

AlMnPd and CdYb icosahedral quasicrystal structure families: state of the art and open questions

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Content

- Stable Al–TM quasicrystals (focus icosahedral – *i*-AlMnPd & *i*-AlCuFe)
 - Proper Mackays are stabilized by Silicon in Al–TM compounds
 - *i*-AlMnPd is 7 Å–edge length canonical cell tiling, made of pseudo-Mackays and Al₁₂Pd icosahedra at its vertices
 - Peculiar atomic structure and chemical ordering in *i*-AlCuFe. Blurred clusters. What does this mean?
 - Natural, untuned implementation of matching rule: decagonal Al₄(Co,Ni)

METHODS 1 (ground floor): Density Functional Theory (DFT)

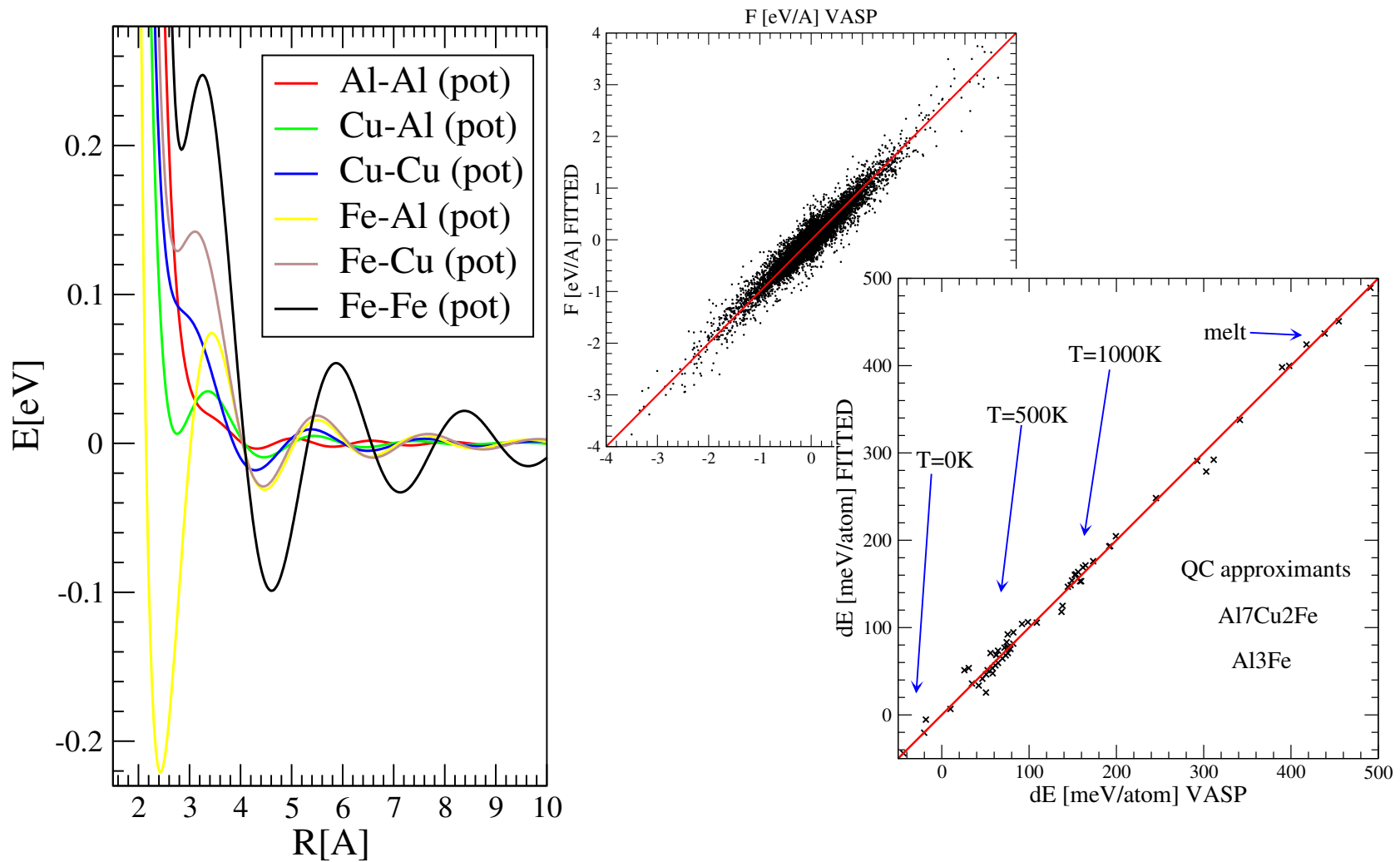
- Usually gives us 1 meV/atom accuracy in energies!
- DFT use 1: data for fitting empirical potentials
- DFT use 2: feedback – check ground state, compute stability, vibrational entropies...
- Limits: handling up to 3×10^3 atoms, excellent parallelization

METHODS 2: Empirical Oscillating Pair Potentials (EOPP)

$$V(r) = \frac{C_1}{r^{\eta_1}} + \frac{C_2}{r^{\eta_2}} \cos(k_* r + \phi_*) \quad (1)$$

- important for QC: captures Friedel oscillation!
- is easy to fit (6 parameters per pair), natural form
- includes *a part* of cohesion (formation energies, for example)
- turns out very accurate for simple metals, simple metal rich alloys, but surprisingly also many other systems
- As of now, good fits are available for 116 alloy systems, including many QC compositions!

Example EOPP fit : ternary AlCuFe



METHOD 3: Shake&Swap annealing method



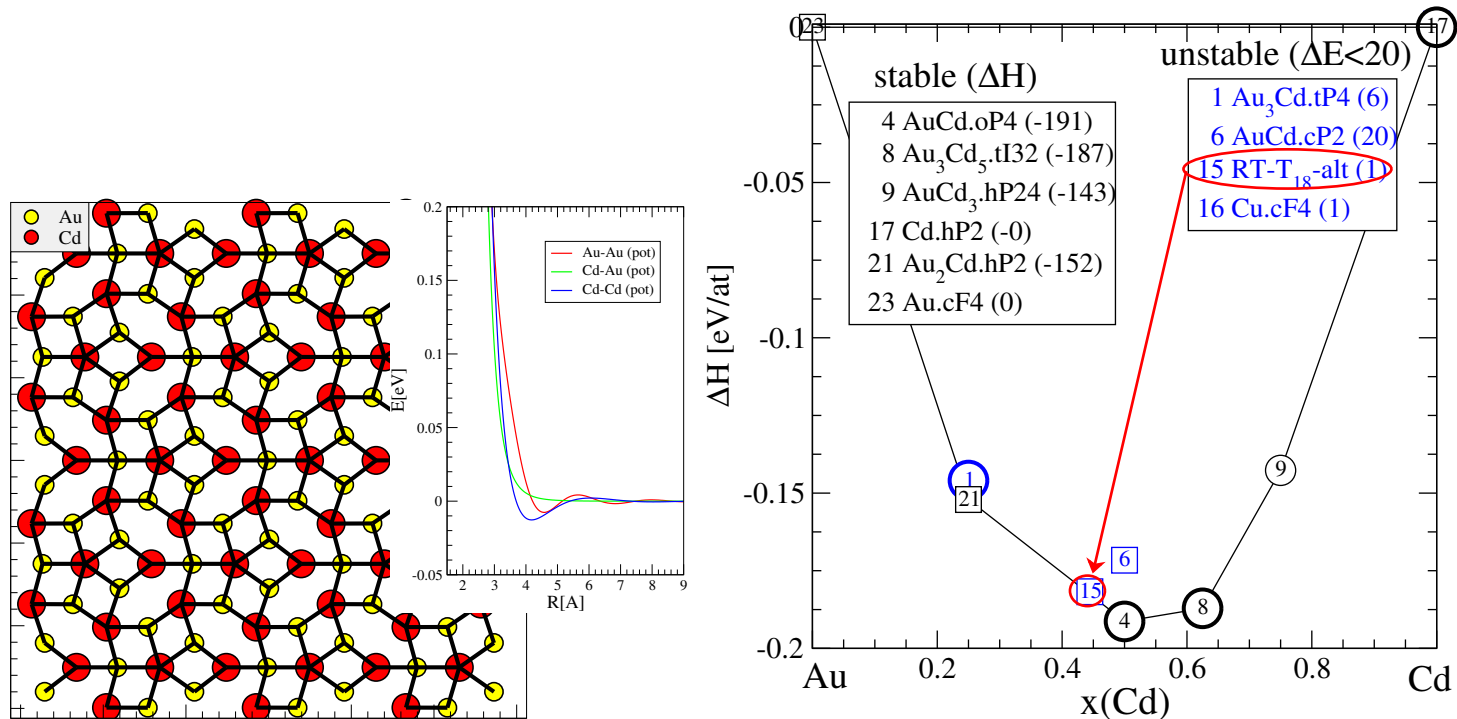
- ▶ SHAKE : molecular dynamics (500 steps per *cycle*, timestep $\Delta t \approx 5$ fs)



- ▶ SWAP : “lattice gas Monte Carlo”: chemical species of two randomly picked atoms are swapped, acceptance controlled by Metropolis crit. Typically 500 swap attempts per atom and per *cycle*

Simulation: 50000 cycles $\rightarrow \sim 125$ ns

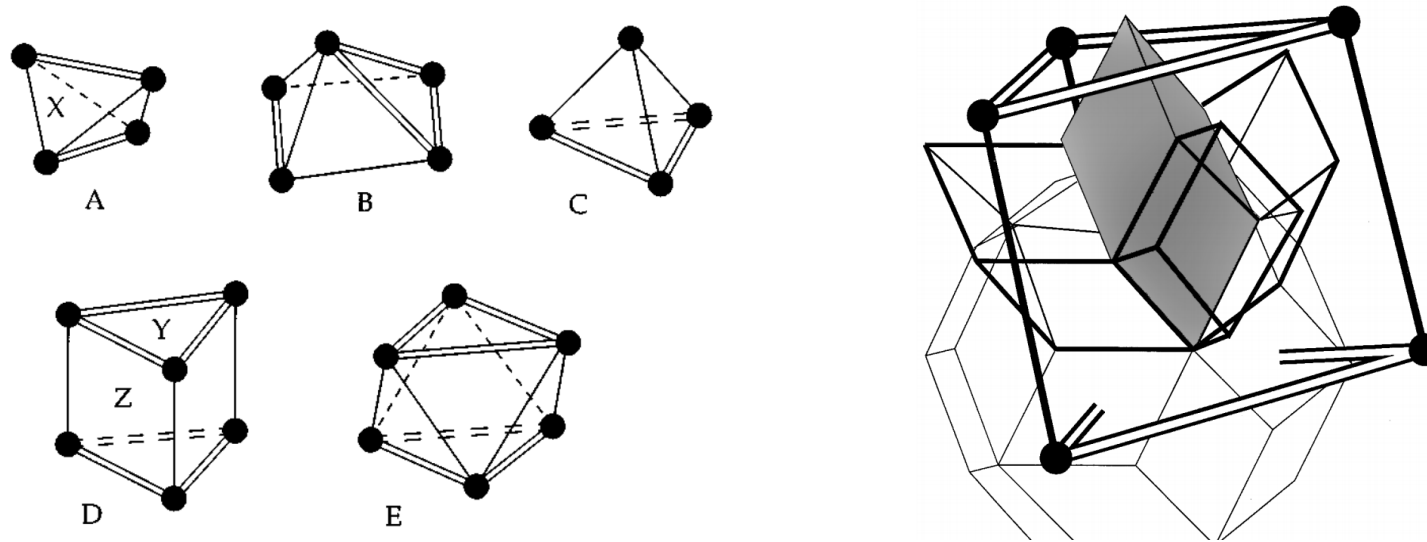
METHOD 4: DFT-based phase diagram



– Stable phases across composition range: convex hull of $E(x)$

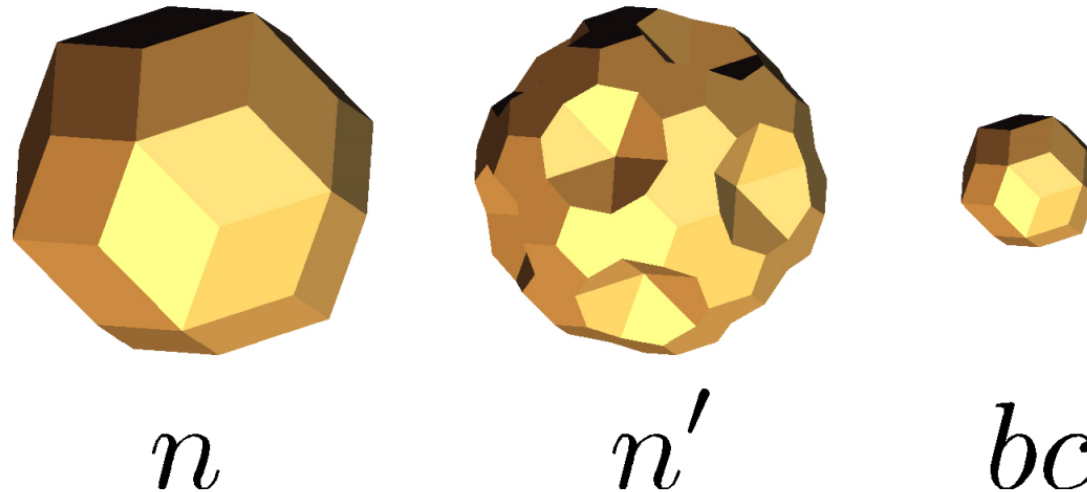
By the way : this is simplest structure of a decagonal quasicrystal ever!

GEOMETRY 1 : Canonical Cell Tiling (CCT)



- Tiling of canonical cells A B C D (Henley, 1991)
- Space divided into cells, that can tile space quasiperiodically or periodically (“tile-tile Hamiltonian” decides)
- Atomic structure : TILING $\times$ DECORATION
- Two fundamental decoration schemes: Triacontahedra+Prolates (*i*-CdYb) or pMI+Icosahedra (Al-TM)

GEOMETRY 2: Katz–Gratias (KG) model for icosahedral quasicrystal



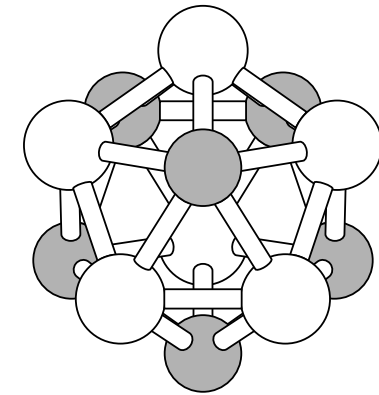
- (Golden standard for many years.) We live in perp space!
- vs CCT : up to $3/2$ approximant size - no difference! But starting from $5/3$, CCT suddenly spreads out in perp space.

Image taken from www-published lecture by D. Gratias

RESULT 1: Proper Mackay Icosahedra are Silicon stabilized!

– based on Sugiyama et al refinement (1998): Si: two classes **Al/Si icosahedron**.
of conjectured Si sites (small icosahedra and “6DBC”)

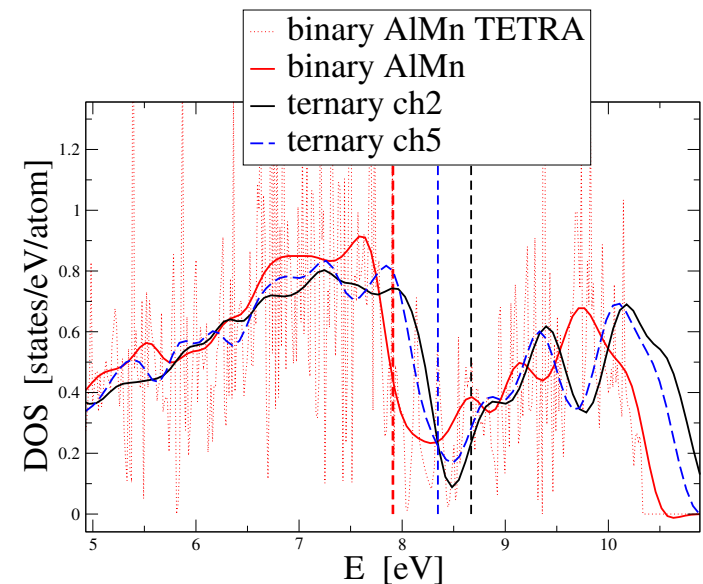
Gray: Si, white: Al



- Si implements 5-fold symmetry of (empty) icosahedron!

- intercluster linkage (2fold) $12.4\text{\AA}$

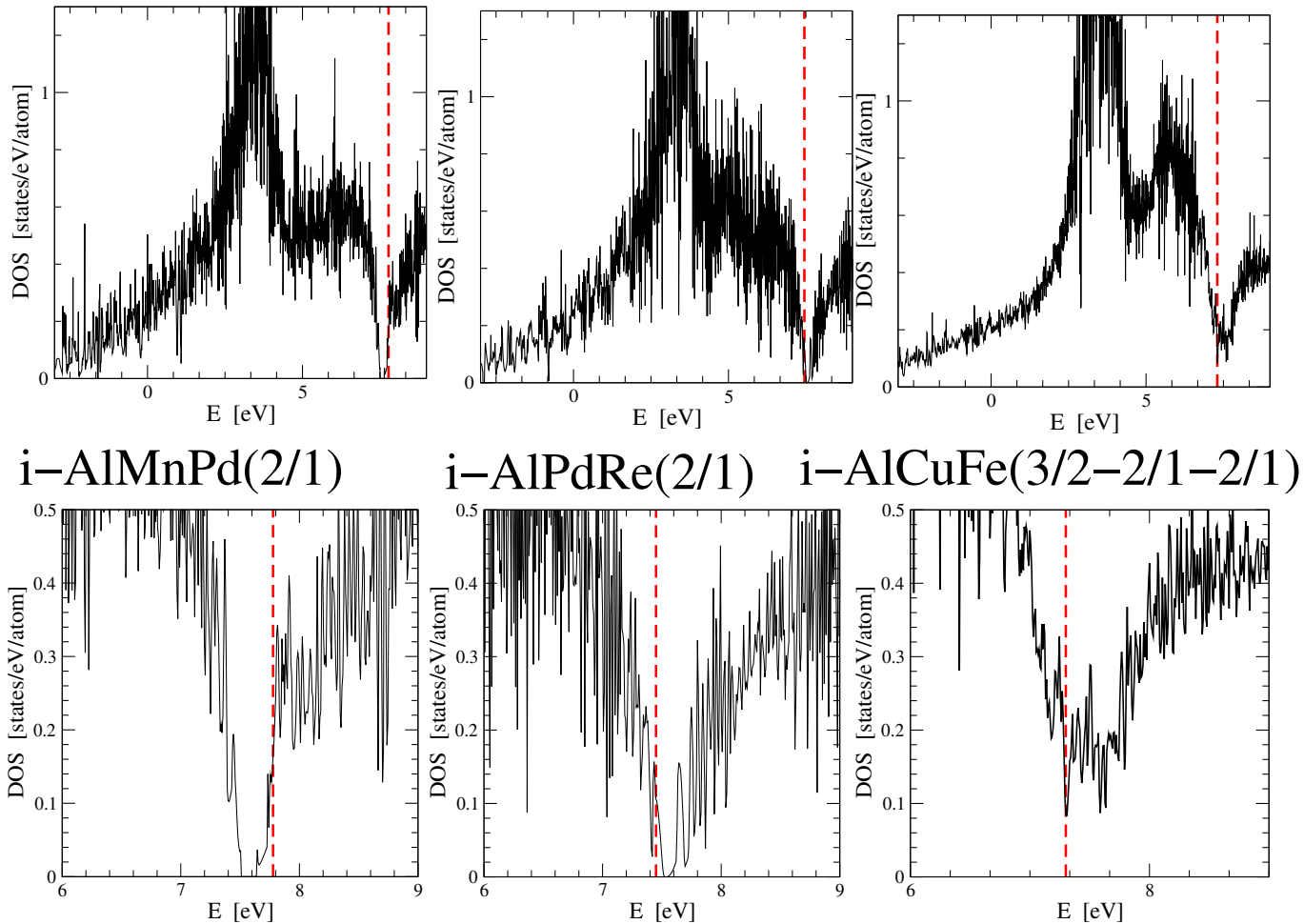
ΔE	x_{Si}	“Si” Al,Si	“M1” Al,Si	“M3” Al,Si	comment
$\mu \rightarrow$		6	12	12	
-4.7	13.0	6,0	6,6	0,12	ch2
7.2	8.7	6,0	12,0	0,12	ch5
14.5	4.3	0,6	12,0	12,0	ch1
16.7	17.4	6,0	0,12	0,12	ch4
15.6	–	6,0	12,0	12,0	BINARY!
–	12.9	0,6	7.8,4.2	4.4,7.6	EXPE



... “Proper Mackay” & Silicon story

- My story: Si–addition $\rightarrow$ “perfect” MI $\rightarrow$ **NO QUASICRYSTAL!**
- Supported by many Mg–TM (TM=Ag,Pd) Mackay phases
- Important bottomline: **(good) quasicrystal requires symmetry breaking inside icosahedral cages!** (... apart from “glue” ...) (*a comment once made by Franz Gähler*)

RESULT 2 : e/a tuning E_F vs bandgap

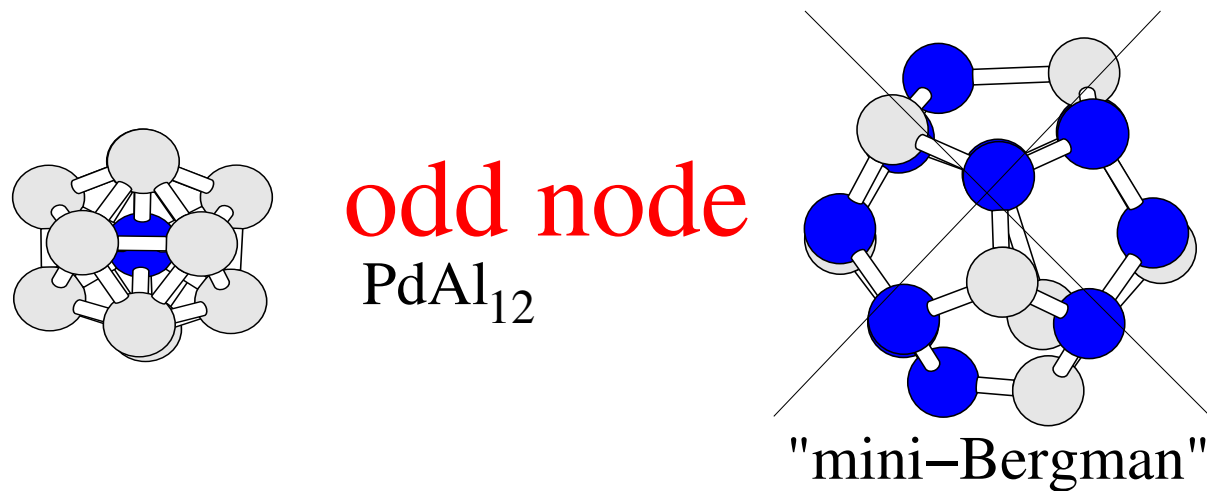
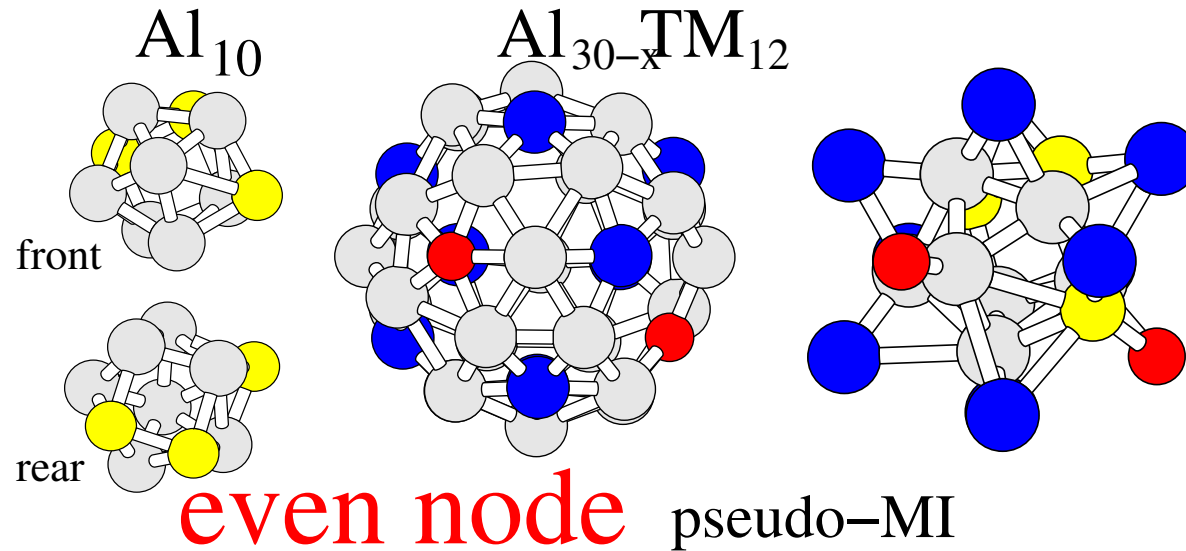


- need exactly correct **atomic density**!
- need exactly correct **Al/TM ratio** (for a given approximant)!
- final e/a tuning done by $x(\text{TM1:TM2})$ – hence ternary.

RESULTS : atomic structures

- rather small approximants “2/1” – “3/2”
- as we believe **DFT-level** proofed realistic local configurations (up to at least 3rd neighbor), at most few meV/atom unstable at $T=0$ against decomposition
- DFT works VERY RELIABLY for Al–TM systems: proved in every detail for all binary systems (Al-Fe, Al-Co, Al-Ni, Al-Pd...).

i -AlMnPd : pseudo-Mackays + CCT!



... More on geometry...

- in fact, the structure coincides with KG model, **EXCEPT for the inner shells of pMI clusters!**
- inner shells contain 9 or 10 atoms. 3 of them can be referred to 6D-projected points.
- Adapted KG model (and matching rule) still possible: inner shell as a molecule attached in a particular way, following attachment sites available

Huge $\text{AlMn}(\text{Fe}, \text{Cr})$ approximant (4500 atoms/cell): CCT!

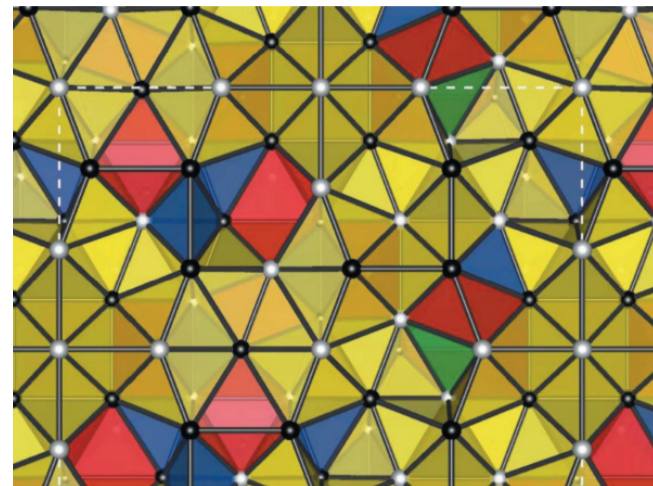
“Cluster–packing geometry for Al–based F–type icosahedral alloys”,
N. Fujita *et al*, Acta Cryst **A69**, 2013

research papers

Table 1

Crystallographic data.

Formula	$\text{Al}_{72.515}\text{Pd}_{22.498}\text{Cr}_{4.928}\text{Fe}_{7.853}$
Molar mass	$5045.2 \text{ g mol}^{-1}$
Temperature of data collection	Room temperature
Space group	$P\bar{a}3$ (No. 205)
Lattice constant, a_{lat}	$40.5405 \text{ \AA}$
Cell volume, Ω	$66629.6 \text{ \AA}^3$
Z	40
Calculated density	5.028 g cm^{-3}
Absorption coefficient	9.294 mm^{-1}
Range of 2θ	$1.74\text{--}53.2^\circ$
Independent reflections	21526
Observed reflections [$I > 3\sigma(I)$]	8454
R_{int} (obs/all)	7.91/13.37
No. of parameters	783
$R(F)$	11.96
$R_w(F)$	12.13
S	4.59
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$	$8.01, -5.38 \text{ e \AA}^{-3}$
$\Delta/\text{e.s.d.}$	0.0002



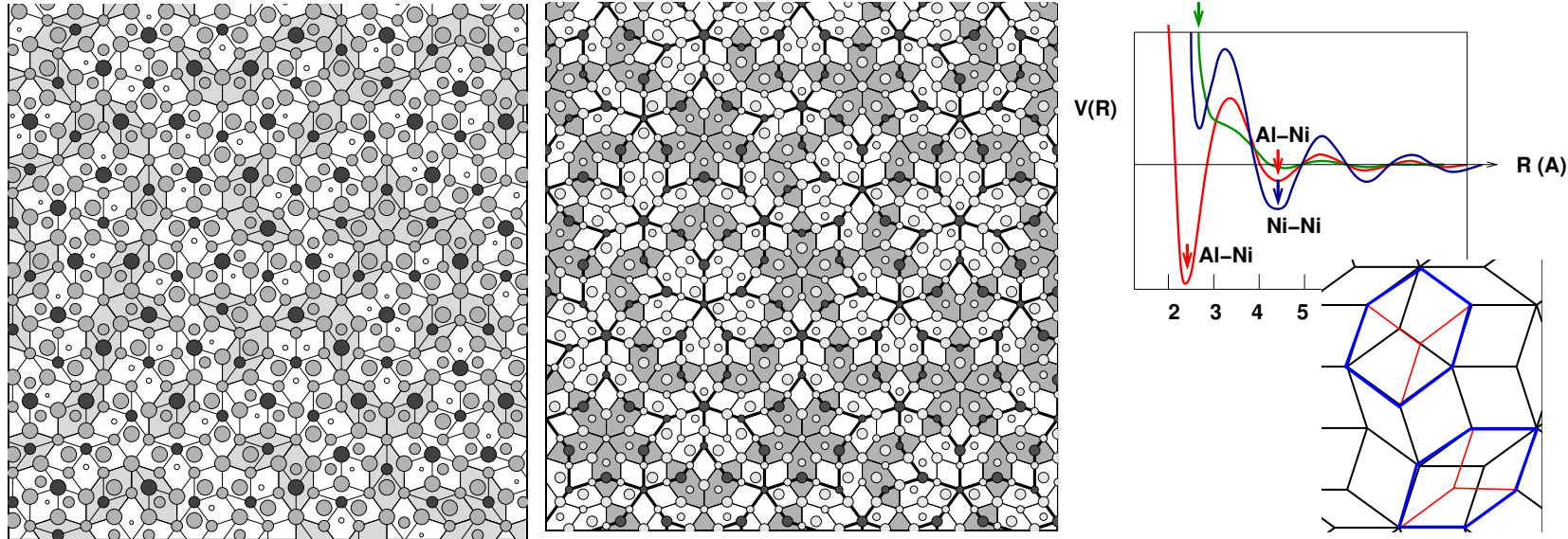
“ $2 \times 2 \times 2 \sqrt{3}/2$ ” Canonical cell tiling with 264 nodes/cell

AlMnPd conclusion

In my notebook, conclusion about AlMnPd is:

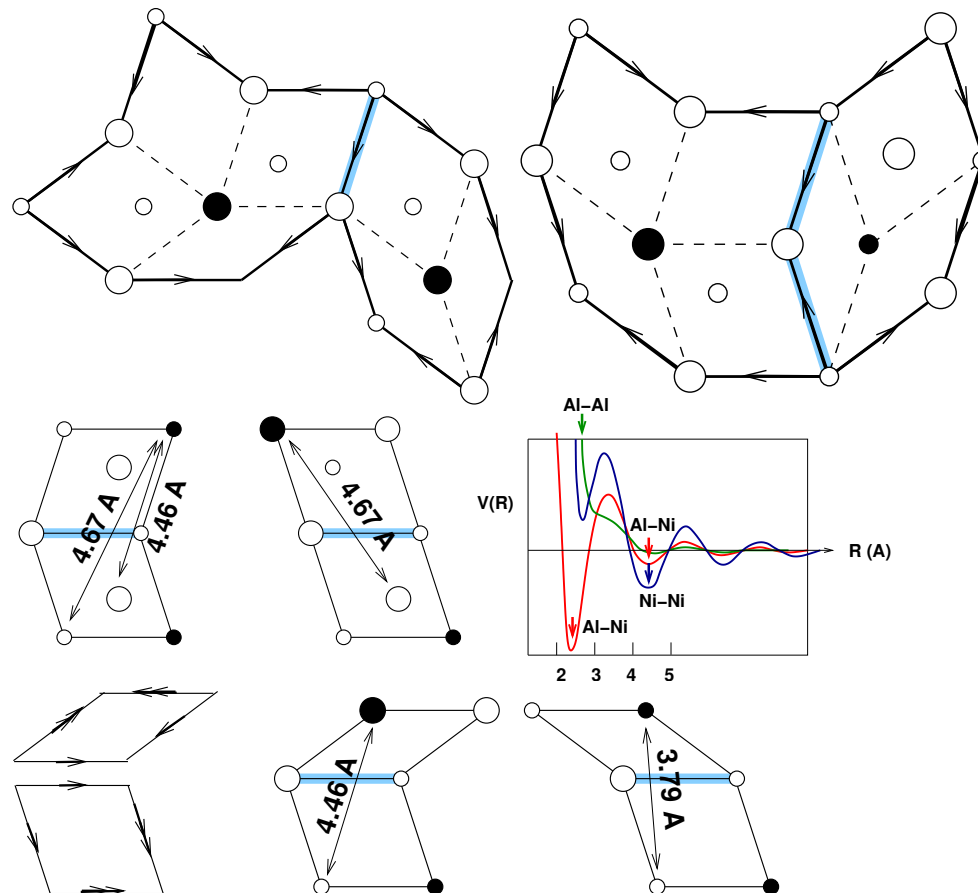
- The structure is canonical cell tiling decoration by pseudo-Mackays
- The standard *i*-AlMnPd is presumably random CCT
- So called F2-phase superstructure related to the superstructure of the observed approximant?
- **consequence for diffraction refinements:** great difficulty due to disorder-averaging

Matching rule quasicrystal by untuned pair potentials



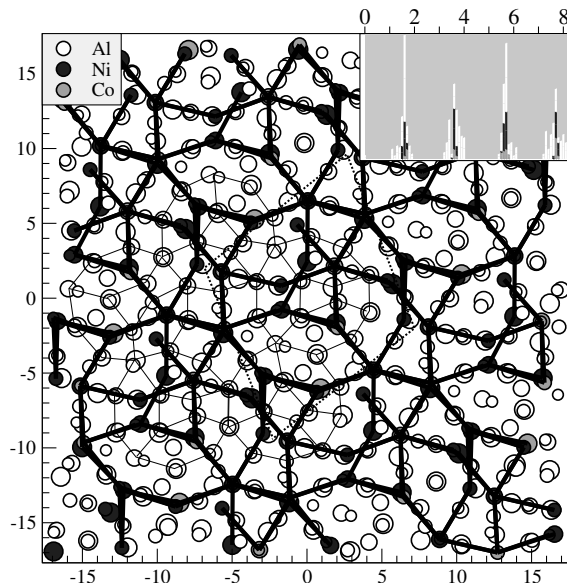
A quasicrystal **CAN** be simple, but so far we know none like that – best real quasicrystals (i-AlMnPd family, i-CdYb “Tsai” family) have *icosahedral cages with symmetry broken central motif*

... arrow matching rules by pair-potentials

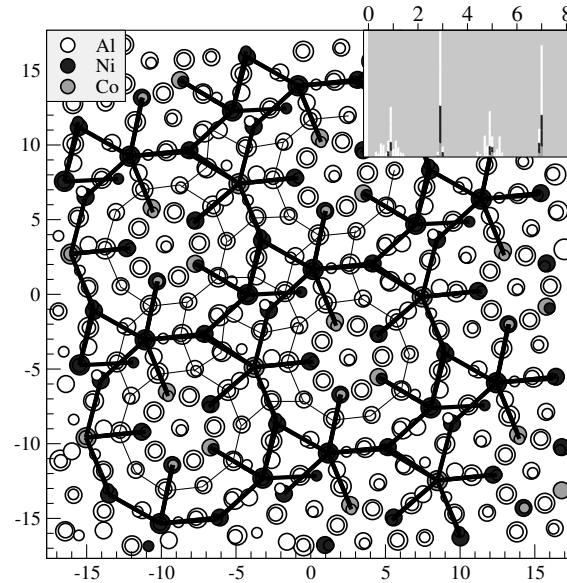


It is **second neighbor interaction** that implemented matching rule.
In reality, this quasicrystal with composition Al_4TM is “killed” by Al_5Co_2 or Al_3Ni crystal structures competition.

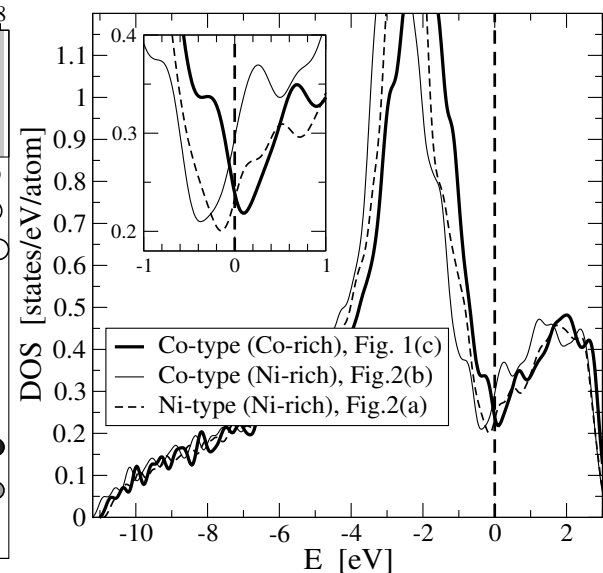
Ni-rich vs Co-rich decagonal: WHY??



(a)



(b)



(c)

Stability is controlled by **atomic density**!

- there is *lower-density* (LD) phase, and *higher-density phase* (HD)
- due to valence excess and pseudogap/Fermi energy interaction, Ni-rich alloy selects LD *decagonal* phase, while Co-rich selects HD
- the so-called Ni-rich “4A”-periodic “perfect” is 8Å within a column, but *lacks correlation from column to column*

Al-TM summary

- Decagonals (roughly speaking) satisfactorily understood:
 - matching rule feasible and CAN be nicely implemented by Friedel oscillation mechanism
 - however important **3D puckering** effect leads to large 20-atom clusters
 - both large clusters + vertical stiffness – **random tiling scenario UNLIKELY!**
- Icosahedrals
 - *i*-AlMnPd and relate are 7.6Å edge length canonical cell tilings
 - Explicit role for fundamental clusters: psuedo-MI and Al₁₂TM icosahedra

- **BUT** in i -AlCuFe there are NO robust clusters, peculiar “reverted” chemical ordering
- We have EOPP for practically ALL important QC systems! We have all needed to tie the two ends: DFT-side and experimental side... NOT DONE!s