Quasicrystals

A story of unusual long-range order

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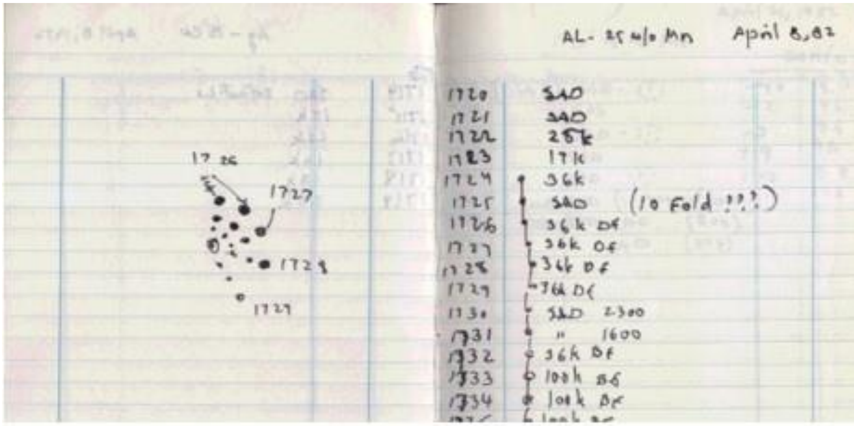
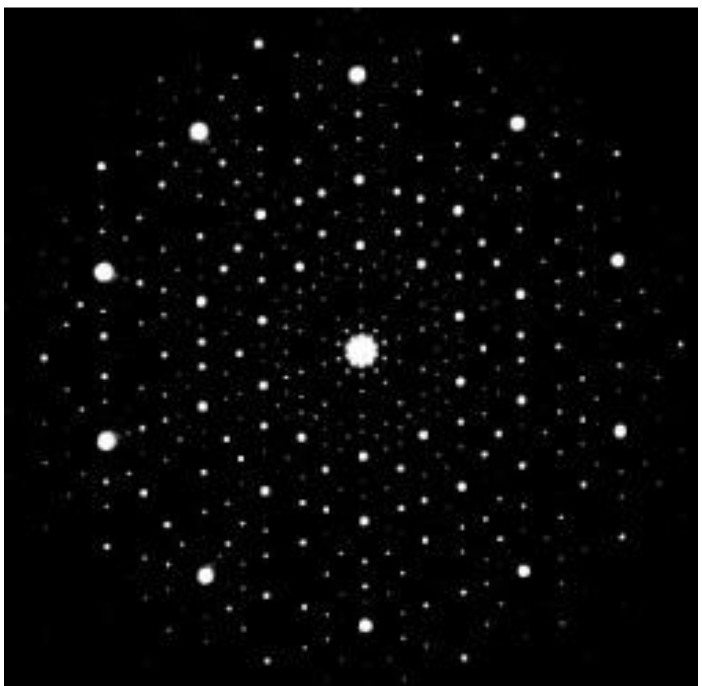
Laboratory for Crystallography
ETH Zurich

Faculty of Physics and Applied Computer Science
AGH Krakow

The story goes back to 1982





Dan Shechtman receiving
2011 Chemistry Nobel Prize

First paper in … 1984

VOLUME 53, NUMBER 20 PHYSICAL REVIEW LETTERS 12 NOVEMBER 1984

Metallic Phase with Long-Range Orientational Order and No Translational Symmetry

D. Shechtman and I. Blech
Department of Materials Engineering, Israel Institute of Technology–Technion, 3200 Haifa, Israel

and

D. Gratias
Centre d'Etudes de Chimie Métallurgique, Centre National de la Recherche Scientifique, F-94400 Vitry, France

and

J. W. Cahn
Center for Materials Science, National Bureau of Standards, Gaithersburg, Maryland 20760
(Received 9 October 1984)

We have observed a metallic solid (Al–14-at.%-Mn) with long-range orientational order, but with icosahedral point group symmetry, which is inconsistent with lattice translations. Its diffraction spots are as sharp as those of crystals but cannot be indexed to any Bravais lattice. The solid is metastable and forms from the melt by a first-order transition.

PACS numbers: 61.50.Em, 61.55.Hg, 64.70.Ew

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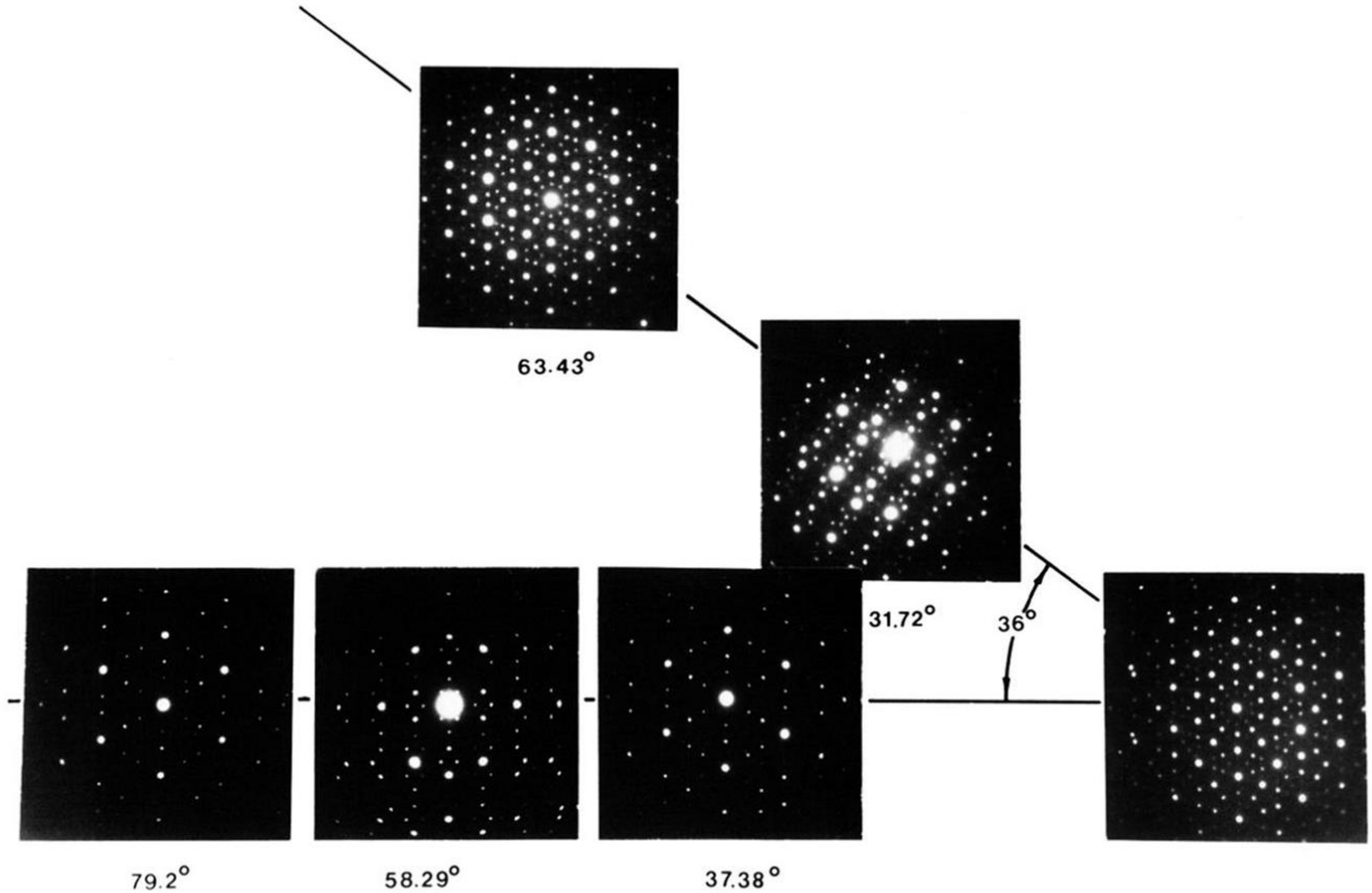

Quasicrystals (QCs)

- What are quasicrystals?
  - According to the definition – they are (aperiodic) crystals!
  - They do not posses 3D periodicity
  - Crystals in general are identified by "an essentially discrete diffraction pattern" (*Comission on Aperiodic Crystals, 1992*)
  - Nobel Prize in Chemistry 2011 for Dan Shechtman
- Icosahedral (IQC)
  - Shechtman *et al*., 1984, Dubost *et al.,* 1986
  - Aperiodic in 3D
  - Mackay-, Bergman-, or Tsai-type
- Decagonal (DQC)
  - Bendersky, 1985; He *et al.*, 1988
  - Aperiodic in 2D, so-called axial QCs
  - 2-, 4-, 6-, 8-layer periodicity
  - Al-based and Zn-Mg-RE

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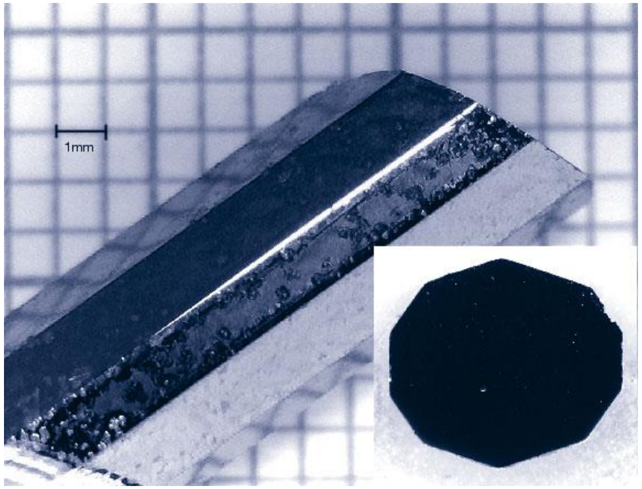
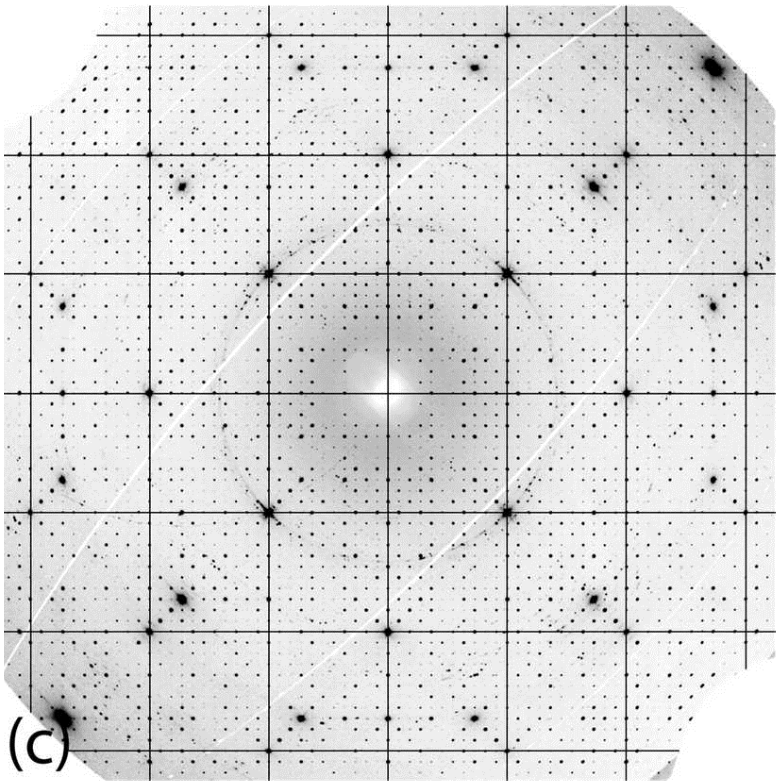


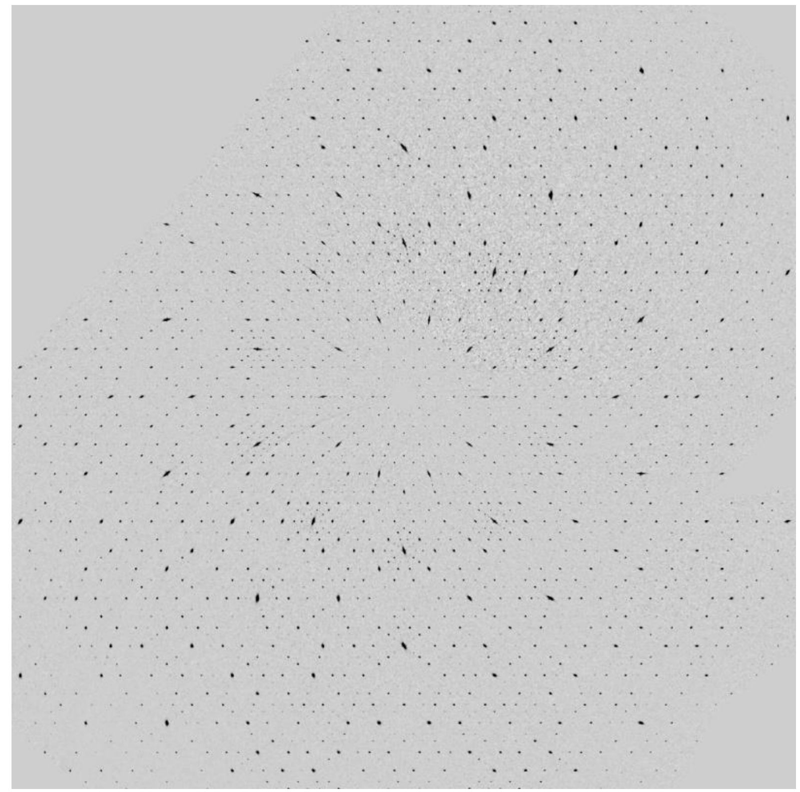
Fot. A.P. Tsai

Structural investigations of quasicrystals

Diffraction pattern.
"classical" crystal *vs. quasicrystal*



Al-Cu-Ta, cubic (a = 71.5 Å)
$F\bar{4}3m$
Weber *et al*., Acta Cryst. B, 2009
PSI, Switzerland, PILATUS (pixel detector)



Al-Cu-Rh, decagonal quasicrystal
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SNBL, ESRF Grenoble, CCD detector

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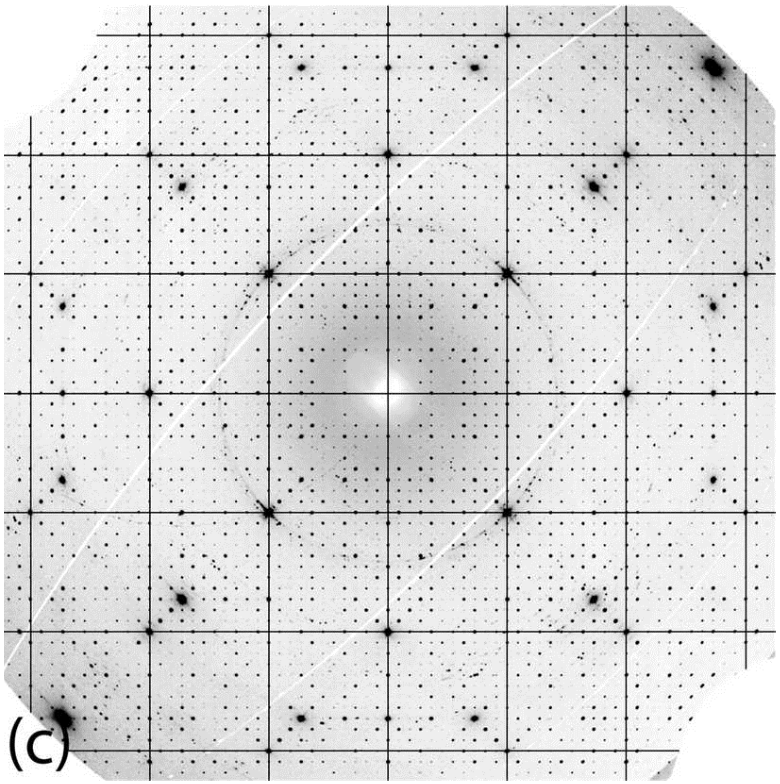

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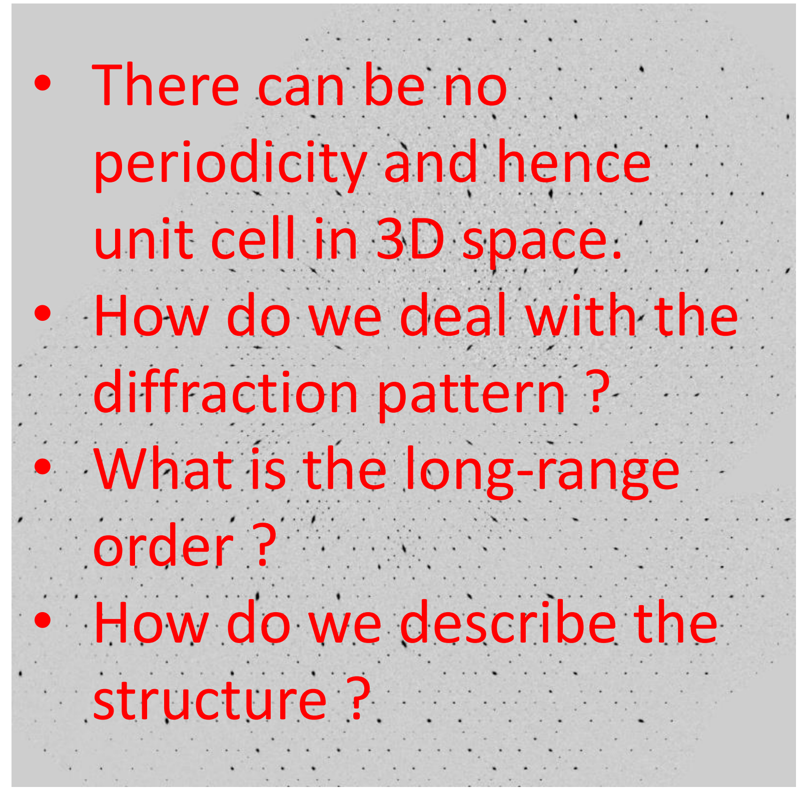

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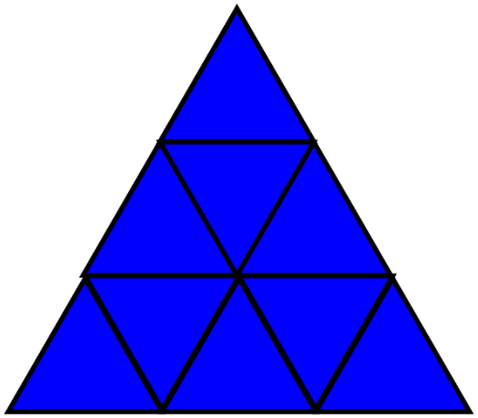
Theoretical problems – (quasi)lattice?



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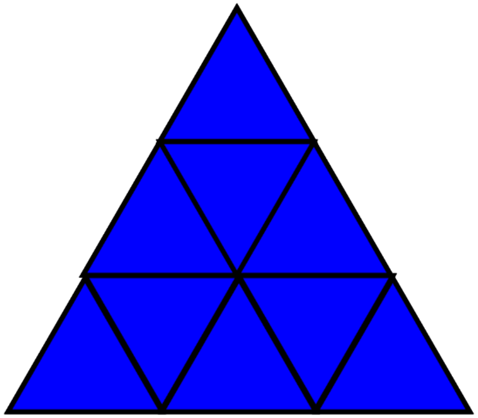

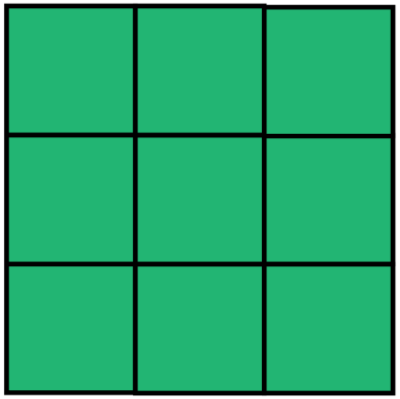

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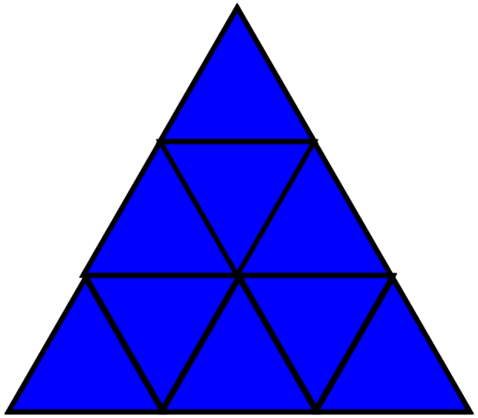

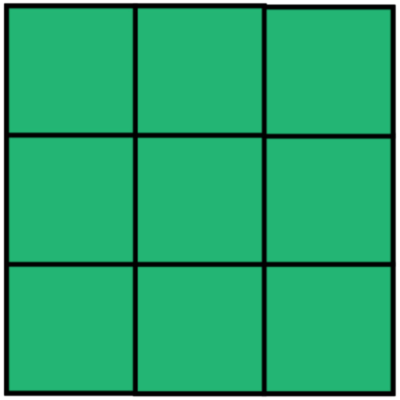

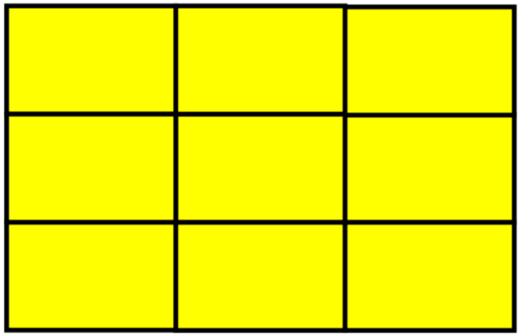

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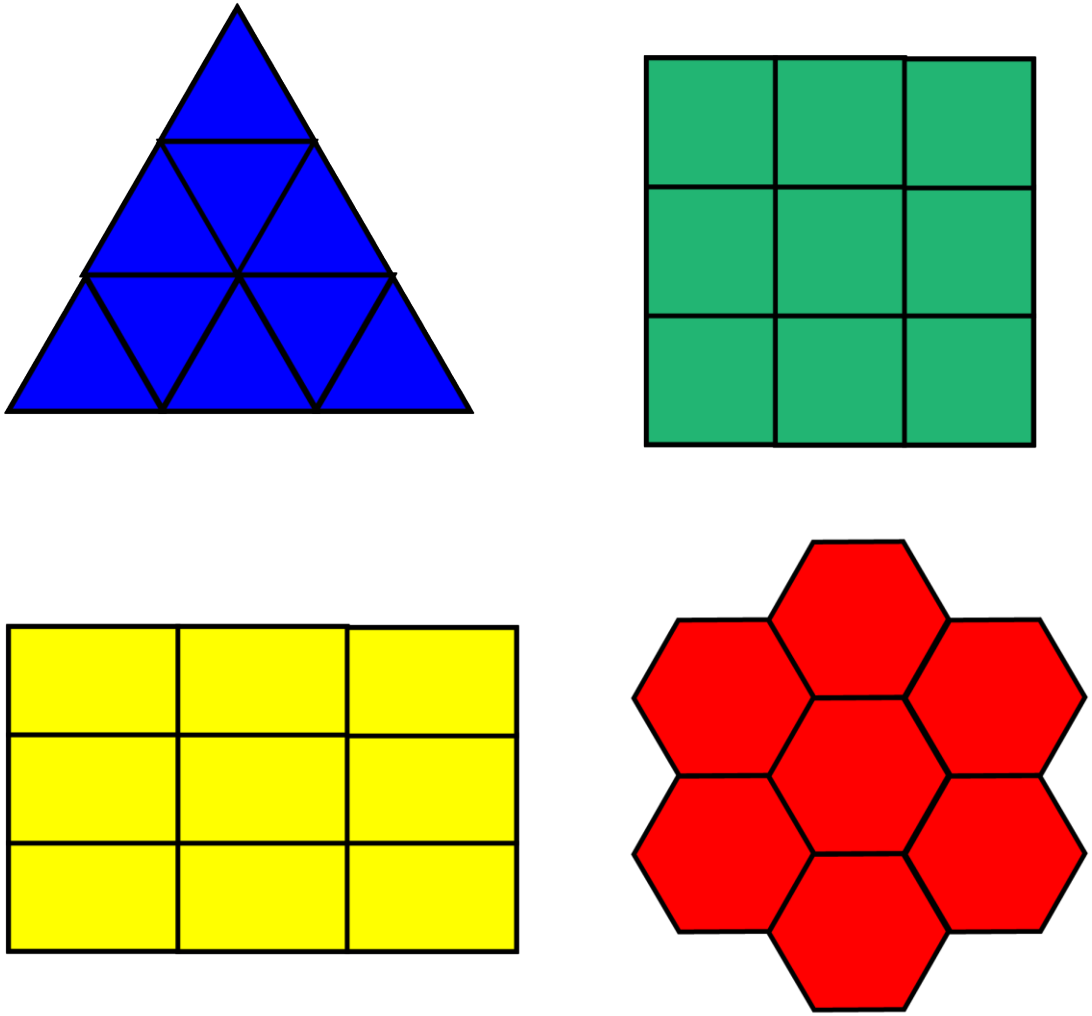

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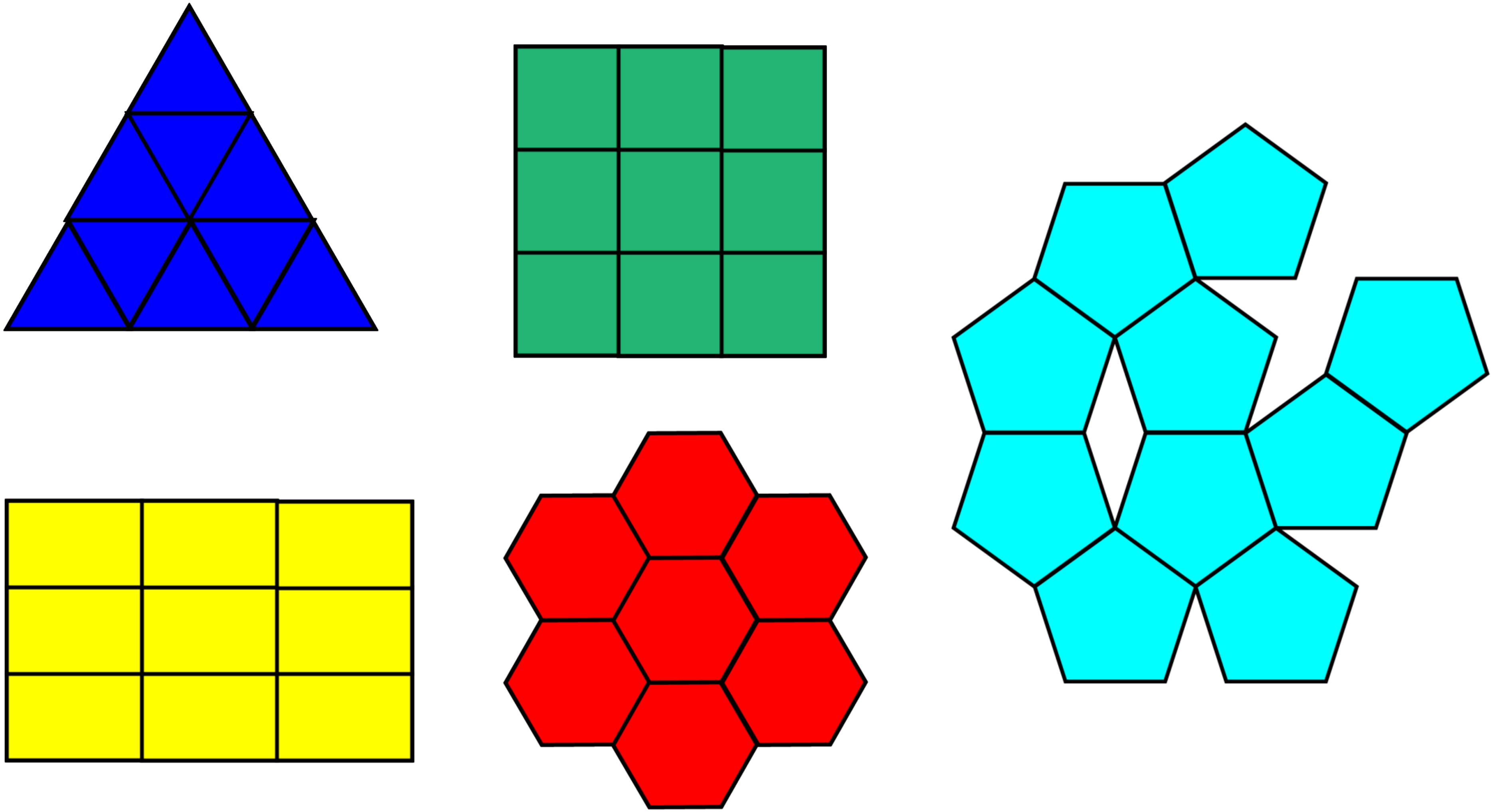
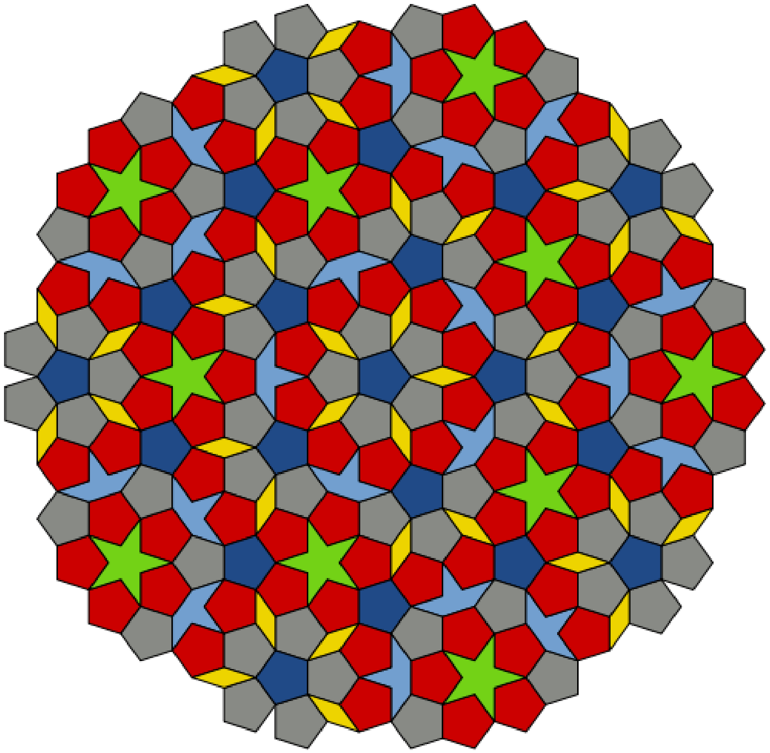
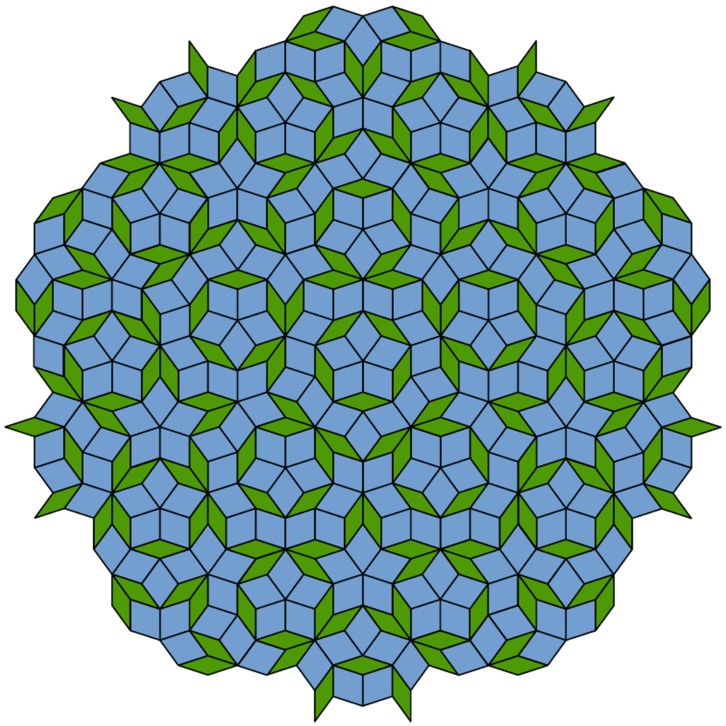


Penrose tilings

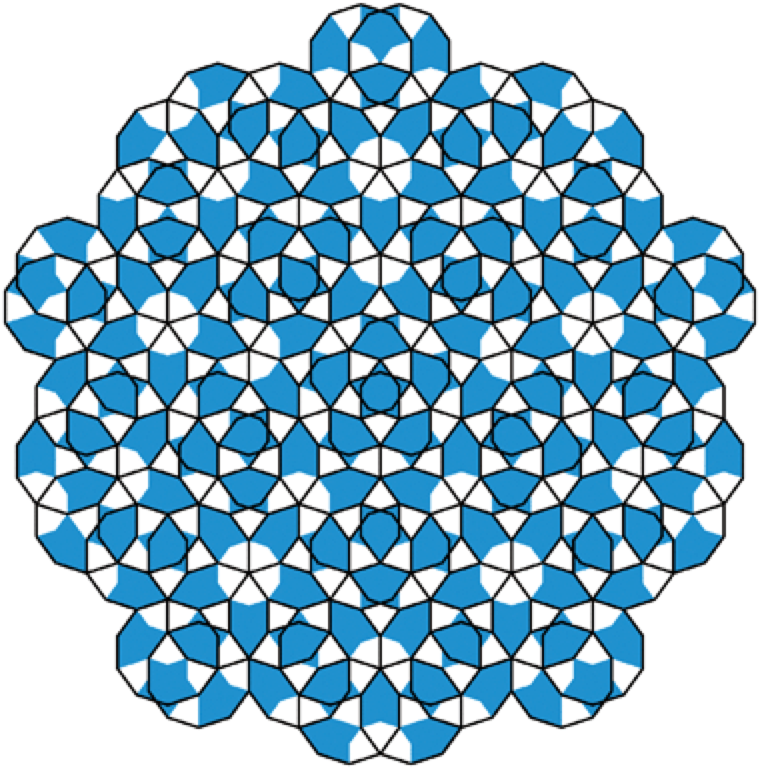


Pentagonal PT



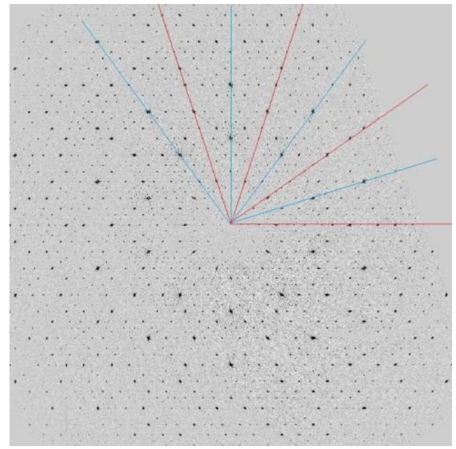
Rhombic PT

Gummelt covering

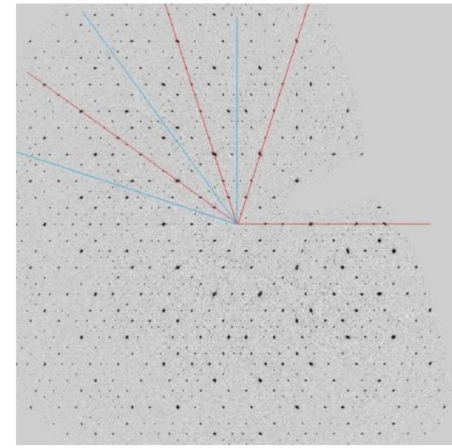


Information obtained from diffraction pattern directly *e.g.* d-Al-Cu-Rh

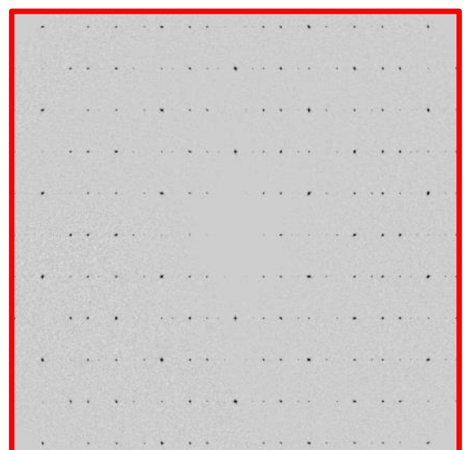
- Periodic stacking of aperiodic layers
- 10/*mmm* Laue class
- Systematic extinctions – screw axis and/or *c*-glide plane present
- Possible space groups
  - $P10_5/mmc$
  - $P10_5mc$
  - $P\overline{10}2c$



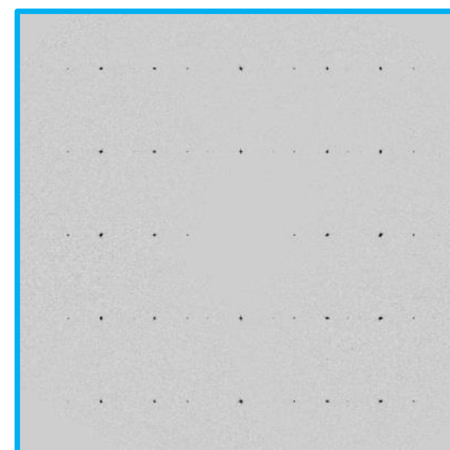
*hk*0



*hk*1



0*kl*



*h*0*l*

Structure solution
Charge Flipping Algorithm & SUPERFLIP

$$I(\mathbf{k}) = |F(\mathbf{k})|^2 \xrightarrow{\mathit{FT}} g(\mathbf{r})$$ *Patterson function*

Structure solution
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$$\rho(\mathbf{r}) \downarrow |\rho(\mathbf{r})|$$

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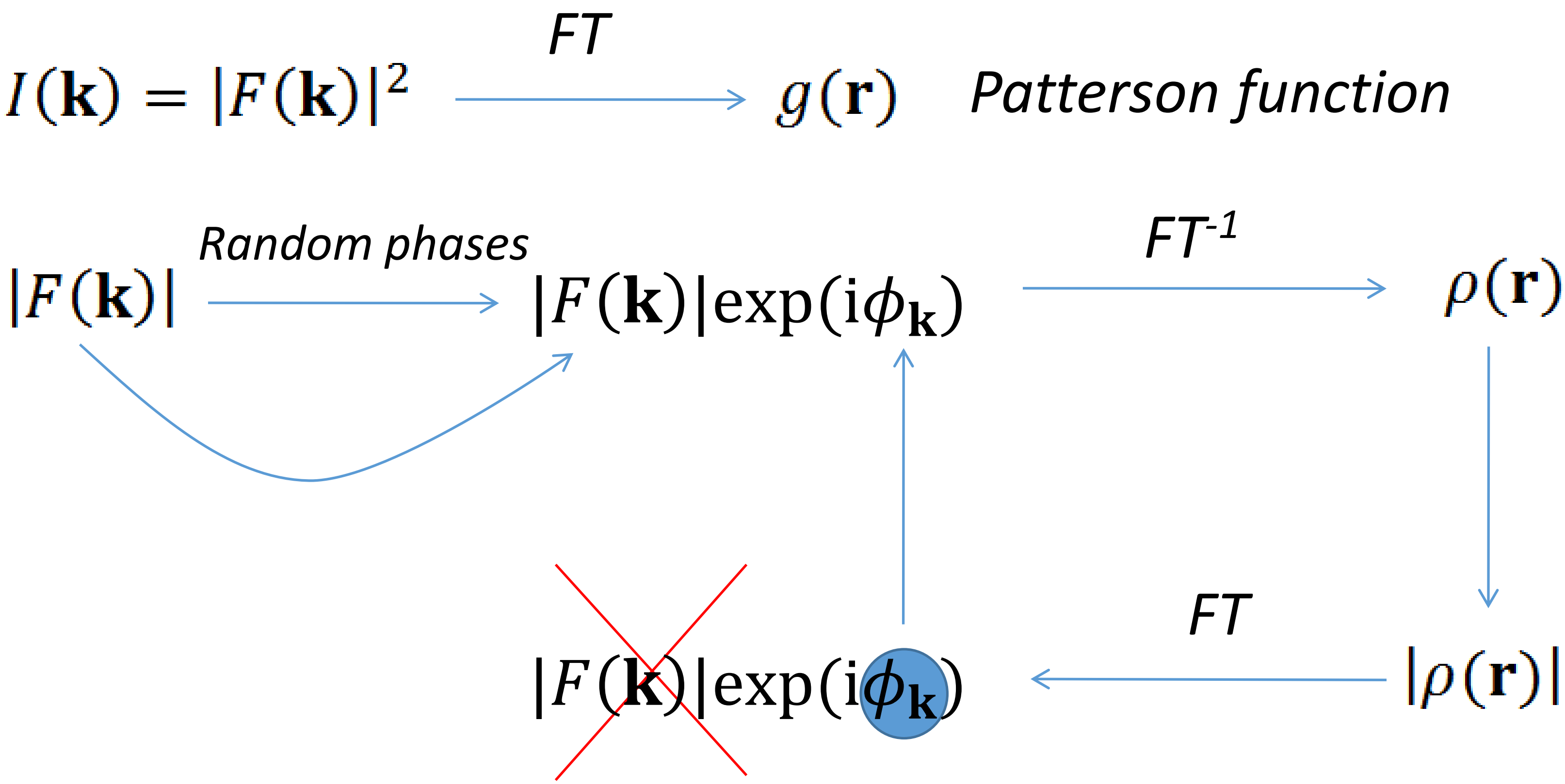
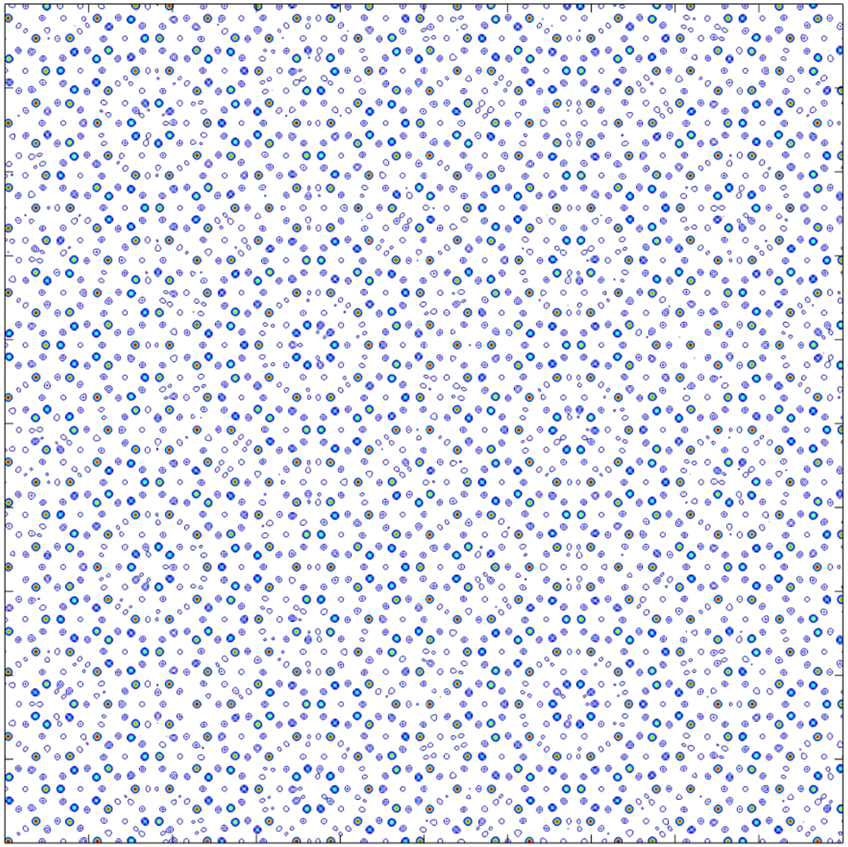


ALGORITHM: Oszlanyi & Suto, 2008

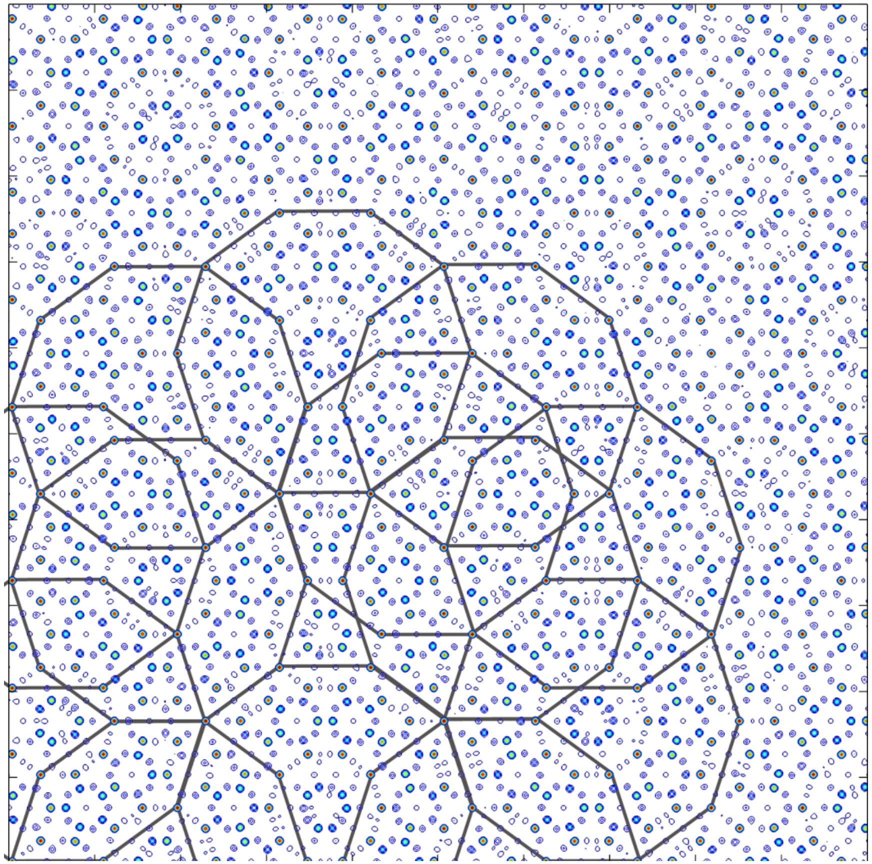
SUPERFLIP PROGRAM: Palatinus & Chapuis, 2007

SUPERFLIP solution
Modeling example d-Al-Cu-Rh



Projection along the tenfold axis

Modeling example: d-Al-Cu-Rh



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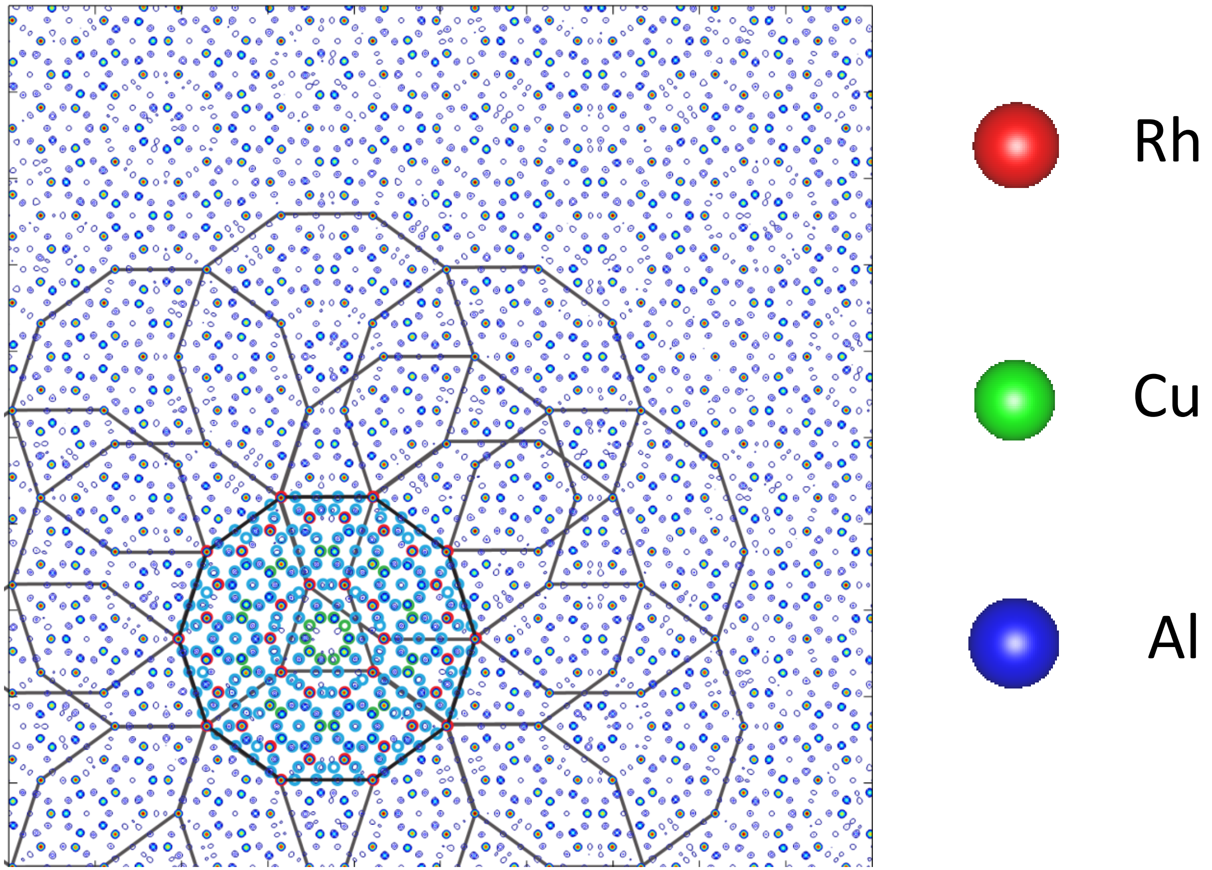
Modeling example d-Al-Cu-Rh; The cluster structure



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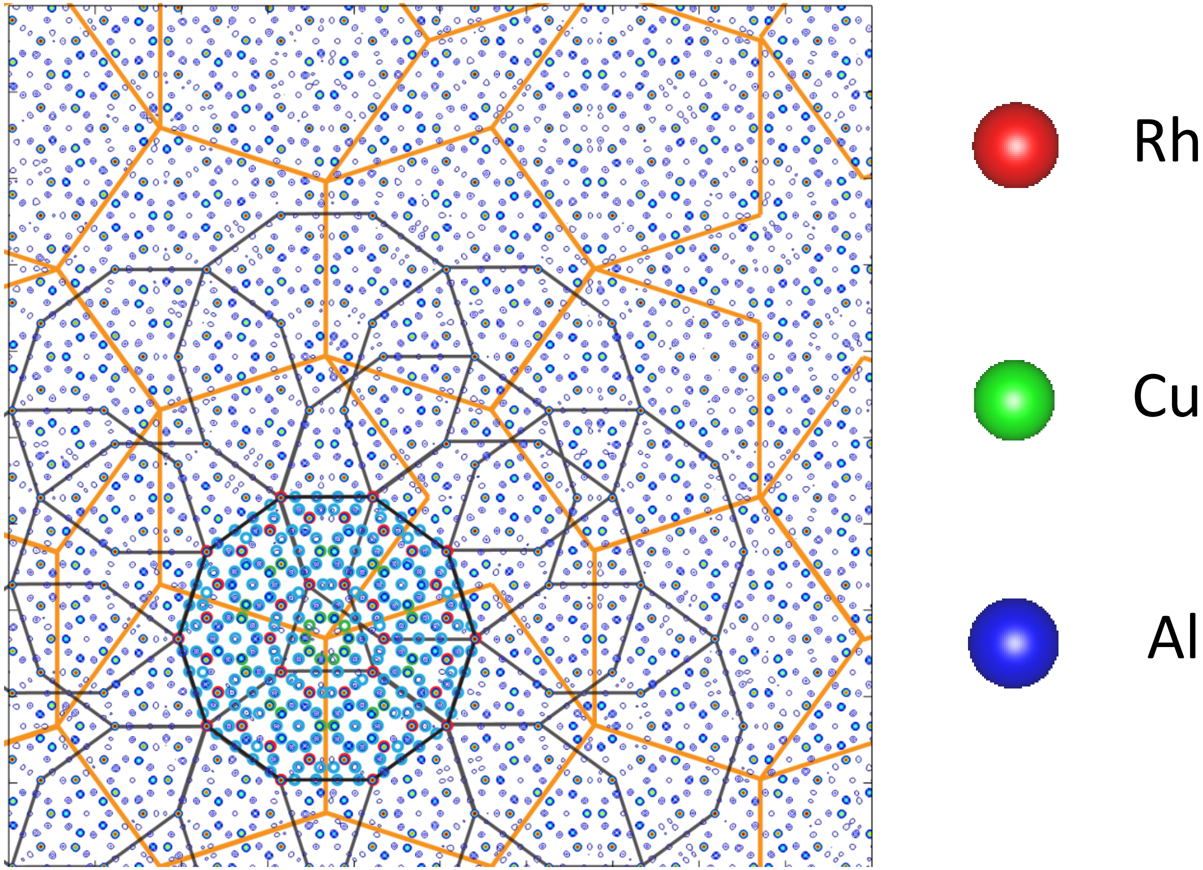

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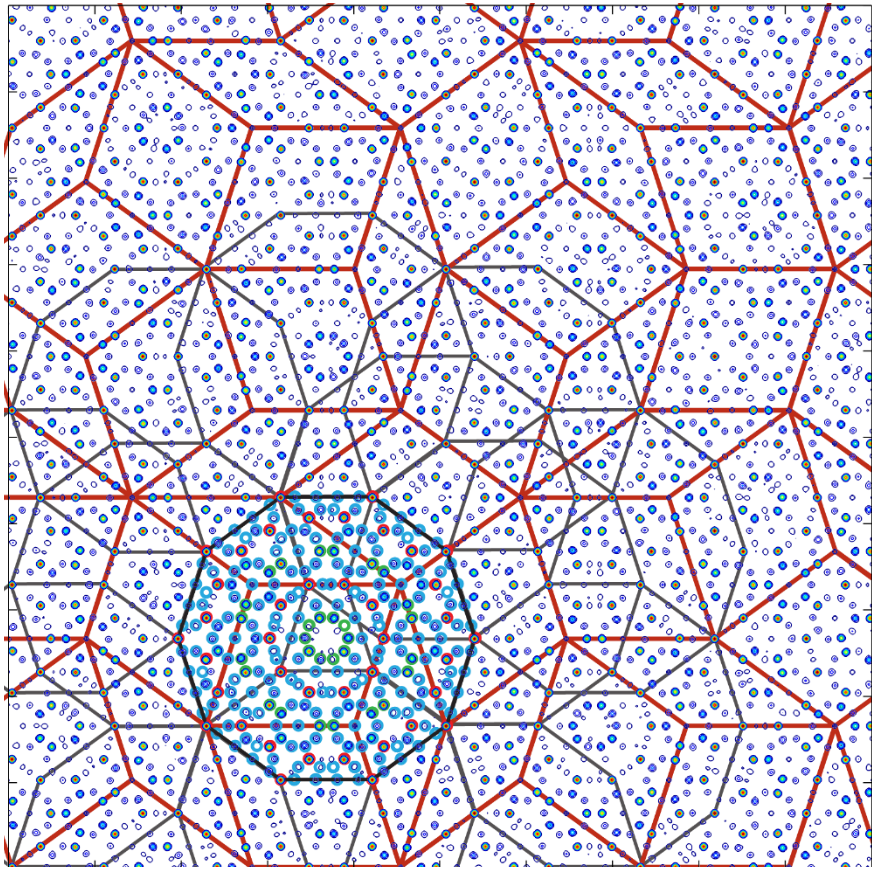
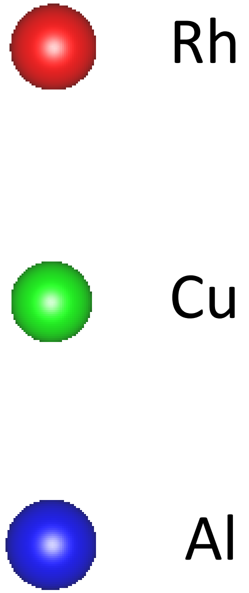
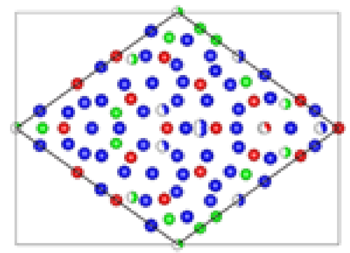
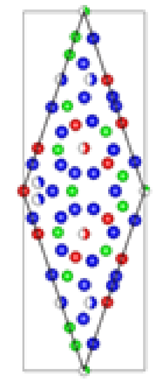




What about the structure factor?



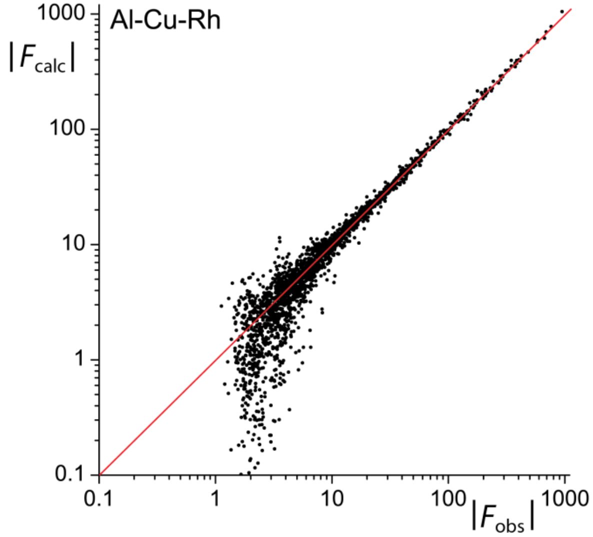


It is possible to calculate the structure factor*

Works of prof. Janusz Wolny &Co.

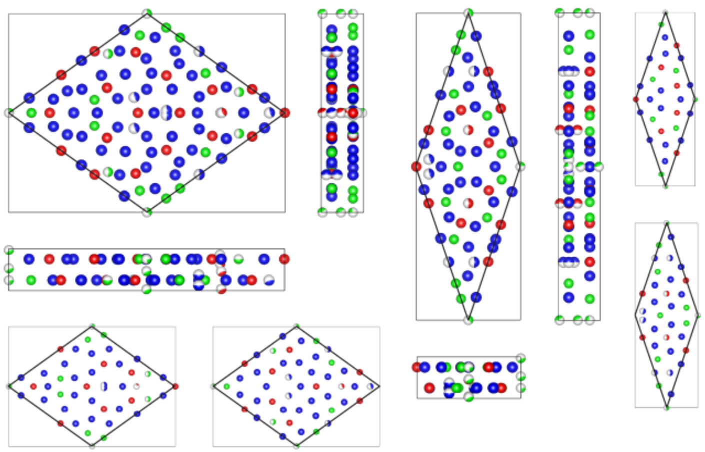
$$FT(\varrho) = \left(\sum_{\alpha} \left(FT(\boldsymbol{L}_{AUC}) \sum_{atoms} f(\mathbf{k}) exp(i\mathbf{k} \cdot \mathbf{r}) \right) + \sum_{\alpha} \left(FT(\boldsymbol{S}_{AUC}) \sum_{atoms} f(\mathbf{k}) exp(i\mathbf{k} \cdot \mathbf{r}) \right) \right)$$

Refinement results d-Al-Cu-Rh

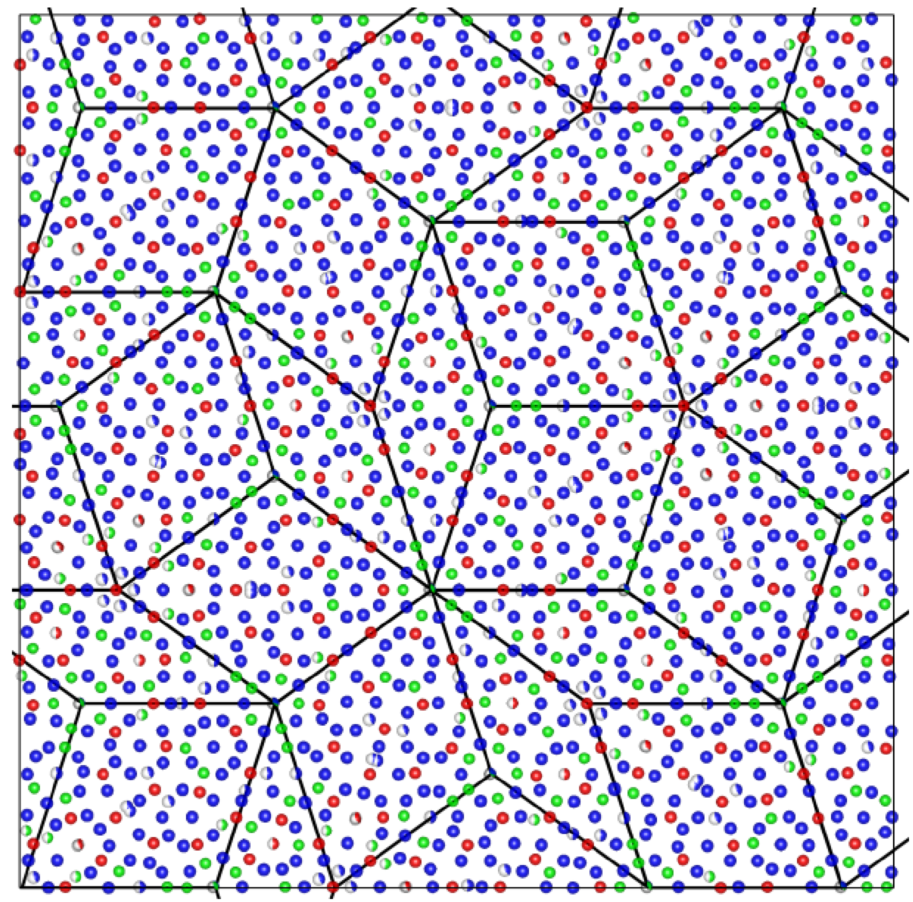


R[|F|/σ > 1]	0.079	No. of refl.	2174
R[|F|/σ > 3]	0.060	No. of params.	245
wR[|F|/σ > 1]	0.086	Chem. comp.	$Al_{61.9}Cu_{18.5}Rh_{19.6}$
wR[|F|/σ > 3]	0.077	Refined comp.	$Al_{60.6}Cu_{19.2}Rh_{20.2}$

Refinement results.



Red – Rh
Green – Cu
Blue - Al



Projection along the tenfold axis

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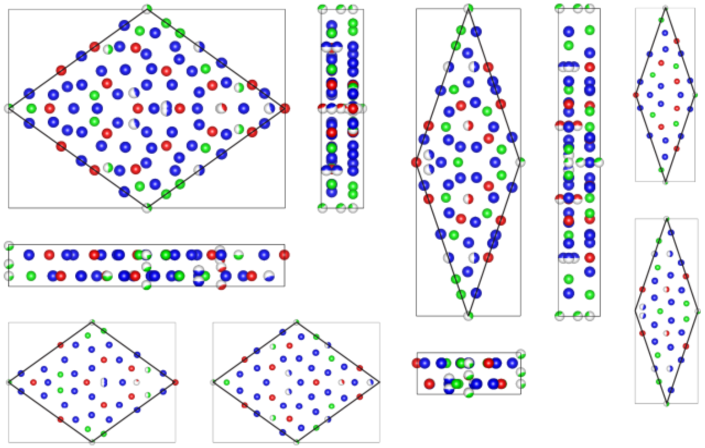

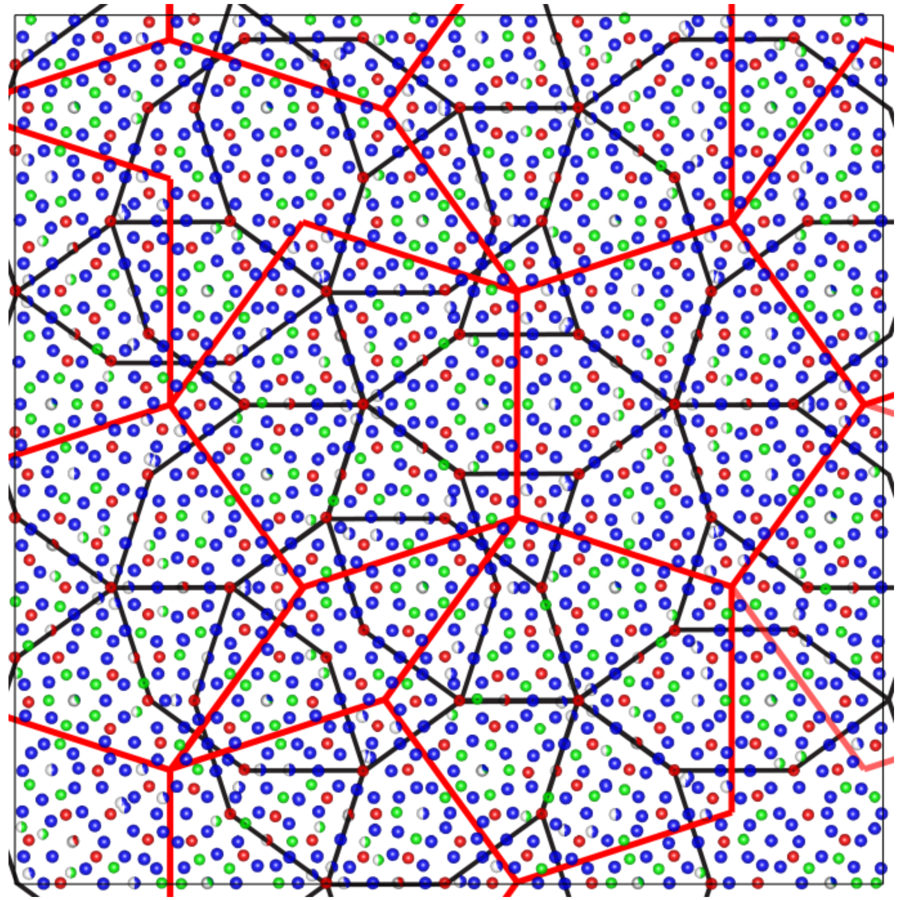

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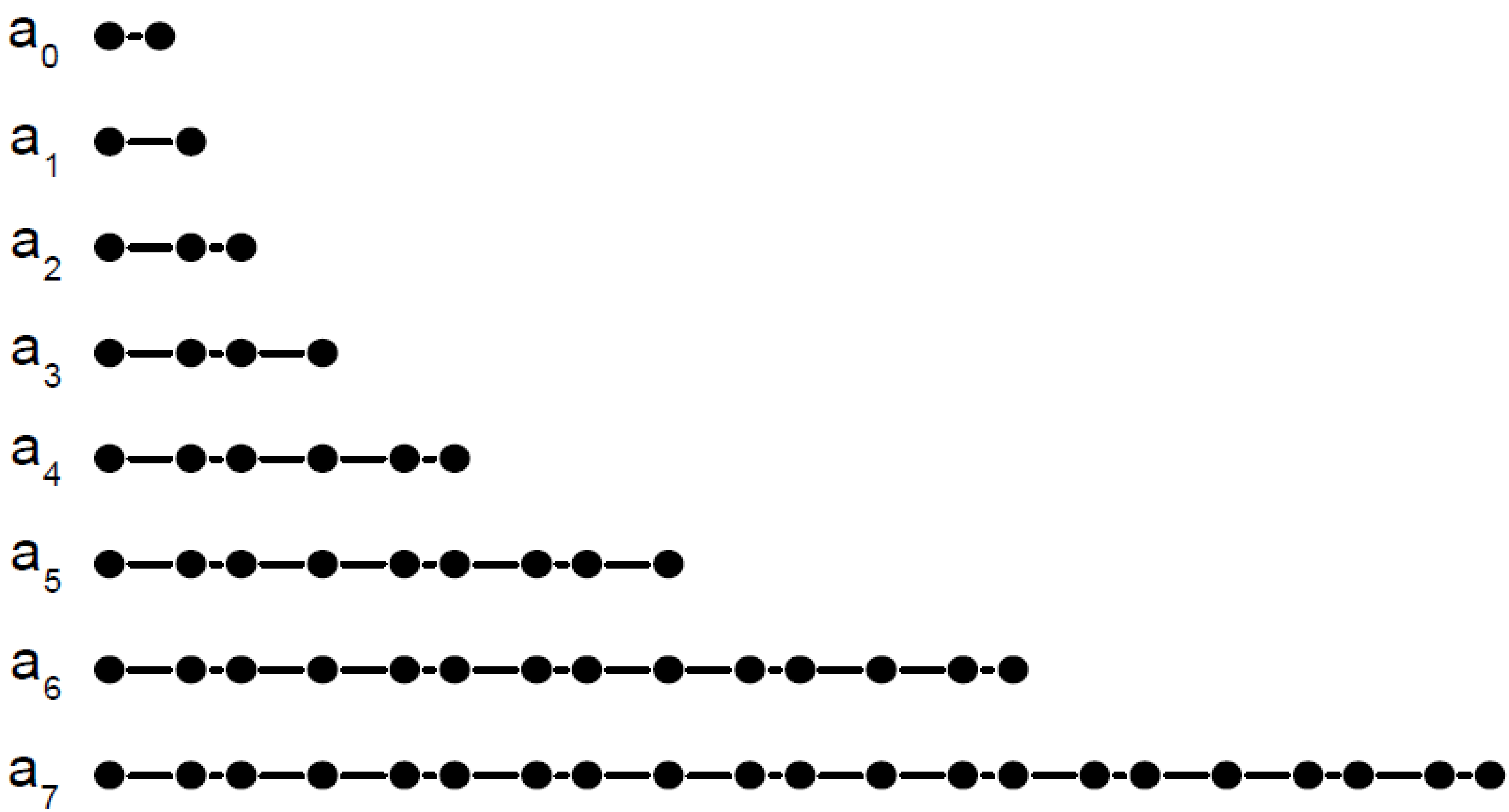
Projection along the tenfold axis

Quasicrystalline long-range order

Monte Carlo simulations

*n*D approach - Fibonacci chain



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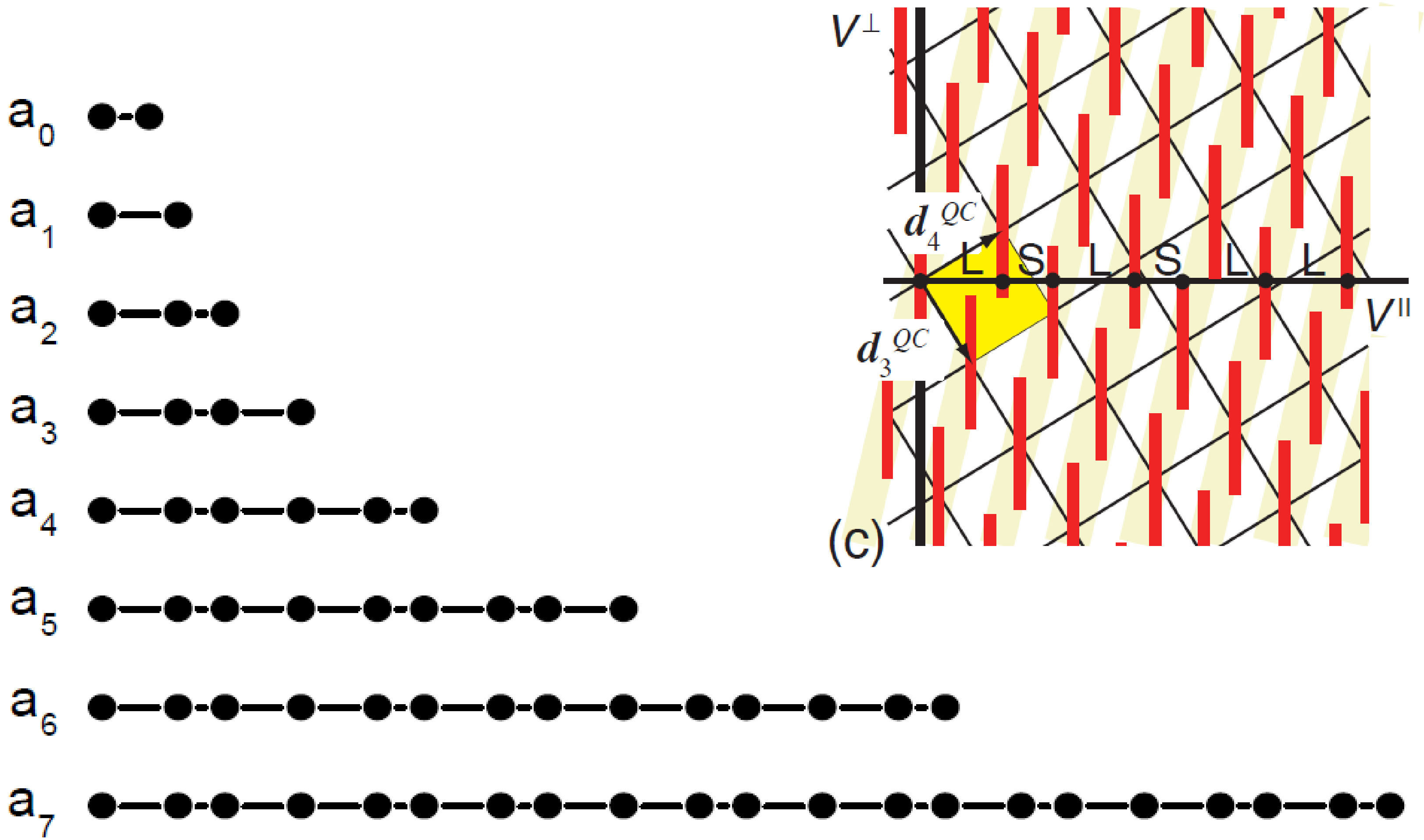
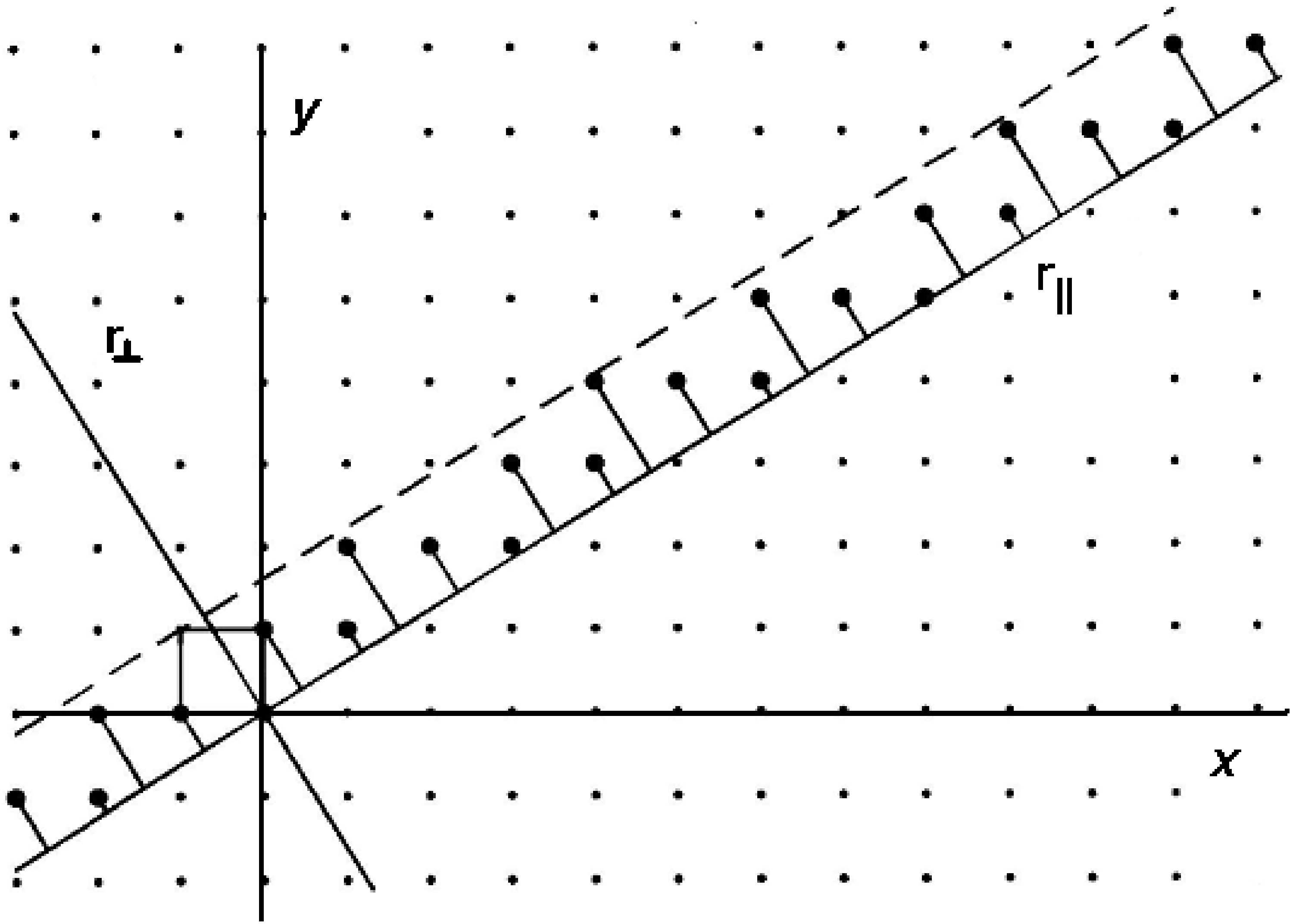


How to quantify the quasiperiodic LRO?



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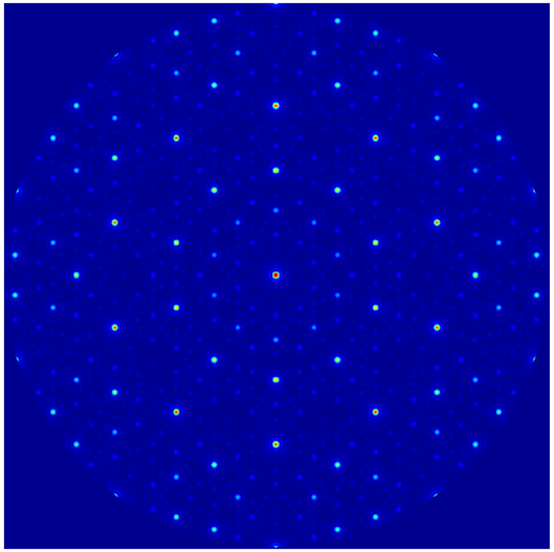

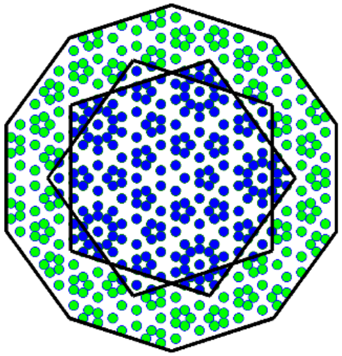

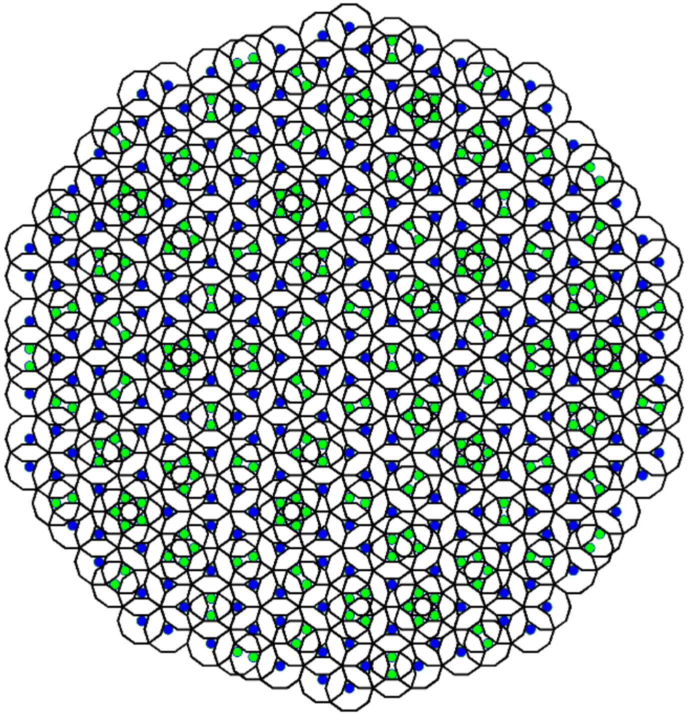

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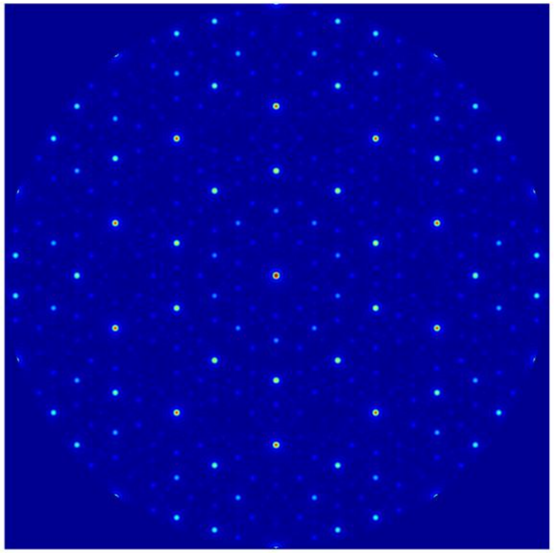
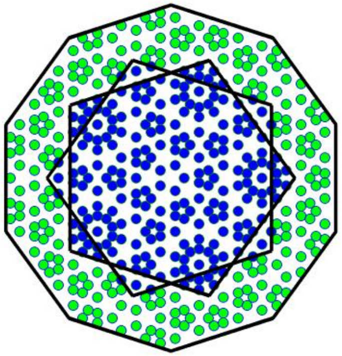
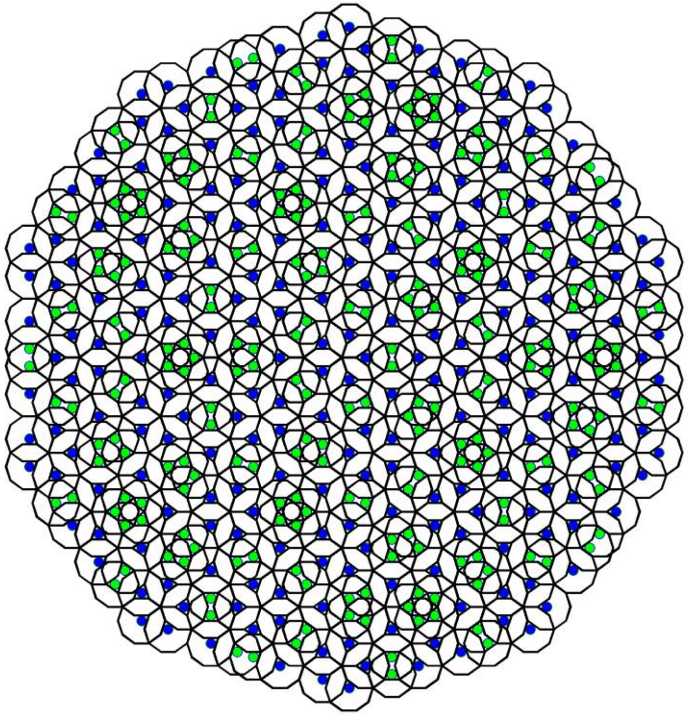
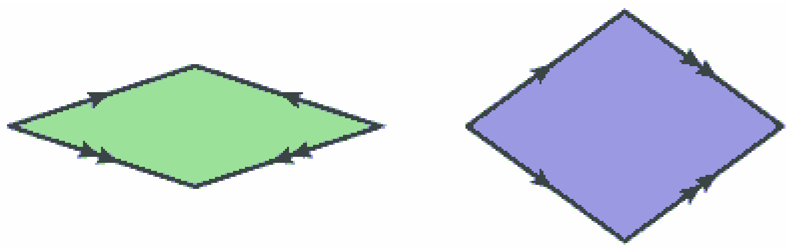






How do we “grow” tilings?

Matching rules / overlap rules



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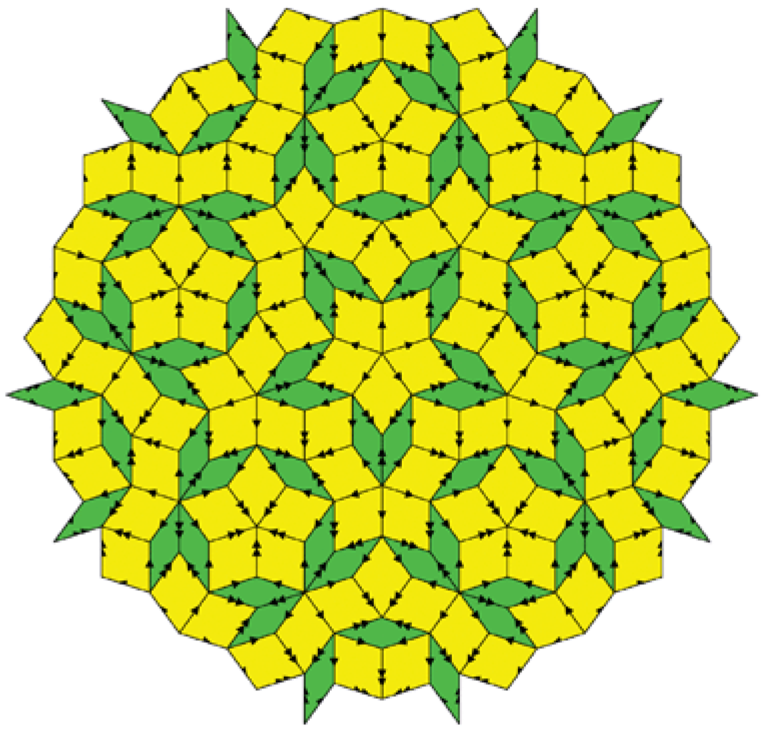

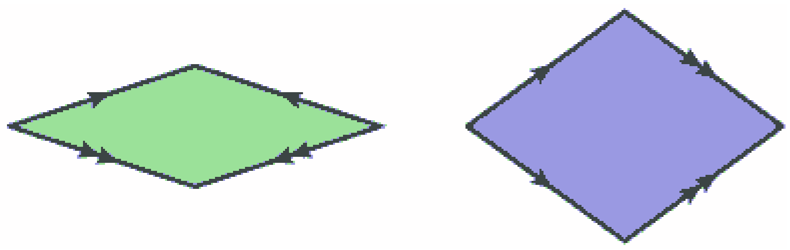

Bake & Grimm, *Chem. Soc. Rev.* (2011) **41** 6821

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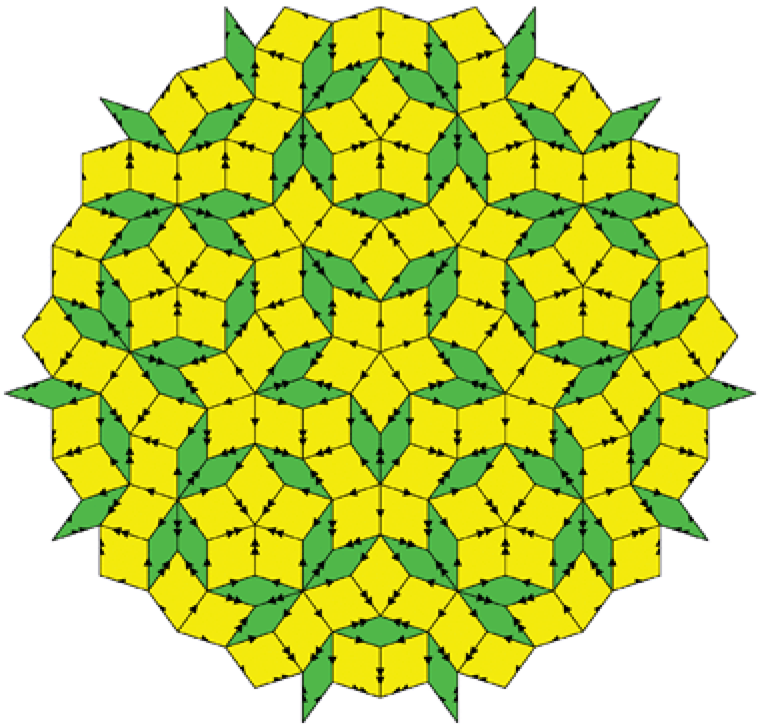

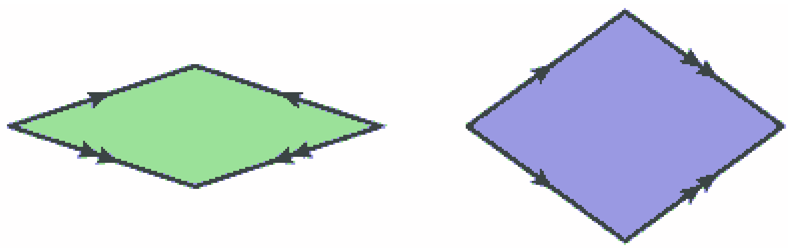

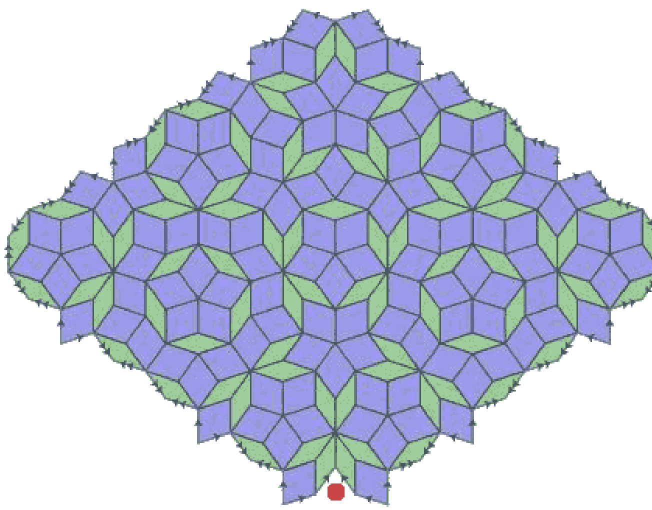

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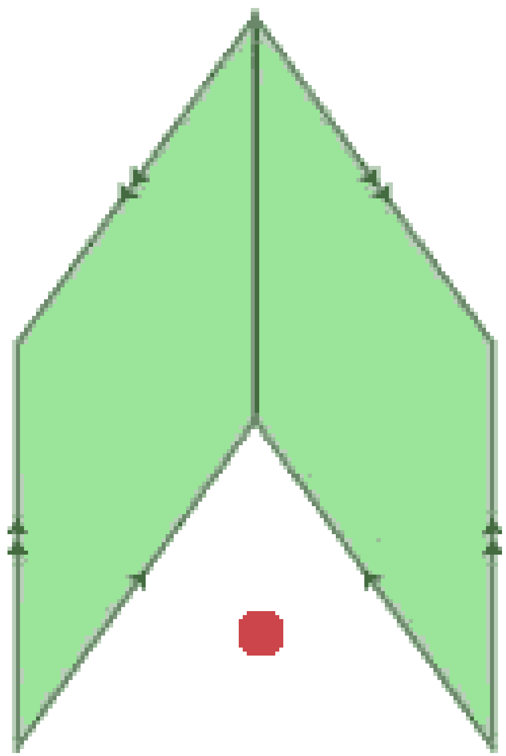
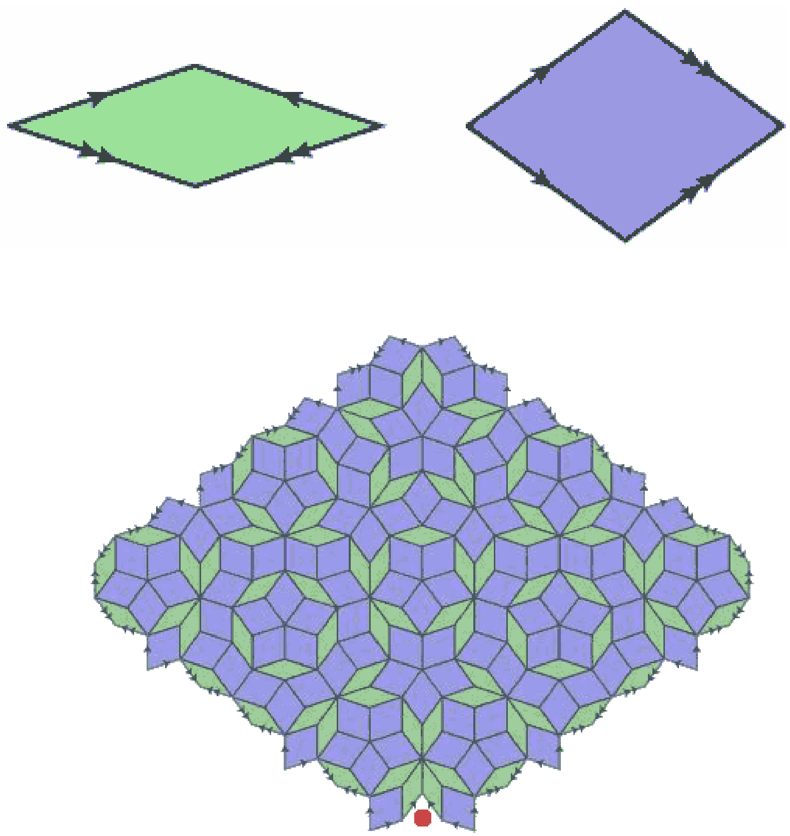
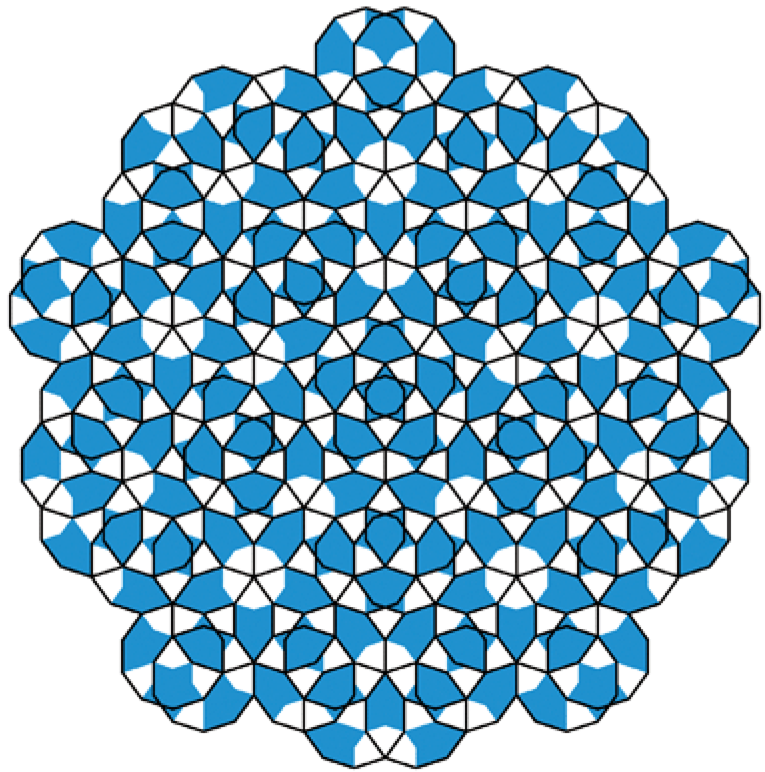
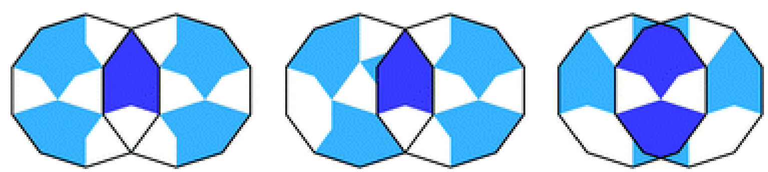




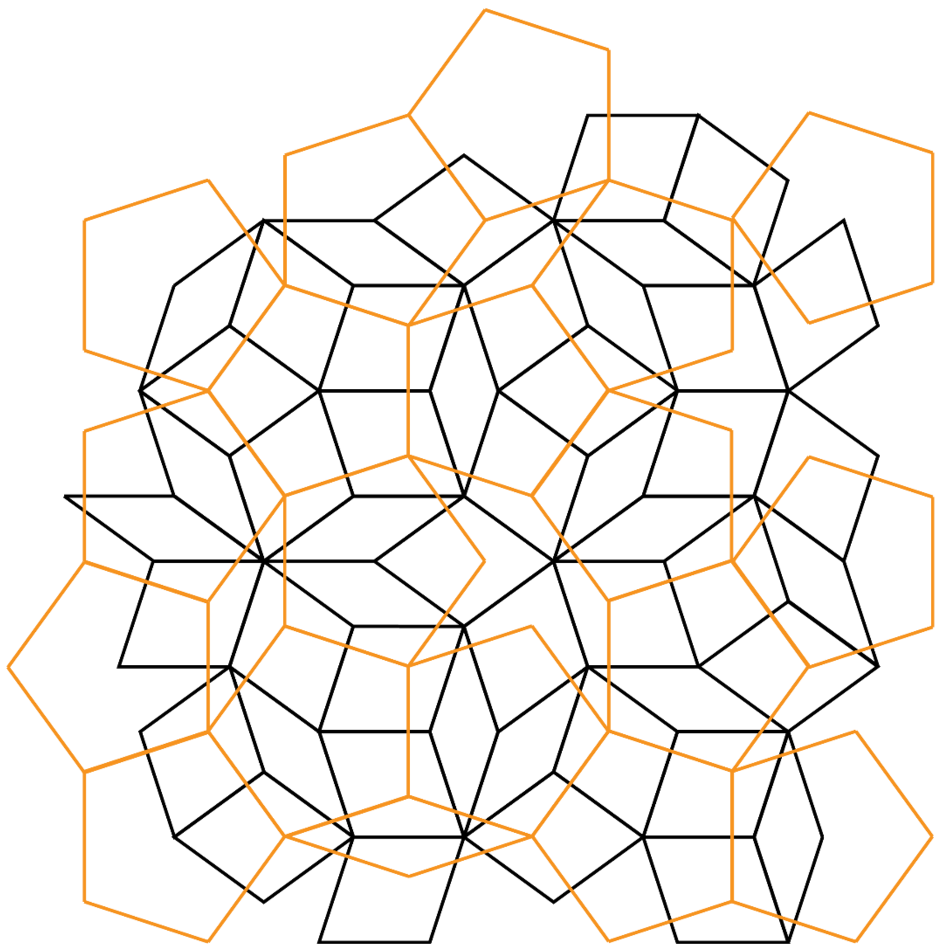
Matching rules / overlap rules



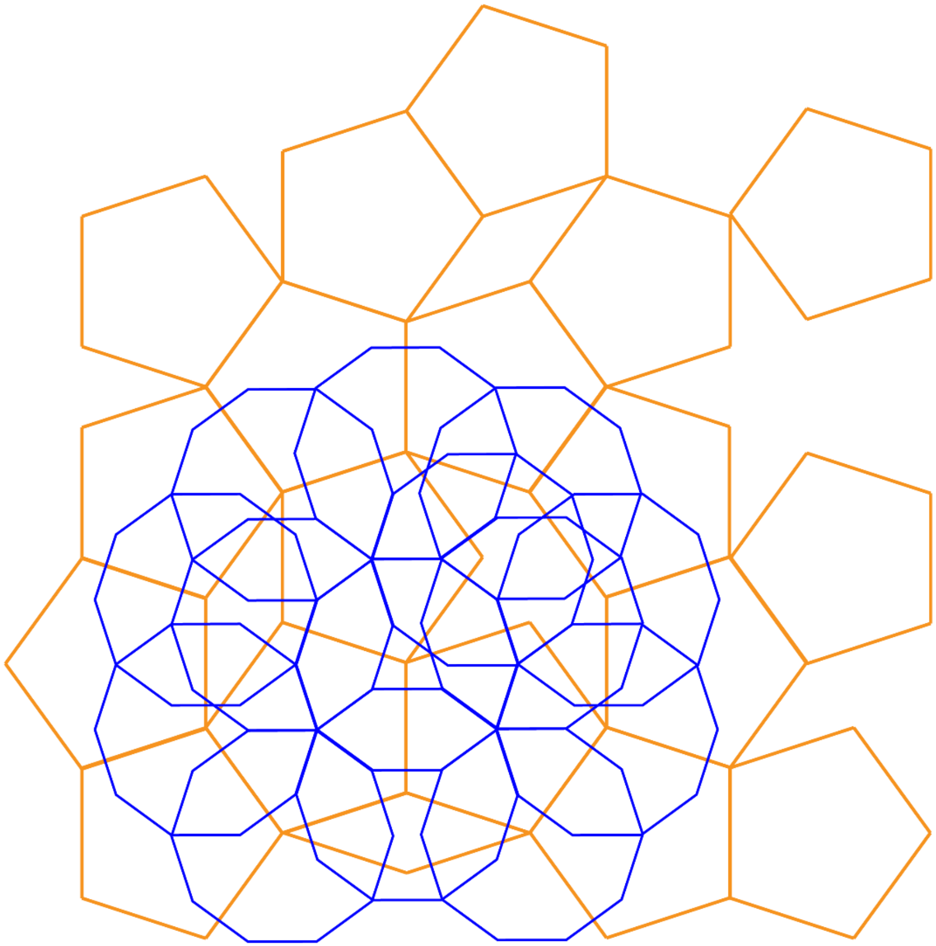


Bake & Grimm, *Chem. Soc. Rev.* (2011) **41** 6821

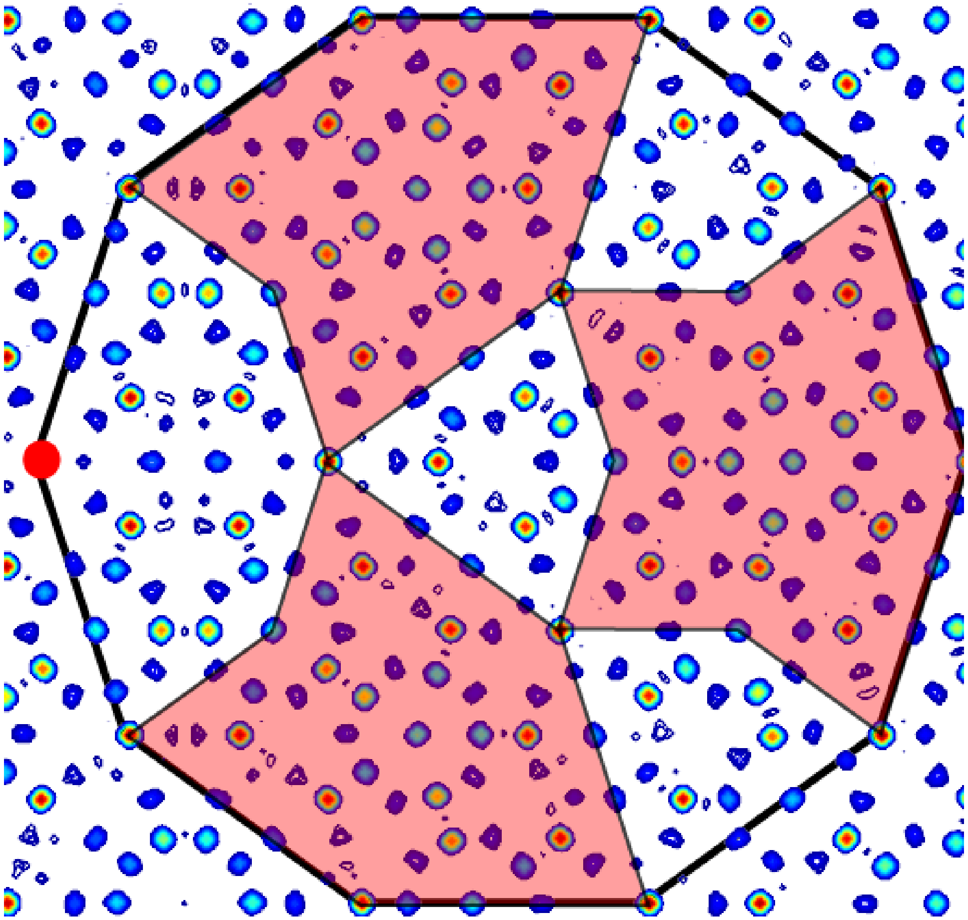
Close relations of RPT, GPR & GC



Close relations of RPT, GPR & GC



How does a real cluster look like?



Kuczera *et. al, Acta Cryst B* (2012) **68** 578

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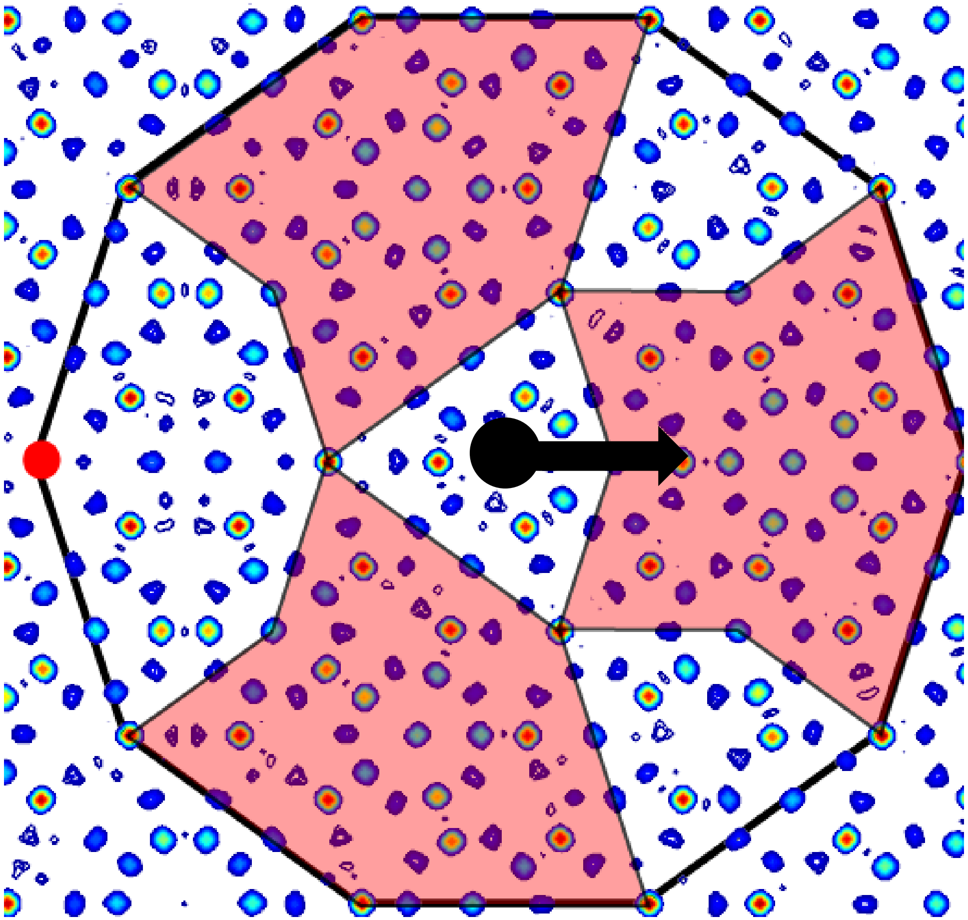

Kuczera *et. al, Acta Cryst B* (2012) **68** 578

Phason Flips

- A tiling/covering can be modified by phason flips:

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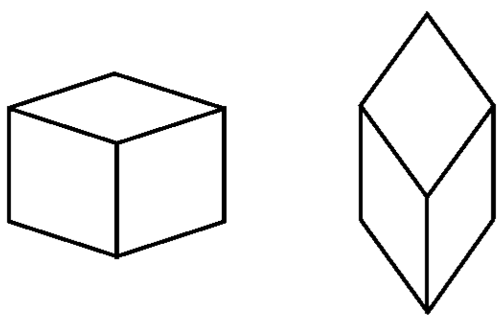

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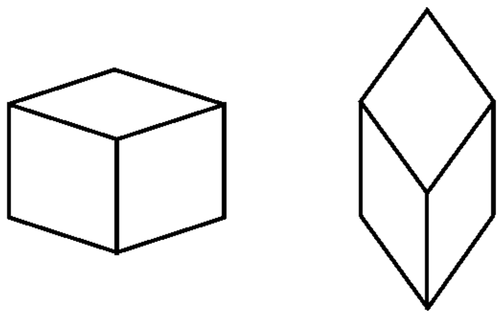

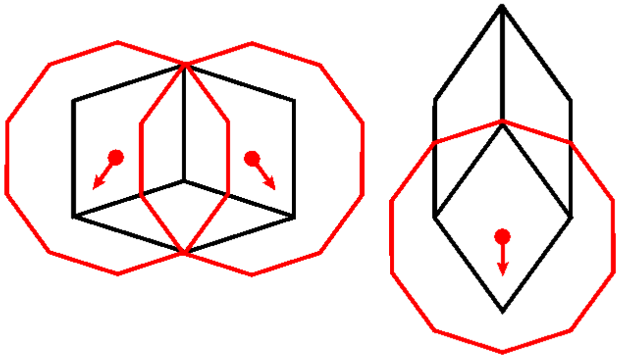

Phason Flips

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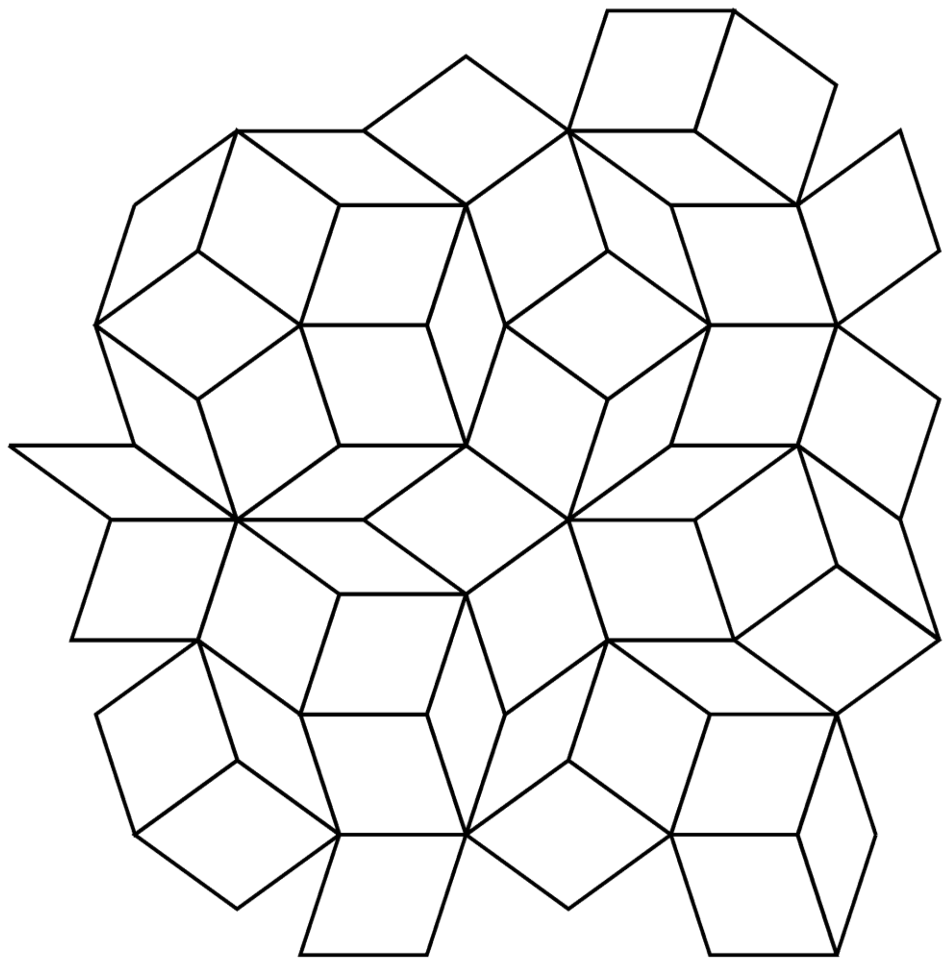
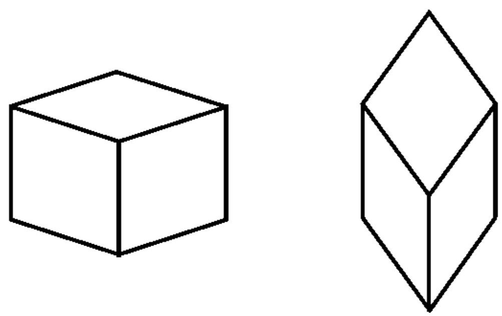
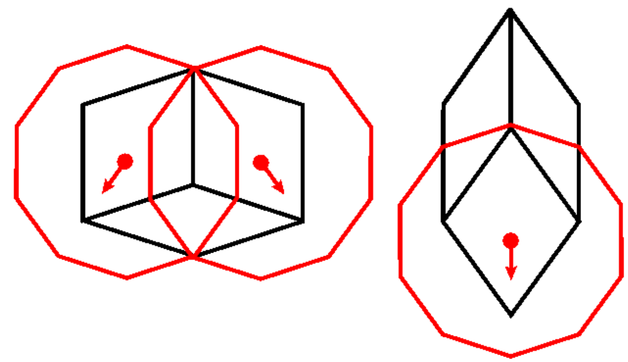


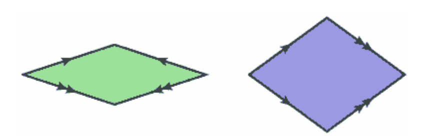
Idea – Monte Carlo simulation

The tiling/covering can be modified by phason flips:





- $E + 1$ for every violation of matching rules



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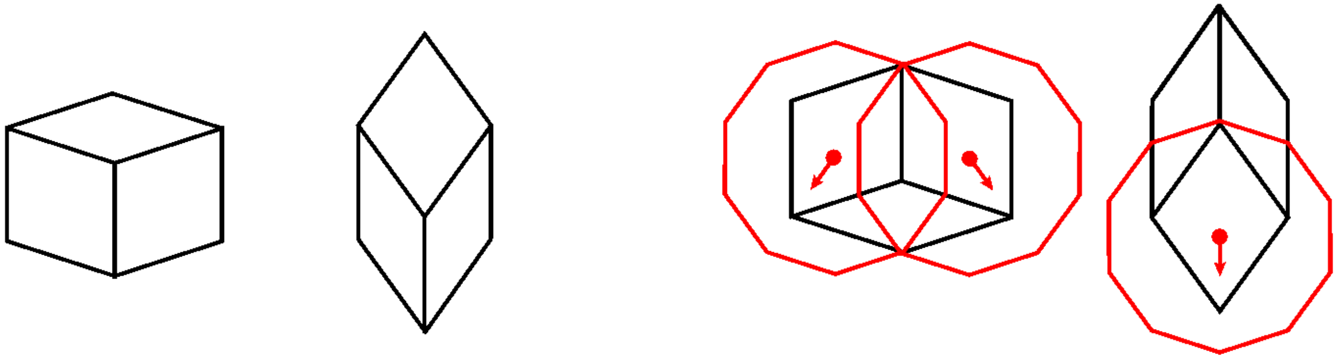


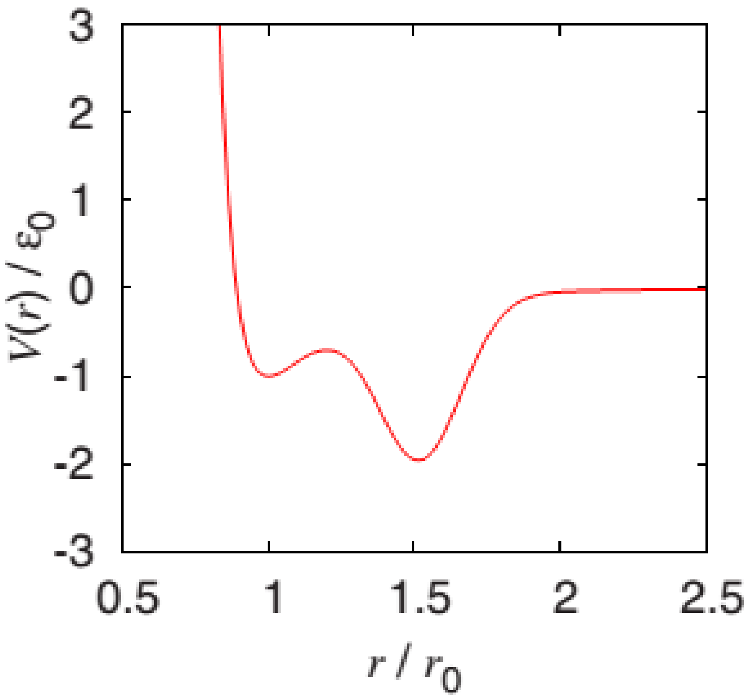
- $E + 1$ for every violation of matching rules

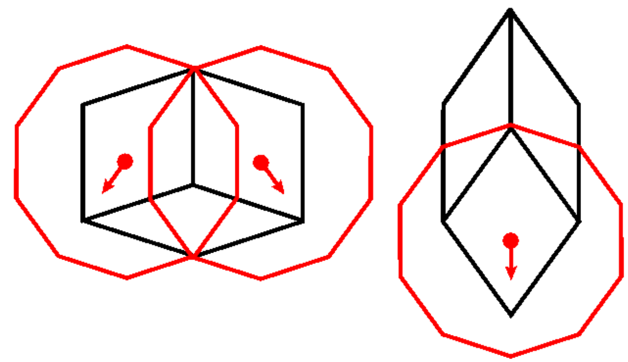
It does not work

Tang & Jaric (1990); Reicher & Gaehler (2003)

Idea – Monte Carlo simulation

The tiling/covering can be modified by phason flips:





ı of matching rules

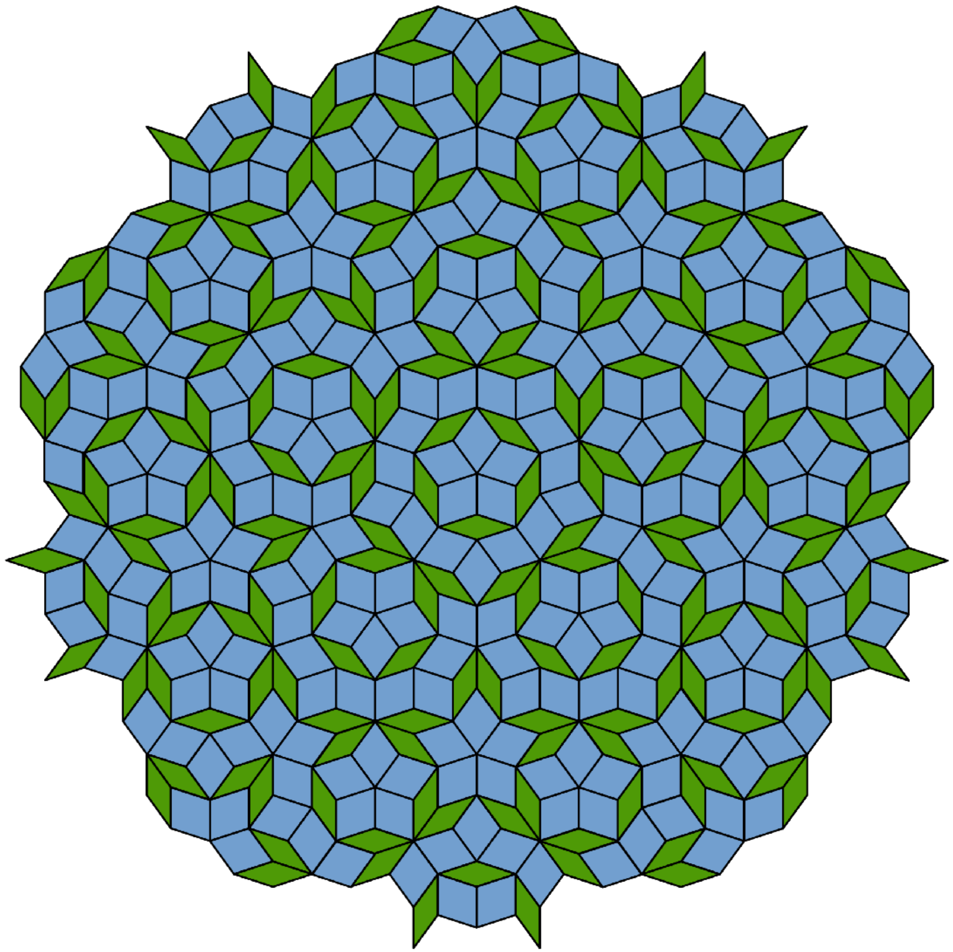
Tang & Jaric (1990); Reicher & Gaehler (2003)

Neither does MD with Lenard-Gauss-Jones pot.

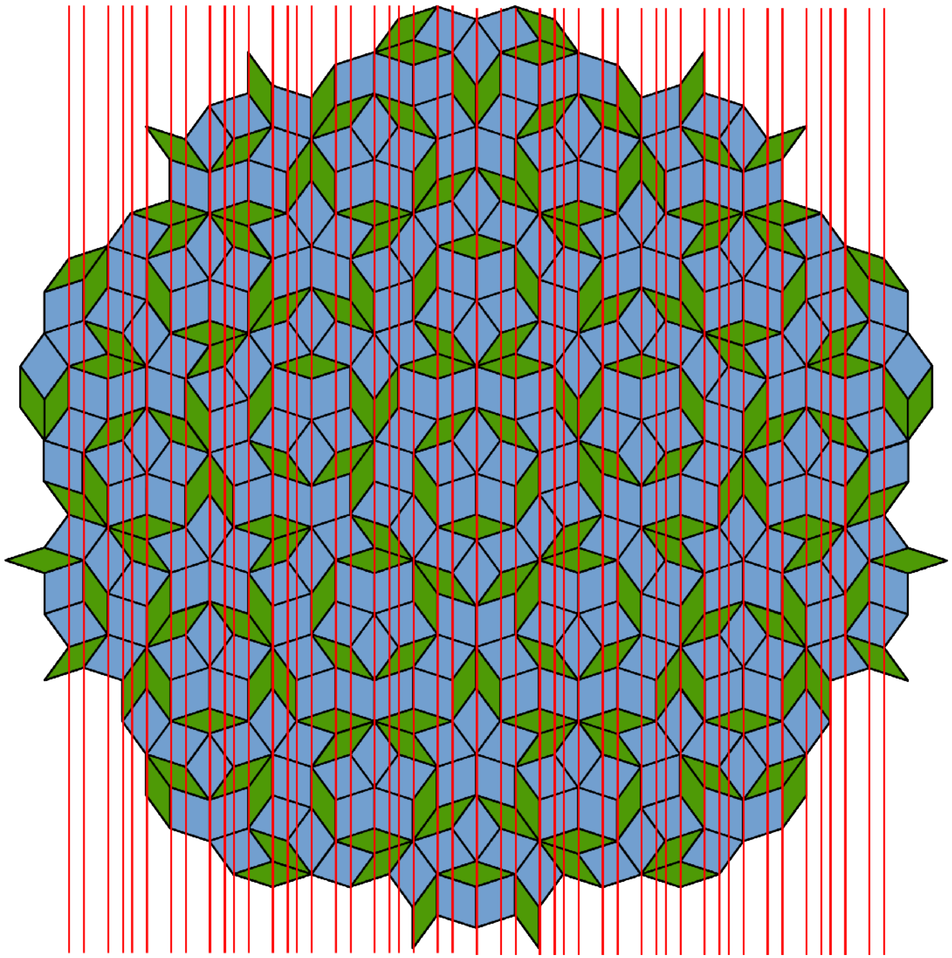
Engel *et al.* (2010); Kiselev *et al.* (2012)

The concept of quasilattice planes
-QLPs-
(*flat atomic layers*)

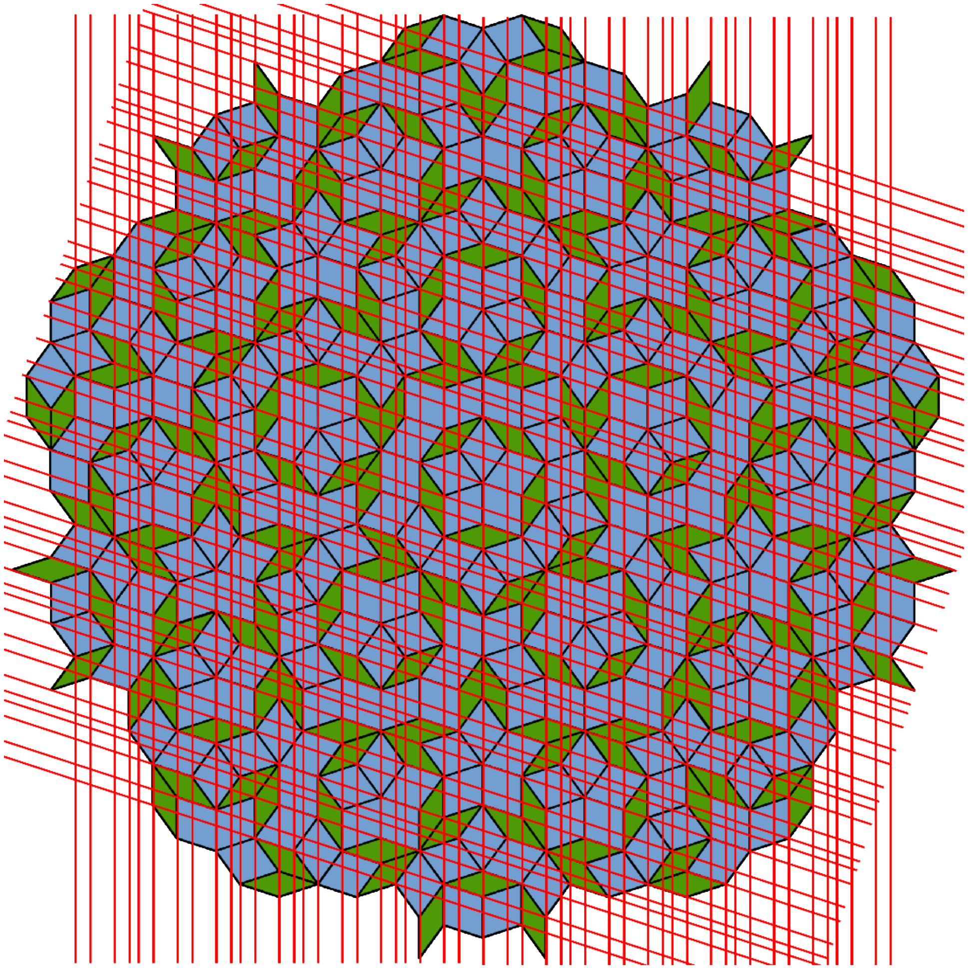
QLPs



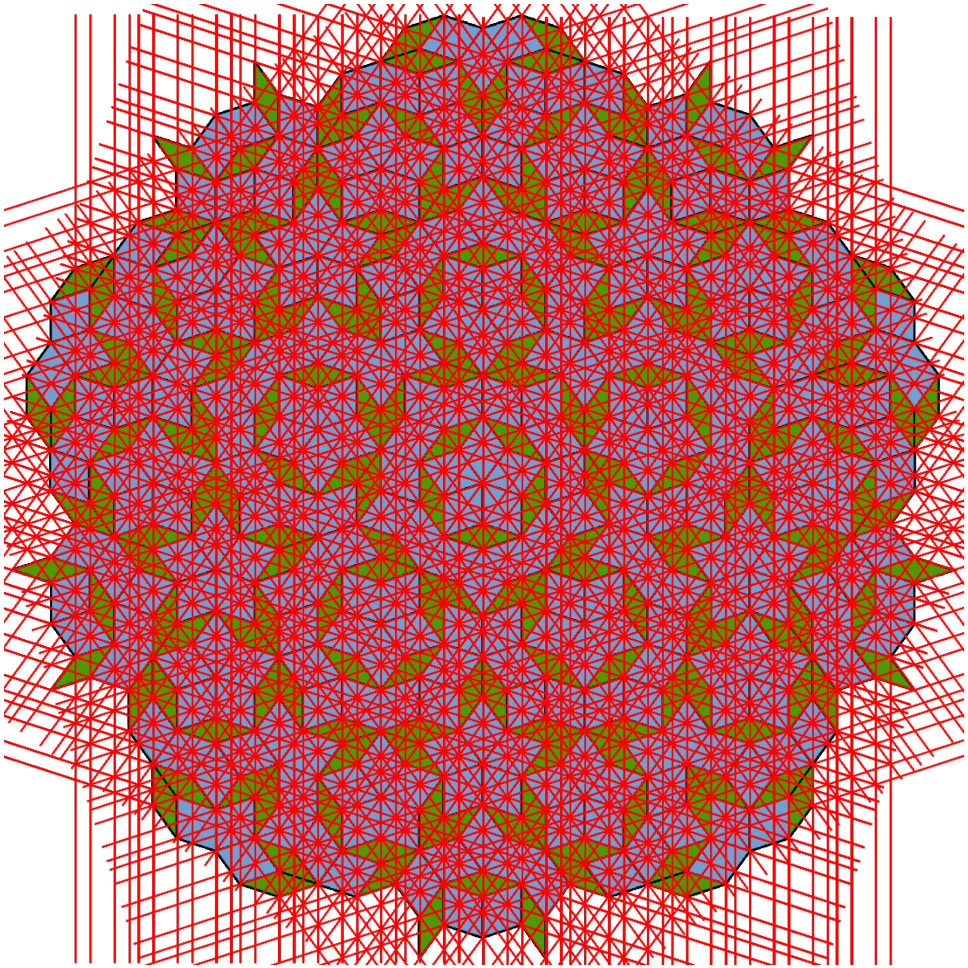
QLPs



QLPs



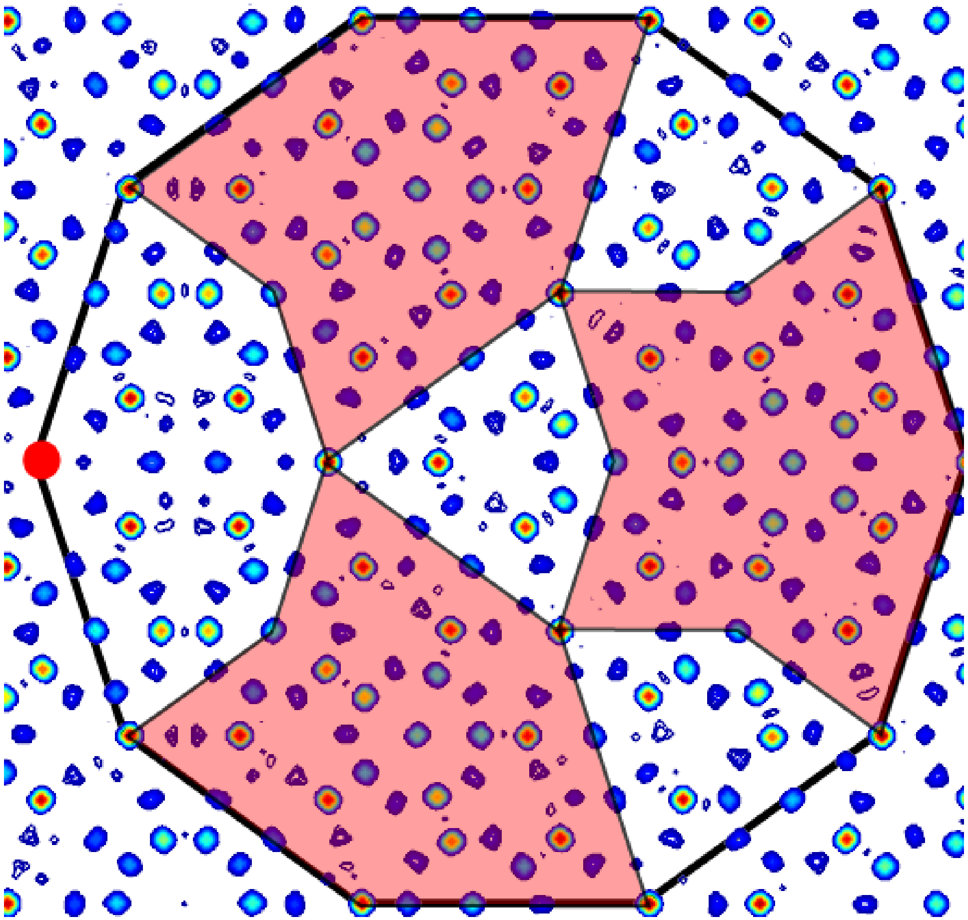
QLPs



- There are three typical interplanar distances between the QLPs: d_1, d_2, d_3
- $d_1 = 0.5 \cdot a(3-\tau)^{0.5}$,
- $d_2 = d_1/\tau$
- $d_3 = d_2/\tau$,
- $\tau \approx 1.618$
- Every second distance is d_2, distances d_1 and d_3 occur according to the Fibonacci sequence

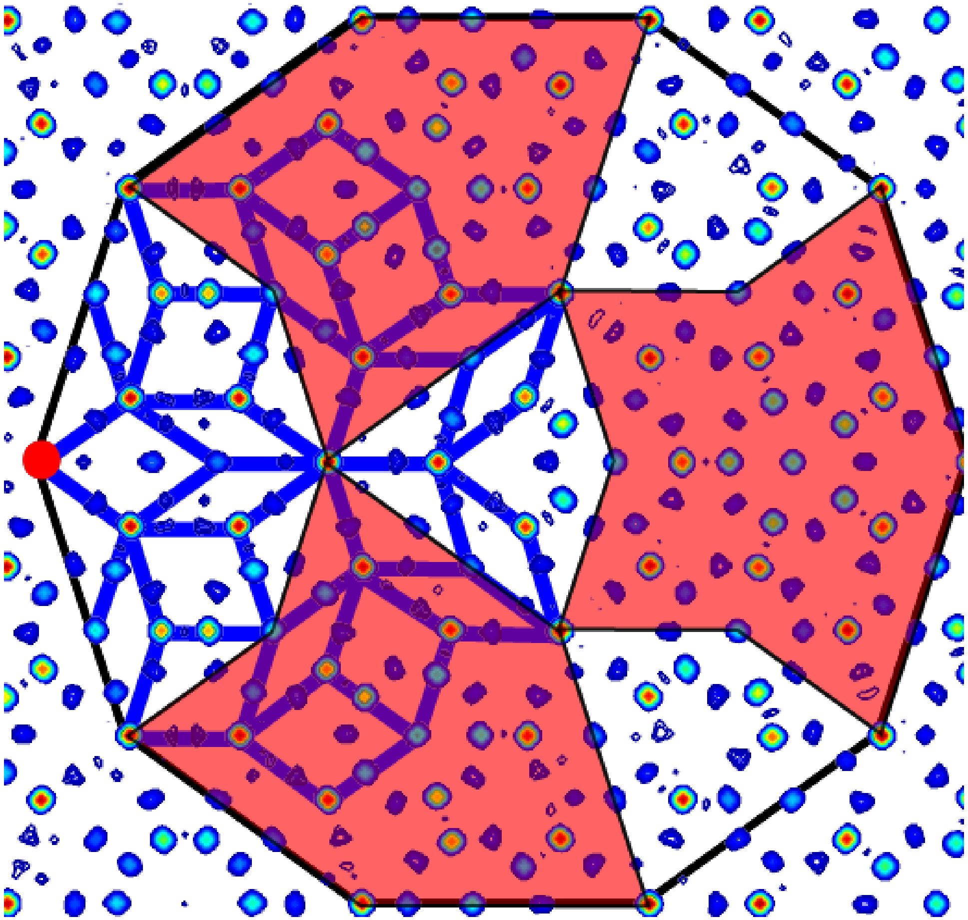
Hoffmann & Trebin, *Phys. Stat. Sol.* B (1992) ,**174** 304

QLPs – How about reality?



Kuczera *et. al, Acta Cryst B* (2012) **68** 578

QLPs – How about reality?



Kuczera *et. al, Acta Cryst B* (2012) **68** 578

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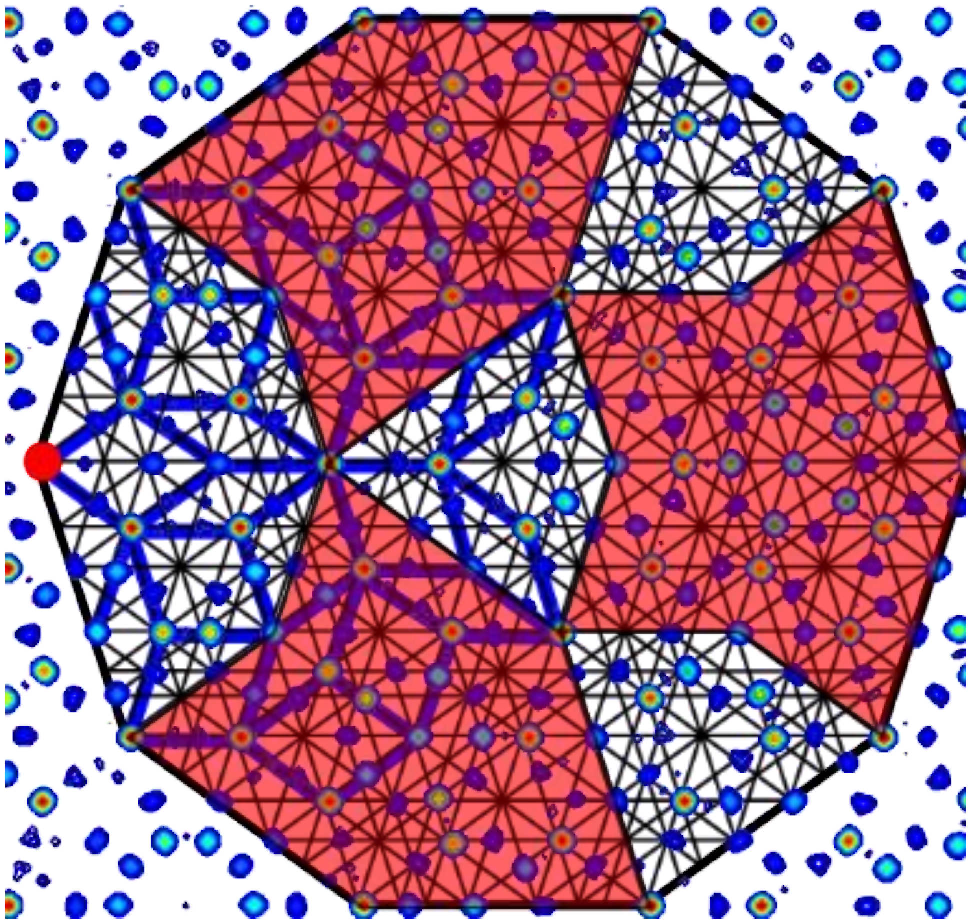
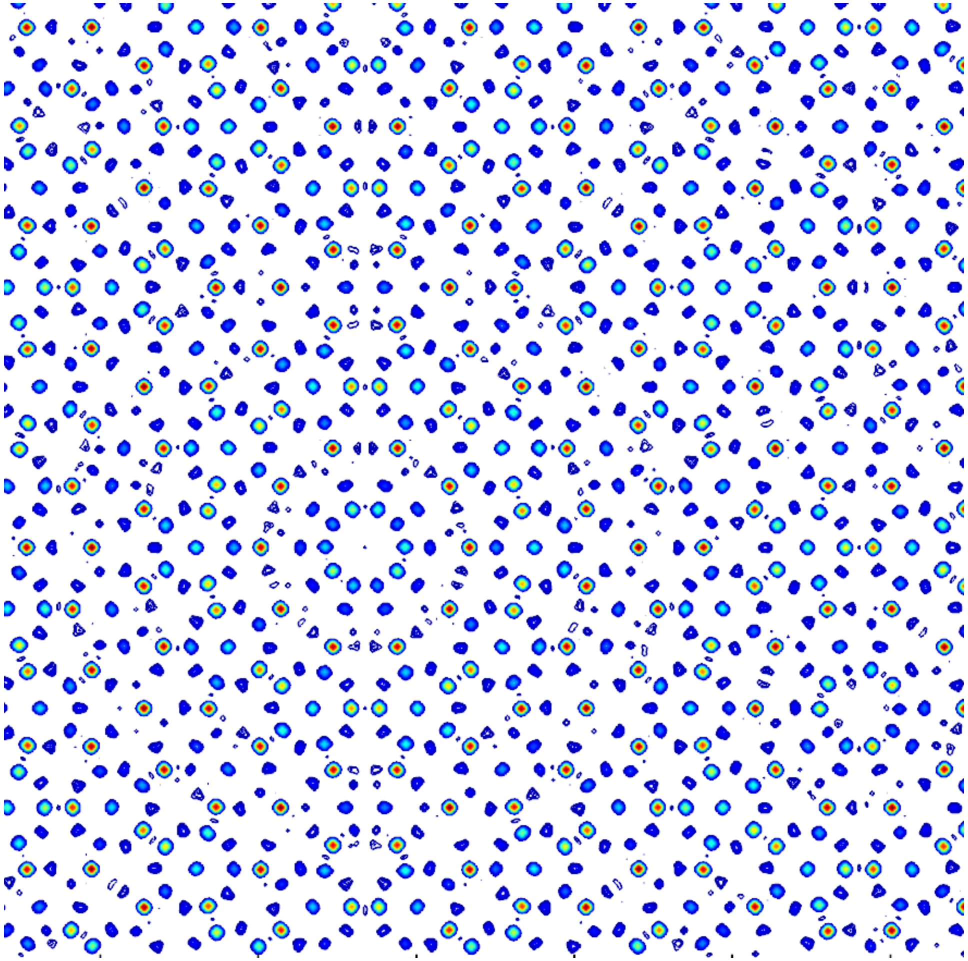


Kuczera *et. al, Acta Cryst B* (2012) **68** 578

QLPs – How about reality?



Kuczera *et. al, Acta Cryst B* (2012) **68** 578

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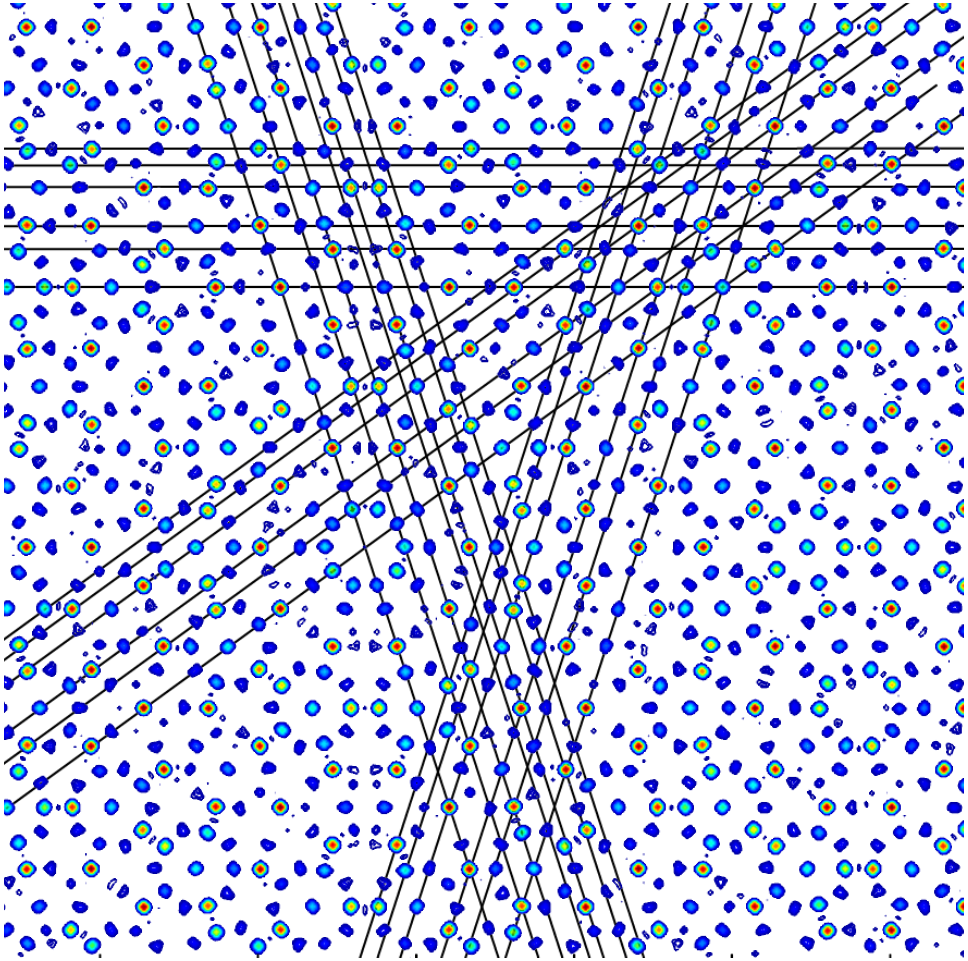

Kuczera *et. al, Acta Cryst B* (2012) **68** 578

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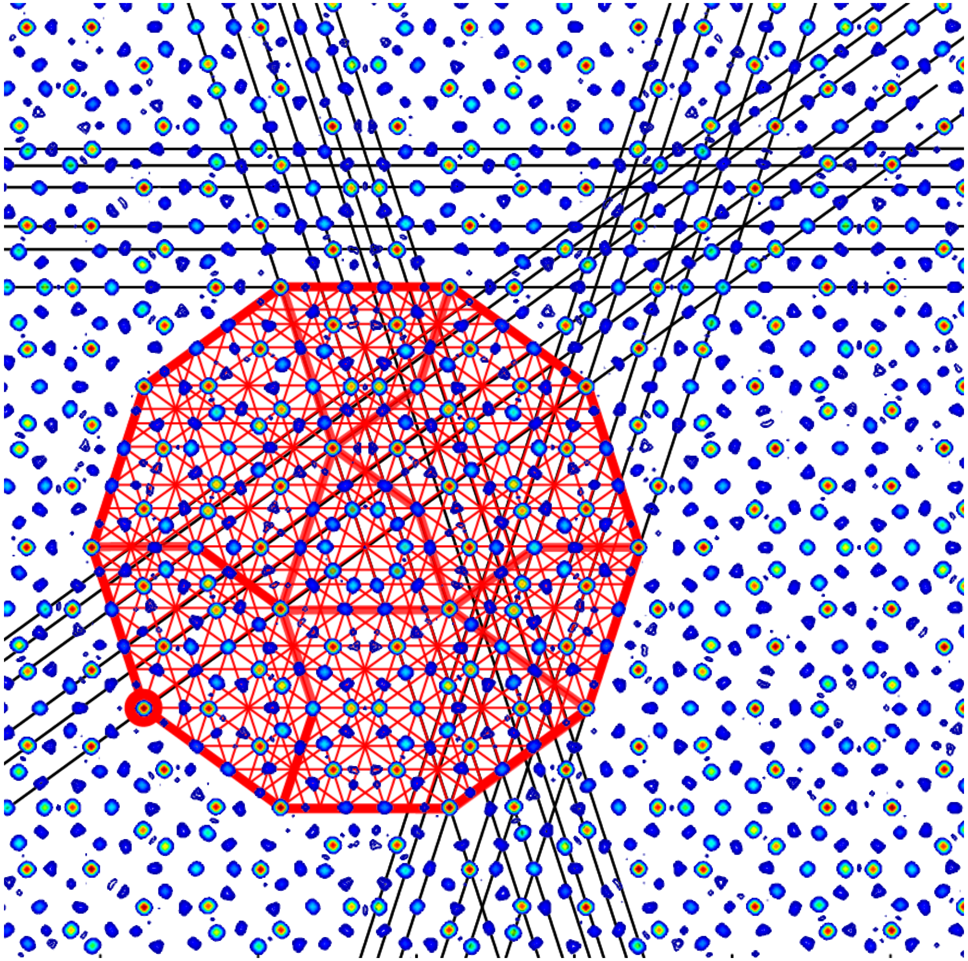

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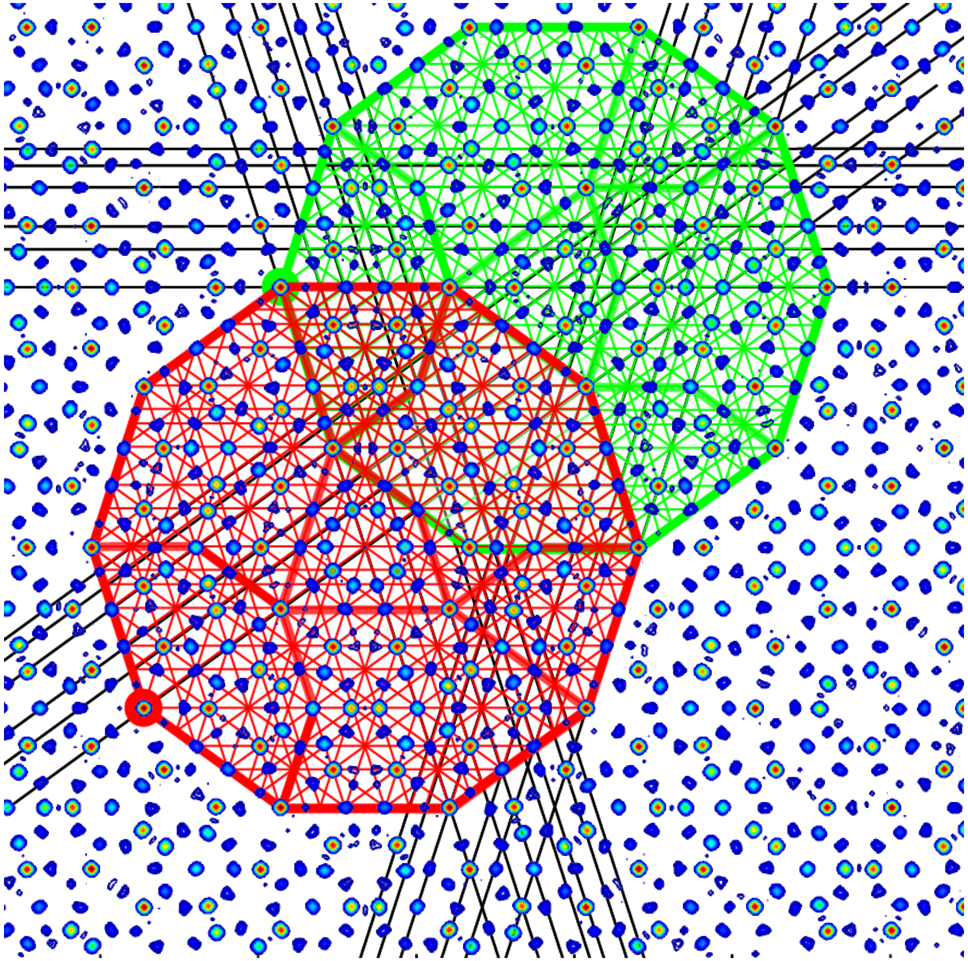

Kuczera *et. al, Acta Cryst B* (2012) **68** 578

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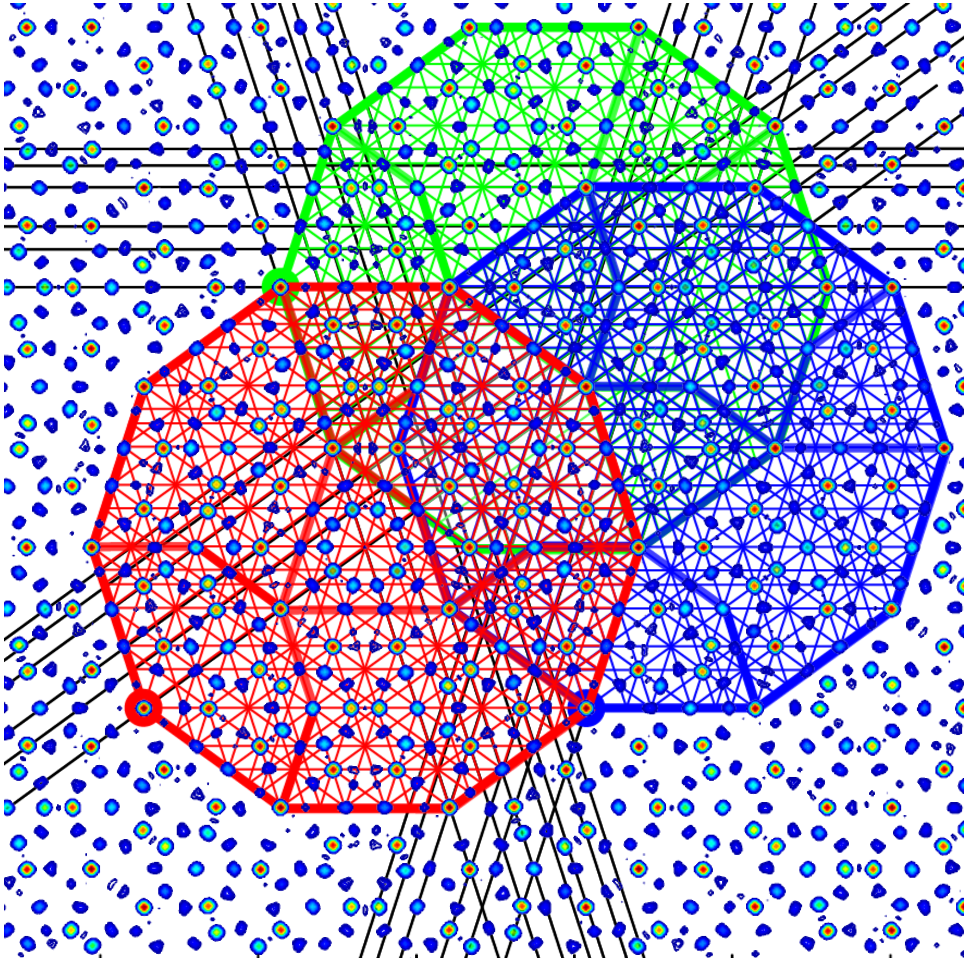
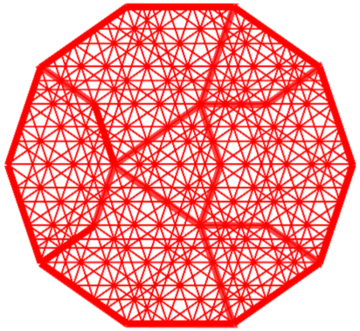
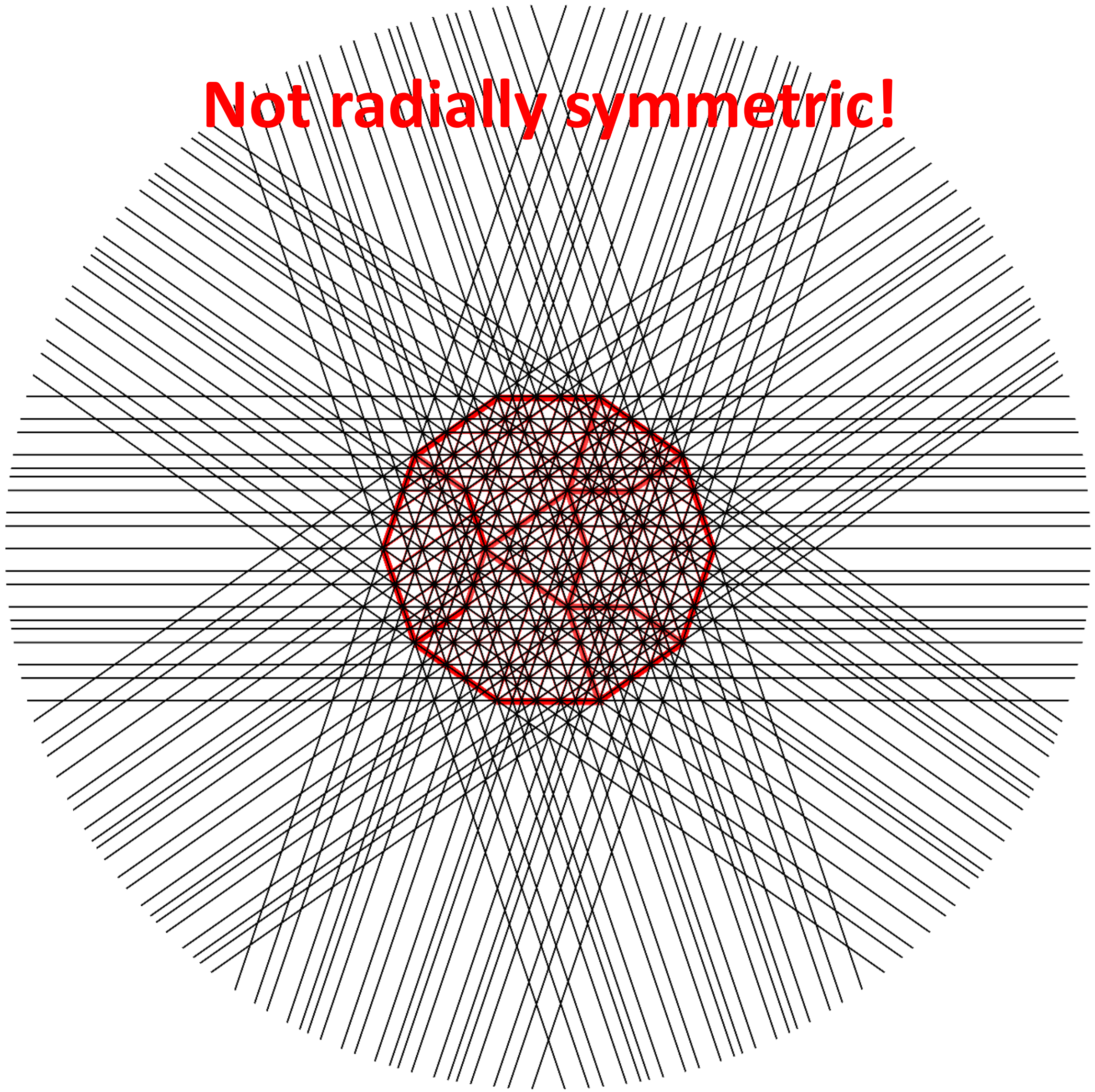


Kuczera *et. al, Acta Cryst B* (2012) **68** 578

A QLP – filed

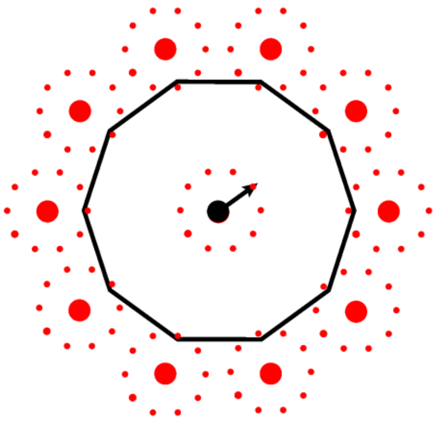


A QLP – filed

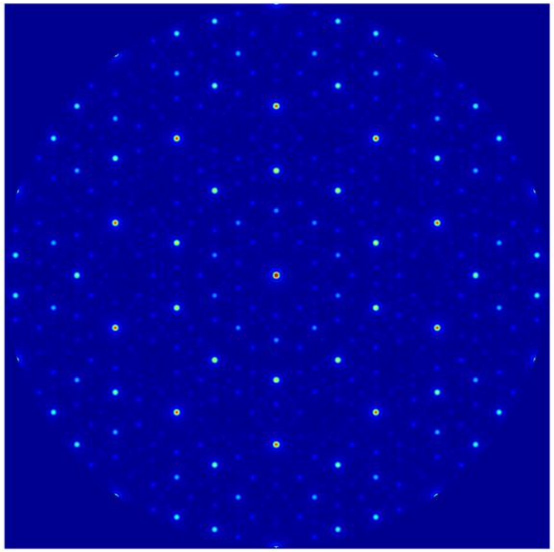


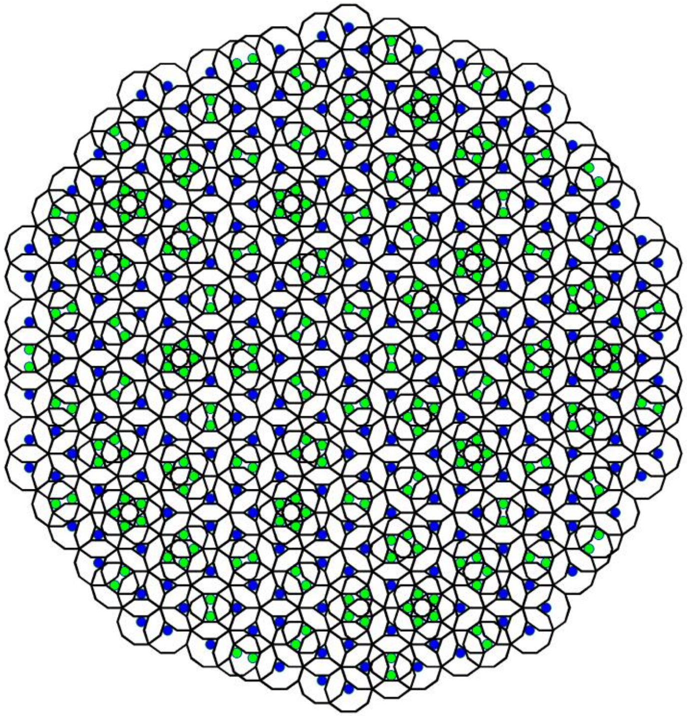
The model

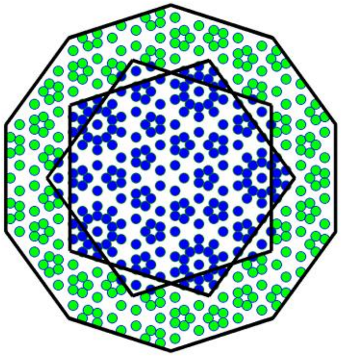
- It is favorable for the clusters to arrange in such a way, that QLPs are continued from cluster to cluster.
- Cluster interact via QLP field (virtual).
- Energy of a cluster is computed based on the MFA
- Every cluster feels the “average” QLP field produced by the remaining clusters.
- Such system is subjected to MC modeling.
- Two models:
  - infinite interaction range
  - finite interaction (r = 3)



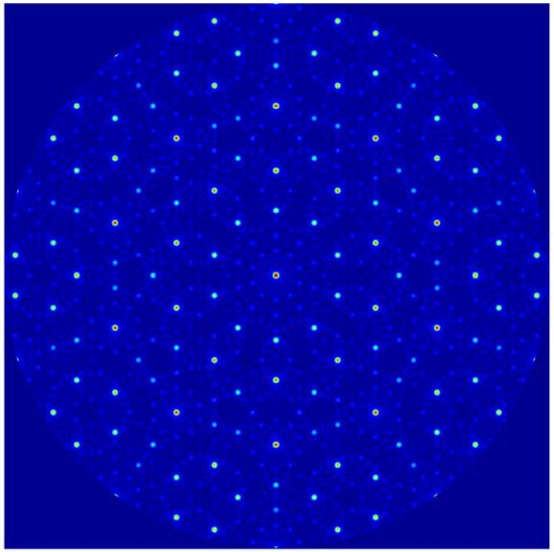
The two sublattices

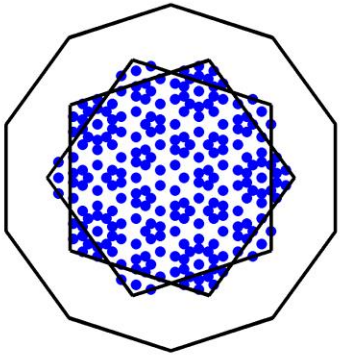


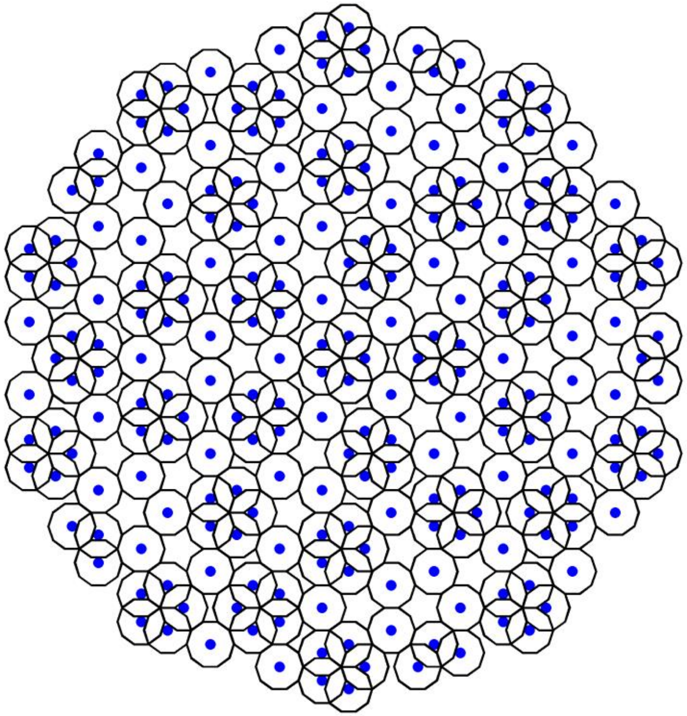




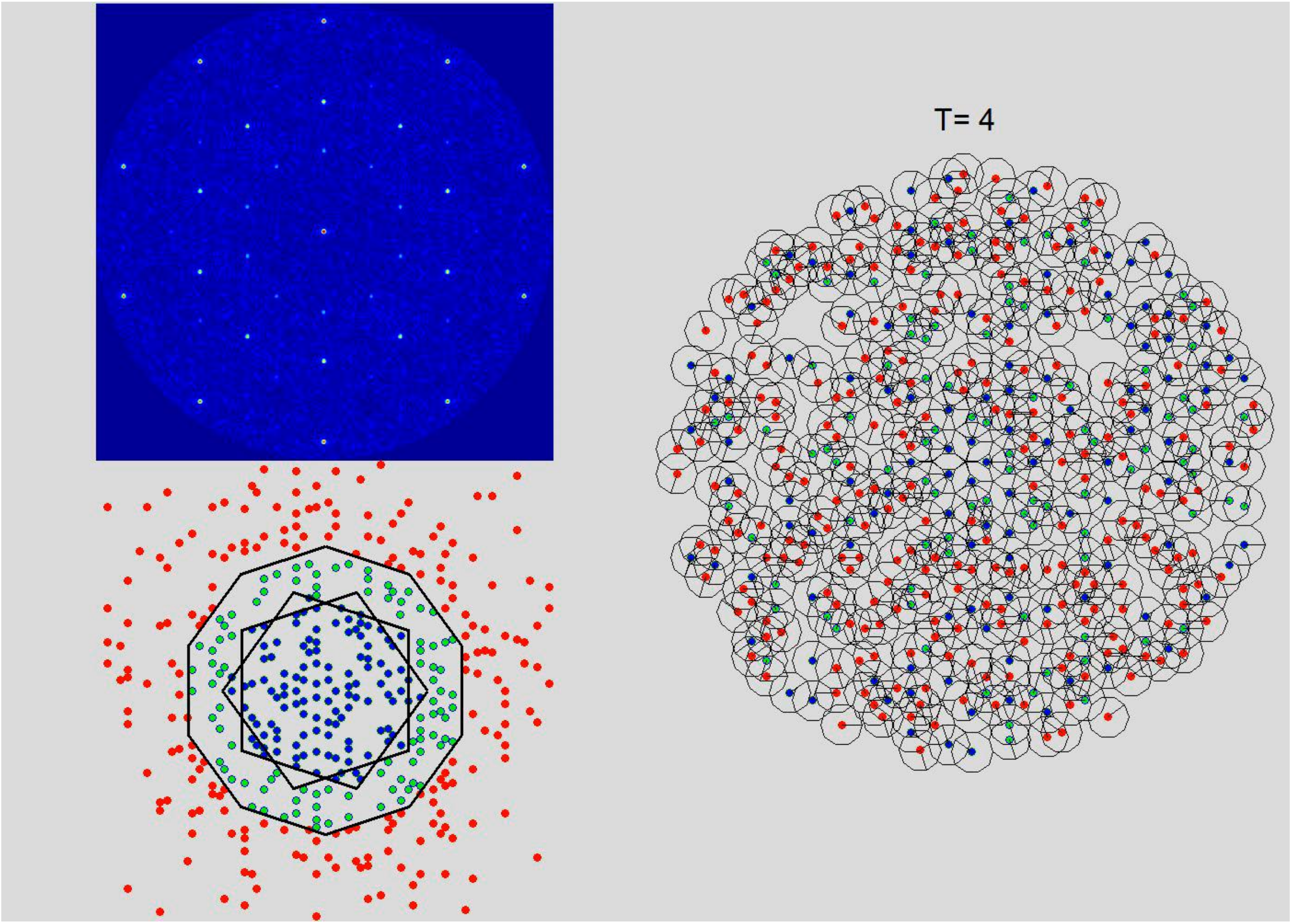
The two length-scales







Order-disorder pahse transition(s)



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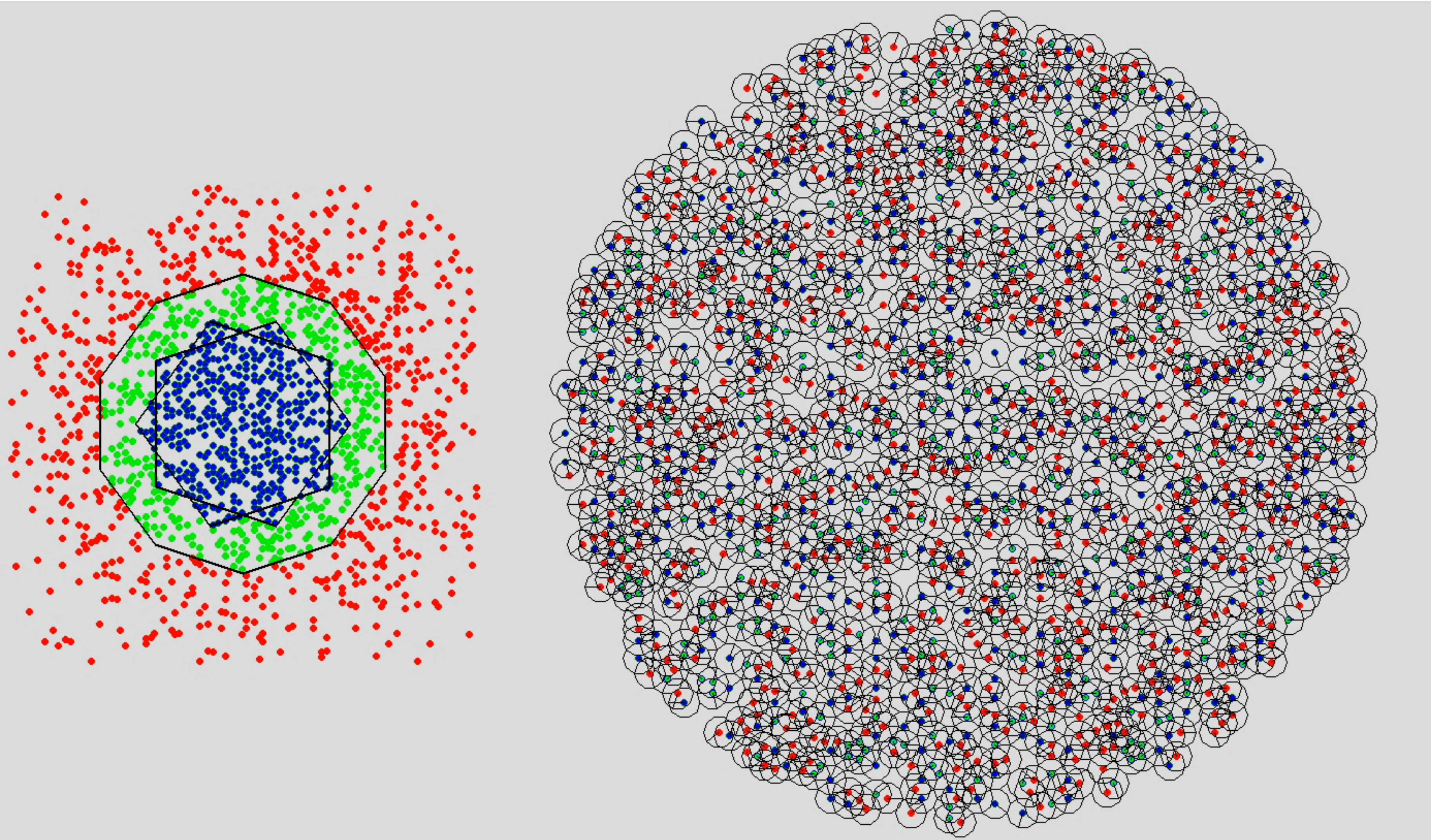
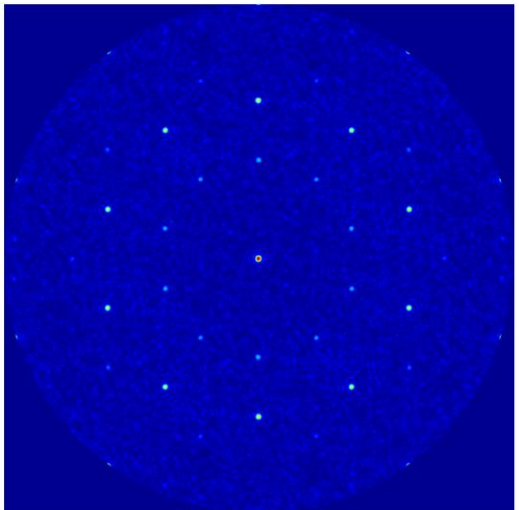
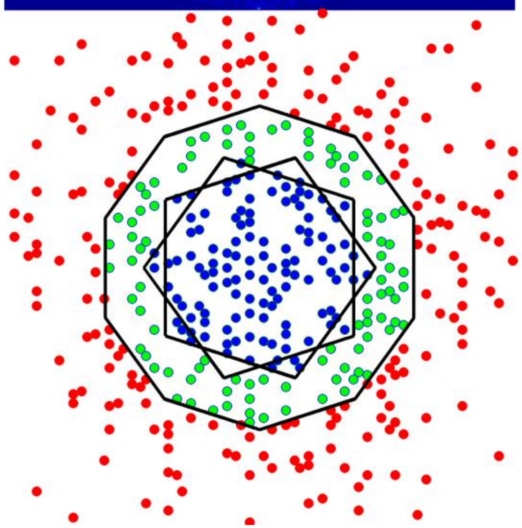
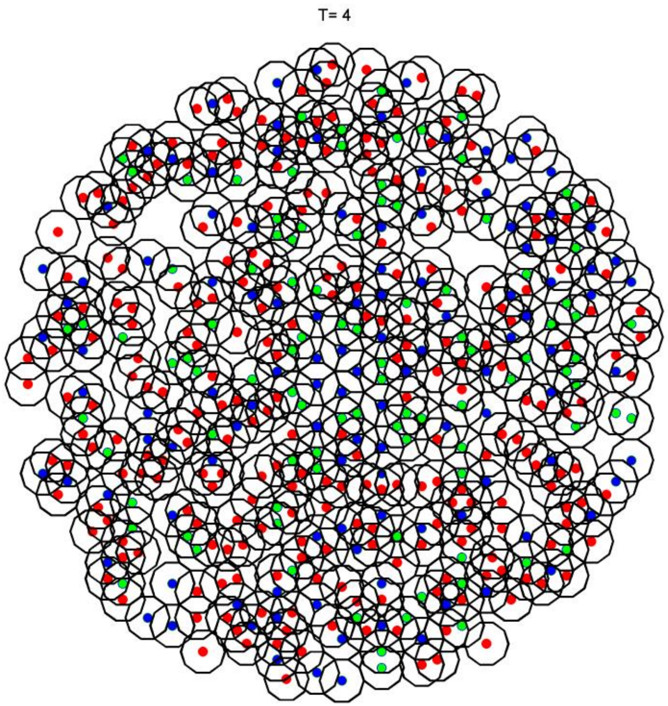


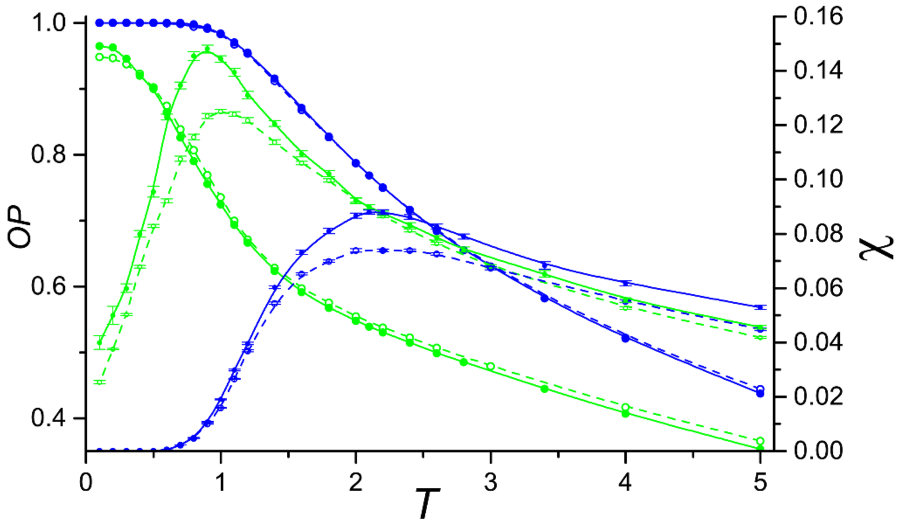
Order-disorder pahse transition(s)

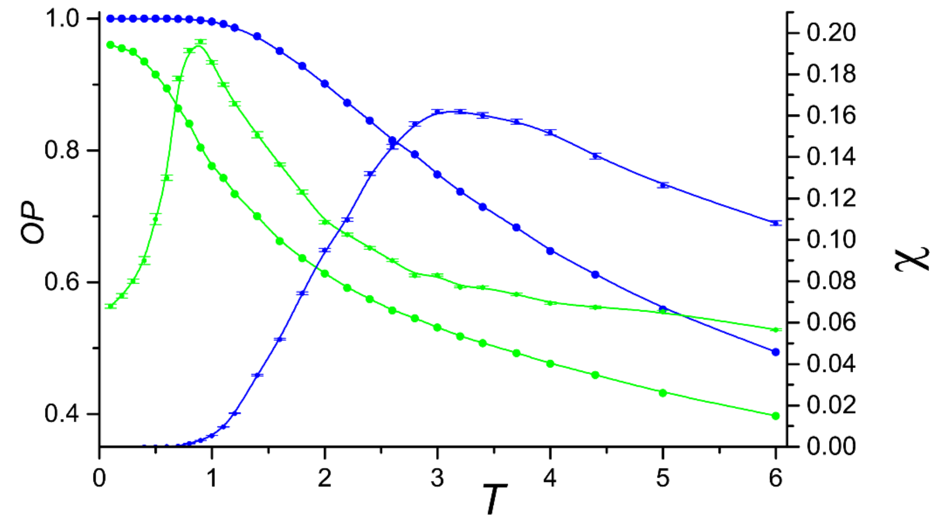






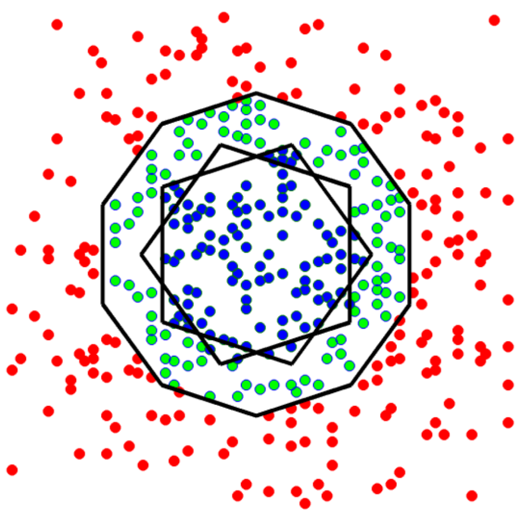
Order parameter, susceptibility





$N = 465, 1585$

$$\chi = \frac{1}{T}(\langle OP^2 \rangle - \langle OP \rangle^2)$$

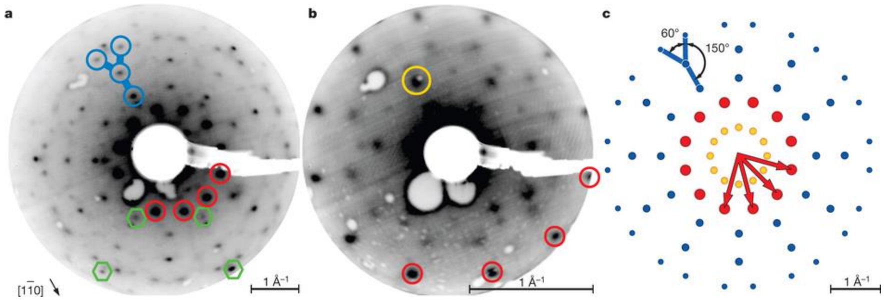


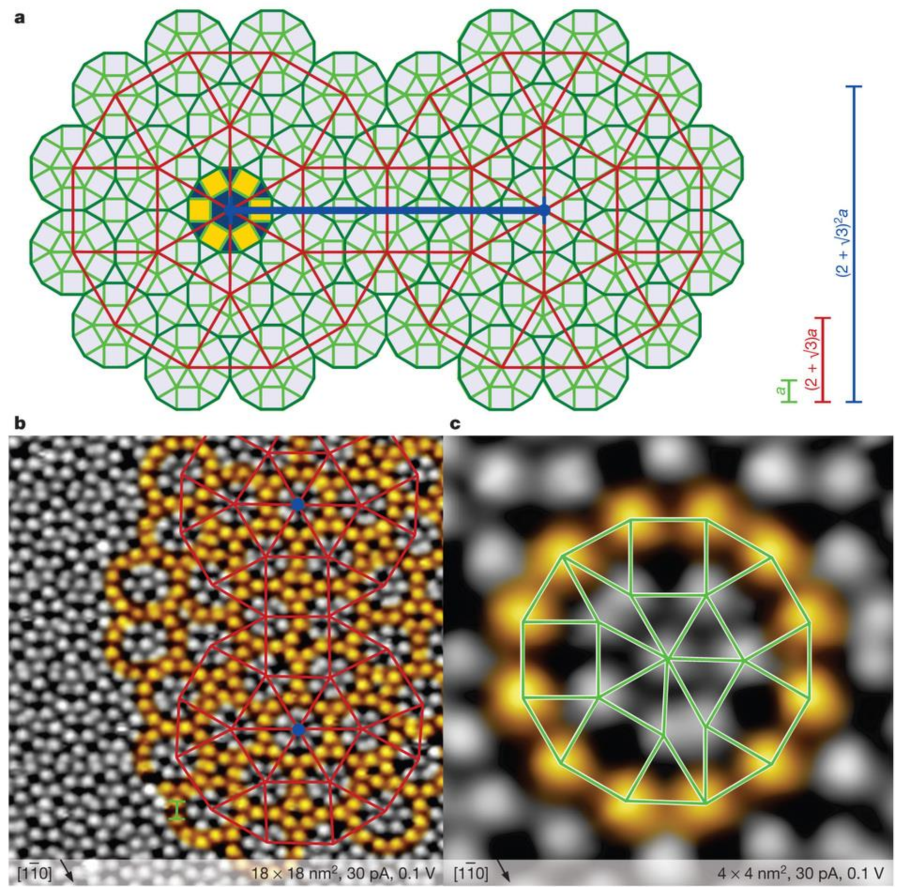
$N = 465$

$$\chi = \frac{1}{T}(\langle OP^2 \rangle - \langle OP \rangle^2)$$

Quasicrystals – recent discoveries

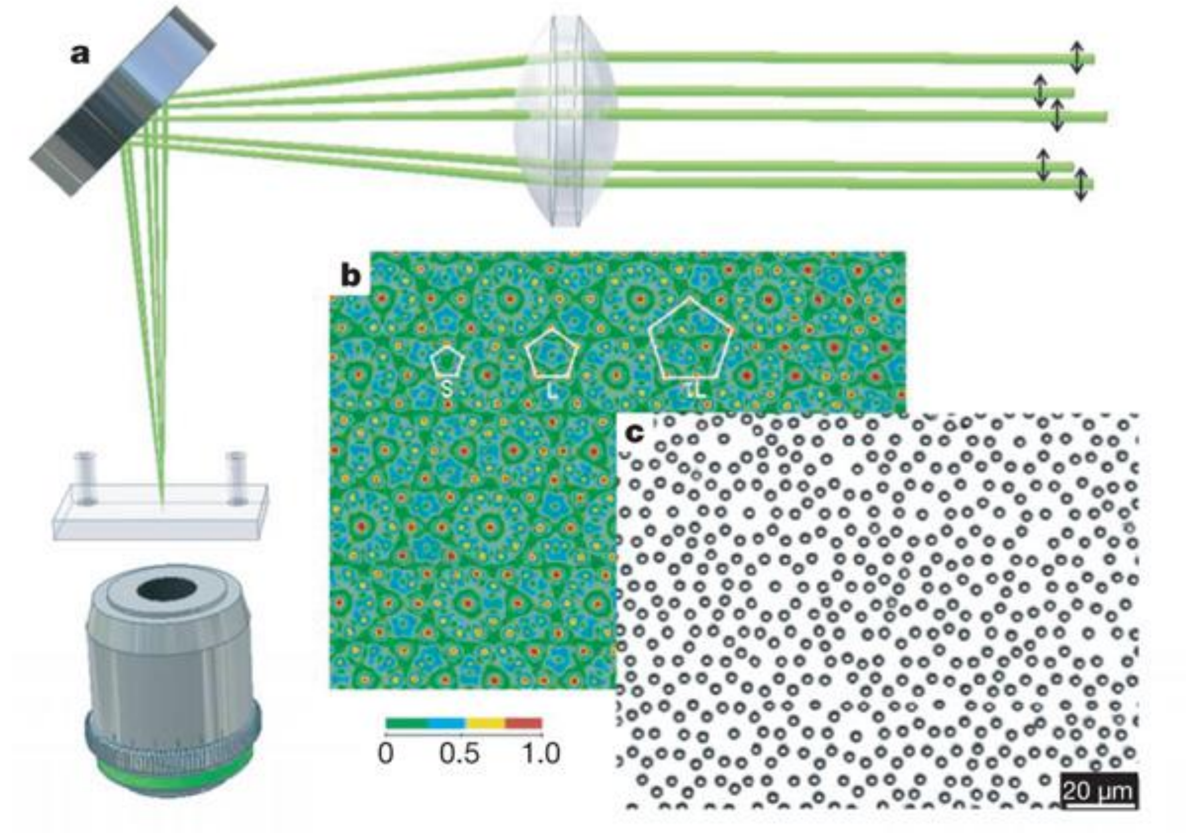
Quasicrystals from oxide surfaces
$BaTiO_3$ on Pt(111)





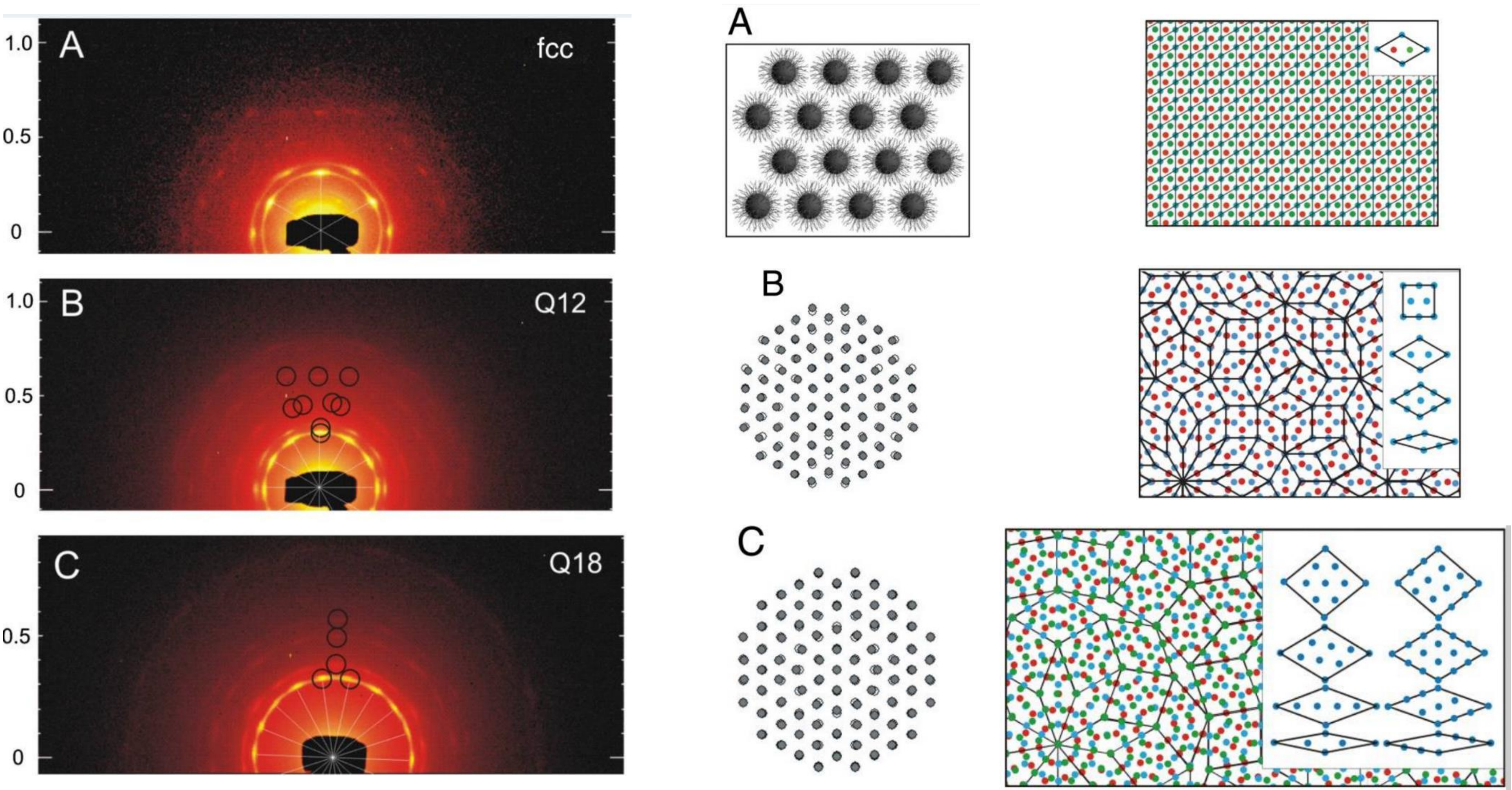
S. Forster *et al.,* Nature **502** (2013), 215-218

Self-assembly of “soft” quasicrystala in laser potential



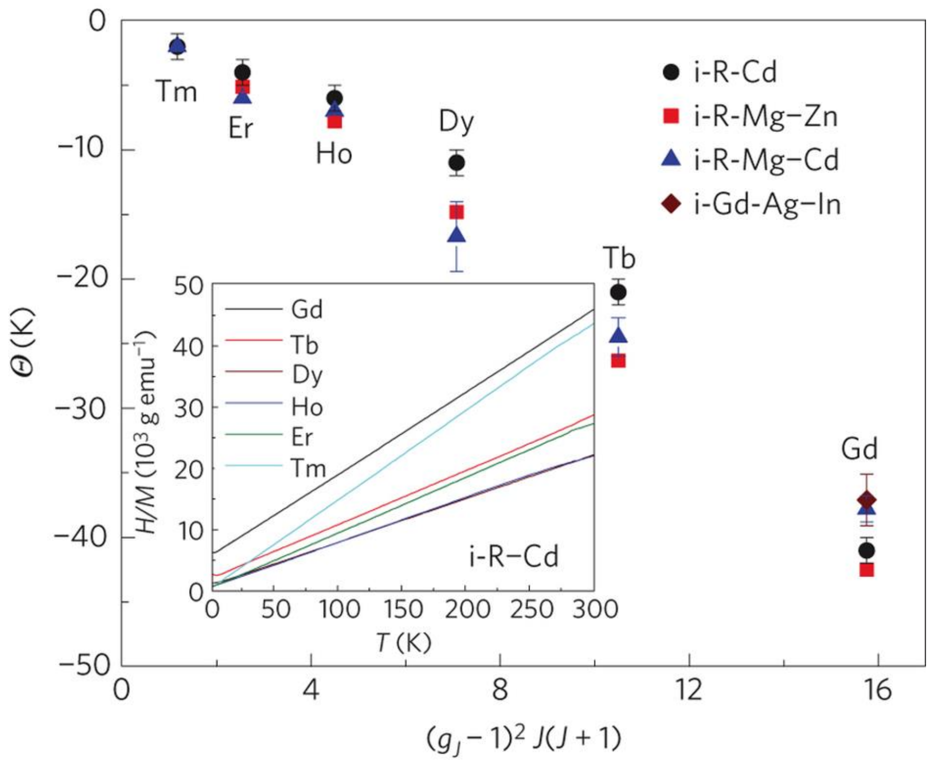
J. Mikhael et al., Nature 454 (2008), 5501-504

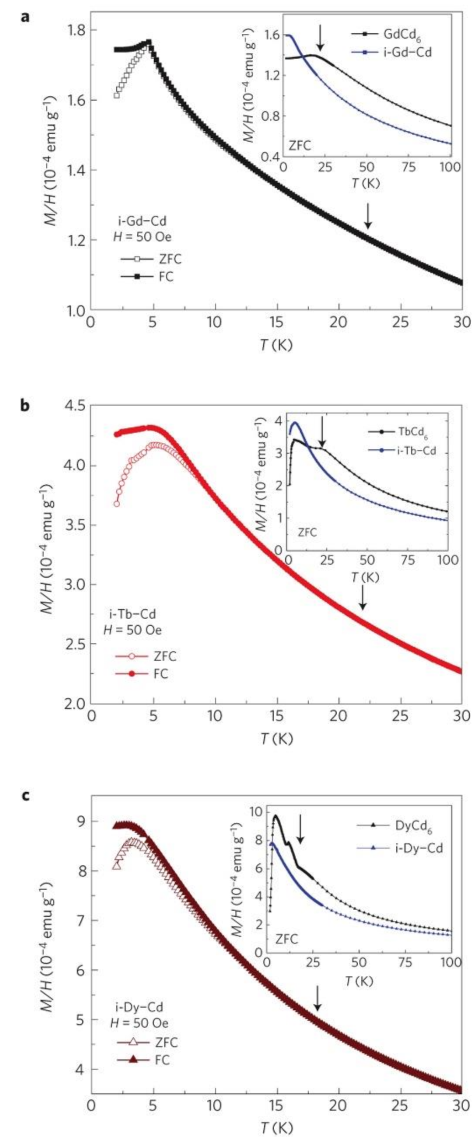
Micles forming
12-fold and 18-fold quasicrystals



S. Fischer et al., PNAS 108 (2011), 1810-1814

RE-Cd magnetic QC low-T spin glass





QC: $RCd_{7.75(0.25)}$
Approximant: RCd_6

A. Glodman et al., Nature Materials 12 (2013), 714-718)

Summary

- The structure of DQC can be refined in the RPT framework – "two unit tiles".
- Using the concept of QLP field and MFA it is possible to obtain a quasiperiodic ground state.
- There are two unlocking phase transitions for the two length scales in the system.
- The key features of the model are:
    - Asymmetricity of the effective interactions.
    - Interaction range – beyond nearest neighbors
- The QLP field computed in a self consistent way
- QLPs could be responsible for propagation of LRO

Acknowledgements

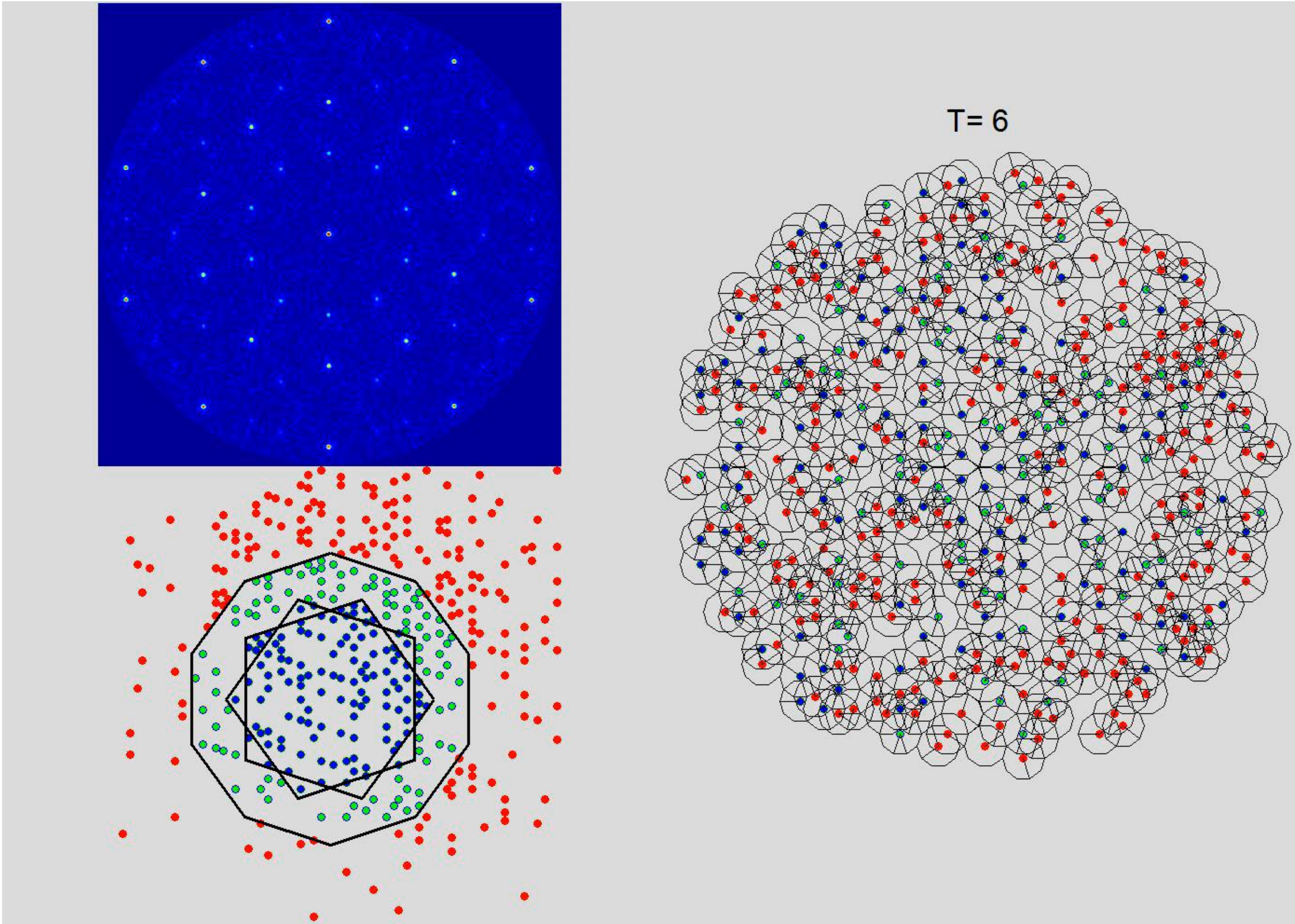
- Group in Krakow:
  - Janusz Wolny, Radoslaw Strzałka, Maciej Chodyń
- Group in Zurich:
  - Walter Steurer, Julia Dshemuchadse, Taylan Ors, Frank Fleisher
- SNBL scientists:
  - Phil Pattison, Dmitry Chernyshov, Vadim Dyadkin
- Founding:
  - SNF
  - SCIEX
  - NCN
- YOU for your attention

The ongoing fight: *E vs. S*?

$$F = E - TS$$

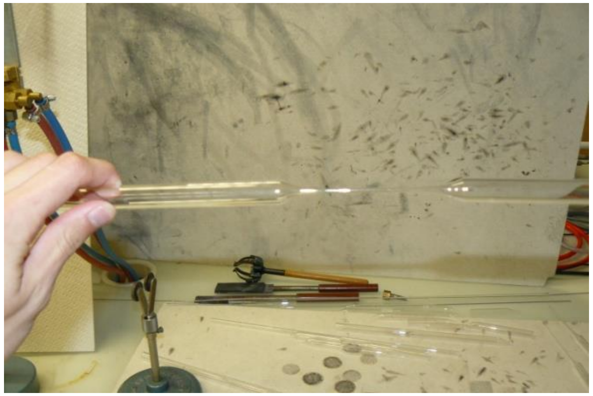
- Each defect increases both *E* and *TS* terms
- Entropy stabilization:
  - Random tiling at high *T*
  - Approximant structure at low *T*

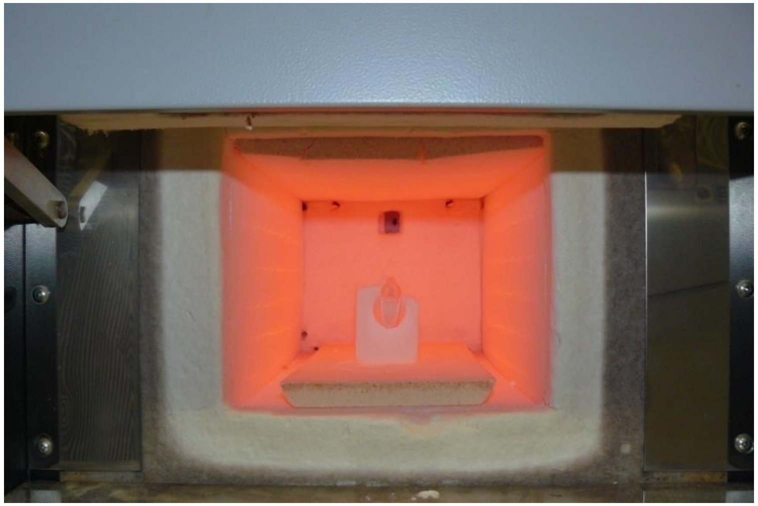
- Energy stabilization:
  - Quasiperiodic long-range ordered ground state (stable at 0K)
  - Possibility of order-disorder phase transition – so called *unlocking* phase transition


T= 6

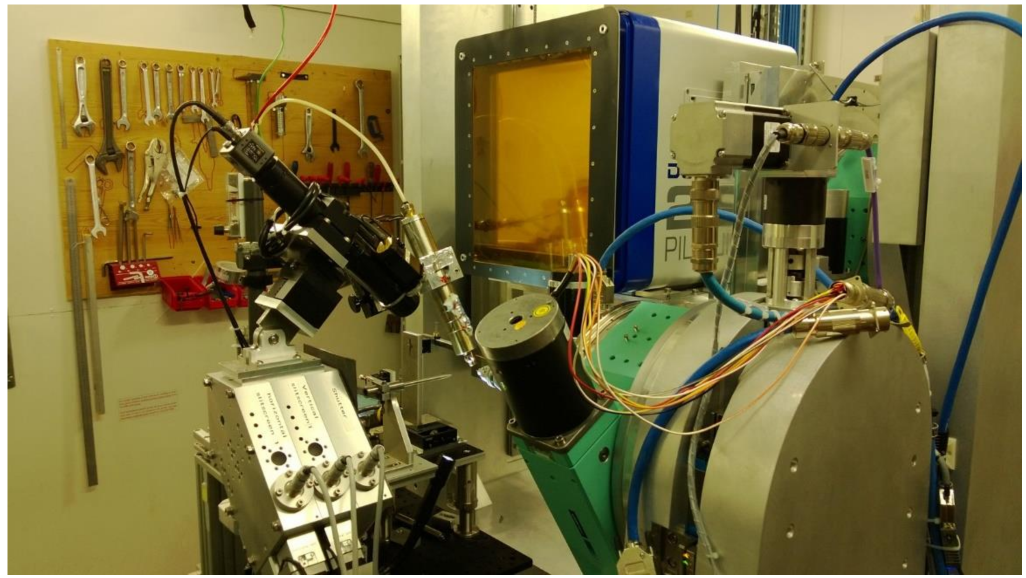
Single crystal growth

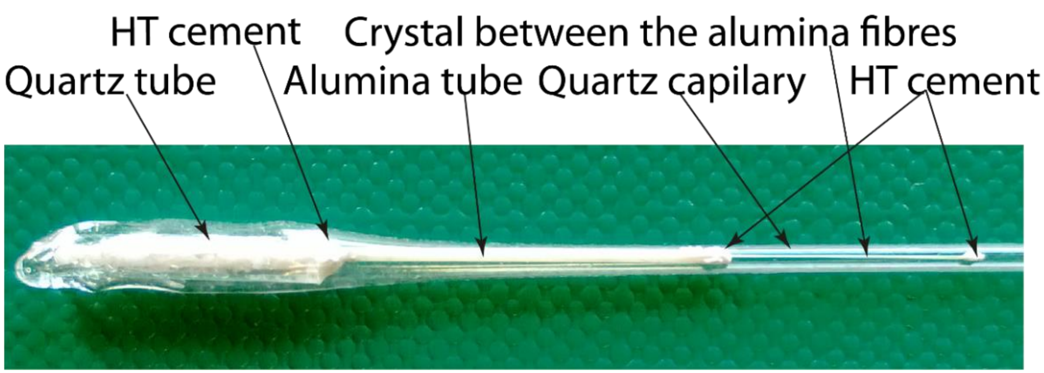
Single crystal growth



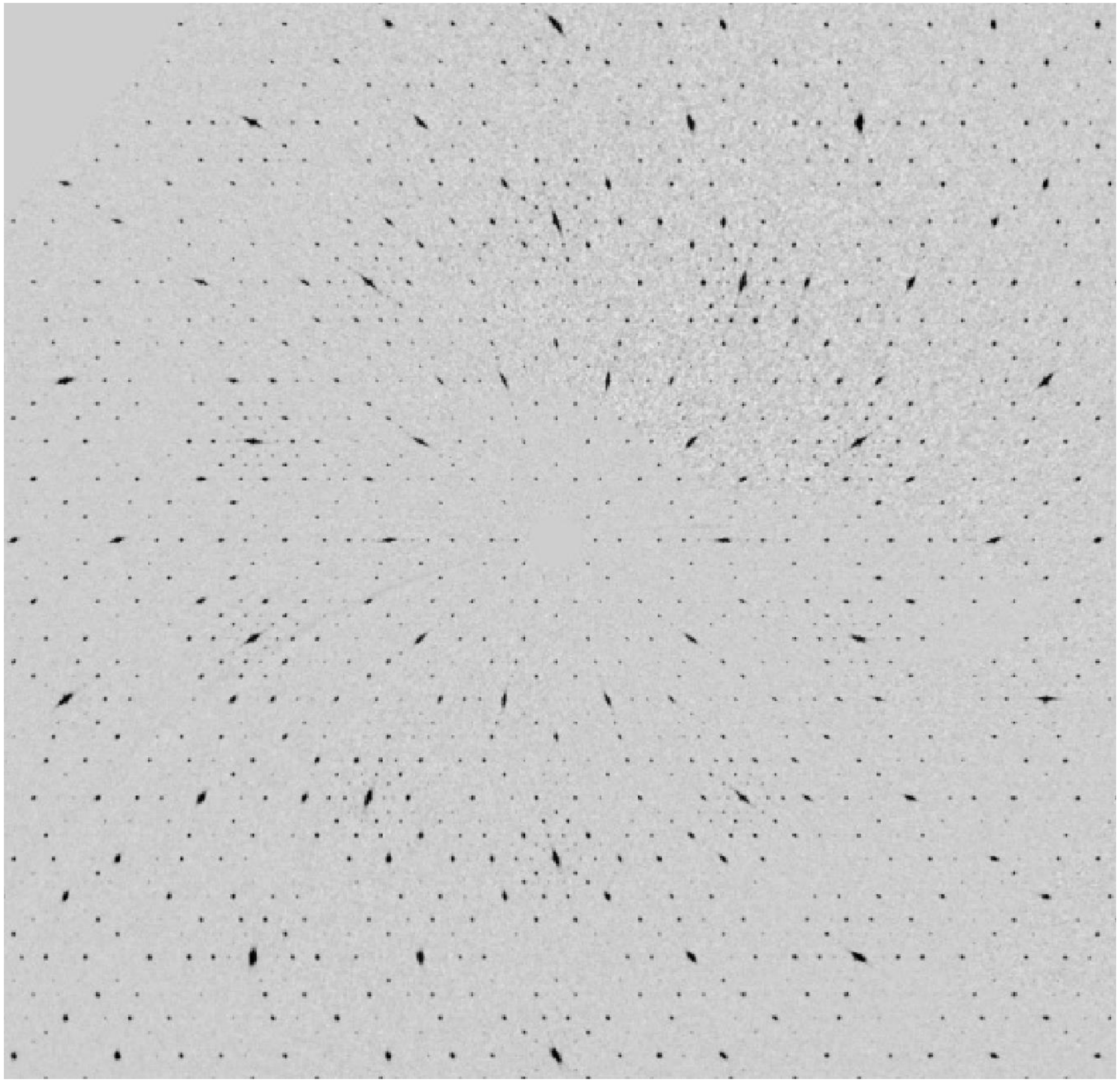


Diffraction measurements @SNBL, Grenoble

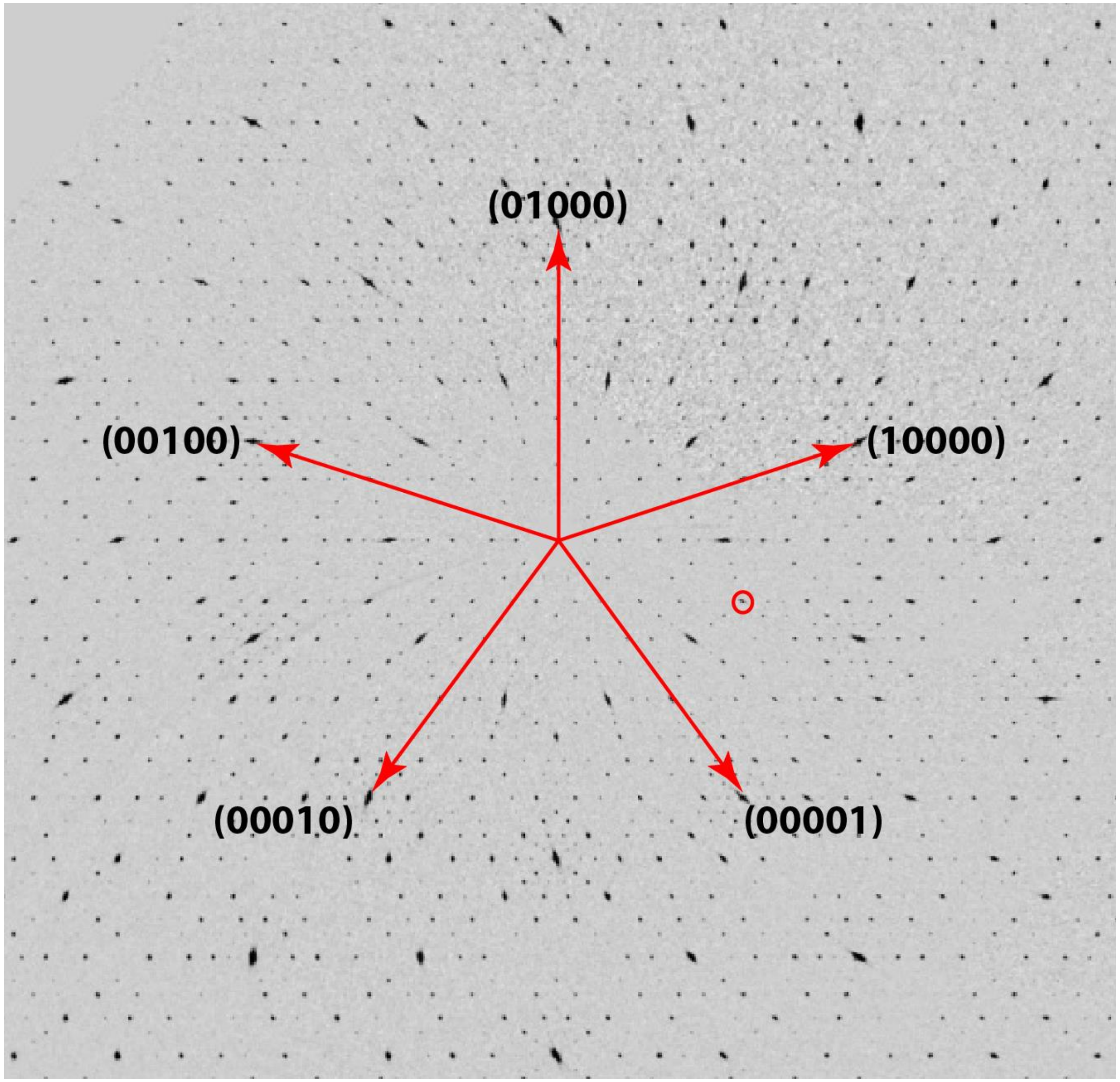




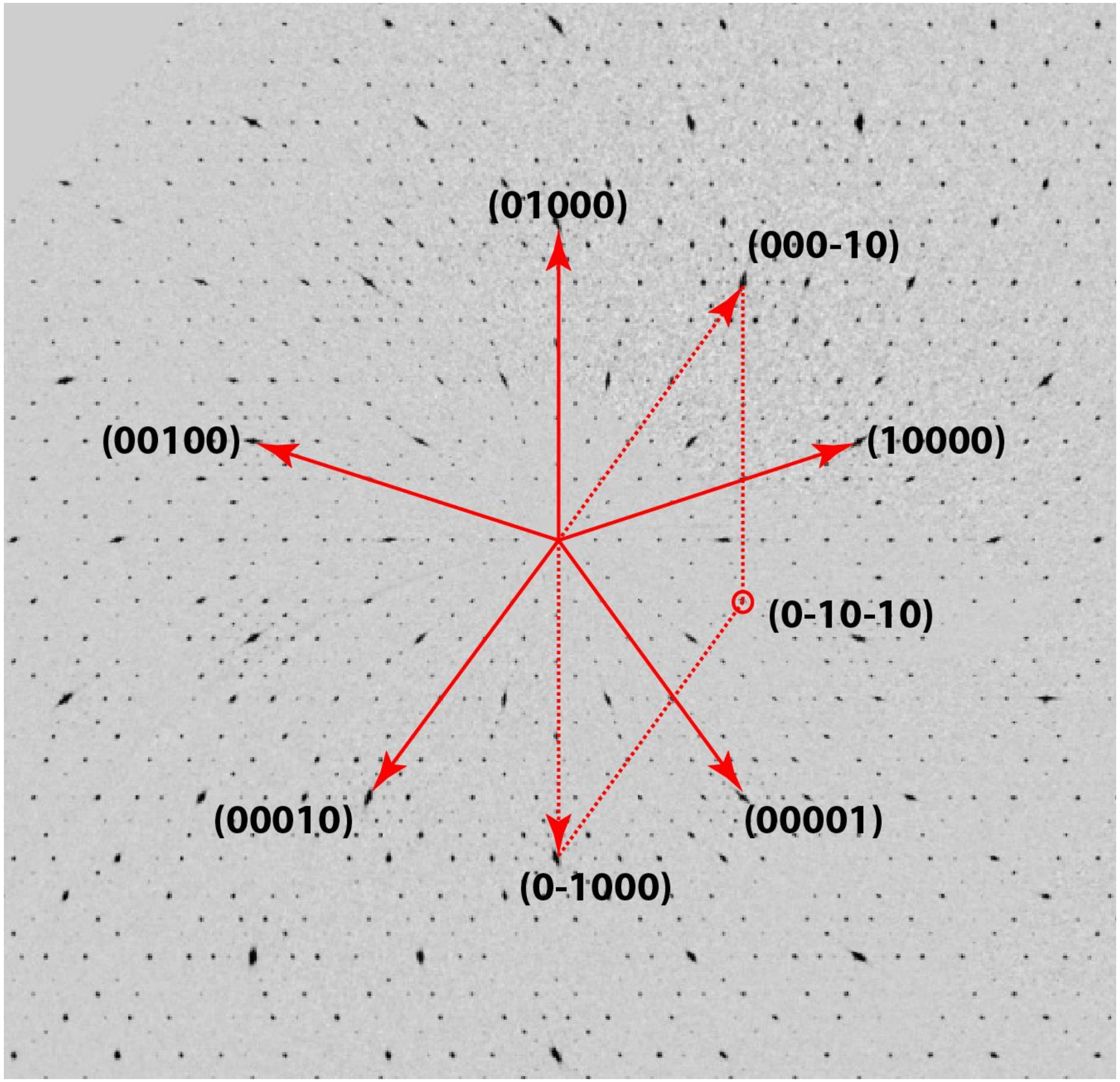
Reciprocal space basis selection



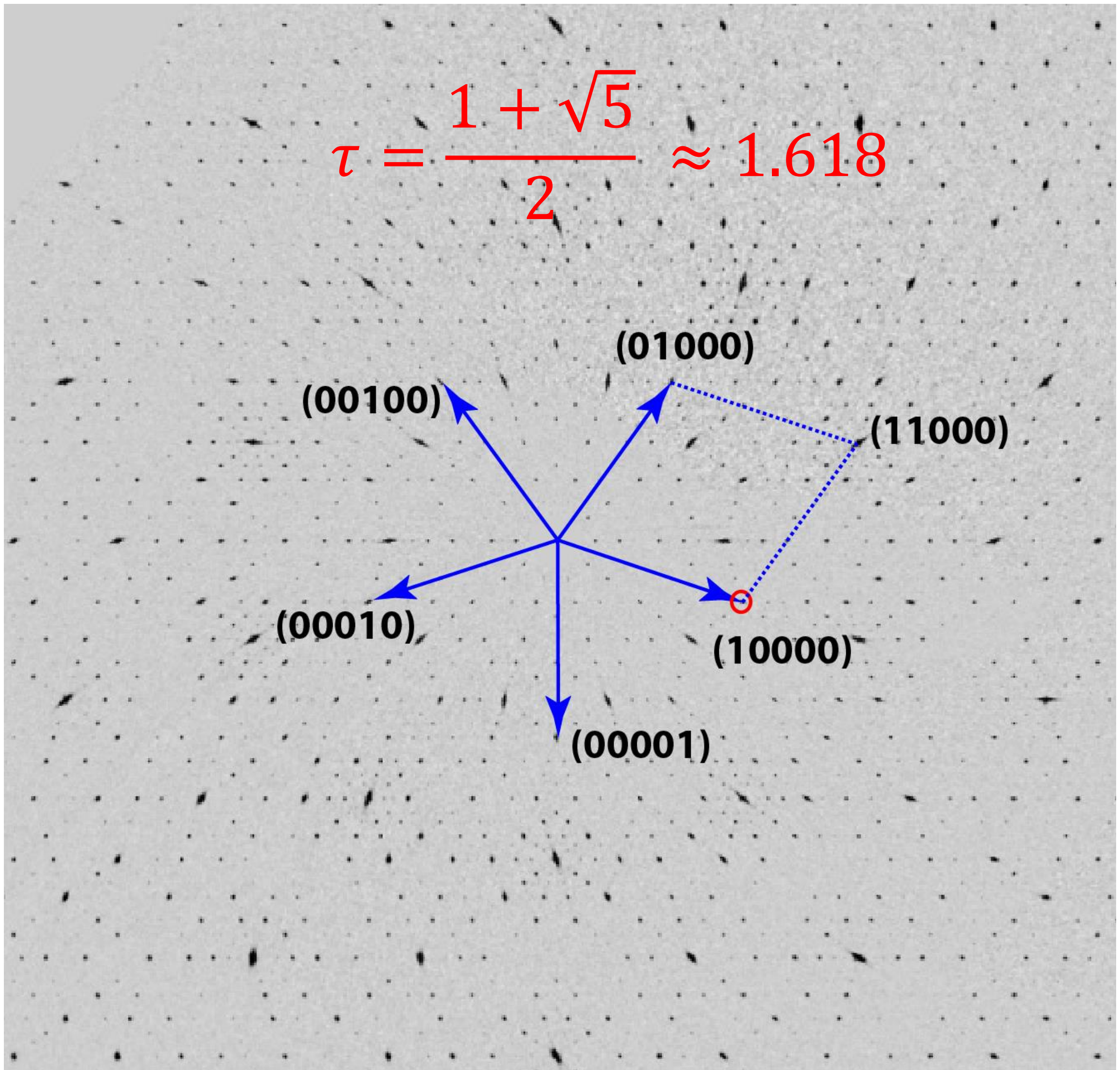
Reciprocal space basis selection



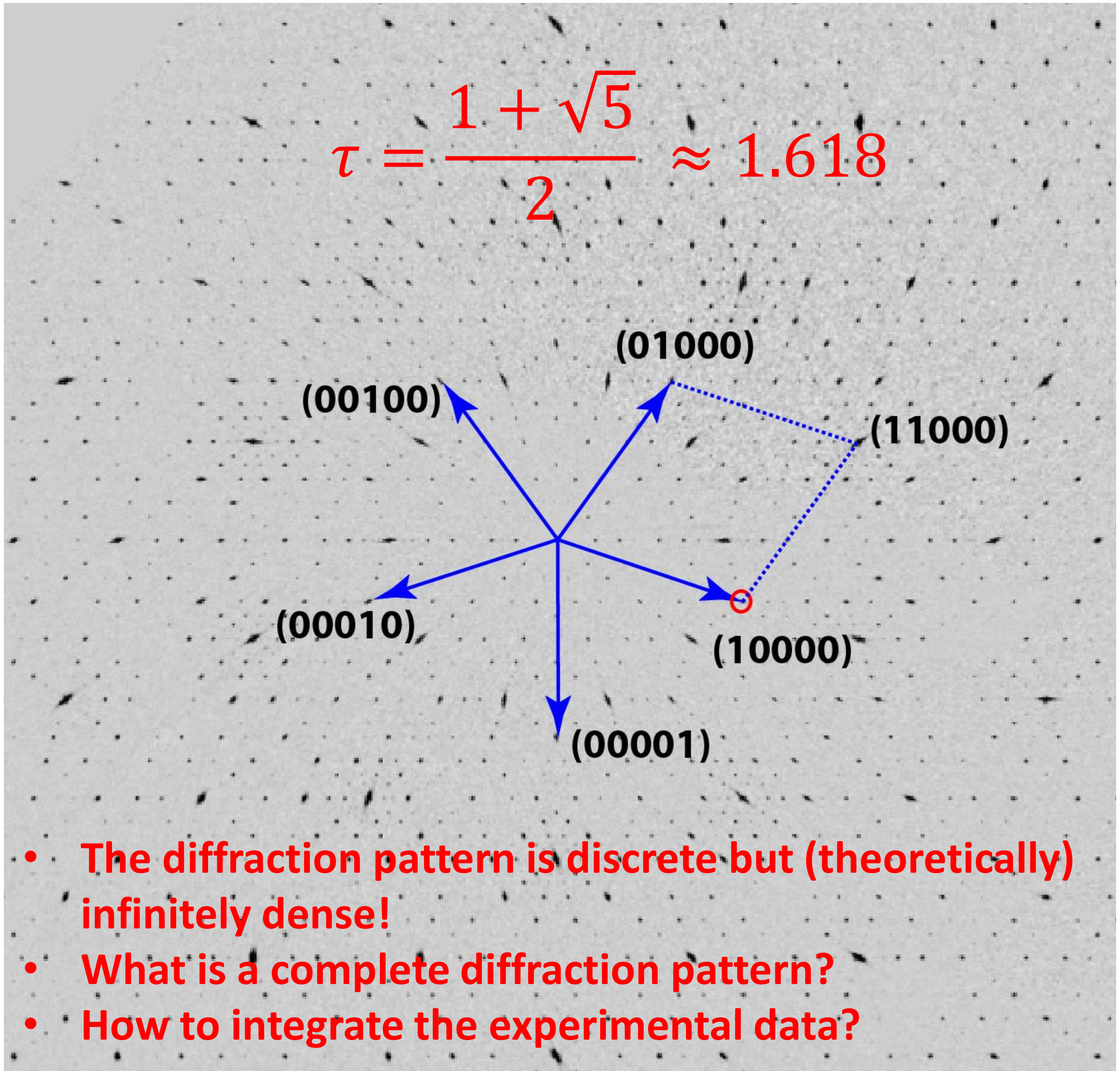
Reciprocal space basis selection



Reciprocal space basis selection



Reciprocal space basis selection



$$\tau = \frac{1+\sqrt{5}}{2} \approx 1.618$$

- **The diffraction pattern is discrete but (theoretically) infinitely dense!**
- **What is a complete diffraction pattern?**
- **How to integrate the experimental data?**

Structure solution
Charge Flipping Algorithm & SUPERFLIP

$$I(\mathbf{k}) = |F(\mathbf{k})|^2 \xrightarrow{FT} g(\mathbf{r})$$ *Patterson function*

Structure solution
Charge Flipping Algorithm & SUPERFLIP

$$I(\mathbf{k}) = |F(\mathbf{k})|^2 \xrightarrow{\textit{FT}} g(\mathbf{r})$$ *Patterson function*

$$|F(\mathbf{k})| \xrightarrow{\textit{Random phases}} |F(\mathbf{k})|\exp(\mathrm{i}\phi_{\mathbf{k}})$$

Structure solution
Charge Flipping Algorithm & SUPERFLIP

$$I(\mathbf{k}) = |F(\mathbf{k})|^2 \xrightarrow{\textit{FT}} g(\mathbf{r})$$ *Patterson function*

$$|F(\mathbf{k})| \xrightarrow{\textit{Random phases}} |F(\mathbf{k})|\exp(\mathrm{i}\phi_{\mathbf{k}}) \xrightarrow{FT^{-1}} \rho(\mathbf{r})$$

$$\rho(\mathbf{r}) \downarrow |\rho(\mathbf{r})|$$

Structure solution
Charge Flipping Algorithm & SUPERFLIP

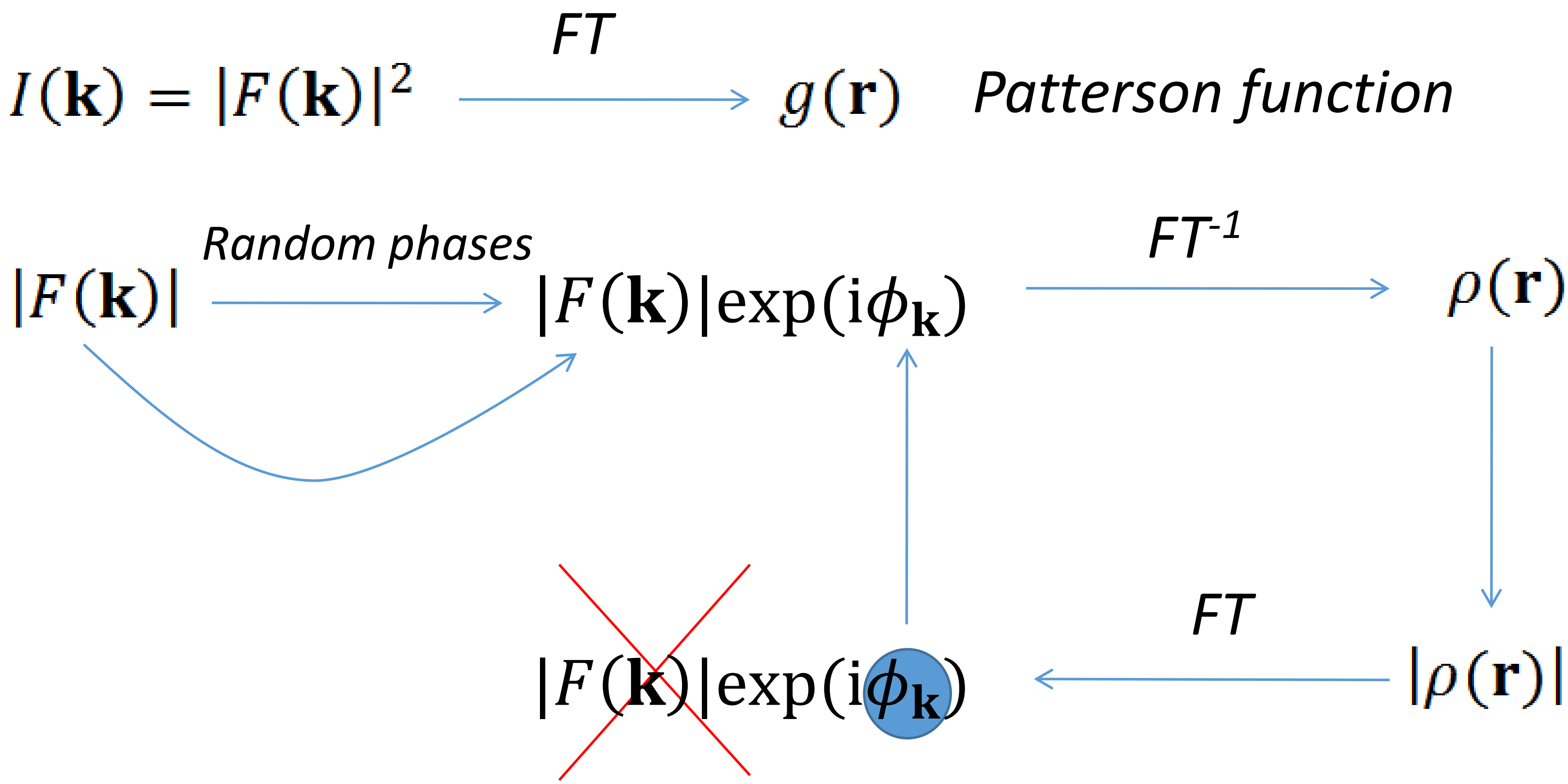
$$I(\mathbf{k}) = |F(\mathbf{k})|^2 \xrightarrow{\textit{FT}} g(\mathbf{r})$$ *Patterson function*

$$|F(\mathbf{k})| \xrightarrow{\textit{Random phases}} |F(\mathbf{k})|\exp(\mathrm{i}\phi_{\mathbf{k}}) \xrightarrow{\textit{FT}^{-1}} \rho(\mathbf{r})$$

$$\rho(\mathbf{r}) \longrightarrow |\rho(\mathbf{r})|$$

$$|F(\mathbf{k})|\exp(\mathrm{i}\phi_{\mathbf{k}}) \xleftarrow{\textit{FT}} |\rho(\mathbf{r})|$$

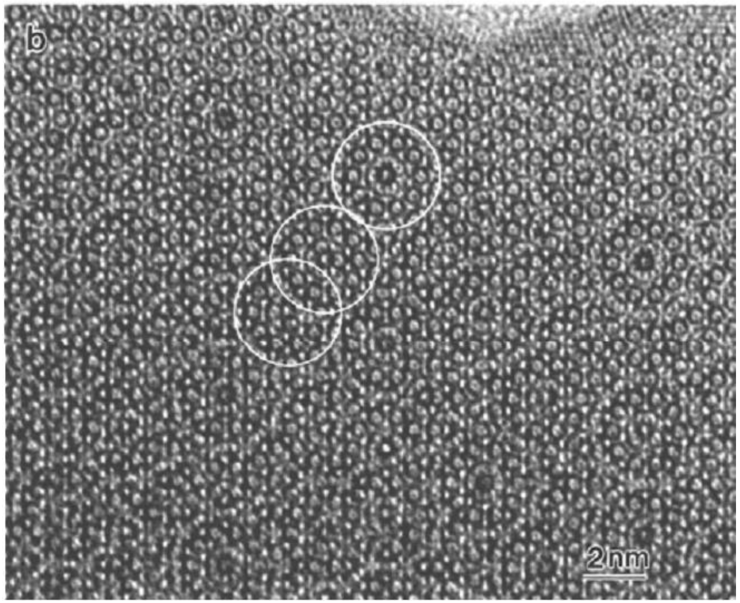
Structure solution
Charge Flipping Algorithm & SUPERFLIP

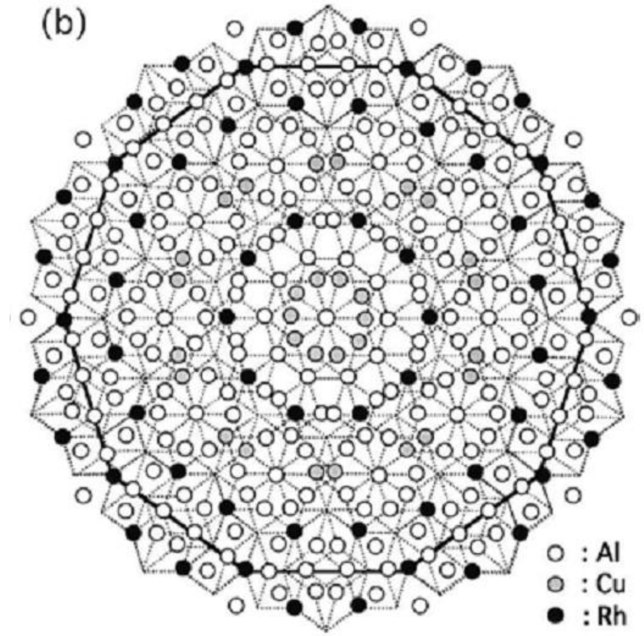


ALGORITHM: Oszlanyi & Suto, 2008

SUPERFLIP PROGRAM: Palatinus & Chapuis, 2007

Modeling example d-Al-Cu-Rh; HRTEM study – 33 Å cluster





Hiraga *et al*., Phil. Mag., 2001