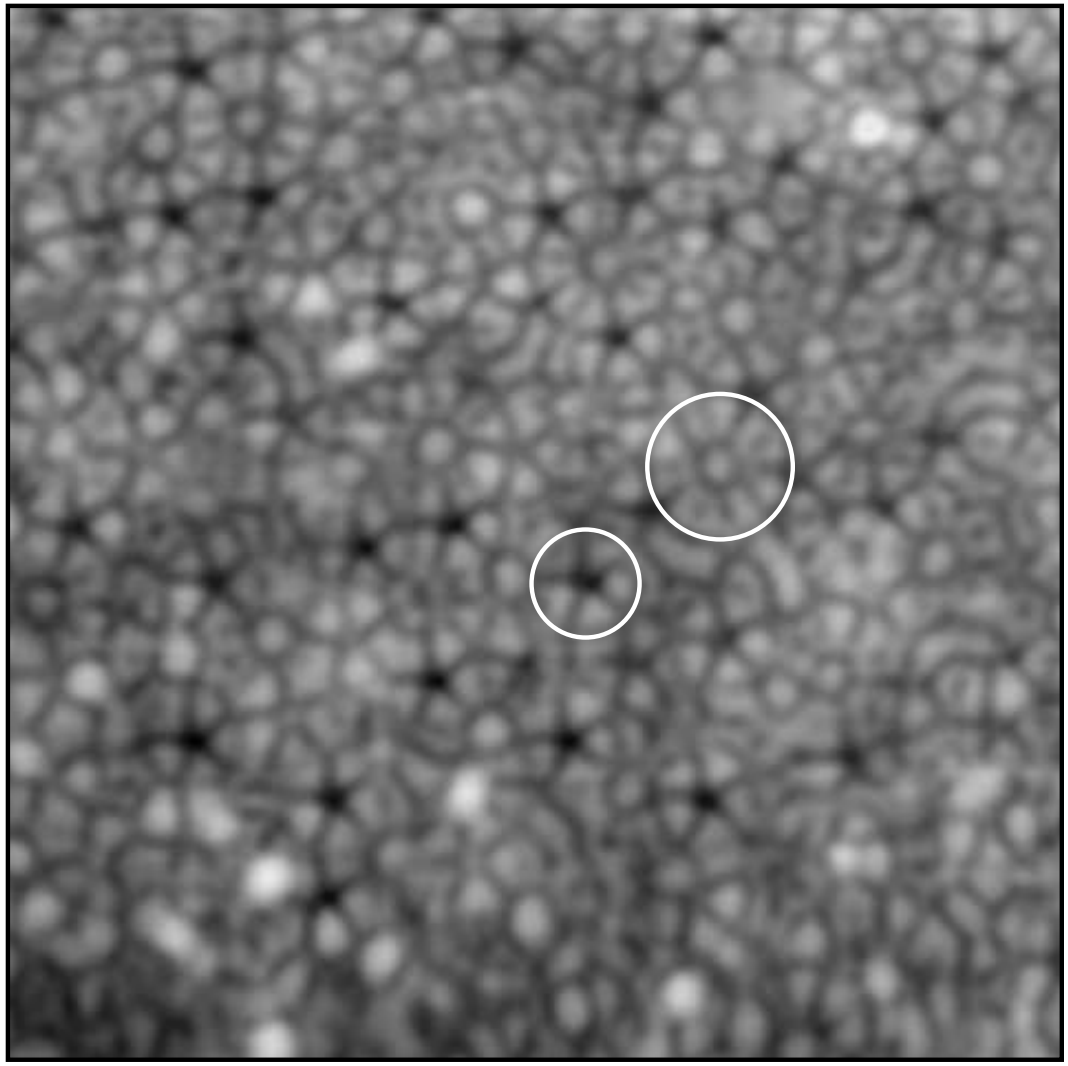
- Quasicrystals - complex metallic alloys $\longrightarrow$ mechanical properties of bulk - brittle
- Despite quasiperiodic order – surfaces are atomically flat
- Surfaces - possible technical applications
- Extraordinary tribological properties (wear, wetting, ...)
- Extraordinary chemical reactivity - adsorption and catalytic properties
- Surface of stable quasicrystals i-AlPdMn and d-AlNiCo - intensively studied.

Low resolution STM image of the surface of i-AlPdMn.



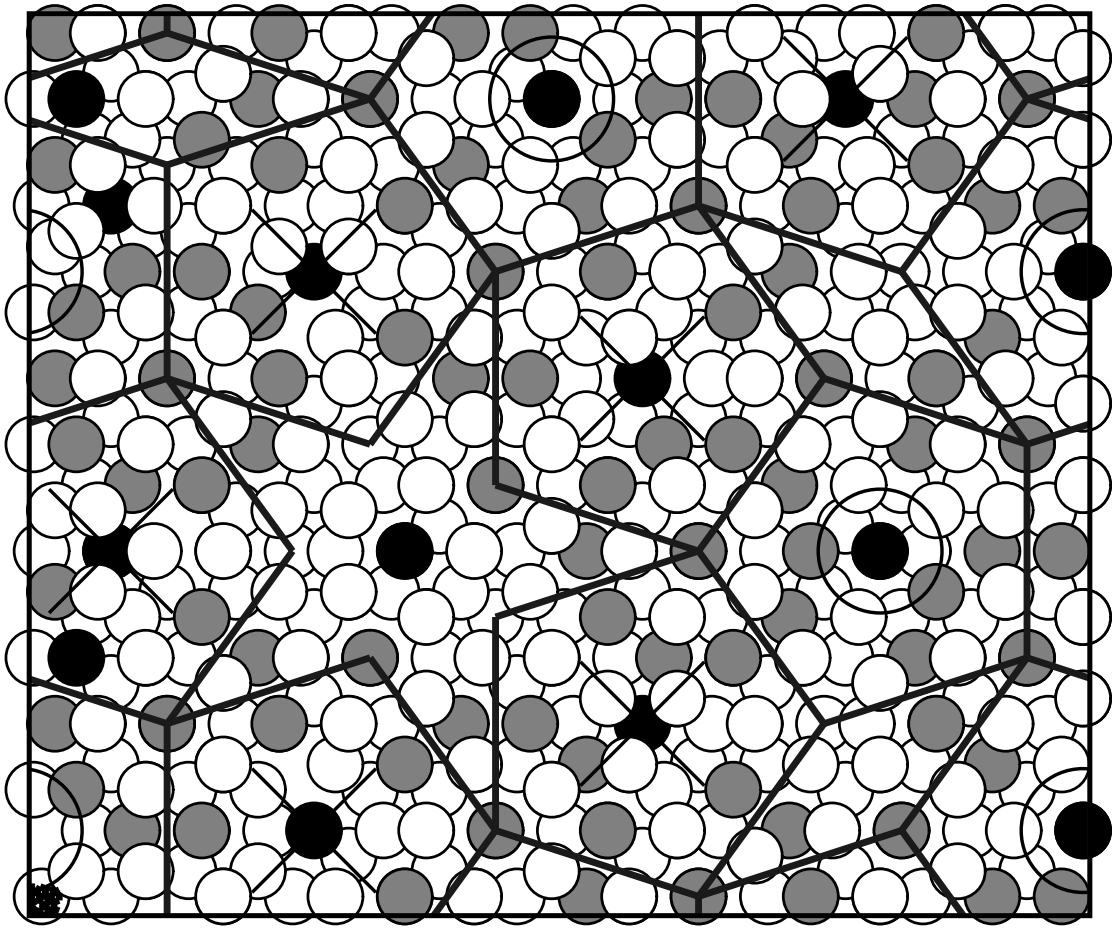
150×150 nm, Thiel and McGrath 2004

High resolution STM image of the surface of i-AlPdMn.



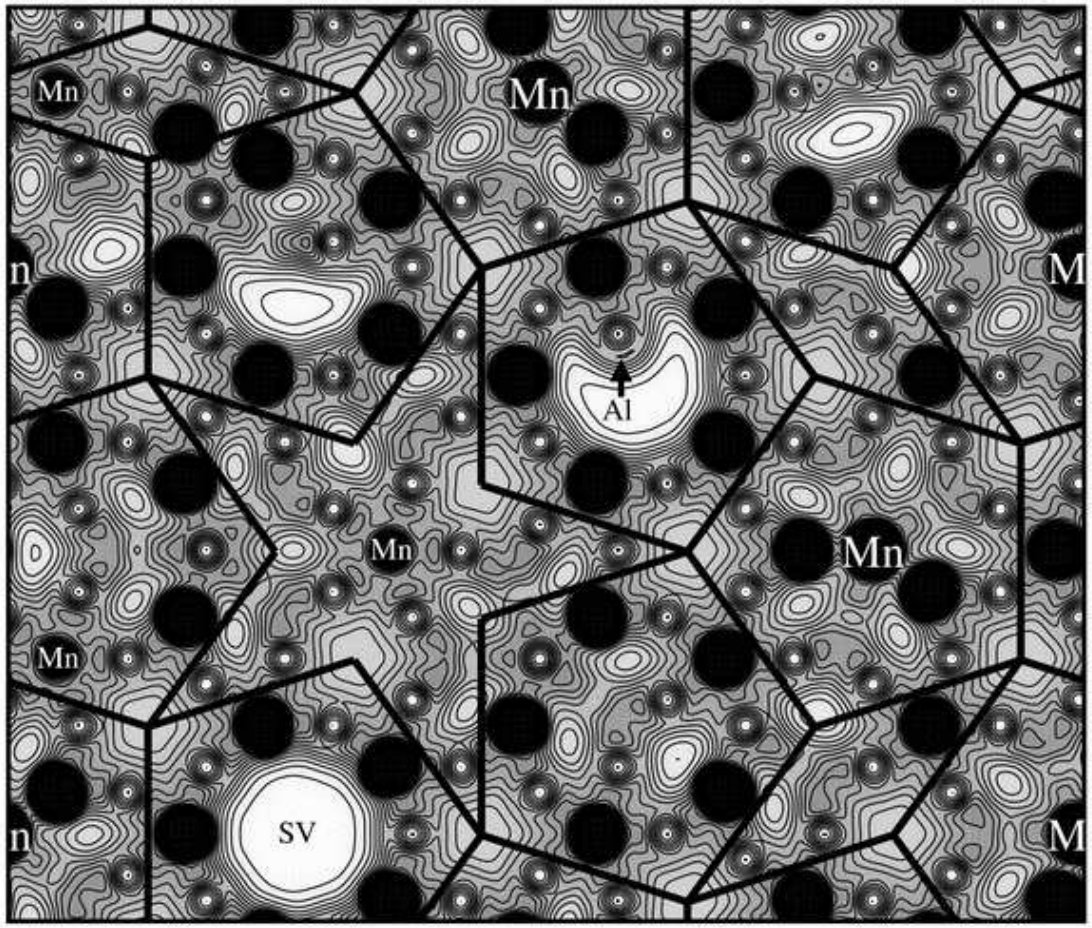
- 10×10 nm
- White flower (WF)
- Dark star (DS)
- Ledieu and McGrath 2005
- Atomic structure not known (from experiment)

Structural model of the 5-fold surface of i-AlPdMn



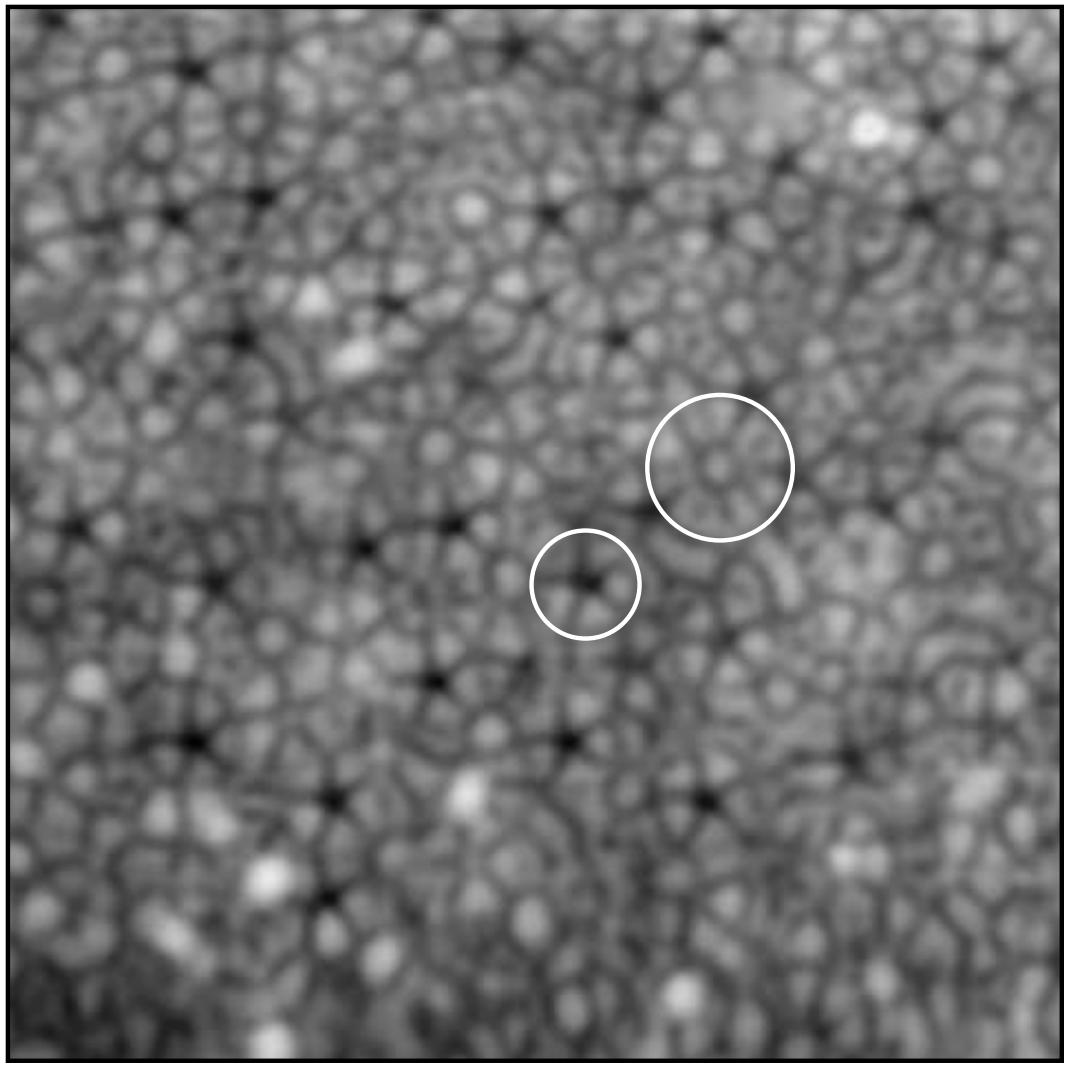
- KGB model
- 3/2-approximant
  38.63 Å×32.86 Å
- Al – open circles
- Pd – gray circles
- Mn – dark circles
- Quasiperiodic order – P1-tiling (Papadopulos et. al 2002)
- Pentagons – "top" and "bottom" orientations

Charge density distribution in a surface layer



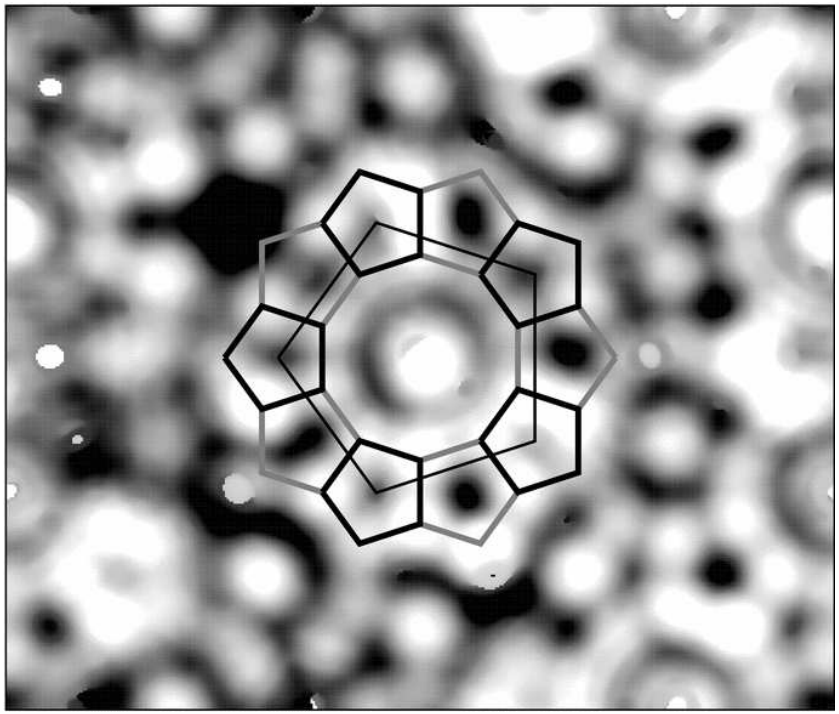
- "top" and "bottom" pentagons - central Mn atom
- pseudo-Mackay (M) and Bergman-type (B) clusters
- Surface vacancies (SV)

High resolution STM image of the i-AlPdMn surface

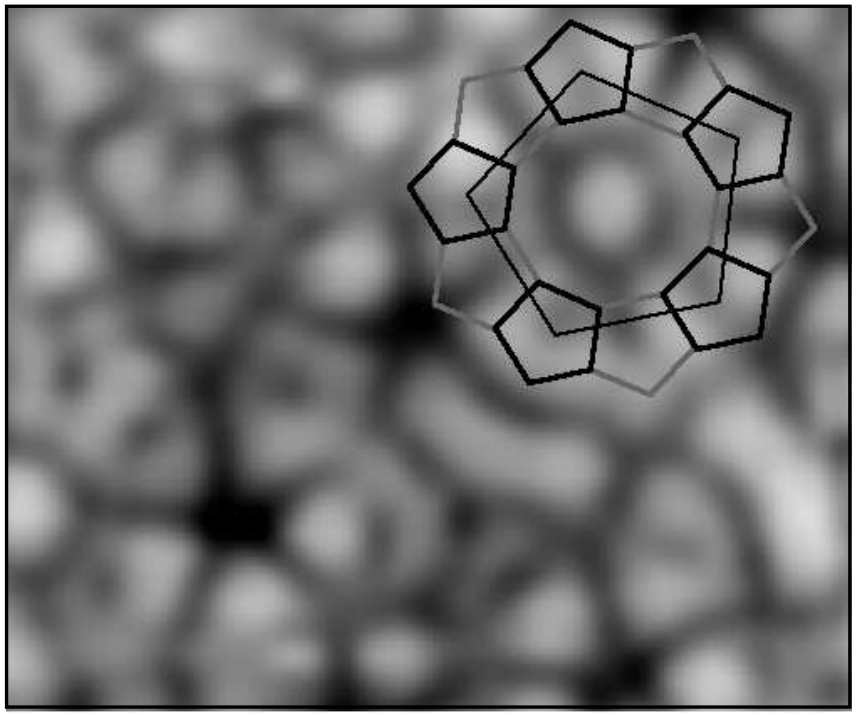


- exp. STM image from Ledieu and McGrath 2005
- 10×10 nm
- White flower (WF)
- Dark star (DS)

Deatil of STM image – white flower (WF)



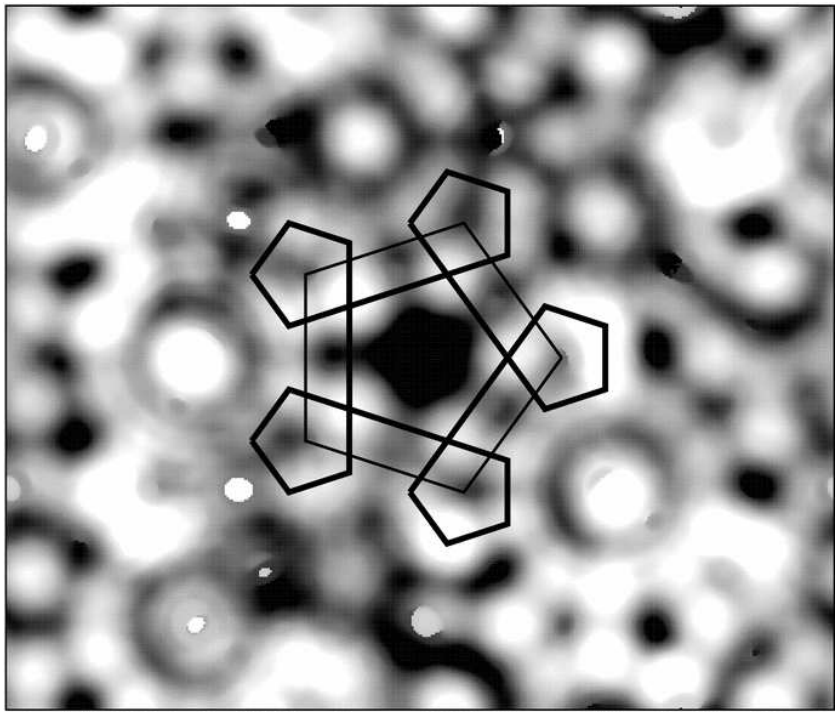
structural model



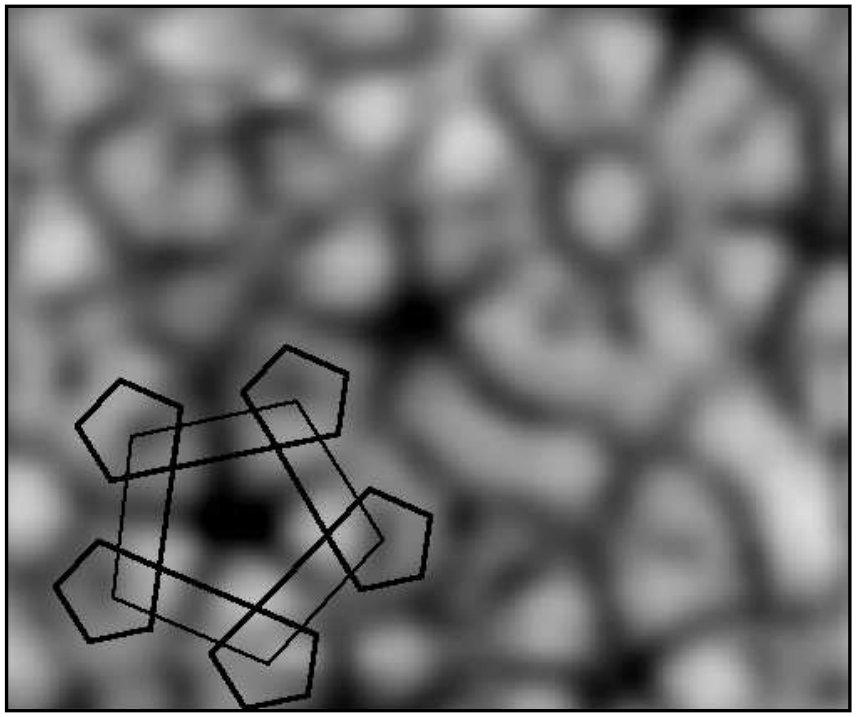
experiment

- Identification of positions and chemical types of individual atoms:
  Small pentagons – Al pentagons with an edge 2.96 Å – leaves of WF
  In the center – a Mn atom
- WF – "top" pentagonal tiles of the P1 tiling
- Experimental STM: Ledieu and McGrath 2005

Deatil of STM image – dark star (DS)



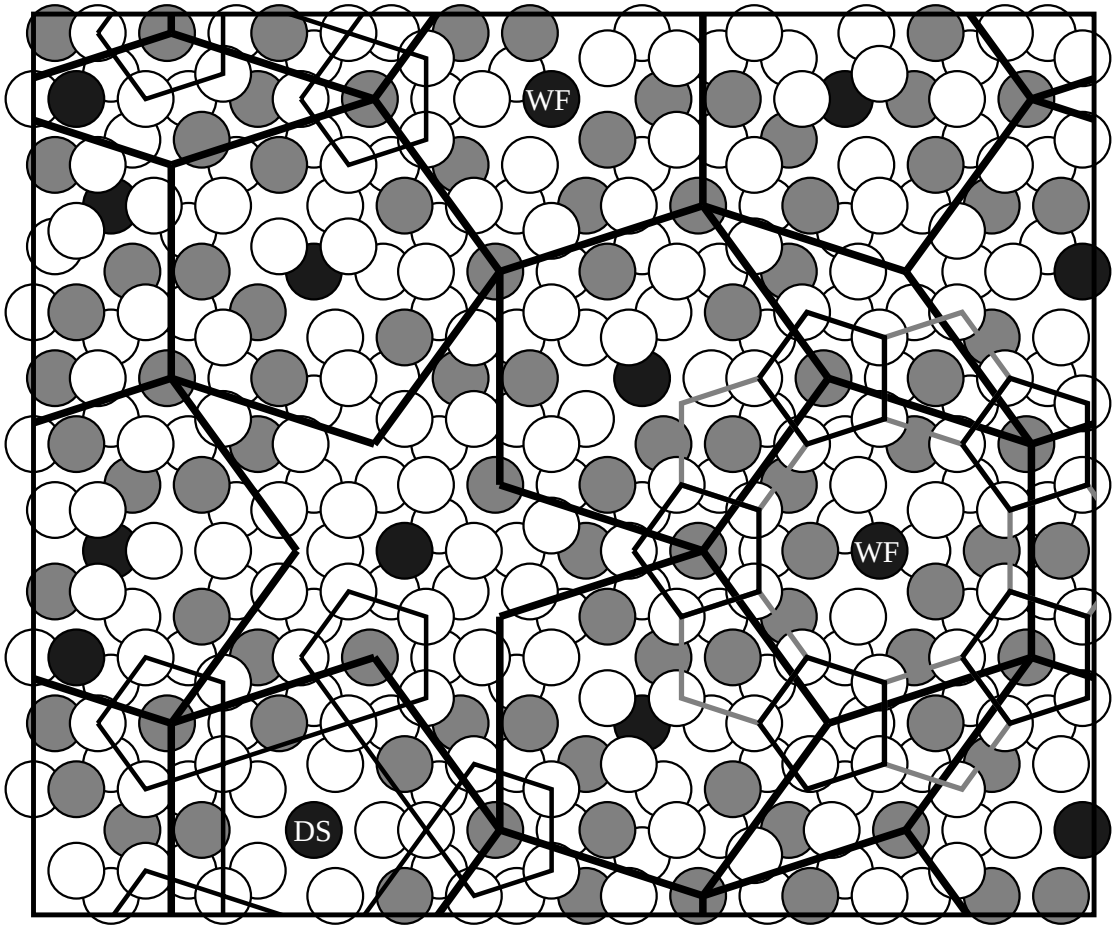
structural model



experiment

- DS – inside some of "bottom" pentagonal P1 tiles
- Atomic structure: surface vacancy surrounded by the ten-fold ring of atoms – a pentagon of Al atoms with the edge 4.79 Å and a pentagon of Pd atoms.
  The contrast between the bright Al atoms and the dark Pd atoms forms the characteristic pentagonal shape of the DS

Structural model of the 5-fold surface of i-AlPdMn



- WF - "top" pentagonal tile
- DS - "bottom" pentagonal tile
- M. K., J. H., J. Ledieu, and R. McGrath: PRB **73** 024202 (2006)

Satisfactorily realistic structural model of clean i-AlPdMn surface

Quasiperiodic monolayers and multilayers

- Ab-initio studies: monolayers on the surface of i-AlPdMn and d-AlCoNi

  - PRB **71** 054202 (2005) : clean i-AlPdMn surface
  - PRB **71** 184207 (2005) : Bi, Sb, and Sn monolayers on i-AlPdMn surface
  - PRB **73** 024202 (2006) : clean i-AlPdMn surface - STM images
  - PRB **73** 134203 (2006) : clean d-AlCoNi surface
  - PRB **73** 184202 (2006) : Bi on d-AlCoNi surface
  - PRB **75** 224205 (2007) : alkali metal monolayers and multilayers on i-AlPdMn
  - PRB **77** 134202 (2008) : monolayers on i-AlPdMn - elements from group I to III
  - PRB **79** 134206 (2009) : alkali metal monolayers on i-AlPdMn - Shukla et al.
  - PRB **79** 165430 (2009) : Pb clusters on i-AlPdMn - Ledieu et al.
  - PRB **81** 085417 (2010) : Pb monolayers on i-AlPdMn - structure and electronic properties

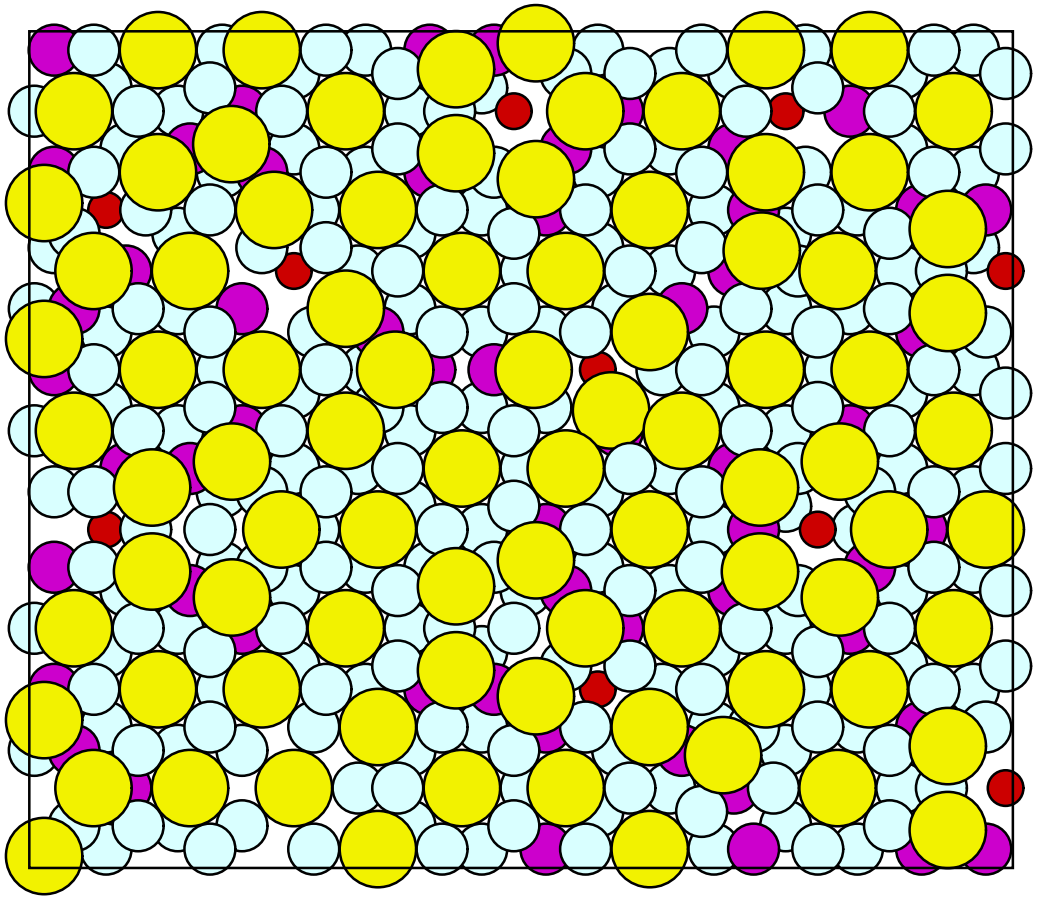
- Experiment: most attempts to grow quasiperiodic overlayers failed!

Which elements form regular quasiperiodic monolayers?

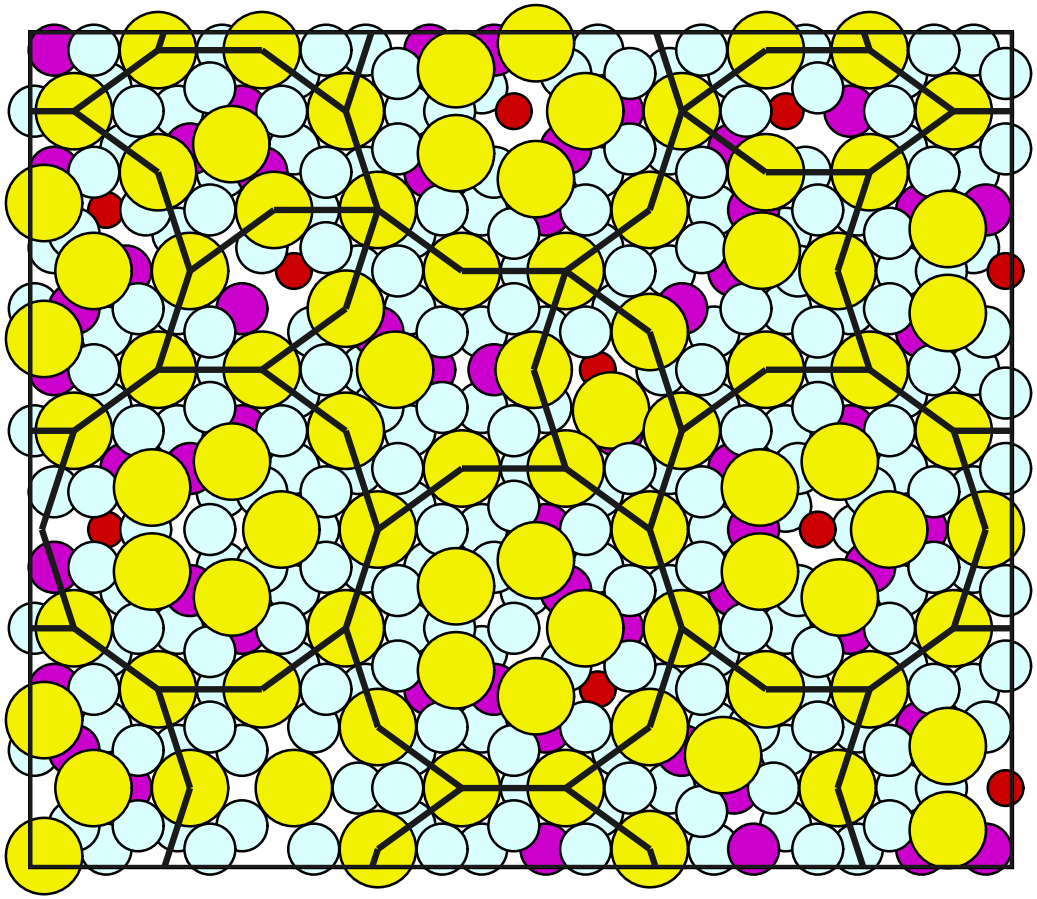
Investigated elements:

- Alkali metals: Li, Na, K, Rb, Cs
- Alkaline earth metals: Be, Mg, Ca, Sr, Ba
- Group 3 elements: Sc, Y, La
- Rare-earth elements: Gd
- Pb group: Pb, Bi

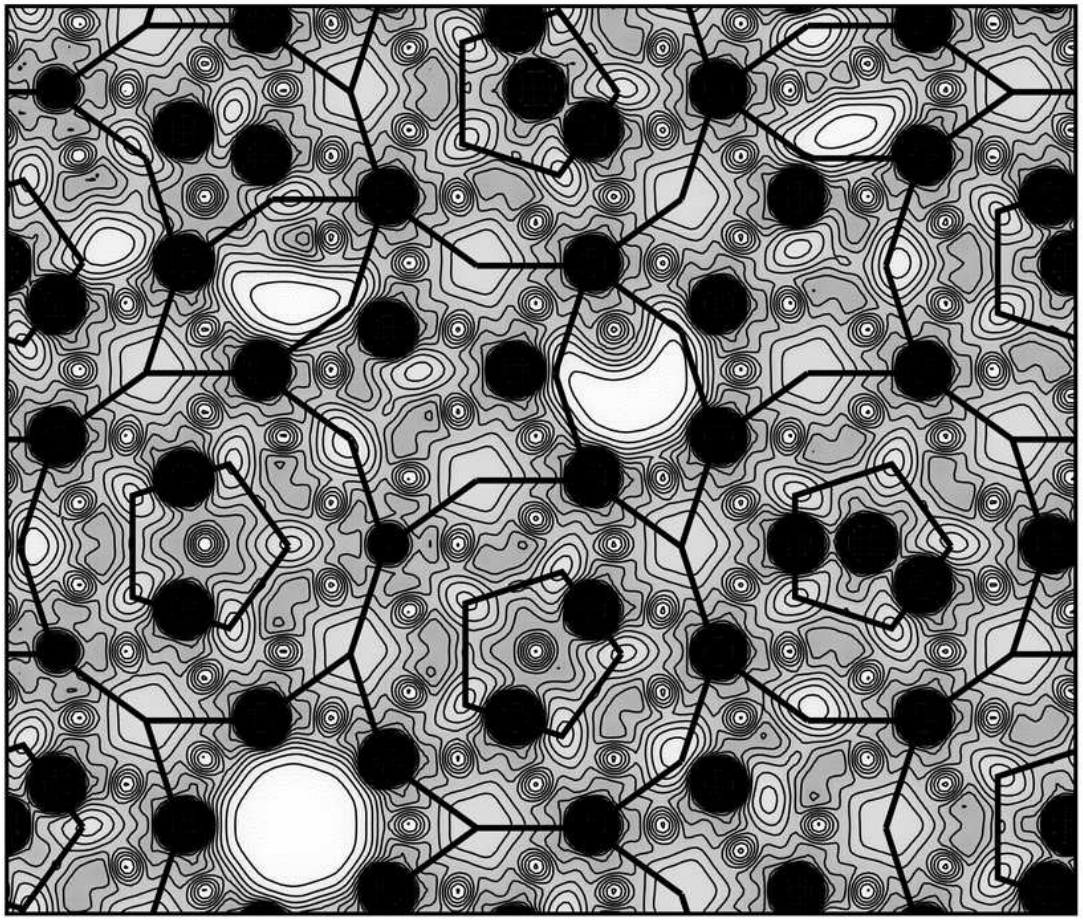
Na monolayer on 5-fold i-AlPdMn surface



Na monolayer on 5-fold i-AlPdMn surface



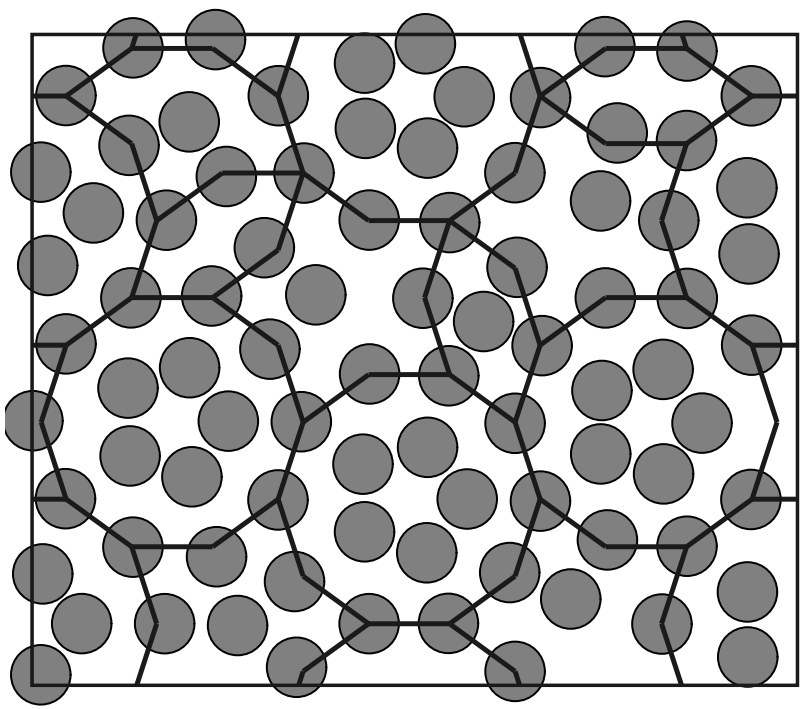
Distribution of adsorption sites



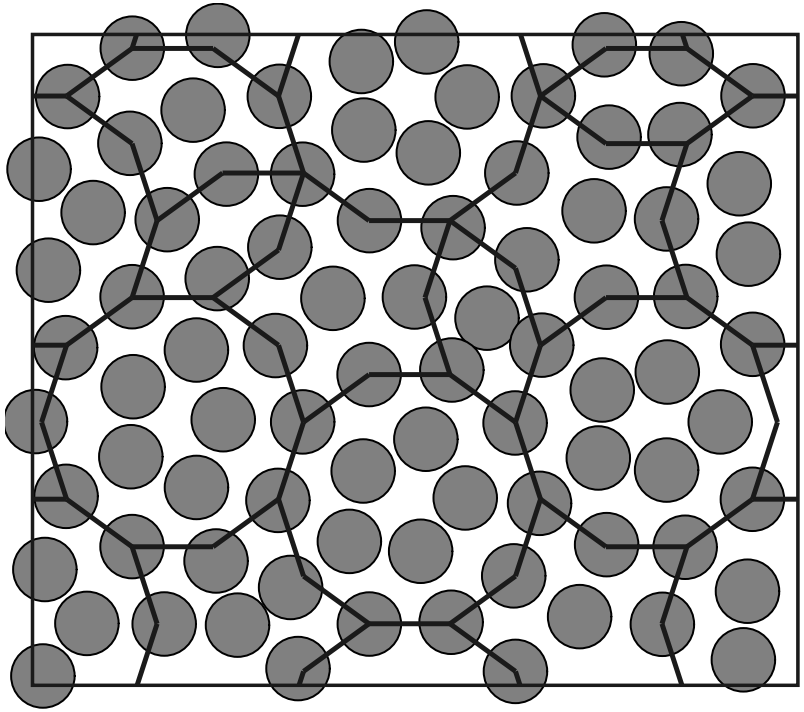
- Sites inside surface vacancies - do not belong to a monolayer
- Hollow sites between Al atoms $\longrightarrow$ DHBS tiling
- Charge density minima $\longrightarrow$ small pentagon inside the D tile

Quasiperiodic ordering in an overlayer enforced by the substrate

Na vs. K monolayer on 5-fold i-AlPdMn surface



Na

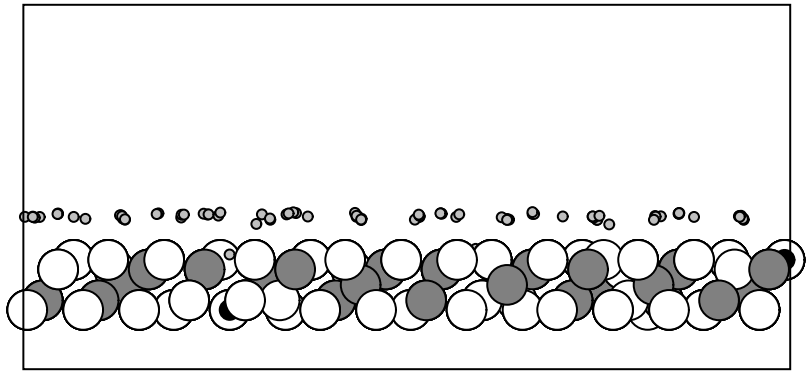


K

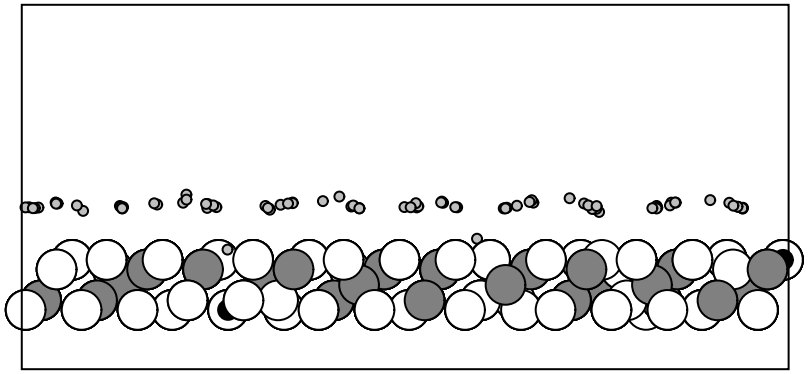
- size of atom d_{Na-Na} ≈3.7 Å vs. d_{K-K} ≈4.6 Å
- atomic density of i-AlPdMn 5-fold surface 0.132 atoms/Å^2
- Na, K coverage 0.066 atoms/Å^2 Θ ≈0.50

Na vs. K monolayer on 5-fold i-AlPdMn surface

side view



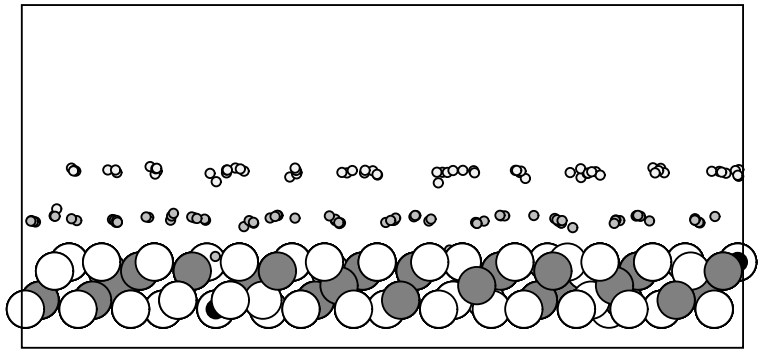
Na



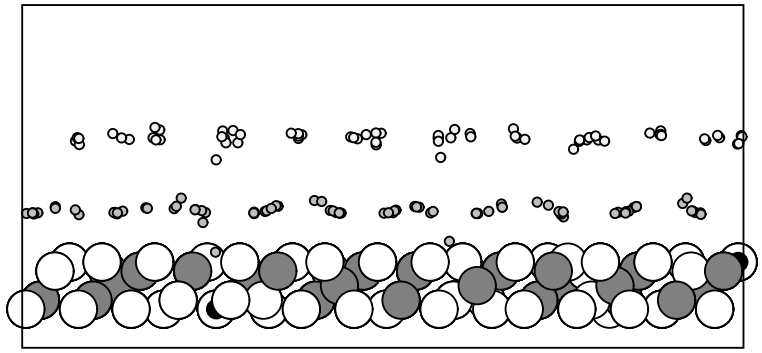
K

Na and K bilayer on 5-fold i-AlPdMn surface

side view

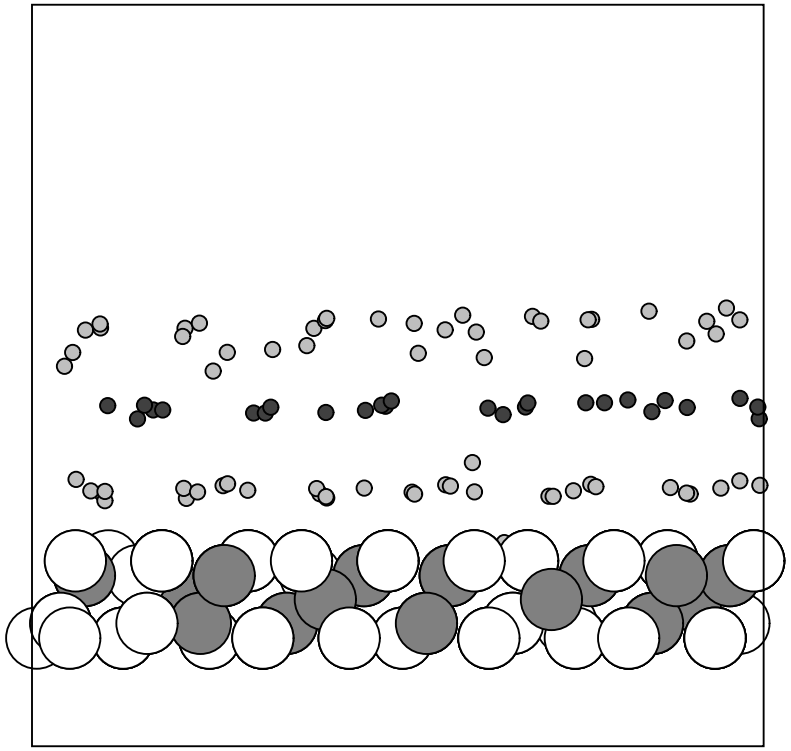


Na

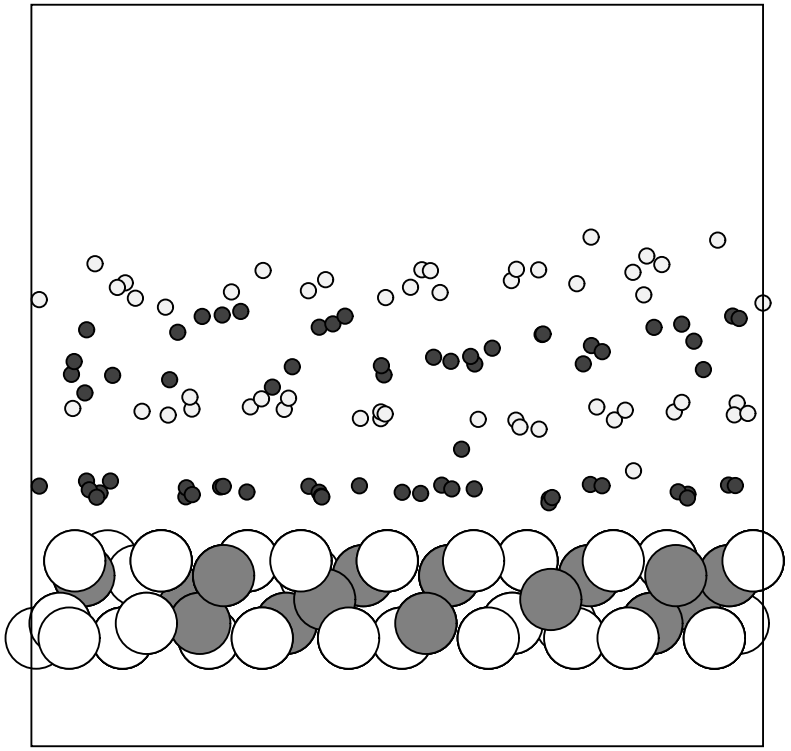


K

Na multilayers on 5-fold i-AlPdMn surface



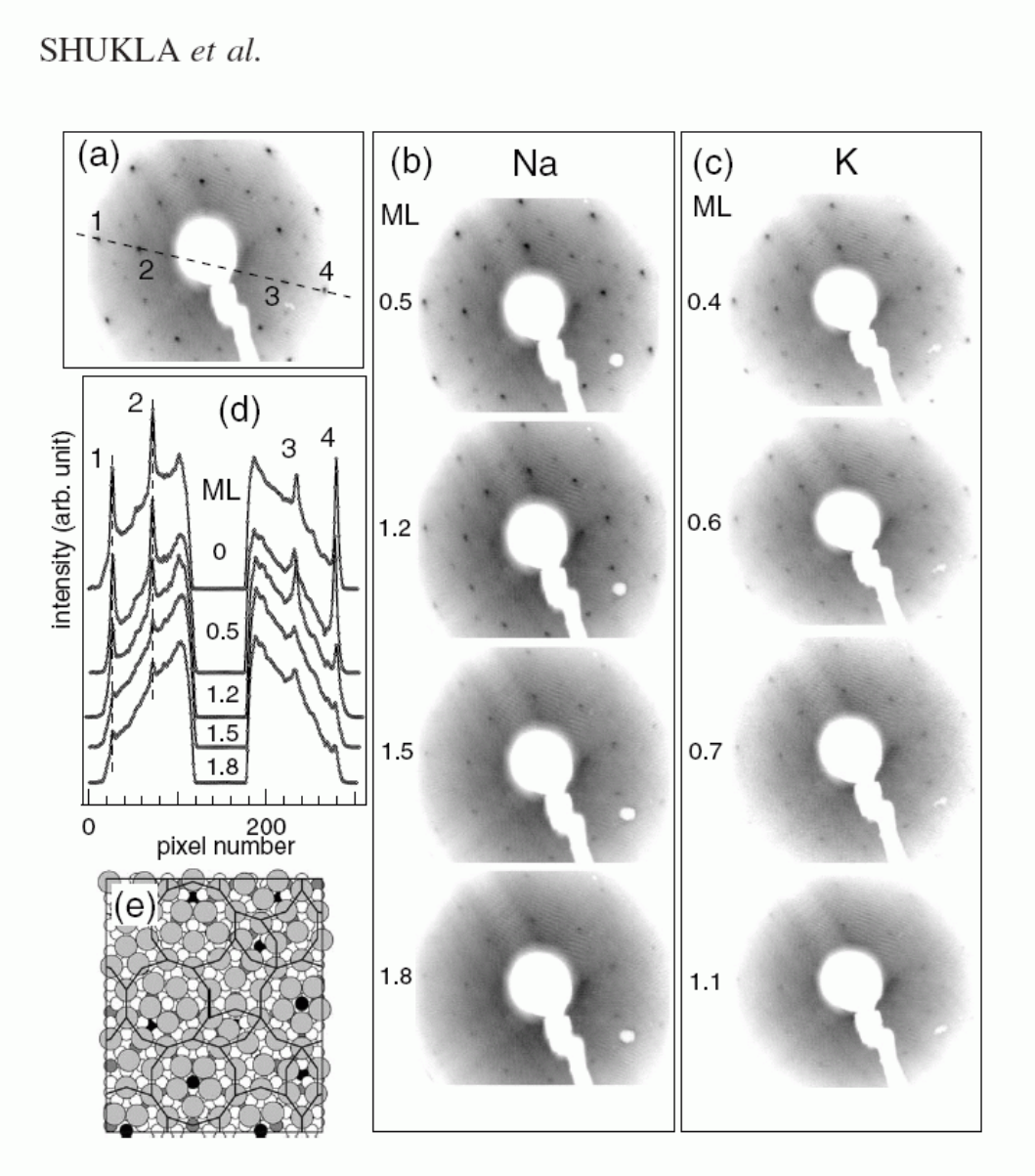
Na - 3 layers



Na - 4 layers

quasiperiodic ordering does not propagate beyond a bilayer

Na and K multilayers on 5-fold i-AlPdMn surface



A. K. Shukla et al.: PRB **79**, 134206 (2009)

Short summary

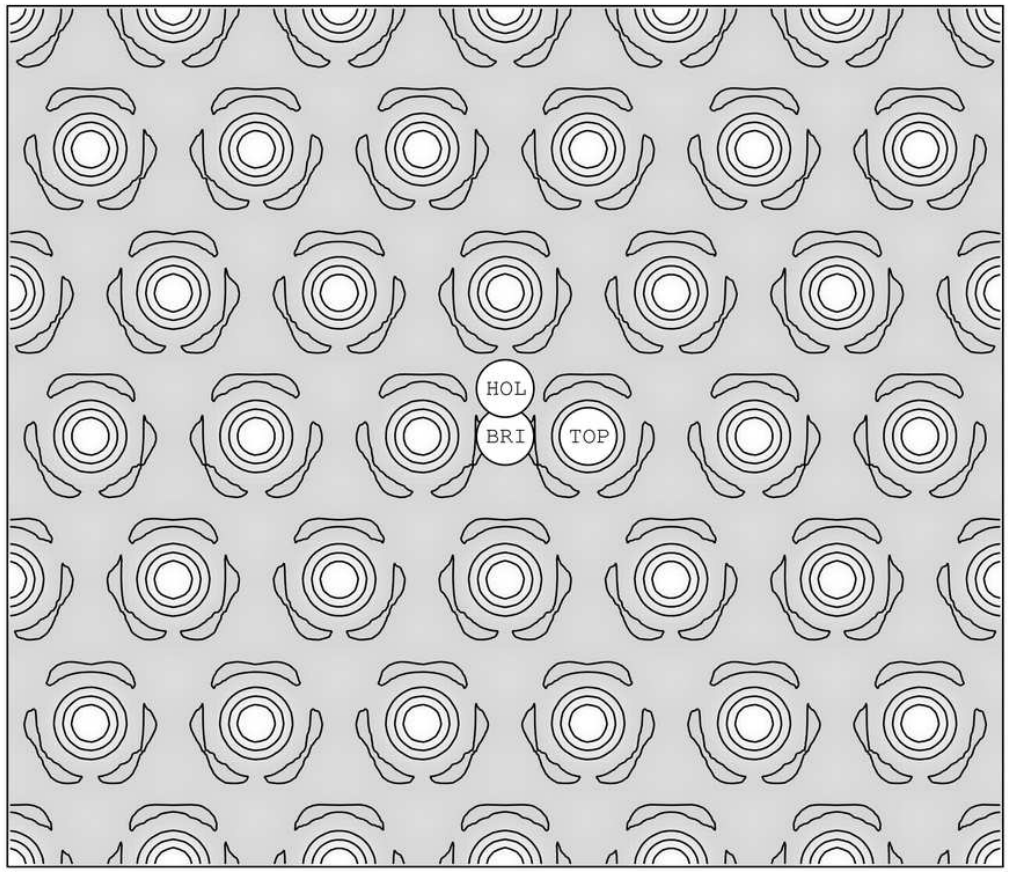
- Quasiperiodic ordering in an overlayers enforced by the substrate
- Unsuported quasiperiodic monolayers - not stable!
- Which atoms form quasiperiodic monolayers?
  - size of adatoms should be comparable with distances between adsorption sites
  - for i-AlPdMn surface optimal size of adatoms 3-4 Å.

Catalytic properties of surface quasicrystaline approximant $Al_{13}Co_4$

Catalytic properties of quasicrystals

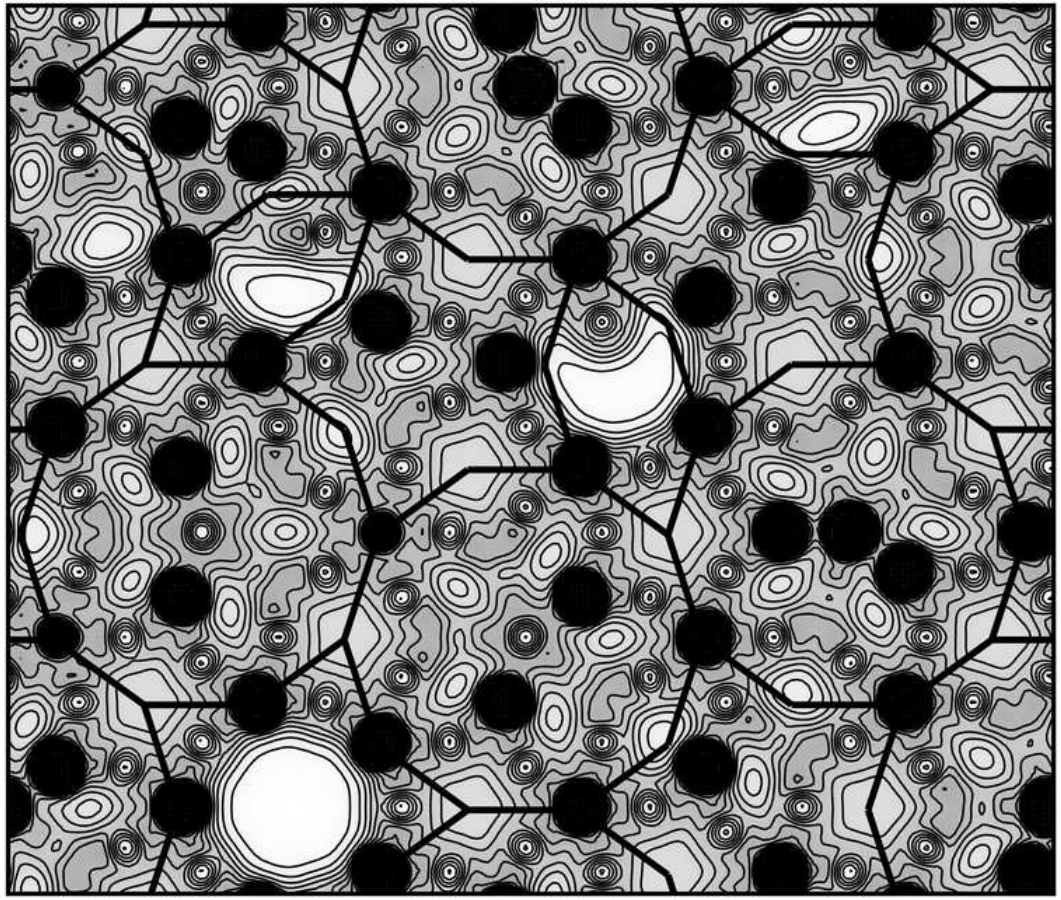
- Surfaces of ordinary metals - few inequivalent adsorption sites
- Surfaces of quasicrystals - many inequivalent adsorption sites
- $Al_{13}Co_4$ - approximant to decagonal AlCoNi quasicrystal
- Experiment: $Al_{13}Co_4$ surface - good catalyst for acetylene hydrogenation

Al(111) surface



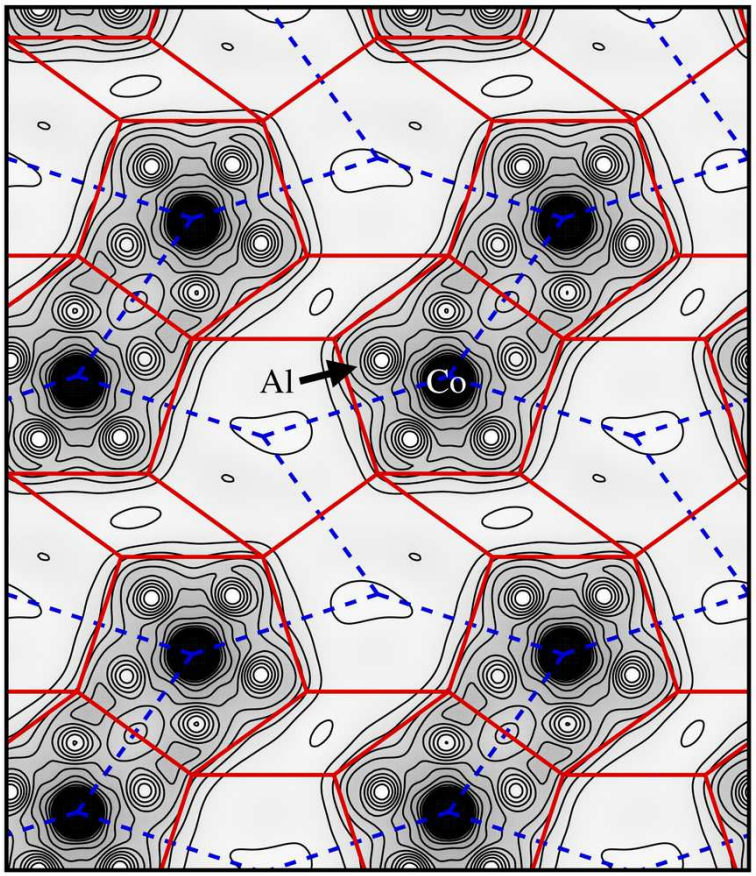
Surface of simple metal

5-fold i-Al-Pd-Mn surface

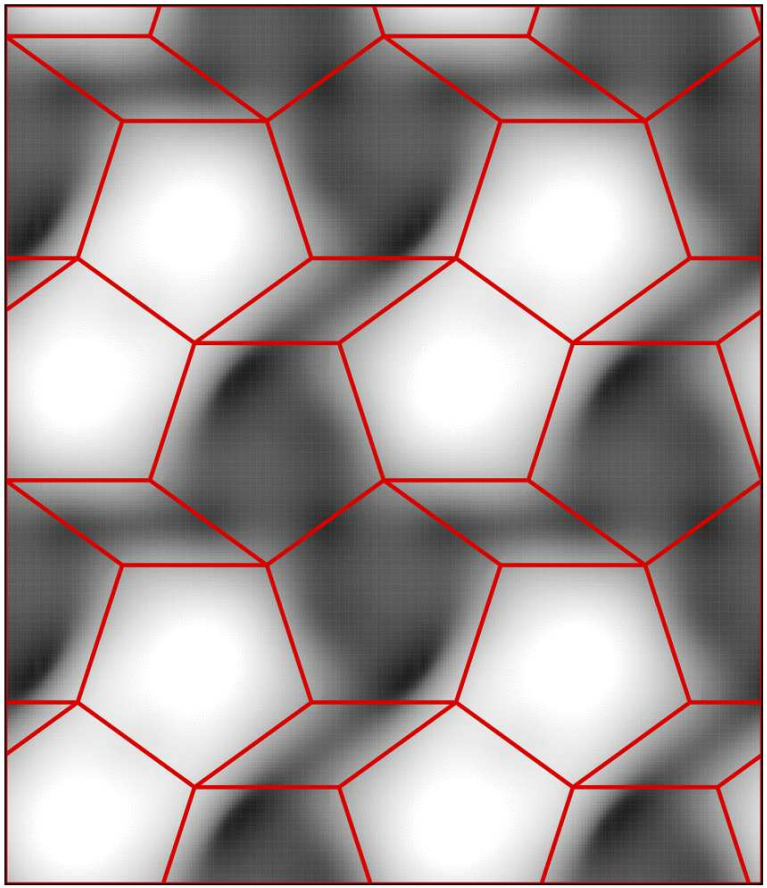


Complex metallic surface

Surface of o-$Al_{13}Co_4$

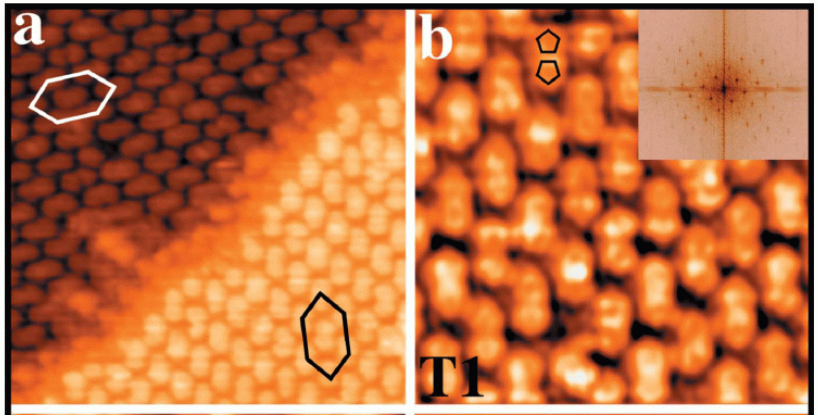


charge density



calculated STM

Surface of o-$Al_{13}Co_4$

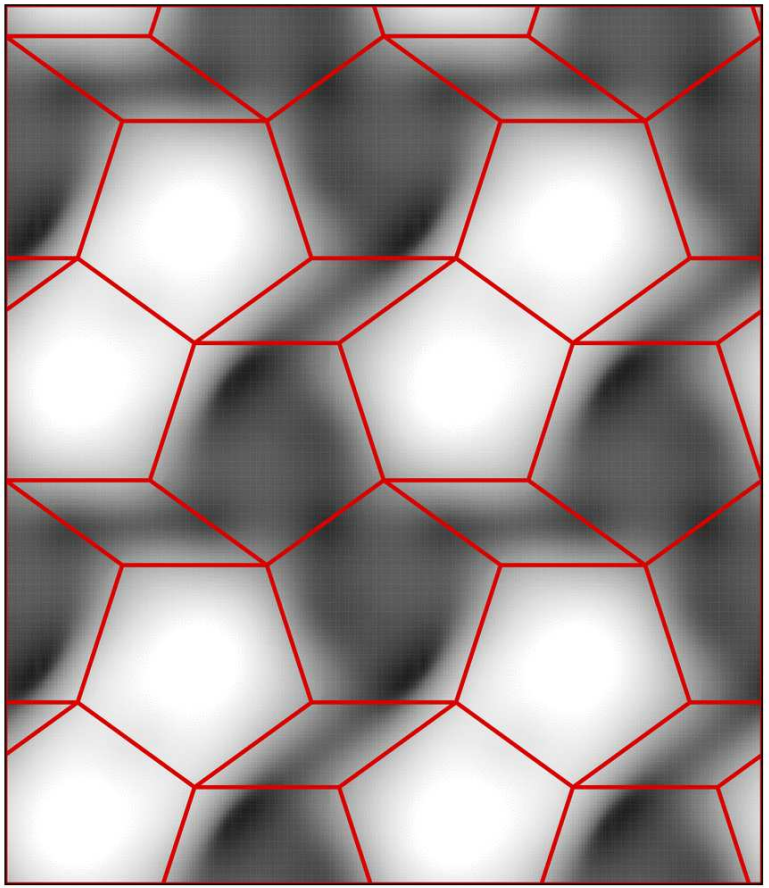


experimental STM

R. Addou et al. : PRB **80**, 014203 (2009)

Interesting catyalytic properties

M. Armbrüster et al. (2009)

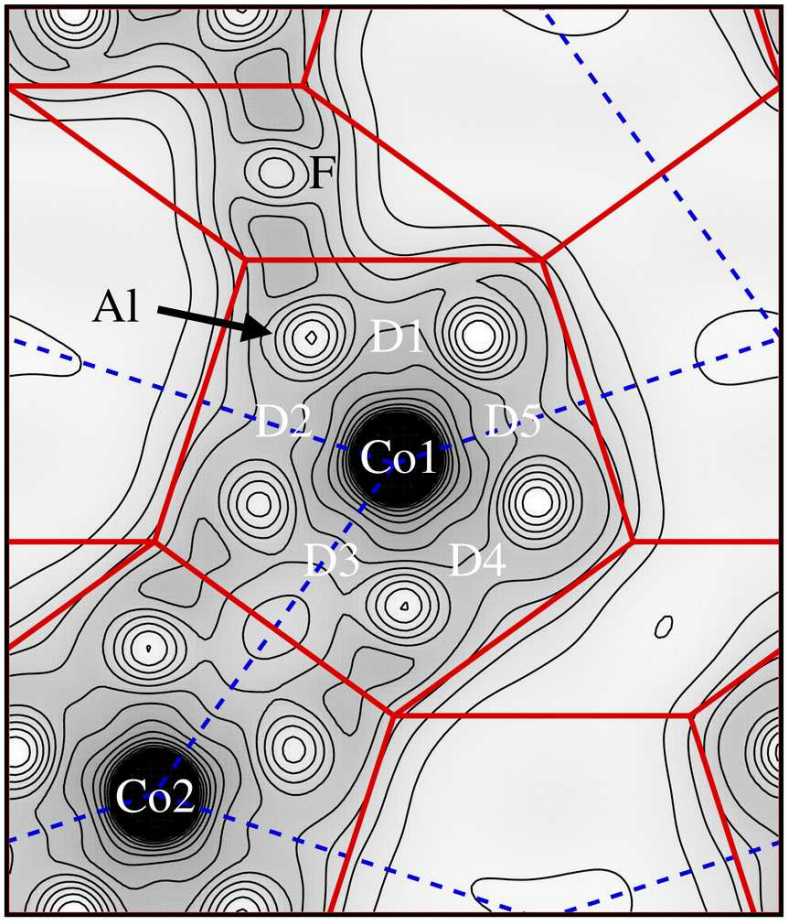


calculated STM

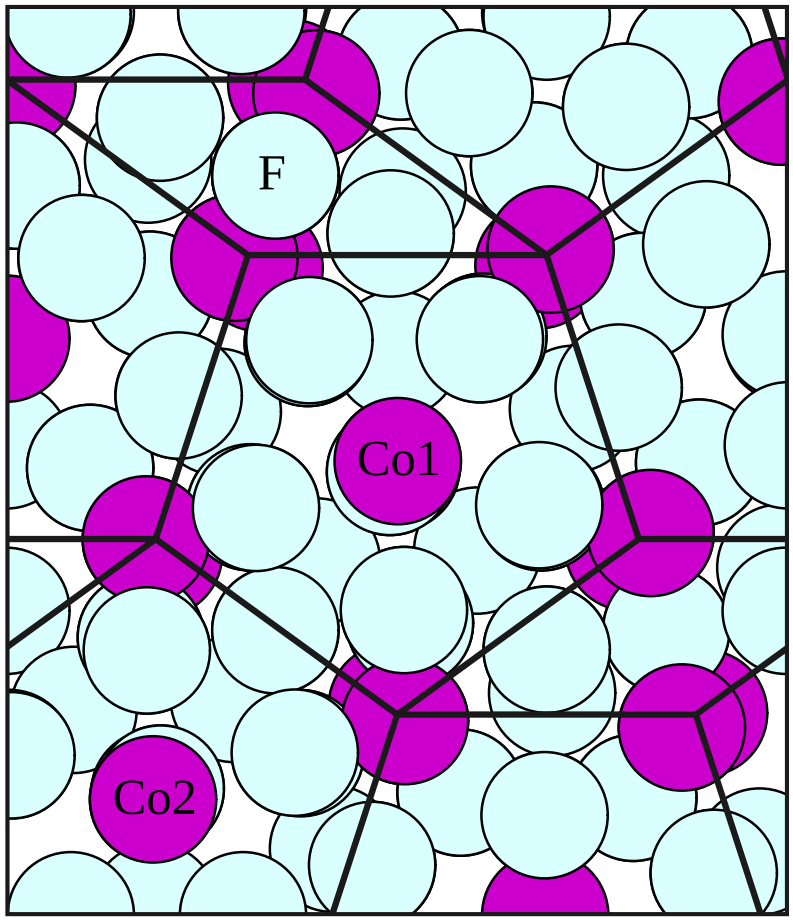
Acetylene hydrogenation

- Acetylene - C_2H_2
- Ethylene (ethen) - C_2H_4
- Hydrogenation $C_2H_2+H_2 \rightarrow C_2H_4$
- Important sub-process at industrial production of polyethylene
- Ethan - C_2H_6
- Hydrogenation $C_2H_4+H_2 \rightarrow C_2H_6$ - undesired
- Pd catalyst - expensive ($\approx$10 000\$/kg)
- Effort to replace Pd by non-precious metals
- Role of the catalyst - reduce activation energy barrier
- Good catalyst - Activity vs. Selectivity

Surface of o-$Al_{13}Co_4$



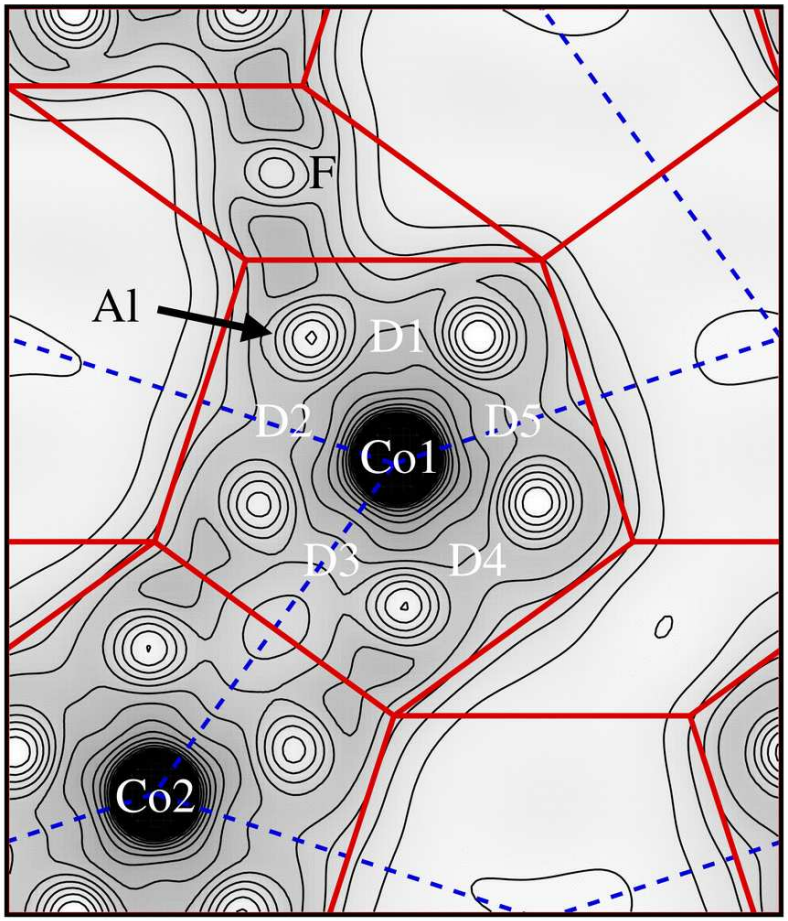
charge density



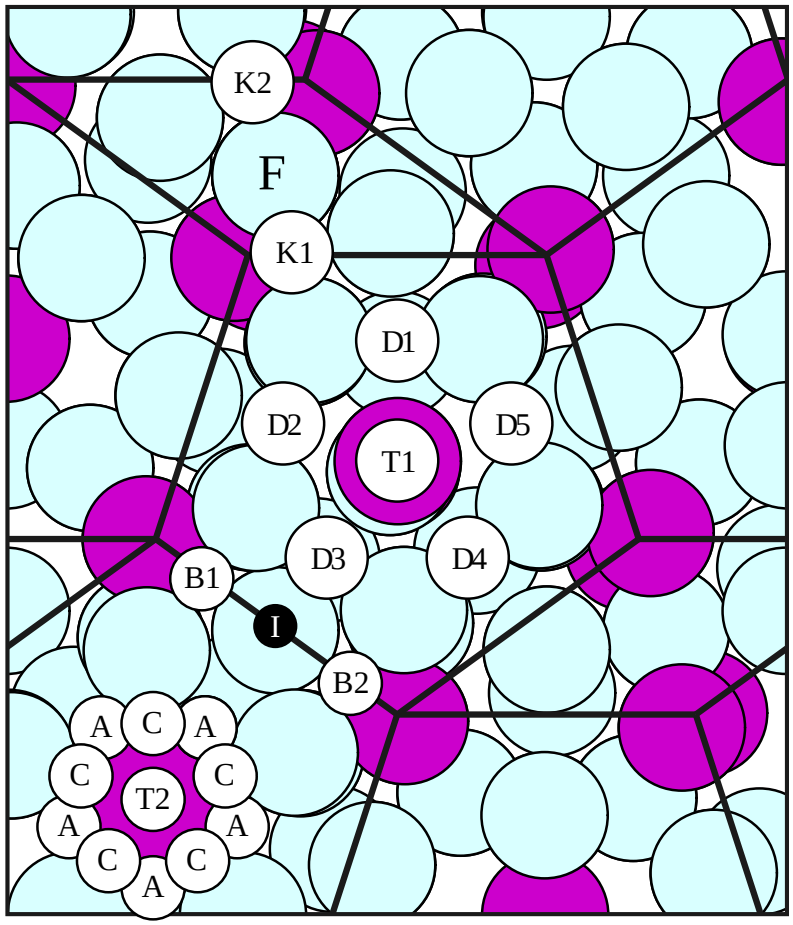
structural model

Preferable adsorption sites for H_2 and C_2H_2 molecules?

Surface of o-$Al_{13}Co_4$



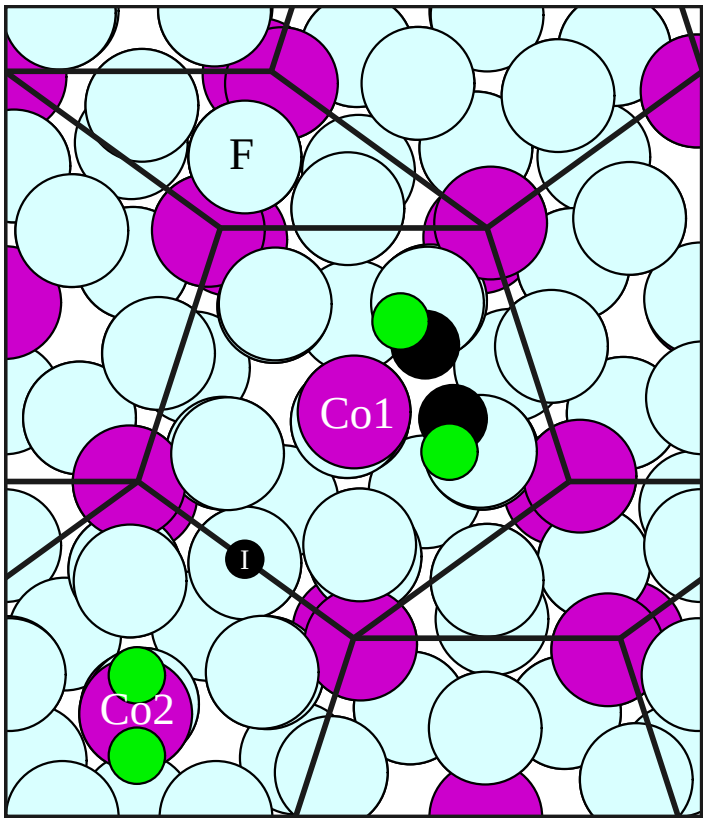
charge density



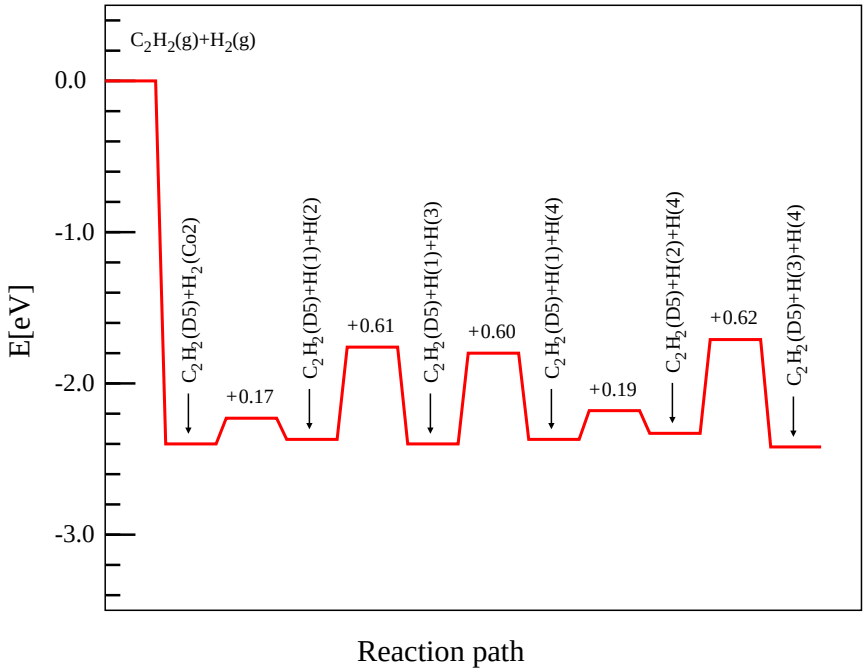
structural model

Preferable adsorption sites for H_2 and C_2H_2 molecules?

Acetylene hydrogenation on the surface of o-$Al_{13}Co_4$



structural model

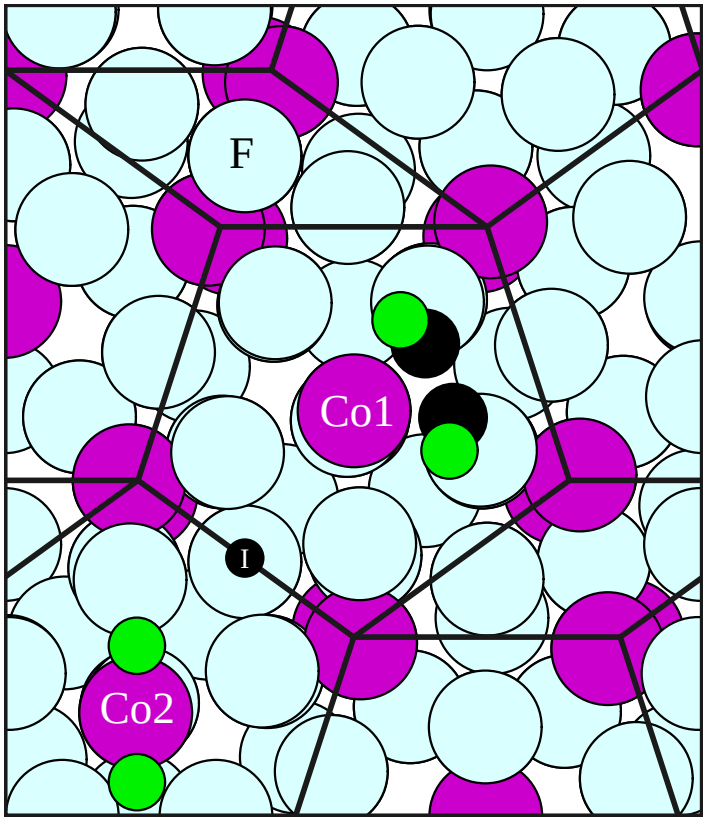


energy profile

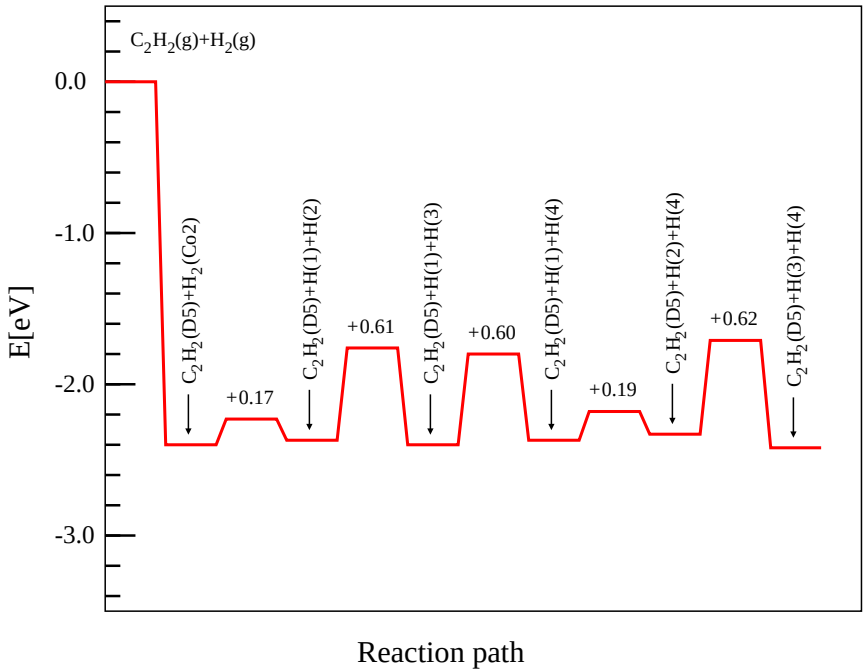
C_2H_2 bonding - di-σ at D5 vs. π-bond at Co1

H_2 at Co2 - easily dissociates

Acetylene hydrogenation on the surface of o-$Al_{13}Co_4$



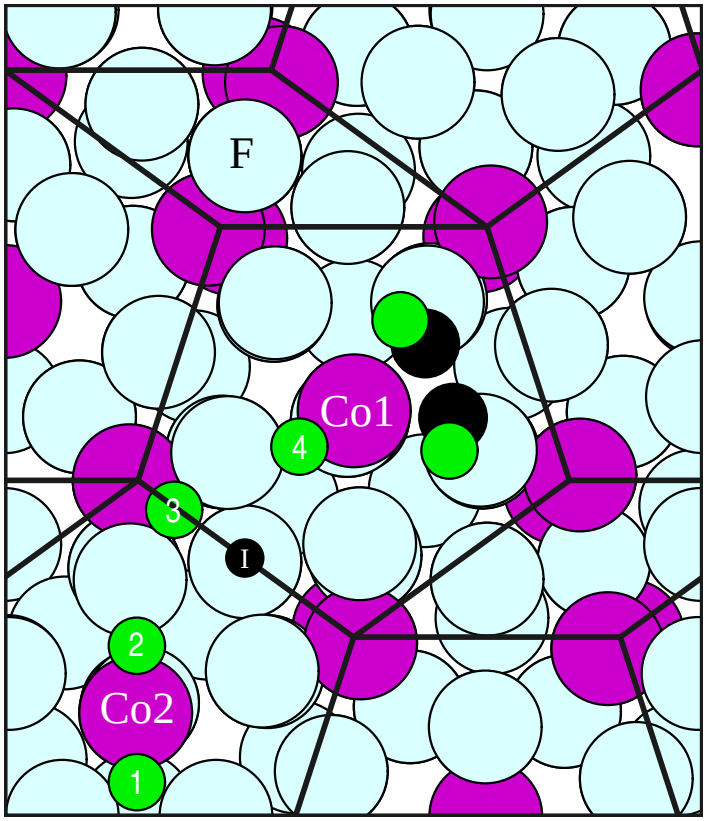
structural model



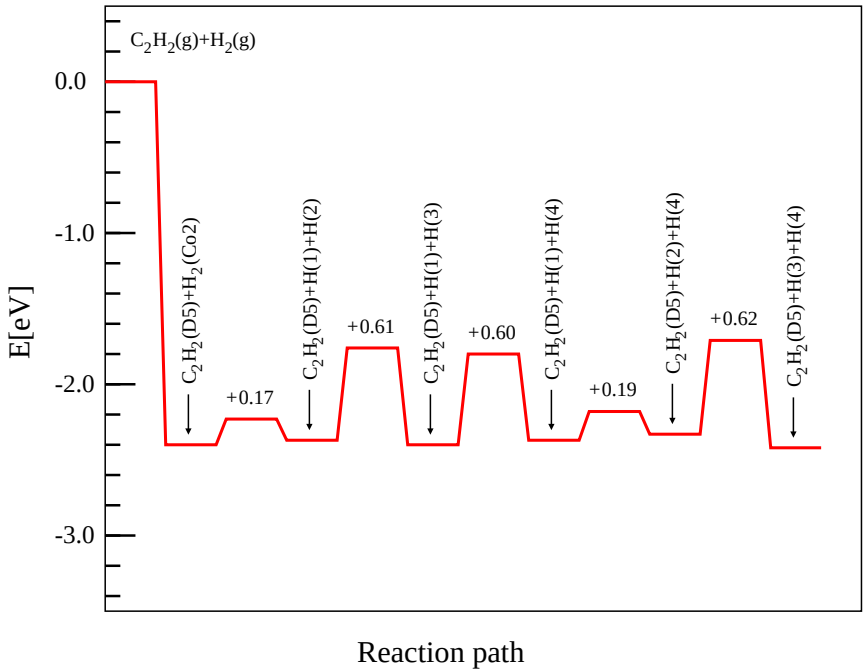
energy profile

H_2 dissociation

Acetylene hydrogenation on the surface of o-$Al_{13}Co_4$



structural model



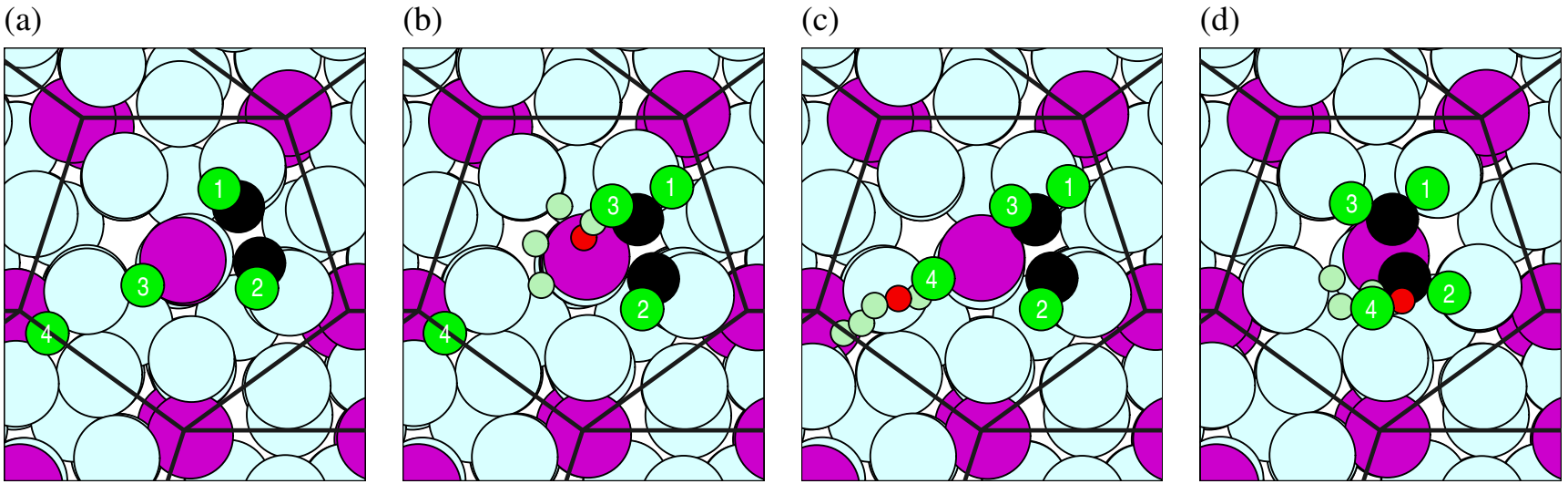
energy profile

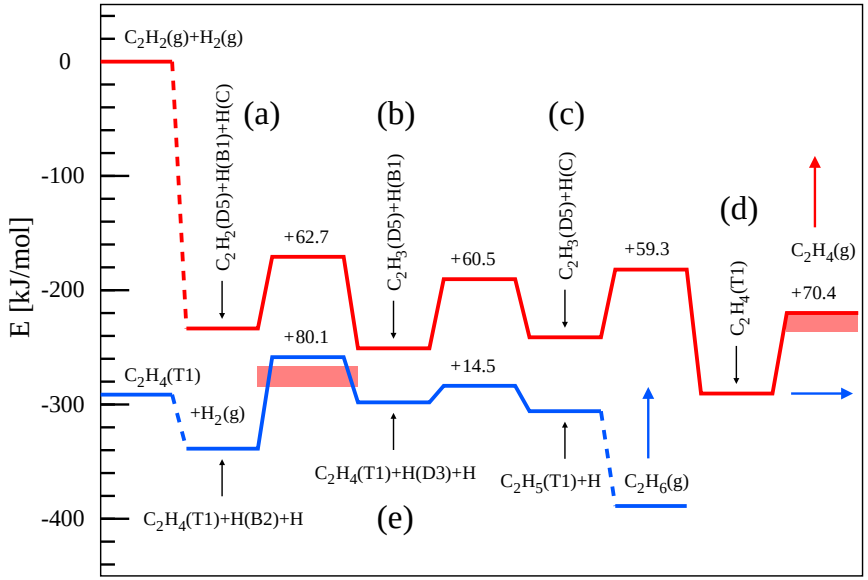
Diffusion jumps of H atoms

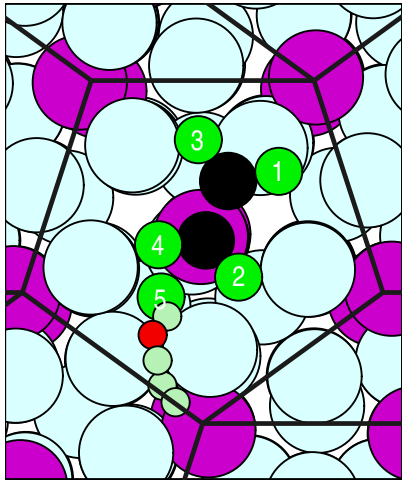
Activation energy barriers $E_a \leq 0.63$ eV $= 60$ kJ/mol

1 eV = 96.5 kJ/mol

$C_2H_2 \rightarrow C_2H_3 \rightarrow C_2H_4$







Comparison with Pd catalyst

Activation energy barriers

	$C_2H_2 \rightarrow C_2H_3$ [kJ/mol]	$C_2H_3 \rightarrow C_2H_4$ [kJ/mol]	desorp. [kJ/mol]	$C_2H_4 \rightarrow C_2H_6$ [kJ/mol]
Pd *	66	74	82	72
$Al_{13}Co_4$	63	61	70	80

* D. Mei et al.: J. Catal. **268**, 181 (2009)

Surface of $Al_{13}Co_4$ - better catalyst than Pd

Higher activity - better selectivity

Short summary

- Surfaces of quasicrystals - various adsorption sites for molecules
- Surface of $Al_{13}Co_4$ - peculiar surface - complex morphology
- Good catalyst: Activity and selectivity
- Acetylene hydrogenation: $C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6$
- Active site - Al_5Co complex
- Surface of $Al_{13}Co_4$ - good catalyst - better than Pd

Methods

- TB-LMTO (Linear Muffin-Tin Orbital Method) - DFT
- VASP (Vienna Ab-initio Simulation Package) - DFT
  - Equilibrium structure - relaxation by interatomic forces
  - Structural stability - clean surface and adsorbants
  - Charge density distribution - chemical bonding
  - Simulated STM images
  - Simulated cleavage - formation of the surface
  - Adsorption energies
  - Activation energy barriers

Thank you for your attention!