北海道大学
HOKKAIDO UNIVERSITY

Introduction to higher dimensional description of quasicrystal structures

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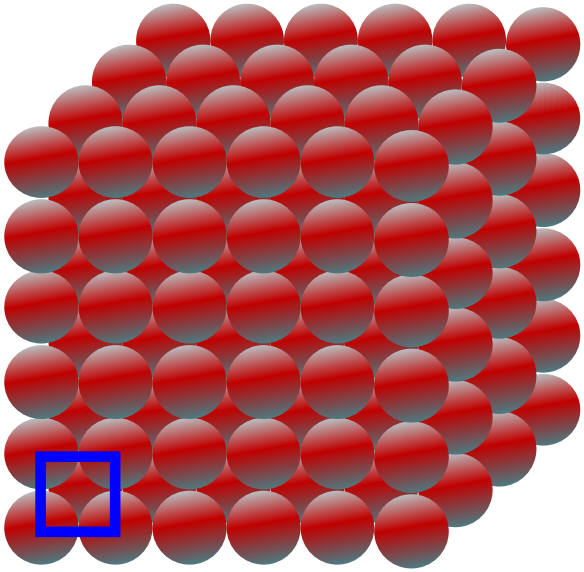
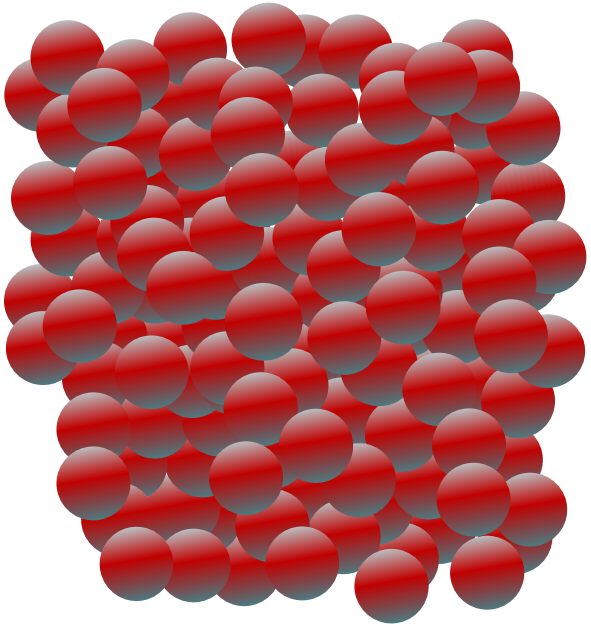
Outline

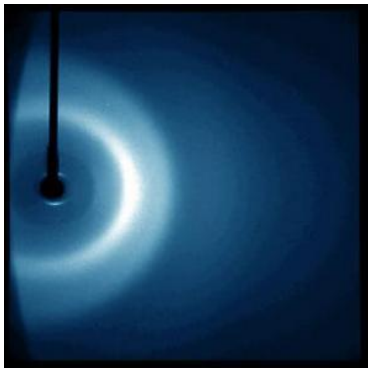
- Diffraction symmetries & Space groups of iQCs
- Section method
- Fibonacci structure
- Icosahedral lattices
- Simple models of iQCs
- Real iQC structures
- Cluster based model of iQCs
- Summary

Crystal



Amorphous





Their diffraction patterns

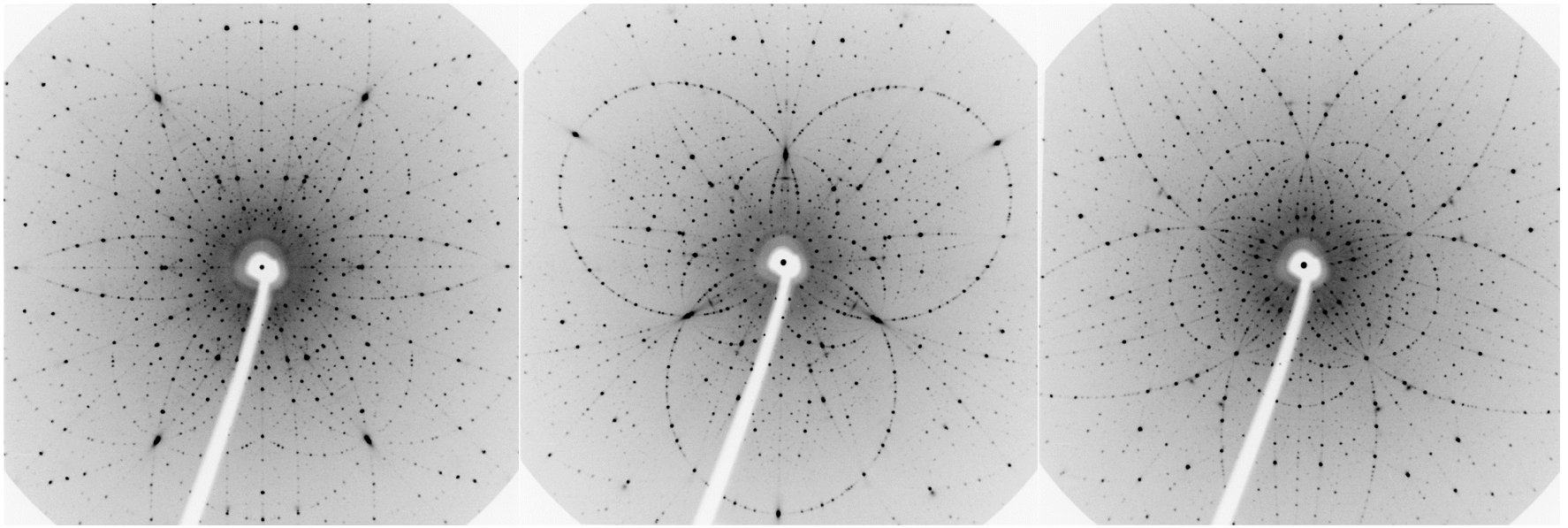
Diffraction symmetries and space groups of iQCs

X-ray transmission Laue patterns of iQC

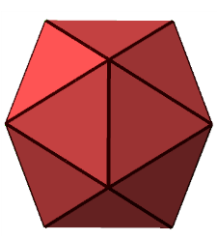
2-fold

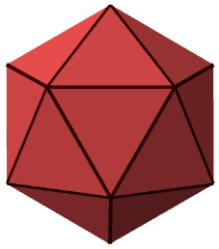
3-fold

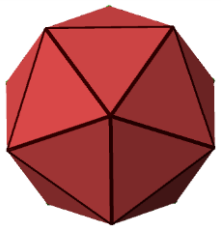
5-fold



i-Zn-Mg-Ho F-type

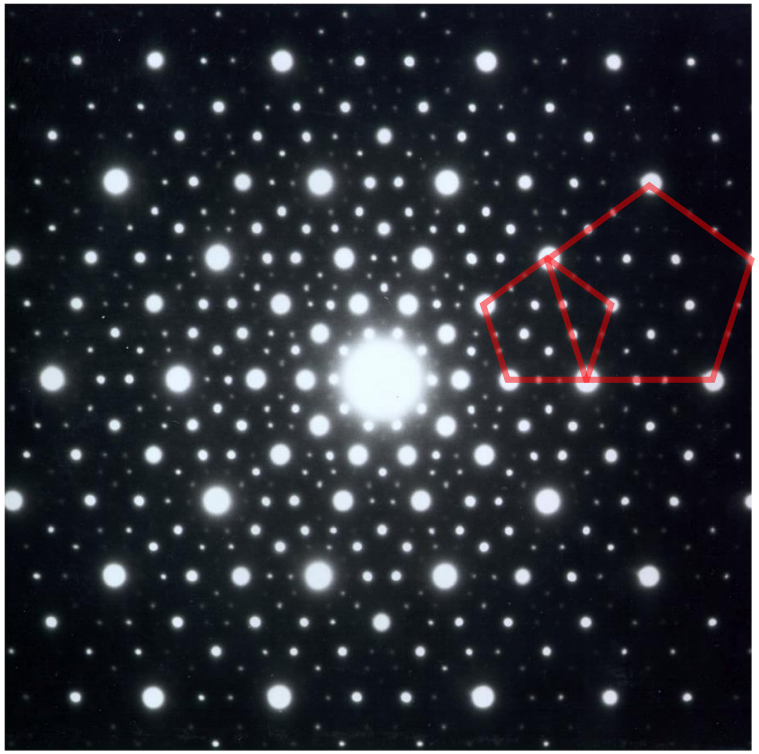


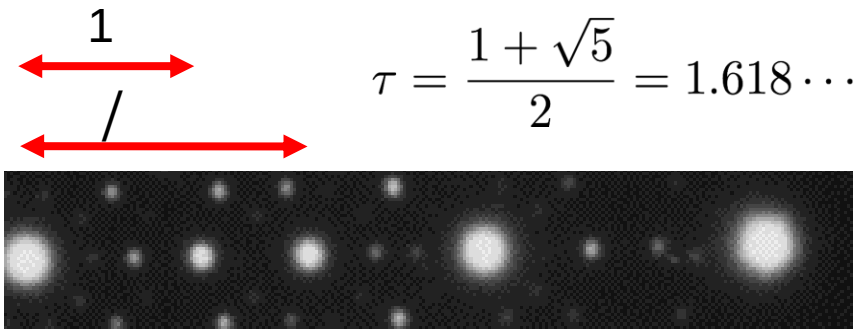




Electron diffraction pattern of iQC

i-AlMn

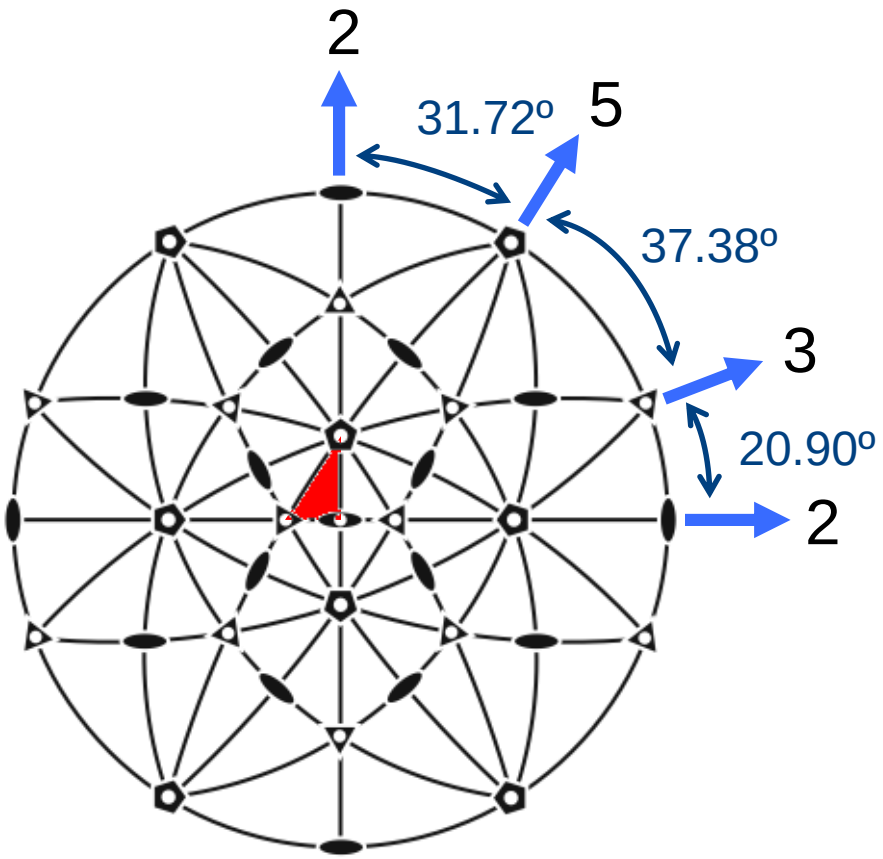




The arrangement of the diffraction spots is not periodic but quasi-periodic.

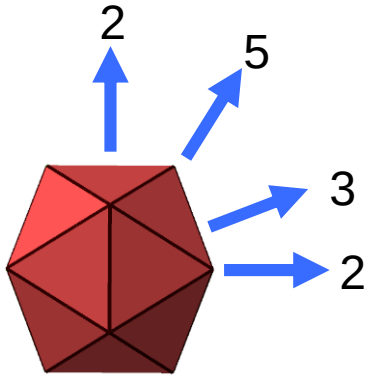
D.Shechtman et al., Phys.Rev.Lett., 53,1951(1984).

Symmetry of iQC



Point group $m\bar{3}\bar{5}$

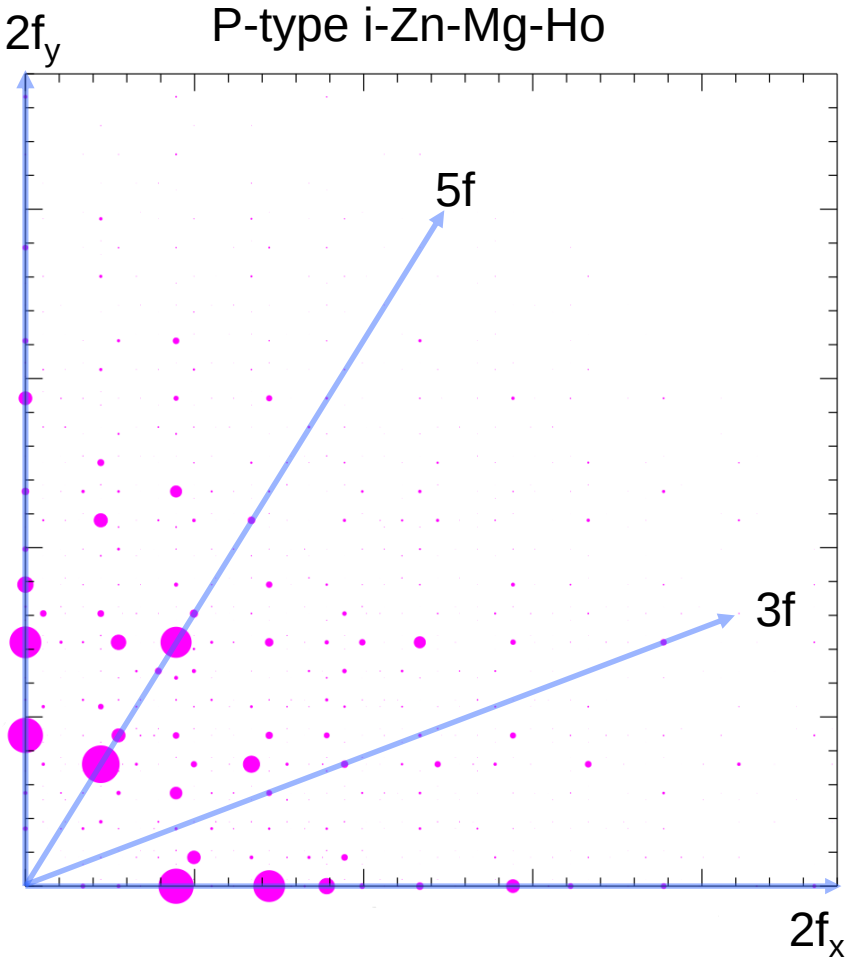
Order : 120

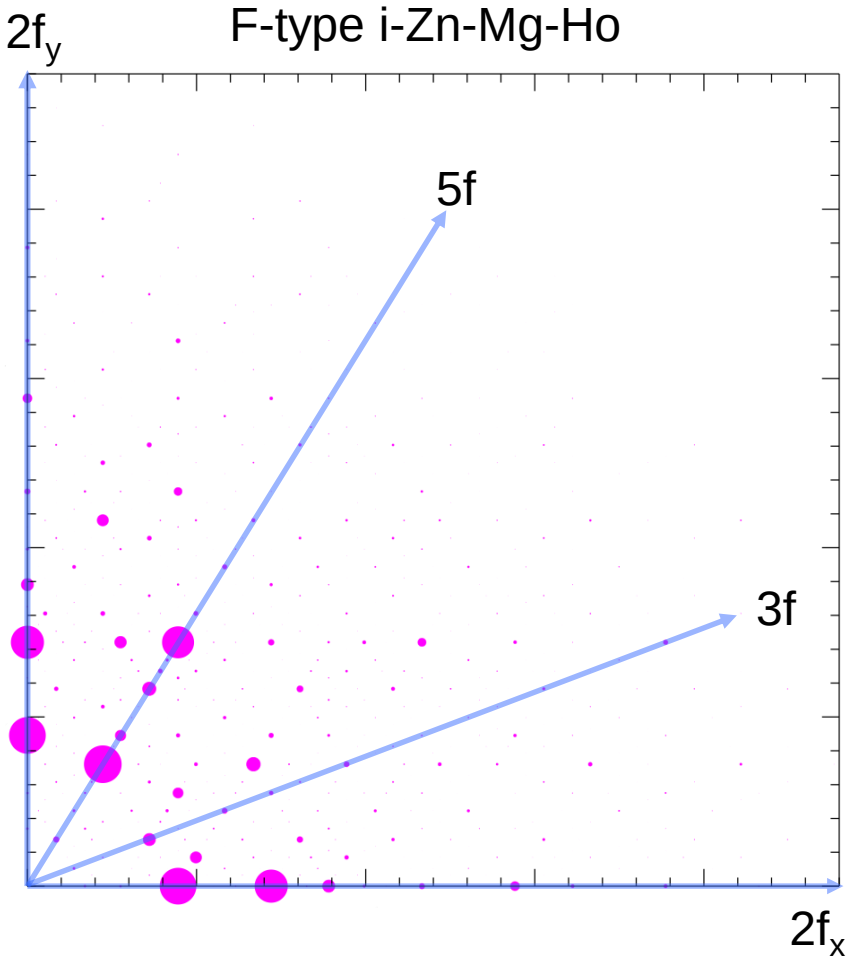


Asymmetric region: $\frac{1}{120}$

6 +10 +15 + *m* + center

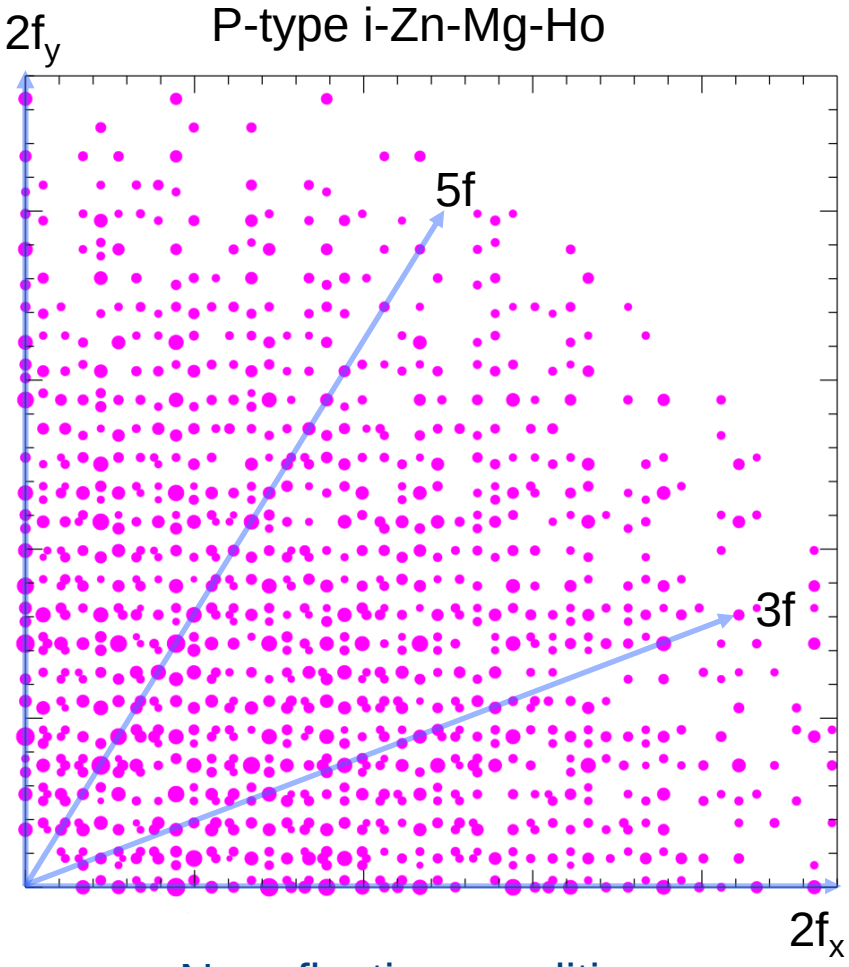
X-ray diffraction patterns of iQCs



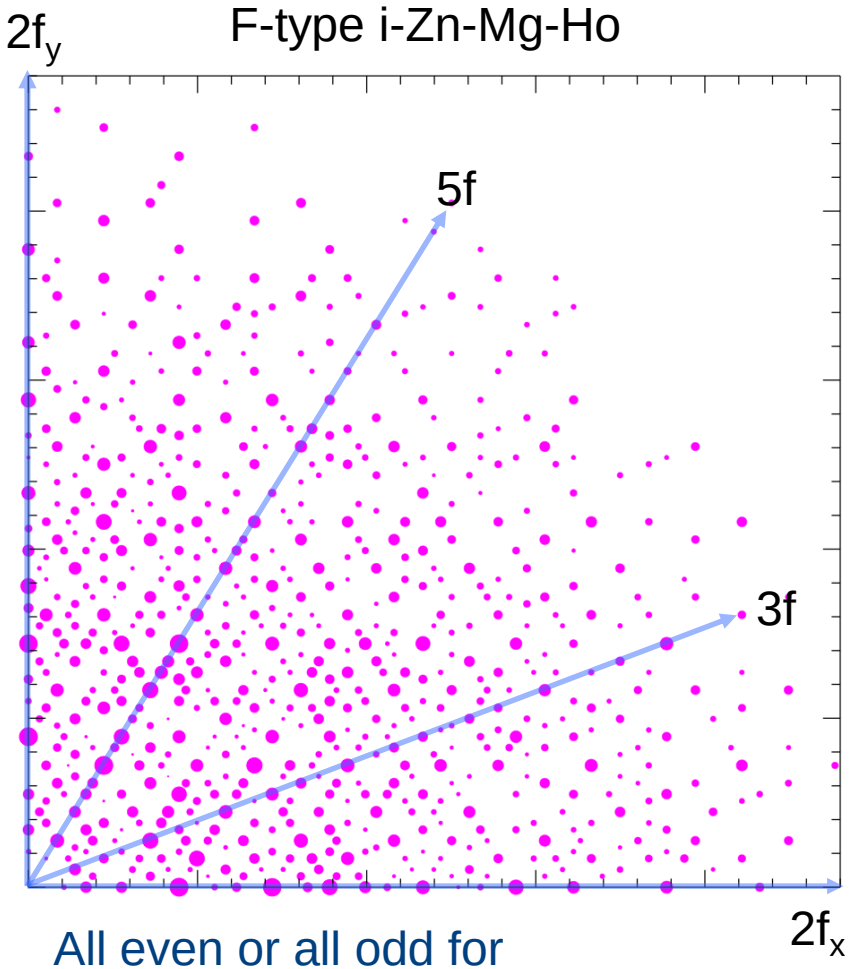


Liner plots

X-ray diffraction patterns of iQCs



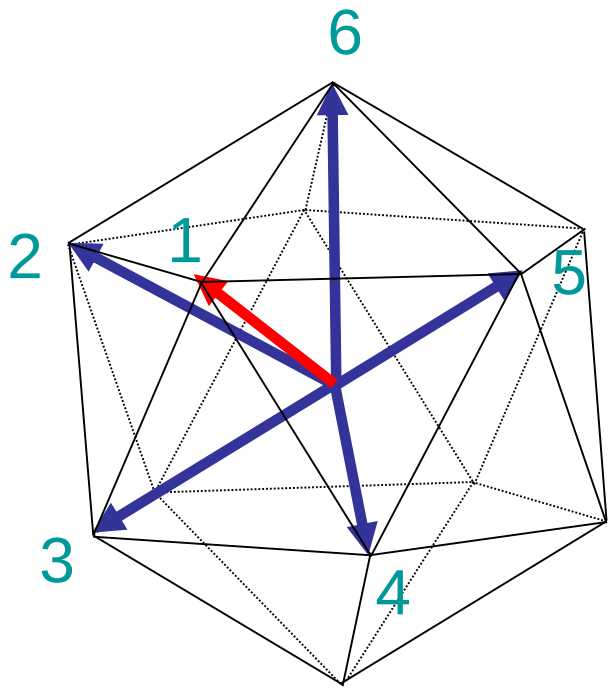
No reflection condition



All even or all odd for $h_1h_2h_3h_4h_5h_6$

Log plots

Vectors used for indexing



Any vectors can be used if all the reflections can be indexed correctly.

Six vectors → 6D reciprocal lattice

The 6D reciprocal lattice must have at least icosahedral symmetry.

6D hypercubic lattice is chosen usually.

6D Icosahedral lattices

Lattice types

- Primitive

  e.g. $Pm\bar{3}\bar{5}$
- Body-centered

  e.g. $Im\bar{3}\bar{5}$
- Face-centered

  e.g. $Fm\bar{3}\bar{5}$

Reflection condition

No condition

$\sum_{i=1}^{6} h_i = 2n$ for $h_1h_2h_3h_4h_5h_6$

All even or all odd for $h_1h_2h_3h_4h_5h_6$

Centering translations in centered lattices

Face-centered
(F-type)

(000000),
$(\frac{1}{2}\frac{1}{2}0000), (\frac{1}{2}0\frac{1}{2}\frac{1}{2}000), \ldots, (0000\frac{1}{2}\frac{1}{2})$,
$(\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}), (00\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}), \ldots, (\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}00)$

32 centering translations

Body-centered
(I-type)

$(000000), (\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2})$

2 centering translations

- *Body-centered lattice has yet to be observed experimentally!*

Recently, an I-type structure has formed as a computer simulated structure:
M. Engel *et al.*, *Nat. mat.* **14**, 109 (2015).

The section method

Fibonacci structure

Recurrence formula

$$F_{n+1} = F_n + F_{n-1}$$

$$F_0 = \mathrm{L}$$

$$F_1 = \mathrm{S}$$

$$(L = \tau S)$$

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

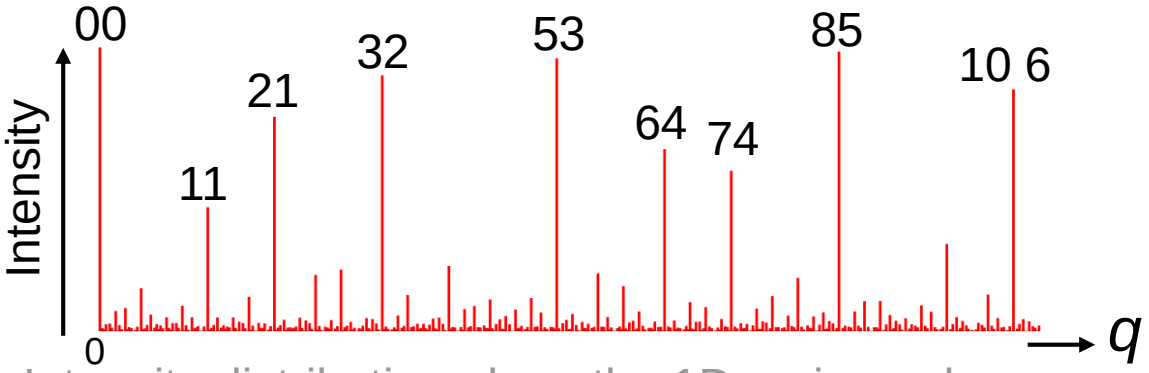
1D quasi-periodic structure

Direct space

Fourier transformation

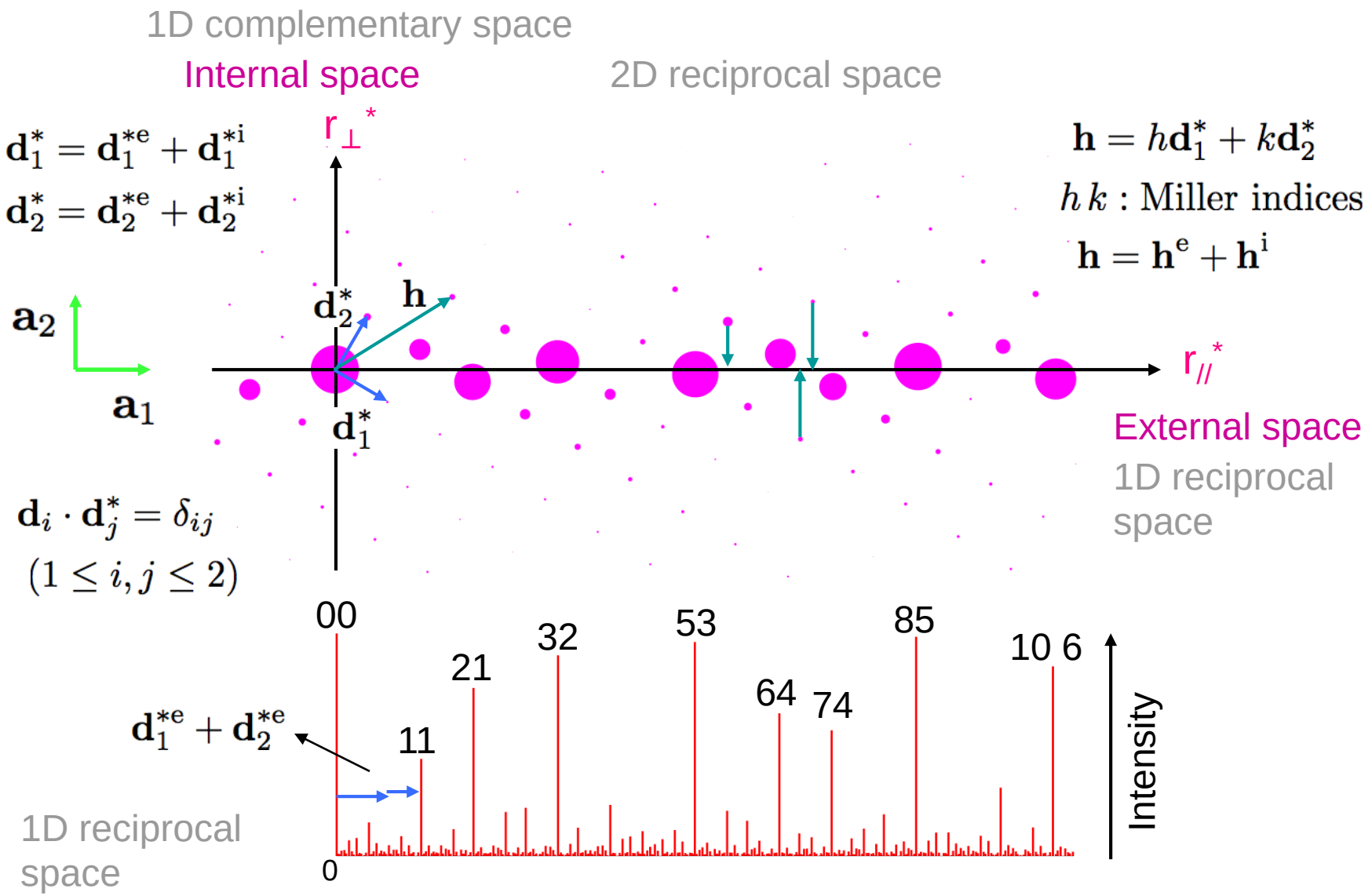
Diffraction pattern

Reciprocal space



Intensity distribution along the 1D reciprocal space

Diffraction pattern of the Fibonacci structure

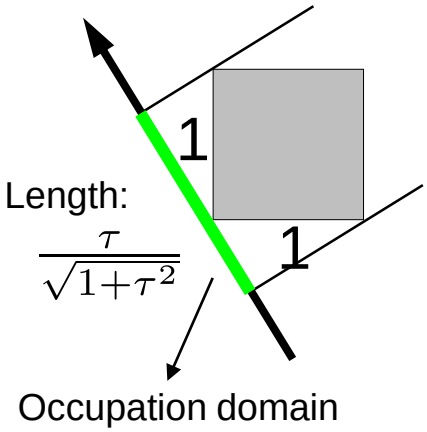


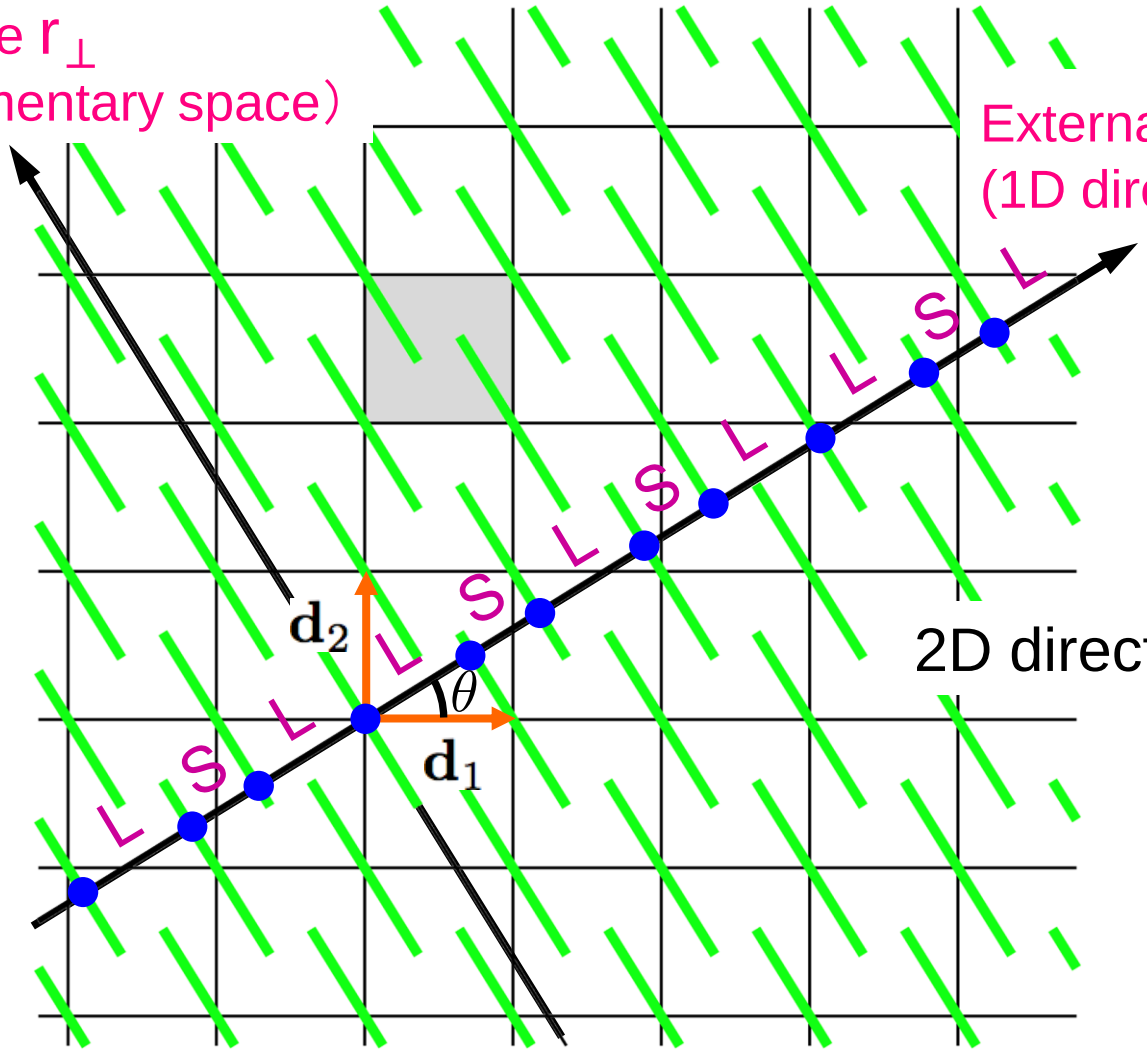
Construction of the Fibonacci structure

Internal space $r_\perp$
（1D complementary space）

External space $r_{//}$
(1D direct space)

$$\mathbf{d}_1 = (\mathbf{d}_1^{\mathrm{e}}, \mathbf{d}_1^{\mathrm{i}})$$
$$\mathbf{d}_2 = (\mathbf{d}_2^{\mathrm{e}}, \mathbf{d}_2^{\mathrm{i}})$$





L = τ
S = 1

2D direct space

$$\mathbf{d}_1 = d_1^{\mathrm{e}}\mathbf{a}_1 + d_1^{\mathrm{i}}\mathbf{a}_2$$
$$\mathbf{d}_2 = d_2^{\mathrm{e}}\mathbf{a}_1 + d_2^{\mathrm{i}}\mathbf{a}_2$$

The angle θ is determined by the formula: $\tan\theta = 1/\tau$.

Relationship between the direct space and the reciprocal space of Fibonacci structure

Direct space		Reciprocal space
2D crystal lattice	Fourier transformation ⟷	2D reciprocal lattice
Periodic		Periodic
Structure		**Diffraction pattern**
1D section of the 2D crystal	Fourier transformation ⟷	Projection onto 1D along the other 1D
Quasi-periodic Fibonacci structure		Quasi-periodic

Construction of the Fibonacci structure

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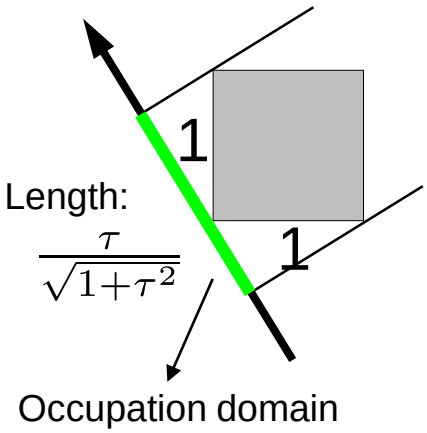

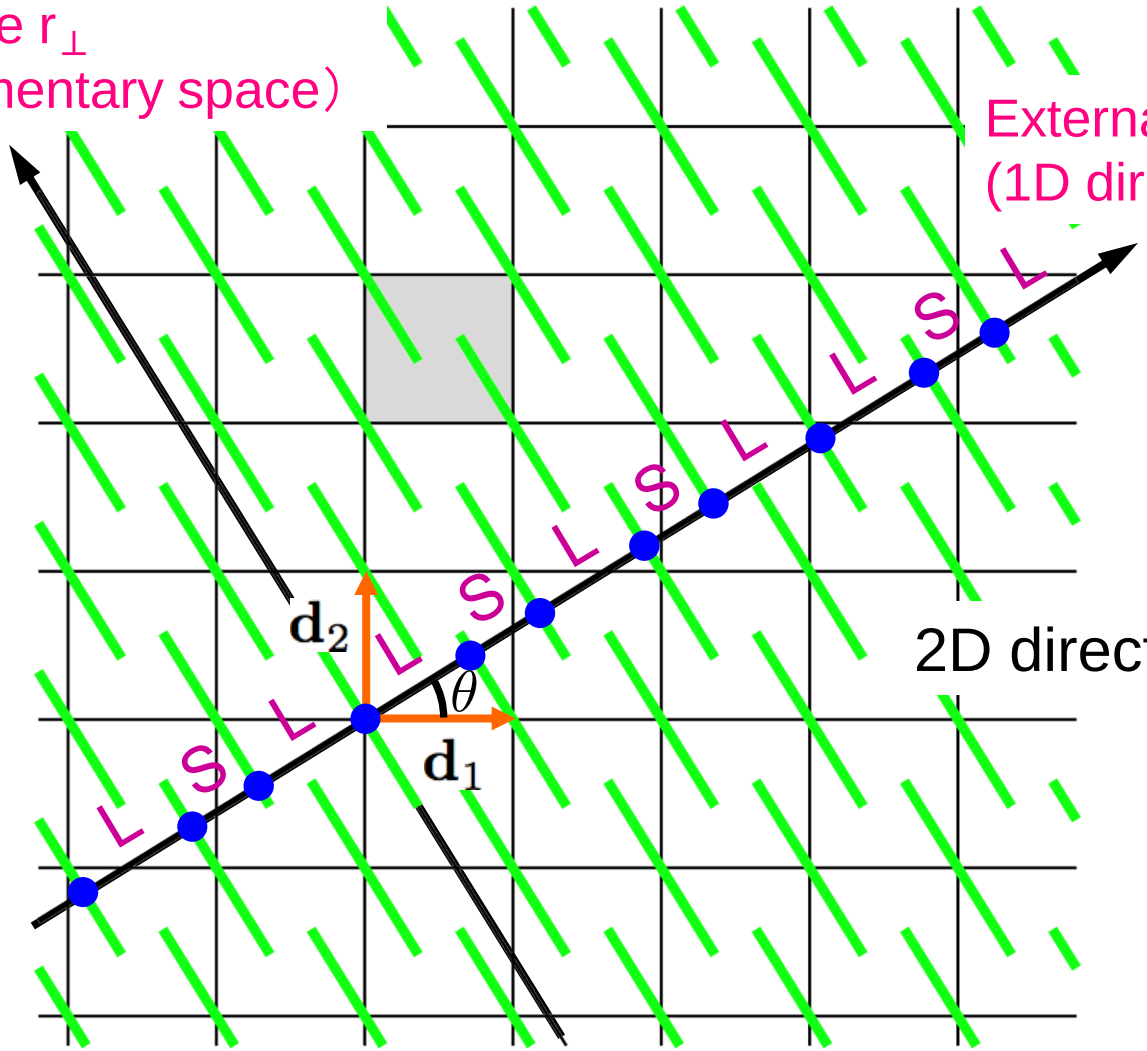

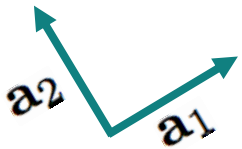

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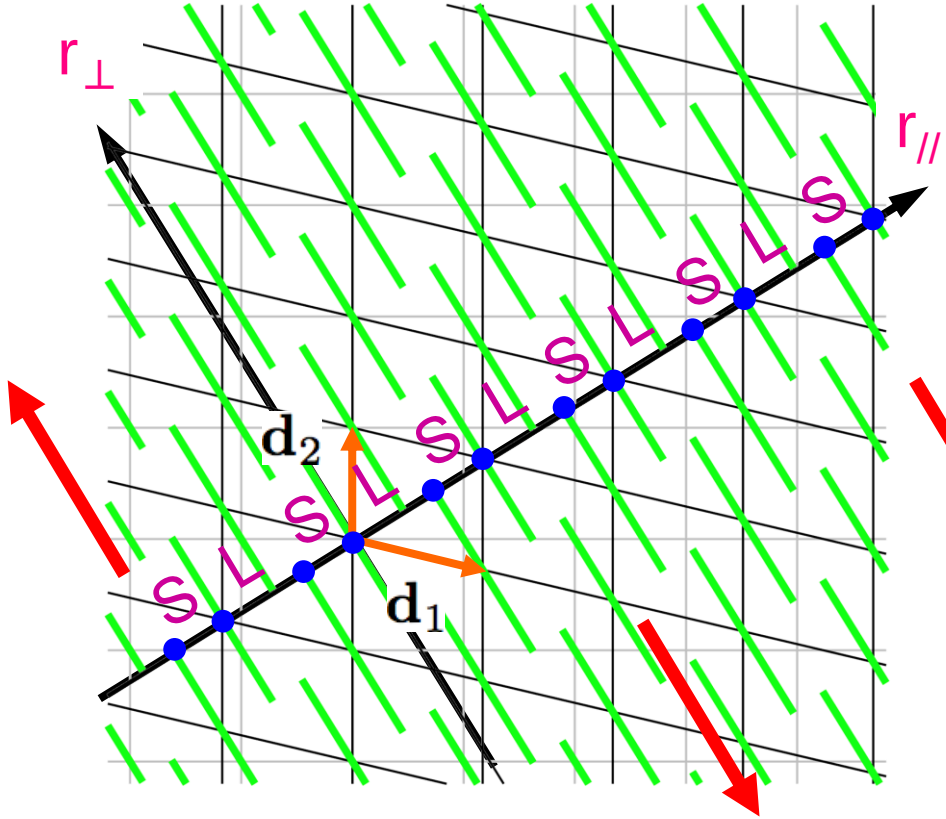
The angle θ is determined by the formula: $\tan\theta = 1/\tau$.

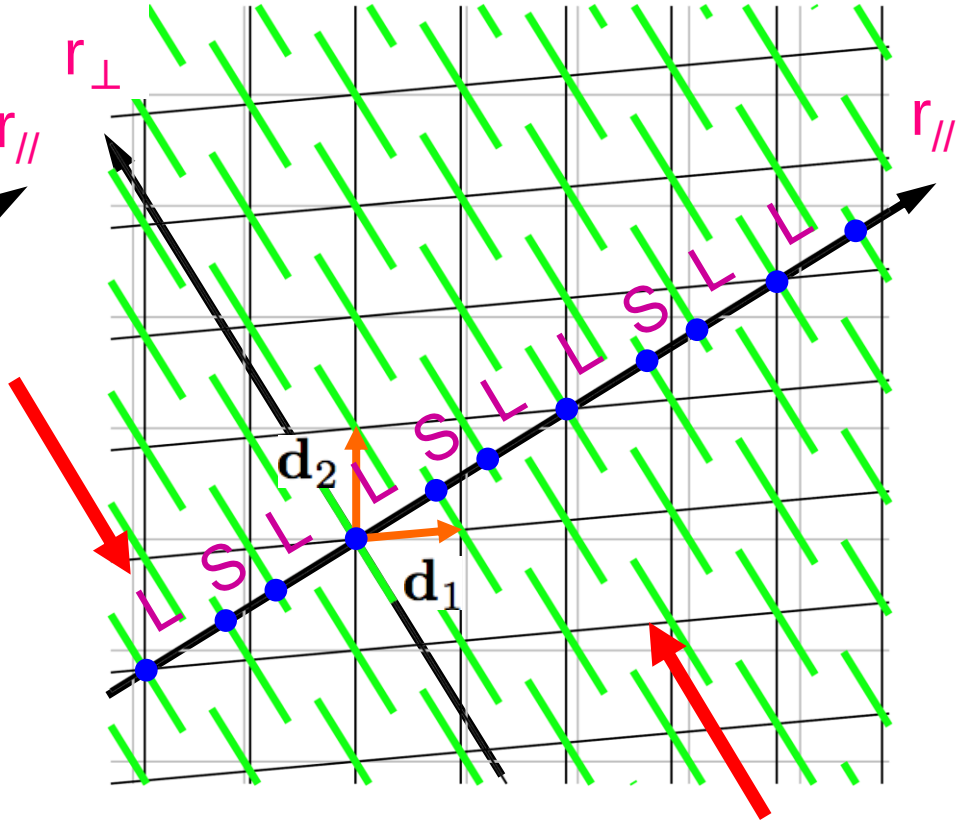
Approximant crystals of Fibonacci structure

A shear strain (liner phason strain) along $r_\perp$ is applied.



1/1 approximant

…LS…



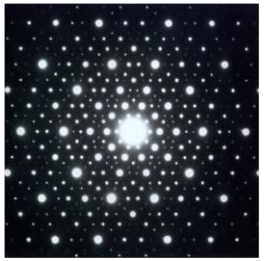
2/1 approximant

…LSL…

Determination of the icosahedral lattice

Determination of the unit vectors of iQCs

Diffraction pattern



reciprocal lattice

Icosahedral lattice in 6D reciprocal space

Icosahedral lattice in 6D direct space

Icosahedral symmetry

$\mathbf{d}_i^{*\mathrm{e}} \quad (i = 1, \ldots, 6)$

6 indices: $h_1 h_2 h_3 h_4 h_5 h_6$

Lattice constant: a^*

$$\mathbf{d}_i^* = \mathbf{d}_i^{*\mathrm{e}} + \mathbf{d}_i^{*\mathrm{i}} \quad (i = 1, \ldots, 6)$$

(external) (internal)

$$\mathbf{d}_i = \mathbf{d}_i^{\mathrm{e}} + \mathbf{d}_i^{\mathrm{i}} \quad (i = 1, \ldots, 6)$$

Lattice constant: $a = \frac{1}{2a^*}$

Unit vectors in 6D reciprocal space

$\mathbf{d}_i^*\ (i = 1, 2, \ldots, 6)$: unit reciprocal lattice vectors

$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{a}_4, \mathbf{a}_5, \mathbf{a}_6$: orthonormal base vectors

$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$: span the external space (3D)

$\mathbf{a}_4, \mathbf{a}_5, \mathbf{a}_6$: span the internal space (3D)

$$\begin{pmatrix} \mathbf{d}_1^* \\ \mathbf{d}_2^* \\ \mathbf{d}_3^* \\ \mathbf{d}_4^* \\ \mathbf{d}_5^* \\ \mathbf{d}_6^* \end{pmatrix} = \frac{a^*}{\sqrt{2+\tau}} \begin{pmatrix} 1 & \tau & 0 & \tau & -1 & 0 \\ \tau & 0 & 1 & -1 & 0 & \tau \\ \tau & 0 & -1 & -1 & 0 & -\tau \\ 0 & 1 & -\tau & 0 & \tau & 1 \\ -1 & \tau & 0 & -\tau & -1 & 0 \\ 0 & 1 & \tau & 0 & \tau & -1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \\ \mathbf{a}_4 \\ \mathbf{a}_5 \\ \mathbf{a}_6 \end{pmatrix}$$

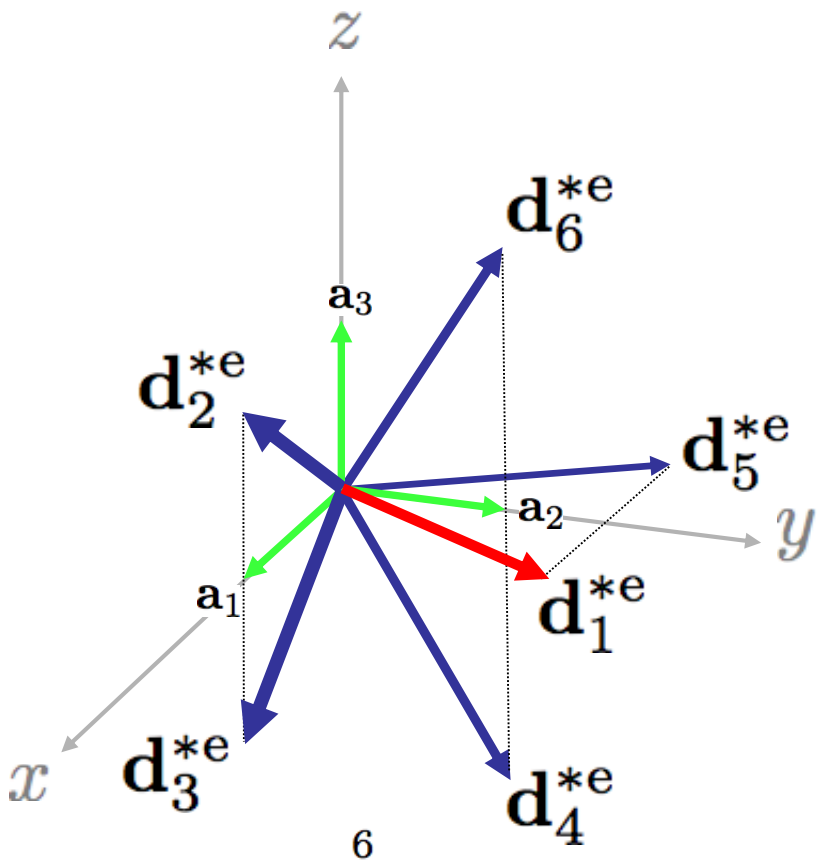
$$\tilde{M}^{-1}$$

a^* : lattice constant in reciprocal space

Projection of the unit vectors $\mathbf{d}_i^*$

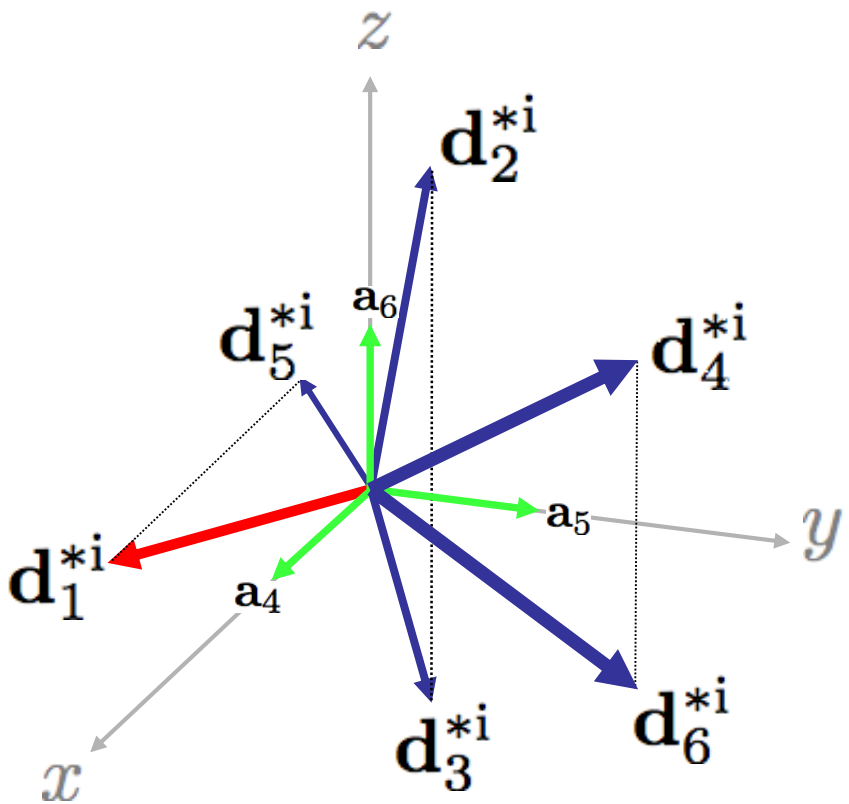
(reciprocal space)

External space (3D) $r_{//}^*$



$$\mathbf{h}^{\mathrm{e}} = \sum_{i=1}^{6} h_i \mathbf{d}_i^{*\mathrm{e}}$$

Internal space (3D) $r_{\perp}^*$



Unit vectors in 6D direct space

Reciprocal lattice vectors

$\mathbf{d}_i^* \ (i = 1, 2, \ldots, 6)$

Direct lattice vectors

$\mathbf{d}_i \ (i = 1, 2, \ldots, 6)$

$$\mathbf{d}_i^* \cdot \mathbf{d}_j = \delta_{ij} \ (1 \leq i, j \leq 6)$$

$$\mathbf{d}_i^* = \sum_{j=1}^{6} \tilde{M}_{ij}^{-1} \mathbf{a}_j \qquad \mathbf{d}_i = \sum_{j=1}^{6} M_{ij} \mathbf{a}_j$$

$$\begin{pmatrix} \mathbf{d}_1 \\ \mathbf{d}_2 \\ \mathbf{d}_3 \\ \mathbf{d}_4 \\ \mathbf{d}_5 \\ \mathbf{d}_6 \end{pmatrix} = \frac{a}{\sqrt{2+\tau}} \begin{pmatrix} 1 & \tau & 0 & \tau & -1 & 0 \\ \tau & 0 & 1 & -1 & 0 & \tau \\ \tau & 0 & -1 & -1 & 0 & -\tau \\ 0 & 1 & -\tau & 0 & \tau & 1 \\ -1 & \tau & 0 & -\tau & -1 & 0 \\ 0 & 1 & \tau & 0 & \tau & -1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \\ \mathbf{a}_4 \\ \mathbf{a}_5 \\ \mathbf{a}_6 \end{pmatrix}$$

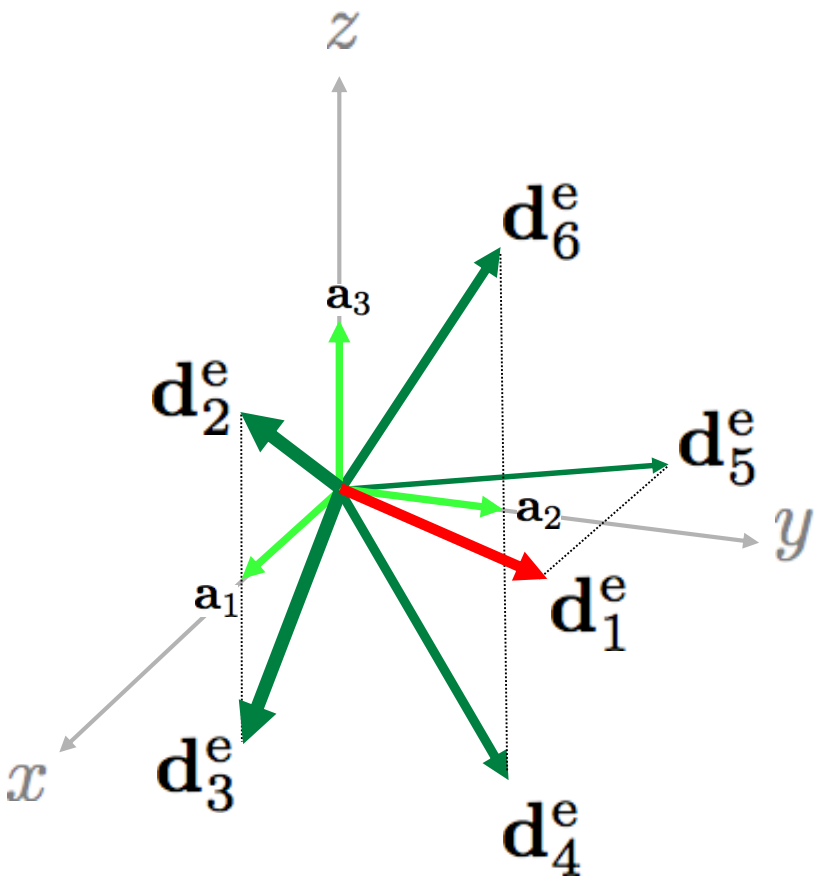
M

$a = \frac{1}{2a^*}$: icosahedral lattice constant

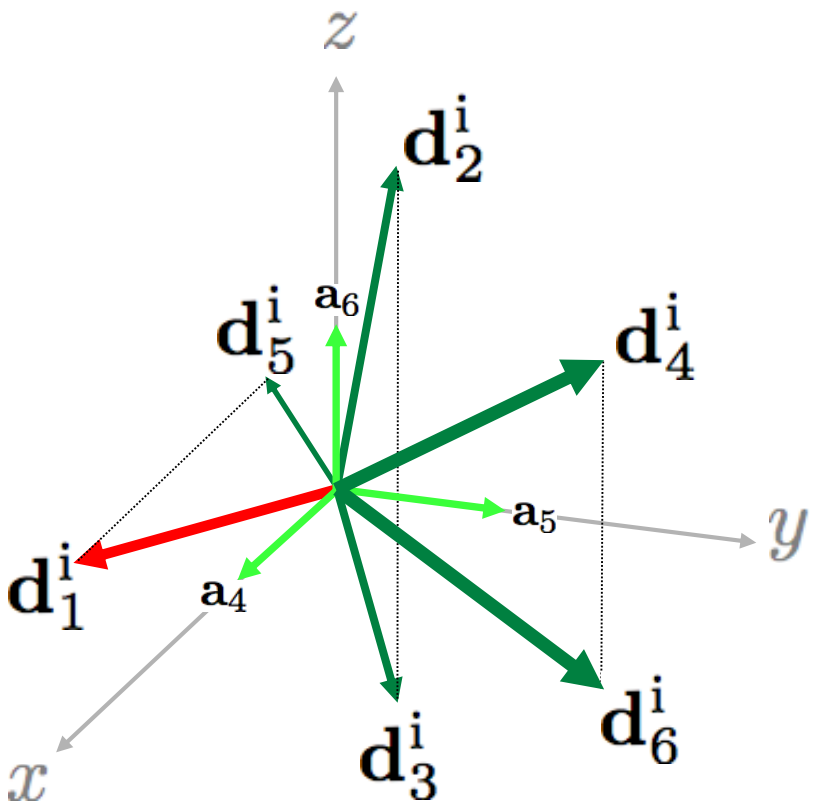
Projection of the unit vectors $\mathbf{d}_i$

(direct space)

External space (3D) $r_{//}$

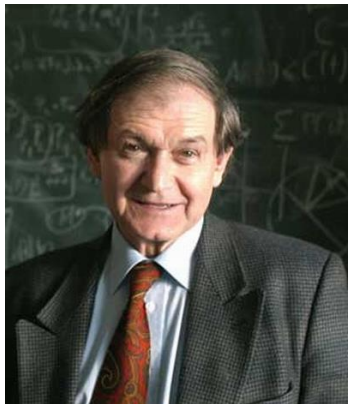


Internal space (3D) $r_{\perp}$



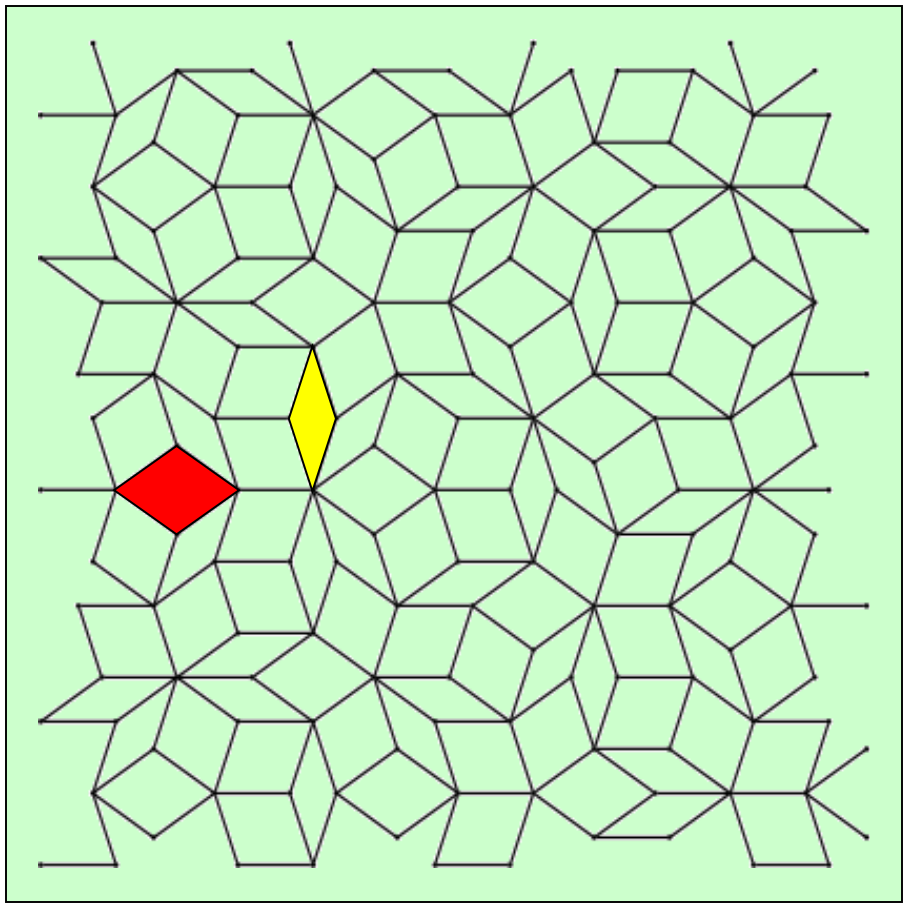
Description of icosahedral quasicrytal structures

Penrose tiling

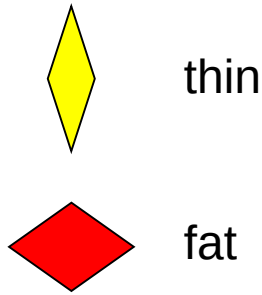


Sir Roger Penrose

Mathematical physicist
Mathematician
Philosopher of science



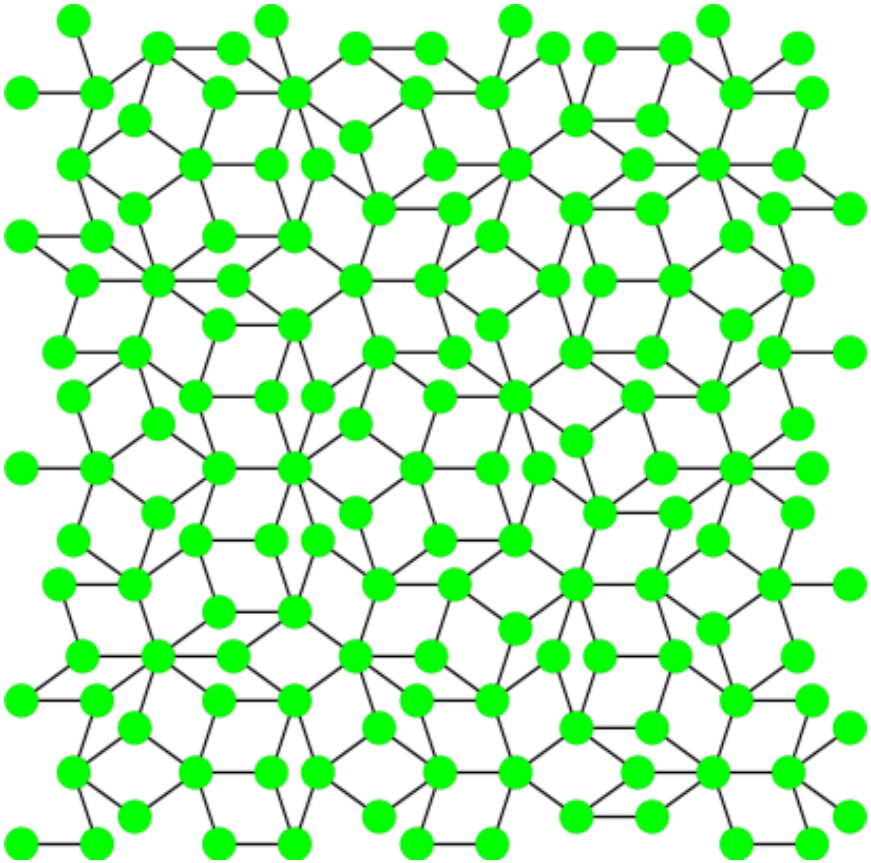
Prototiles



A Penrose tiling is an example of quasiperiodic 2D tiling that consists of two types of prototiles.

Decoration of the Penrose tiling with atoms

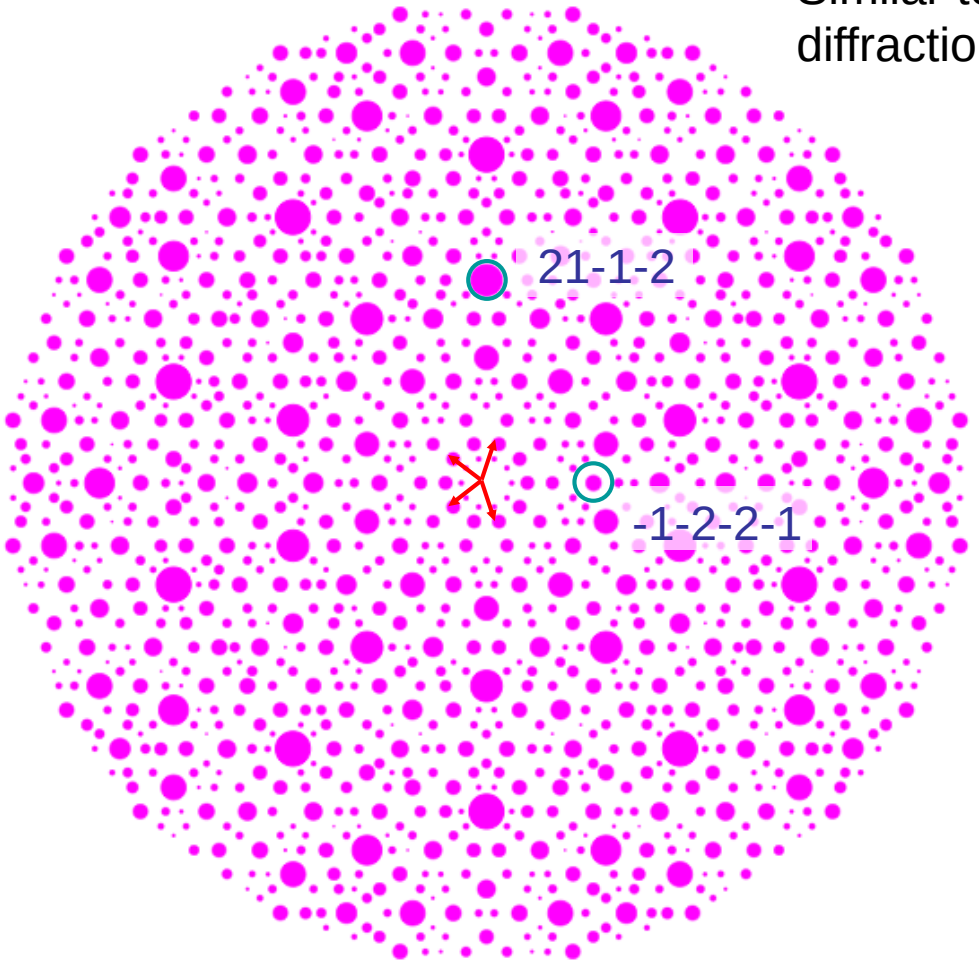
A 2D quasiperiodic atom arrangement is realized.

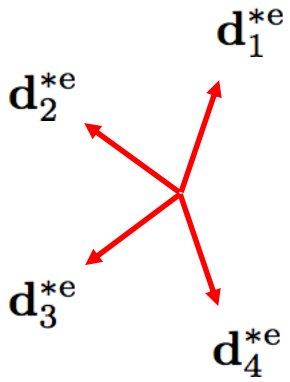


Vertex decoration model

Diffraction pattern of the Penrose tiling

Similar to $h_1h_2h_3h_4 0$
diffraction plane of real dQCs

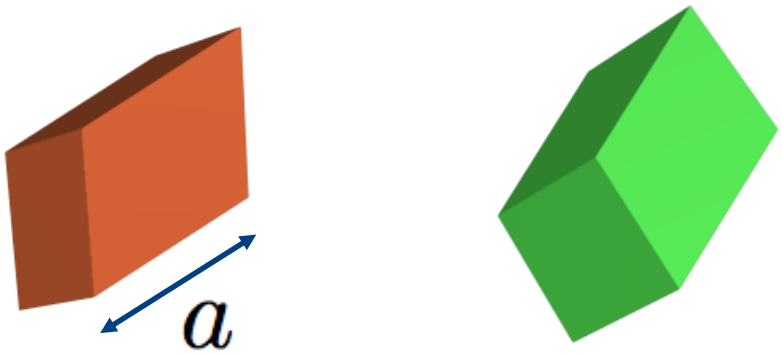




Vertex decoration with point scatters

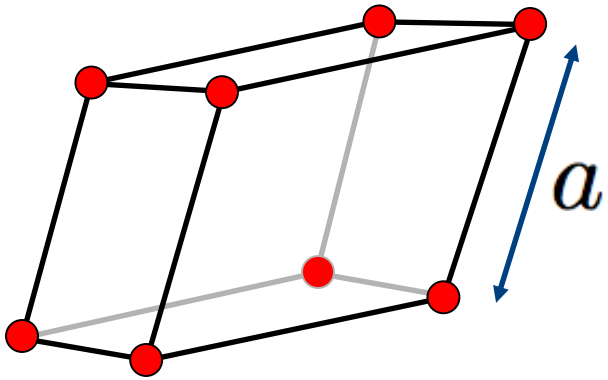
3D Ammann-Kramer-Neri tiling

- A 3D analog of Penrose tiling.
- The AKN tiling consists of two primitive rhombohedra:
  the acute rhombohedron (AR) and the obtuse rhombohedron (OR).
- Space-filling structure with icosahedral symmetry.

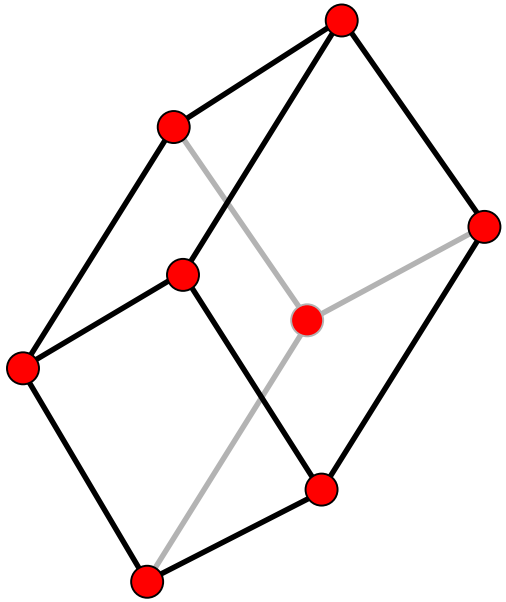


AR OR

Vertex decoration of the rhombohedra



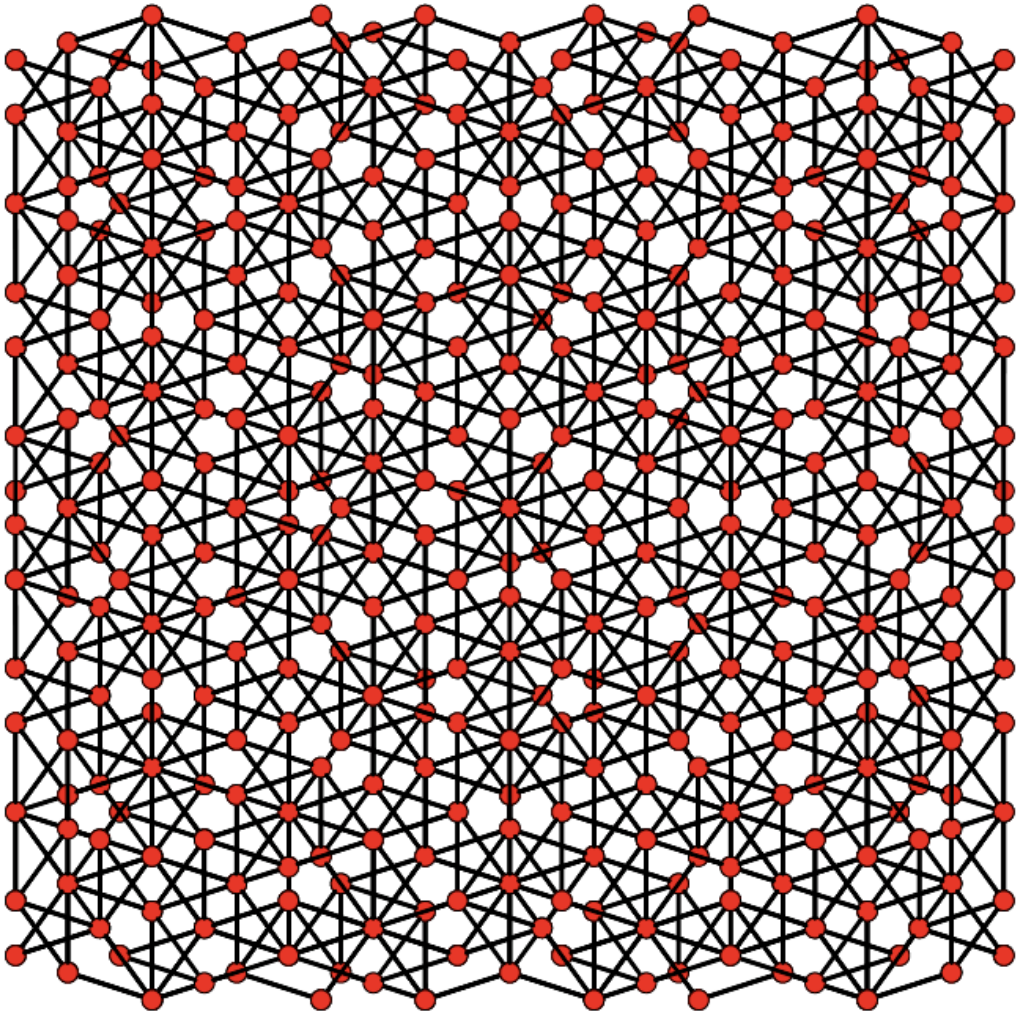
AR



OR

Put atoms at every vertex of the AKN tiling.

A naïve model of iQC (vertex decoration model of AKN tiling)

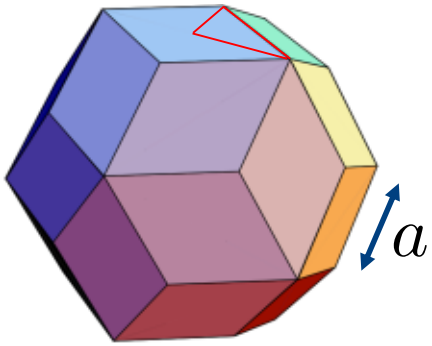


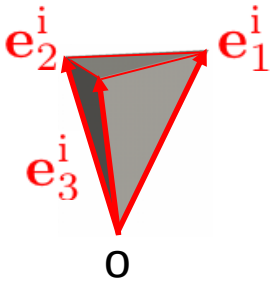
Projected view of the structure along a 5f axis.

Construction of AKN tiling by the section method

(Generate the vertices of the AKN tiling)

Occupation Domain





Asymmetric part

Corner vectors

$$\mathbf{e}_1^{\mathrm{i}} = (1, \bar{1}, \bar{1}, \bar{1}, \bar{1}, \bar{1})^{\mathrm{i}}/2$$
$$\mathbf{e}_2^{\mathrm{i}} = (1, 1, \bar{1}, \bar{1}, \bar{1}, \bar{1})^{\mathrm{i}}/2$$
$$\mathbf{e}_3^{\mathrm{i}} = (1, 0, \bar{1}, \bar{1}, 0, \bar{1})^{\mathrm{i}}/2$$

Basis: $\mathbf{d}_i^{\mathrm{i}} \quad (i = 1, \ldots, 6)$

Position

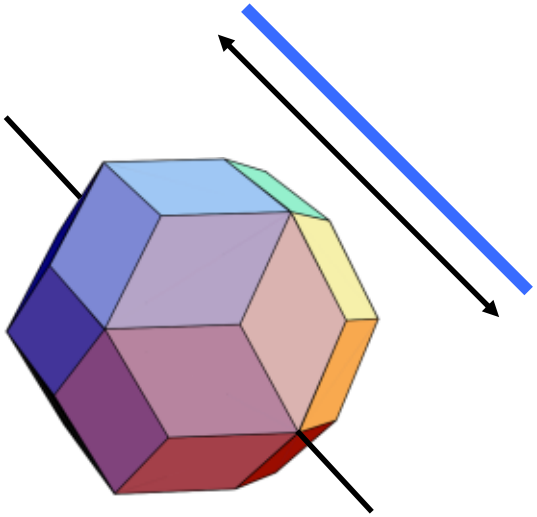
$$(0, 0, 0, 0, 0, 0)$$

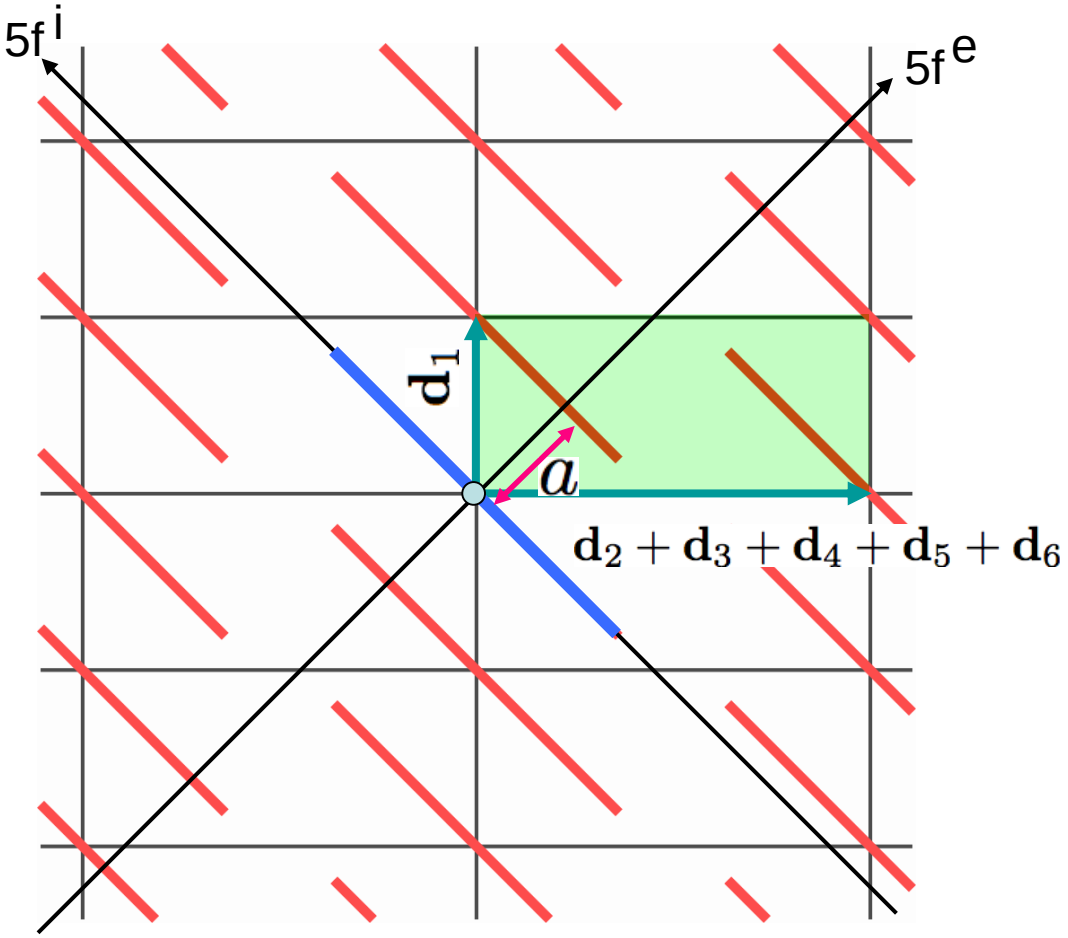
Site-symmetry group:

$$m\bar{3}\bar{5}$$

This rhombic triacontahedral OD corresponds to the projection of the 6D unit cell onto the 3D internal space.

2D section of the 6D structure including 5f axes

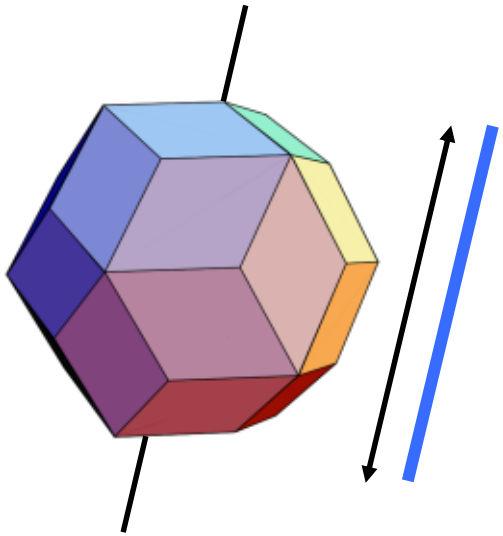




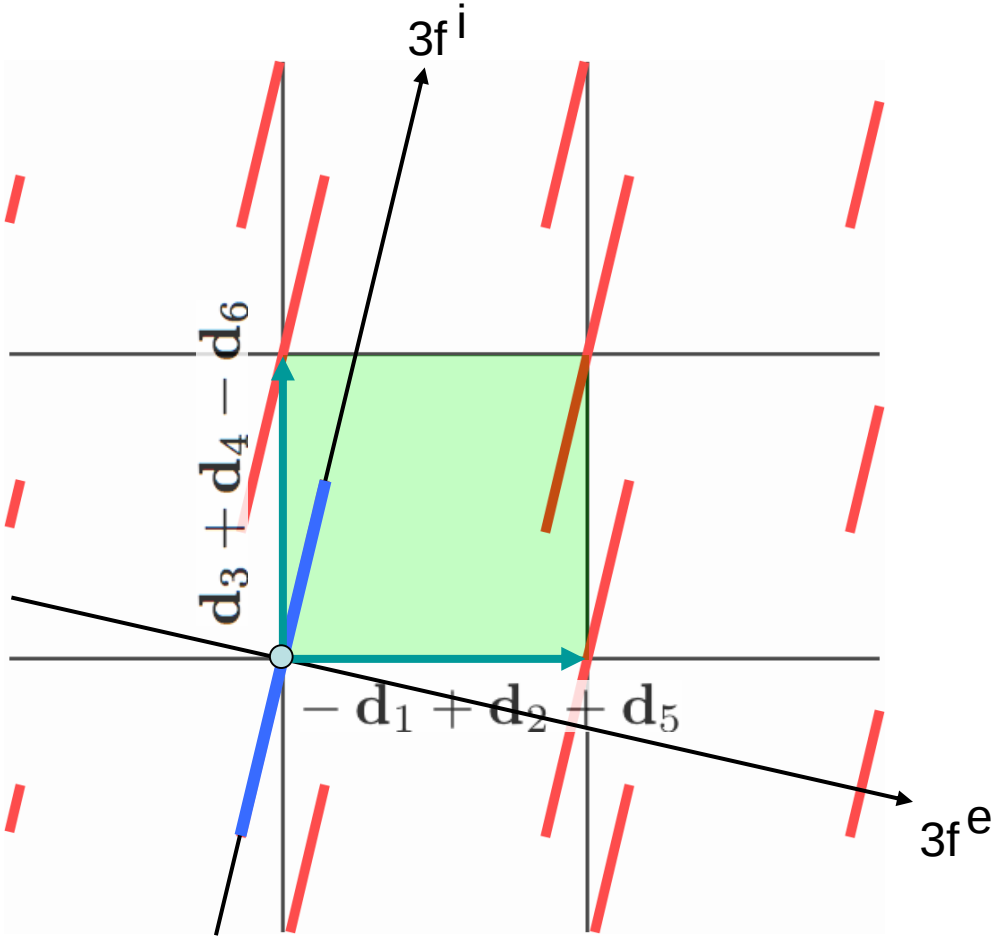
The line segment is the 1D section of the OD along a 5f axis in the internal space.

Note that any direction in the plane has 5-fold rotational symmetry.

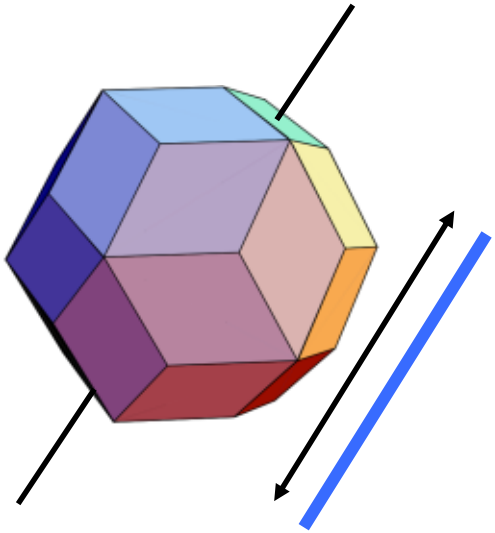
2D section of the 6D structure including 3f axes



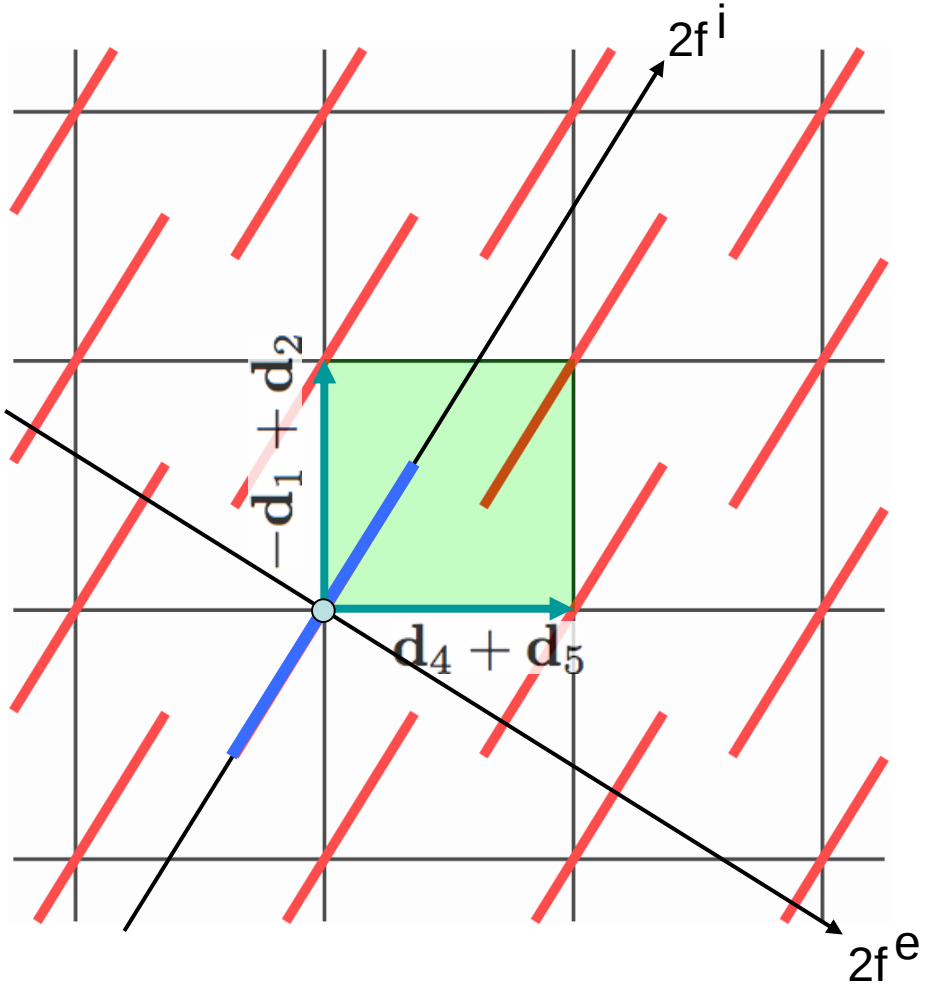
The line segment is the 1D section of the OD along a 3f axis in the internal space.



2D section of the 6D structure including 2f axes

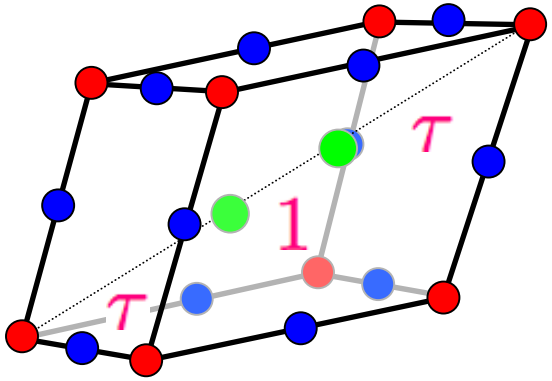


The line segment is the 1D section of the OD along a 2f axis in the internal space.

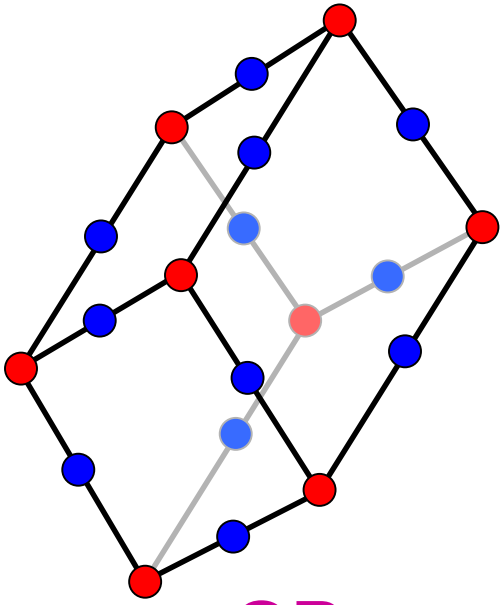


Simple decoration model of icosahedral QC based on the AKN tiling

Atomic decoration of two rhombohedra in the case of simple decoration model



AR

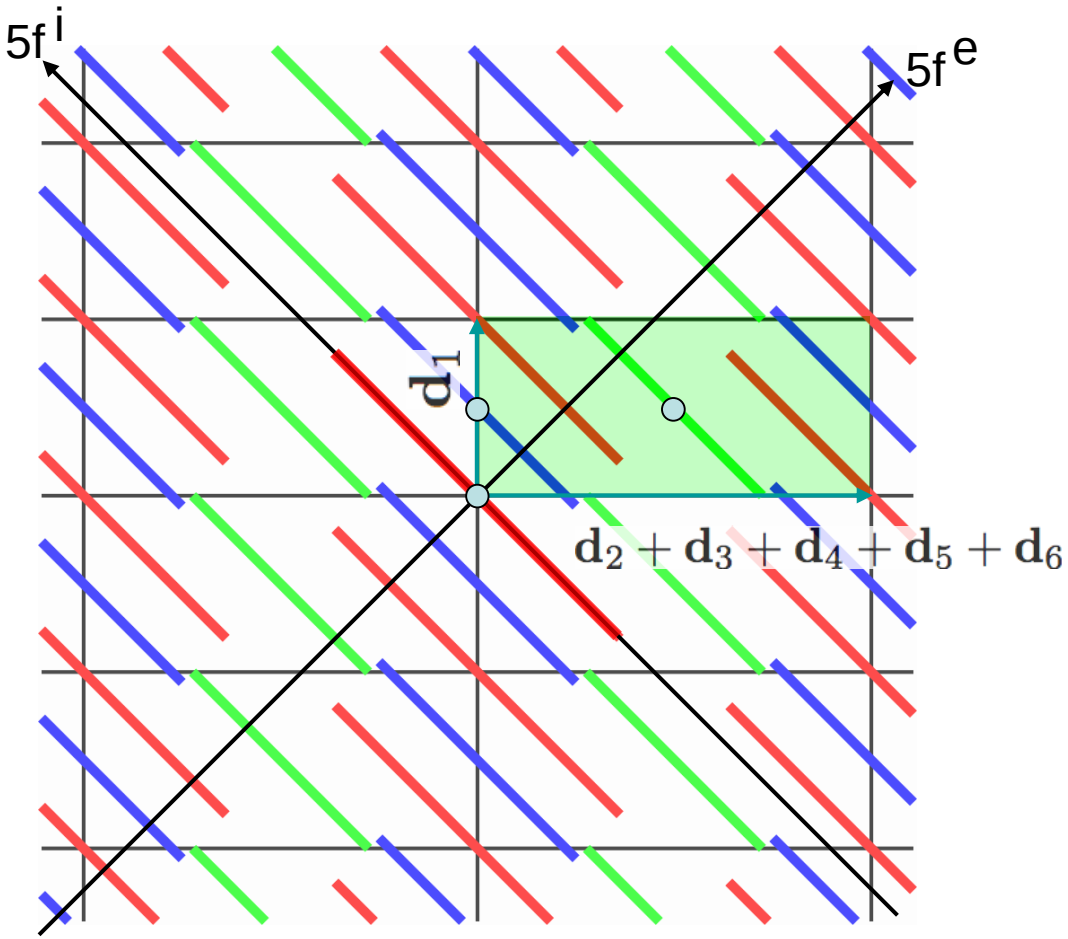


OR

- Vertices
- Mid edges
- Body diagonal two positions in ARs

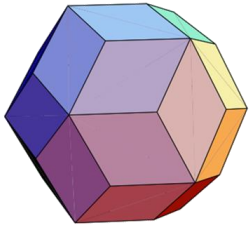
This model was proposed as the structure model of i-Al-Cu-Li iQC (Bergman type cluster) at the early stage.

Simple decoration model of iQC in 6D

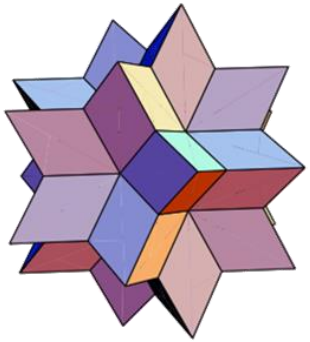


Three large occupation domains characterize the 6D structure.

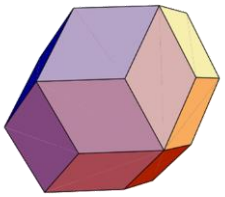
Site-symmetry group

RT  $m\bar{3}\bar{5}$

V: $(0,0,0,0,0,0)$

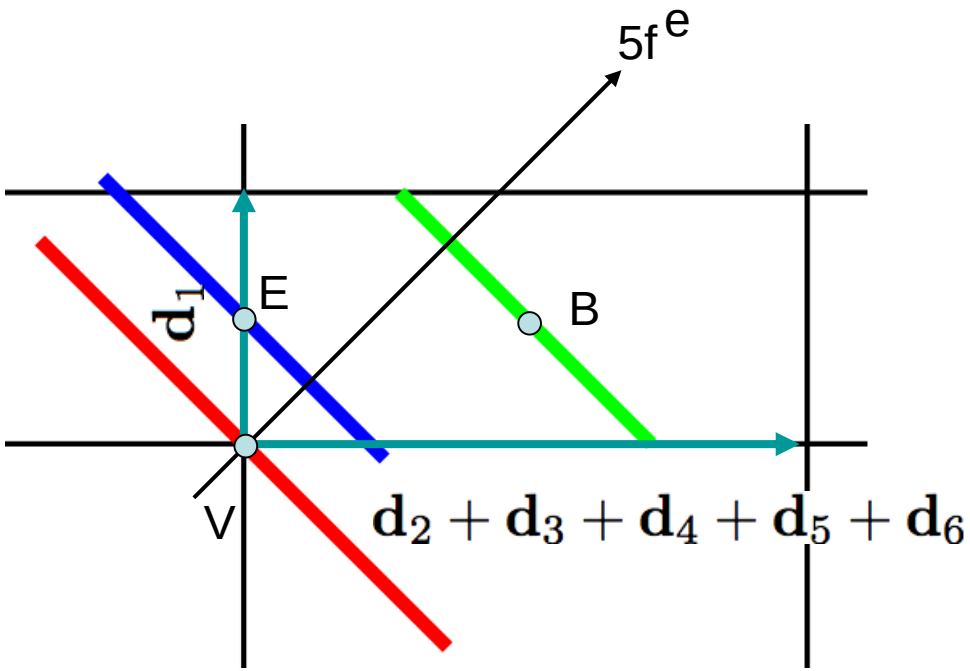
FD  $m\bar{3}\bar{5}$

B: $(\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2})$

RI  $m\bar{5}$

E: $(\frac{1}{2},0,0,0,0,0)$

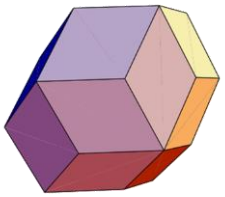
Independent occupation domains and their shapes in the internal space.



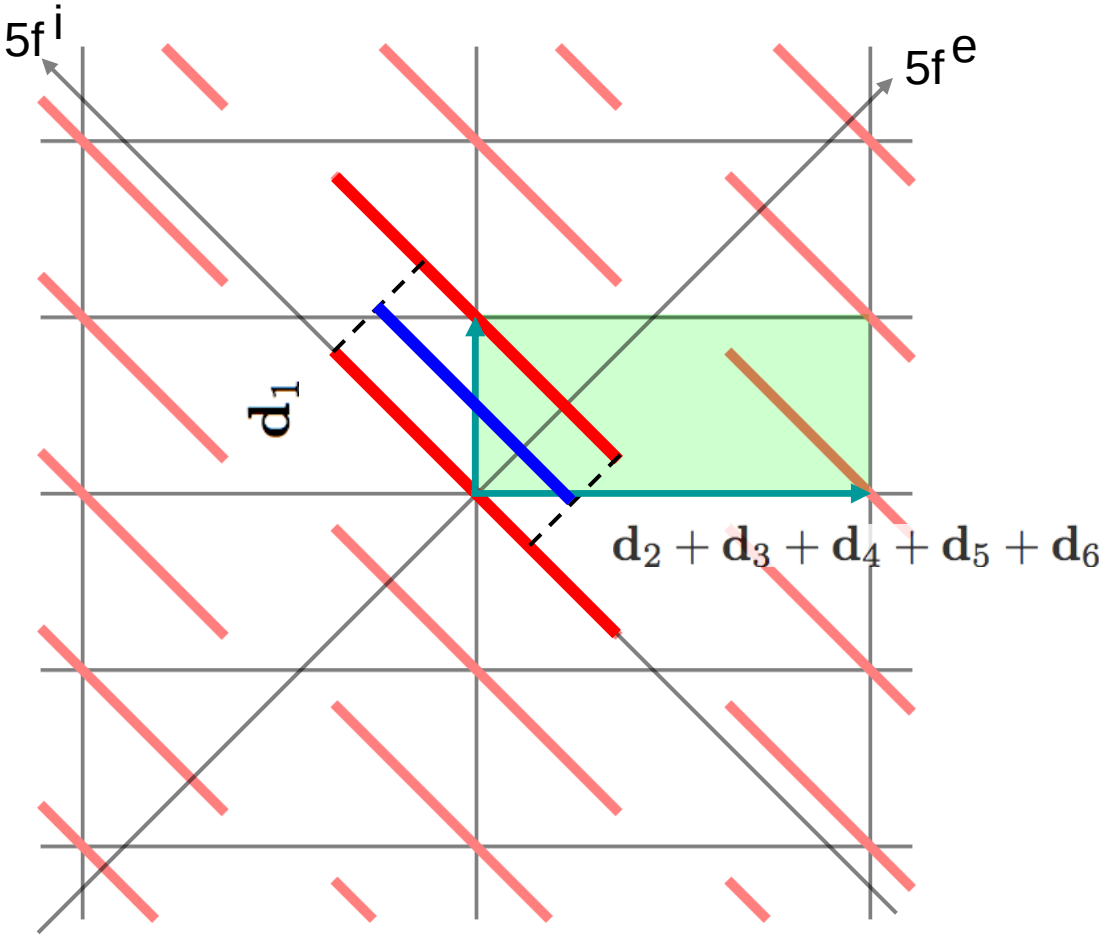
The symmetry of the occupation domain is equal to or higher than the site symmetry.

How to obtain the OD at E

Rhombic icosahedron



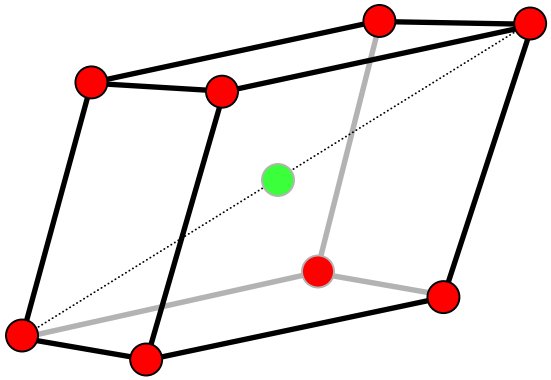
$(\frac{1}{2}, 0, 0, 0, 0, 0)$

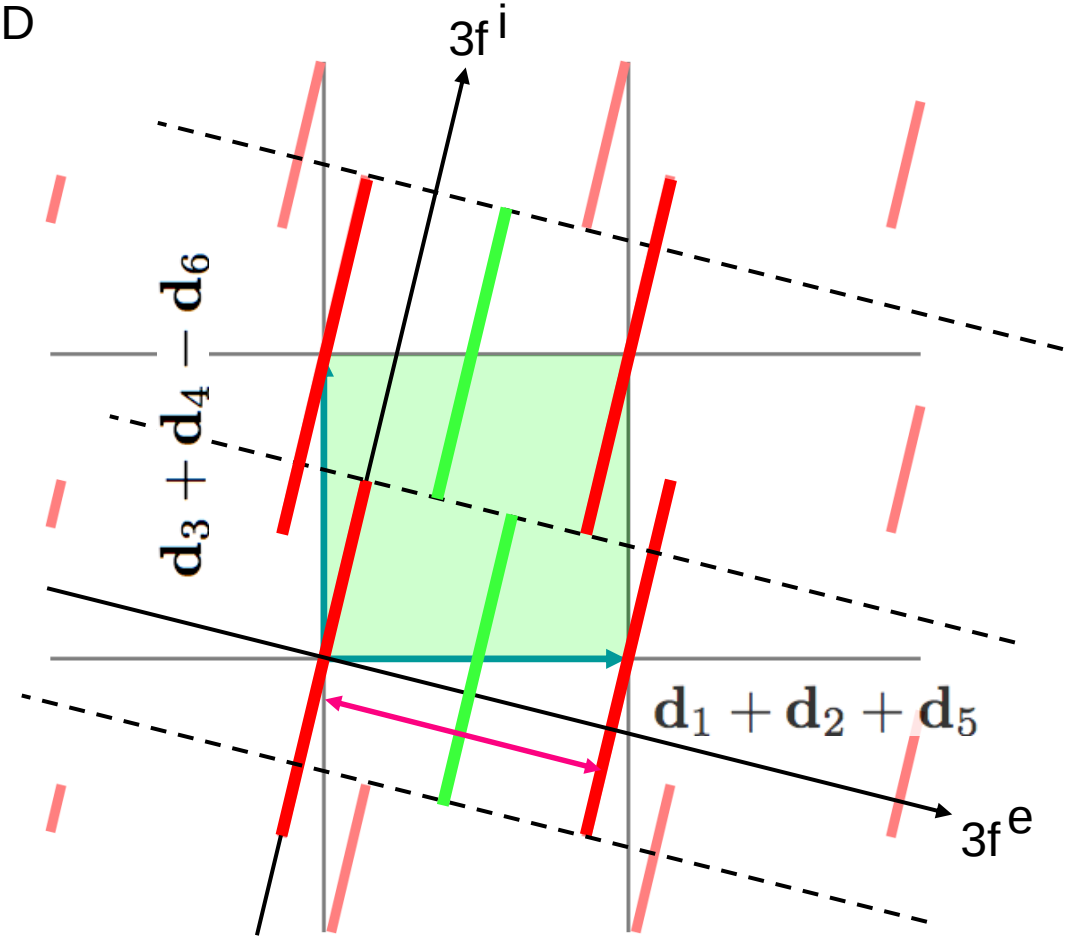


How to obtain the OD at B
(step no.1)

Acute rhombohedral-shaped OD

Center: $(\frac{1}{2}, \frac{1}{2}, 0, 0, \frac{1}{2}, 0)$





Length of the diagonal: $|\mathbf{d}_1^{\mathrm{e}} + \mathbf{d}_2^{\mathrm{e}} + \mathbf{d}_5^{\mathrm{e}}| = (1+\tau)a$

(step no.2)

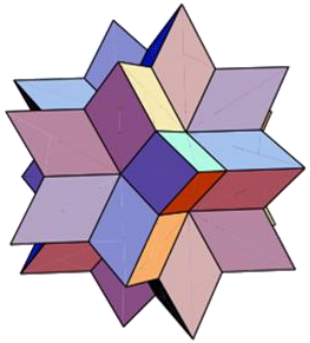
20AR

Center: $(\frac{1}{2}, \frac{1}{2}, 0, 0, \frac{1}{2}, 0)$ + shift along E-space

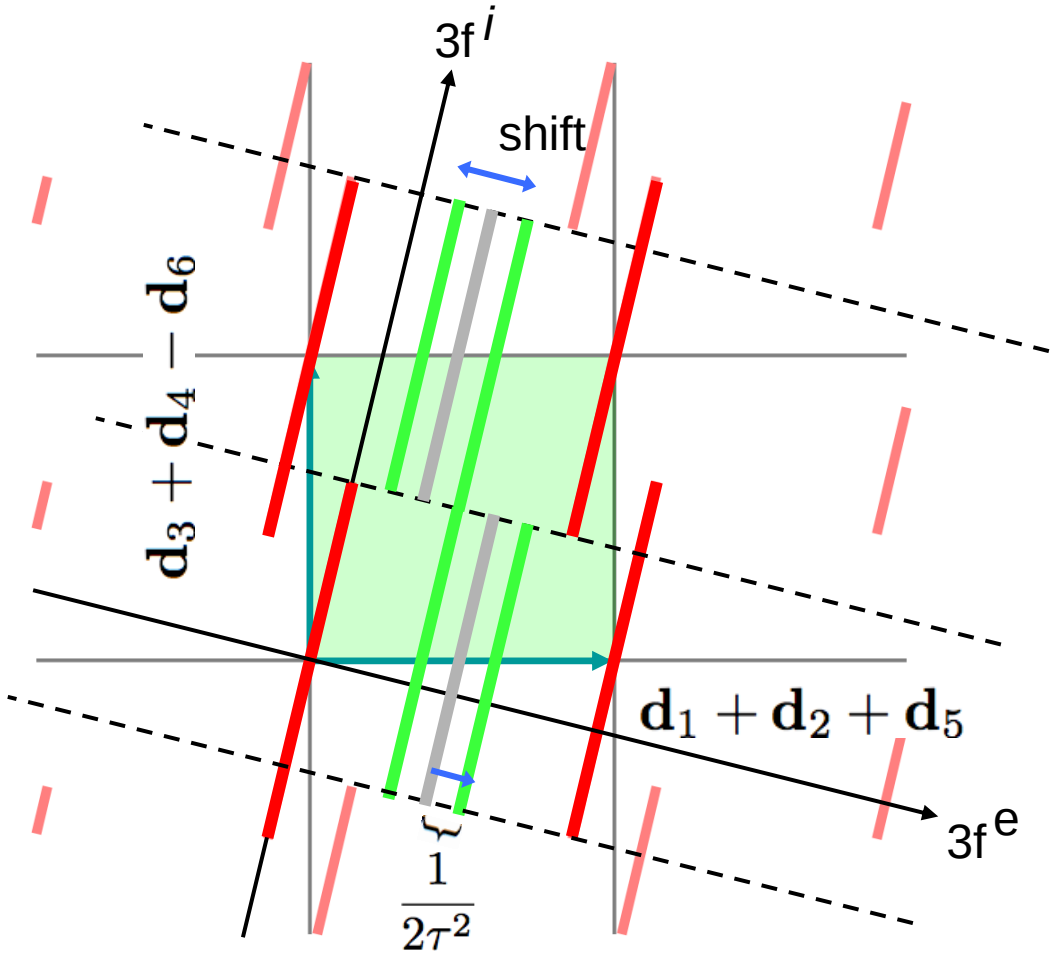
$\cdots$

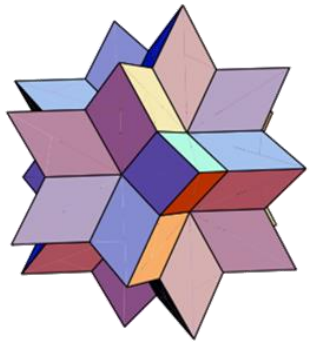
$\cdots$

FD

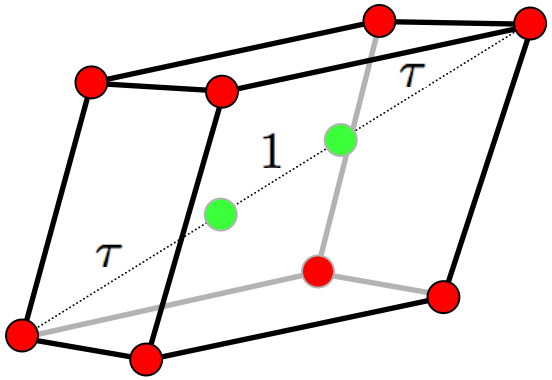


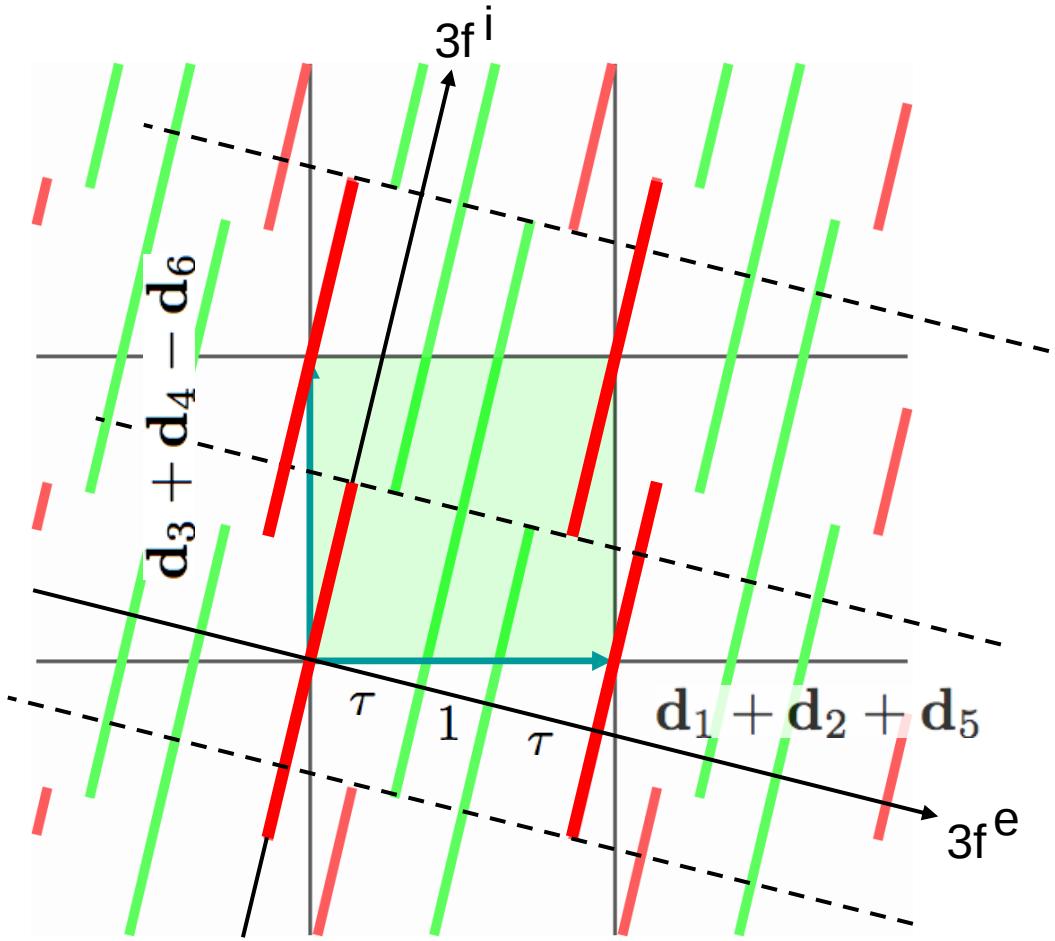
Center: $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$





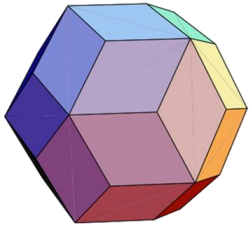
$(\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2})$



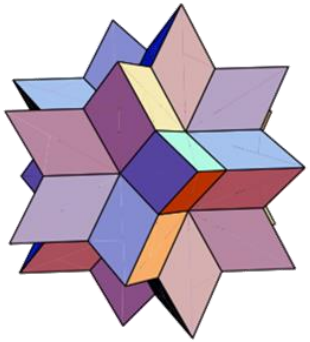


The result is equivalent to put an OD with FD shape on (1,1,1,1,1,1)/2 instead of putting ODs with AR shape at the original positions in the 6D unit cell.

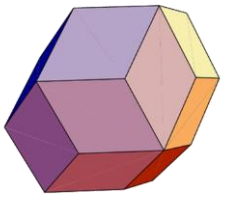
Site-symmetry group

RT  $m\bar{3}\bar{5}$

V: $(0,0,0,0,0,0)$

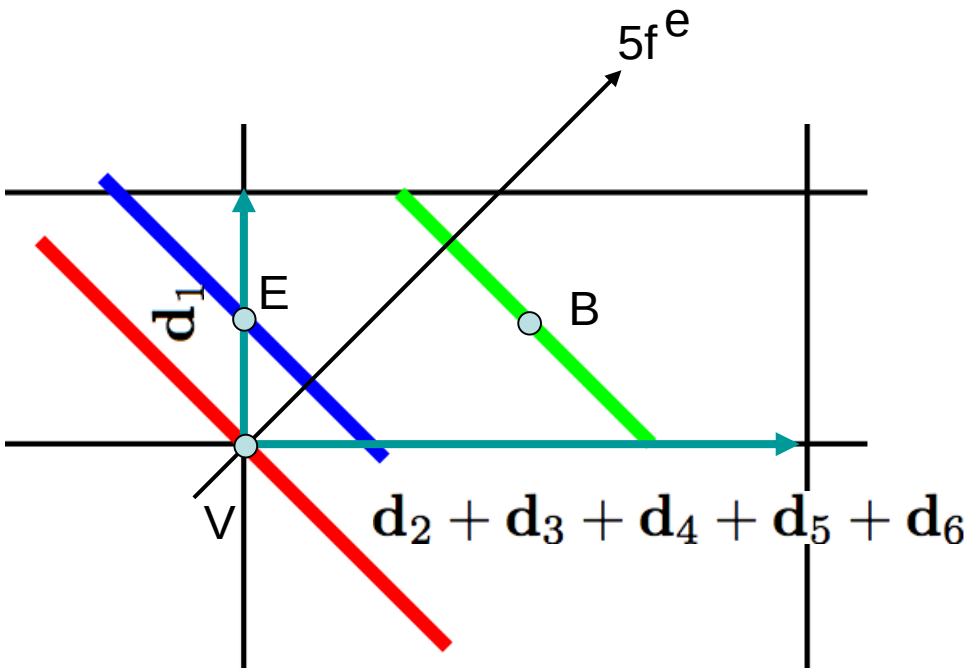
FD  $m\bar{3}\bar{5}$

B: $(\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2})$

RI  $m\bar{5}$

E: $(\frac{1}{2},0,0,0,0,0)$

Simple decoration model



What is important to remember

- iQCs can be described as 6D periodic crystals.
- Occupation domain (OD) can be considered as atom in the 6D periodic crystal.
- Each OD has a specific size and shape.
- The symmetry of OD is equal to or higher than the site-symmetry.

Structure factor formula for QCs

Structure factor formula

$$F(\mathbf{h}) = \sum_{\mu} \sum_{\{R|\mathbf{t}\}^{\mu}} f^{\mu}(\mathbf{h}^{\mathrm{e}}) p^{\mu} \exp\{-B^{\mu}(\mathrm{h}^{\mathrm{e}})^2/4\}$$
$$\times \exp\{2\pi i\, \mathbf{h}\cdot(R\,\mathbf{r}^{\mu} + \mathbf{t})\} F_0^{\mu}(R^{-1}\mathbf{h})$$

μ : Independent occupation domain

$\{R|\mathbf{t}\}^{\mu}$: Symmetry operators of space group which generate the equivalent occupation domains in a unit cell from the independent occupation domain μ

$f^{\mu}(\mathbf{h}^{\mathrm{e}})$: Atomic scattering factor

p^{μ} : s.o.f

B^{μ} : ADP

Provided that the occupation domain consists of ν independent triangles (or tetrahedra), it is given by

$$F_0^{\mu}(\mathbf{h}) = \sum_{i=1}^{\nu} \sum_{R'} F_{0i}^{\mu}(R'^{-1}\mathbf{h})$$

R' : Rotational part of the site-symmetry operator

Real structure of icosahedral quasicrystals

Phase problem in QCs

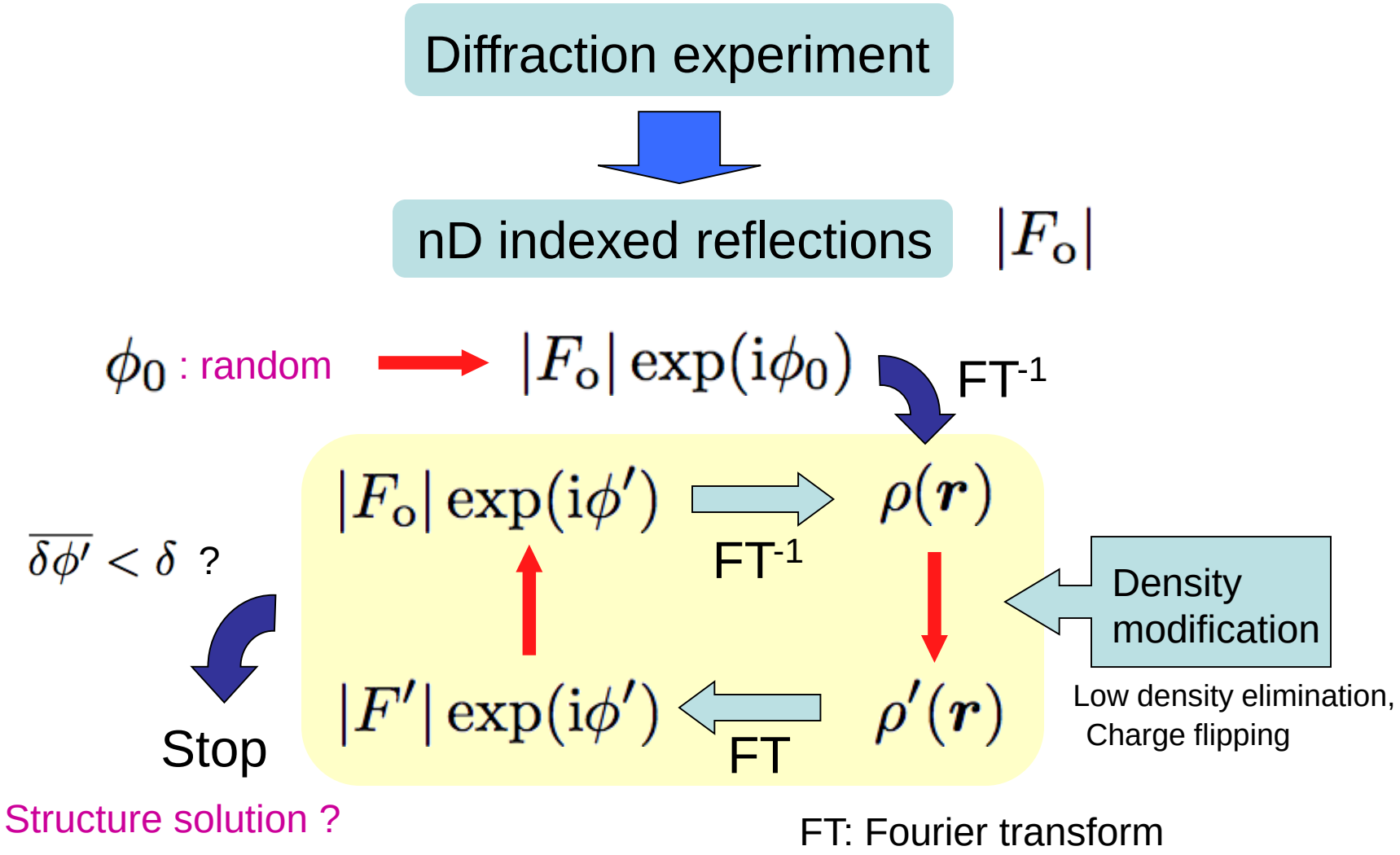
Unavoidable loss of phase information in the diffraction intensity.

$$\begin{cases} F(\boldsymbol{k}) = \int \rho(\boldsymbol{r}) \exp(2\pi i \boldsymbol{k}\cdot\boldsymbol{r})\ \mathrm{d}\boldsymbol{r} \\ \rho(\boldsymbol{r}) = \dfrac{1}{V}\int F(\boldsymbol{k}) \exp(-2\pi i \boldsymbol{k}\cdot\boldsymbol{r})\ \mathrm{d}\boldsymbol{k} \end{cases}$$

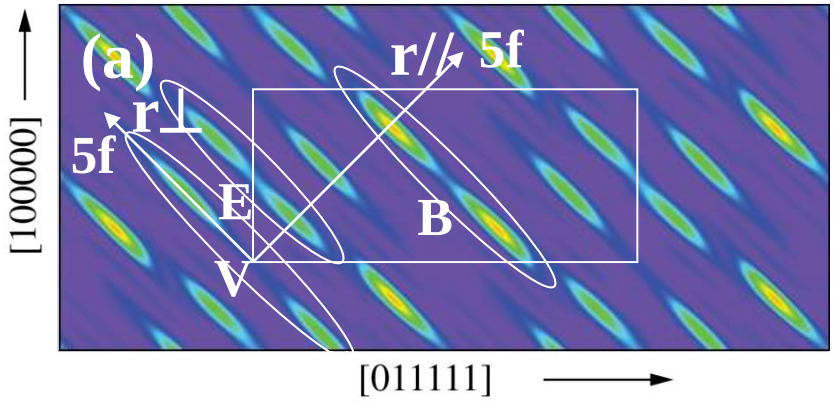
$$F(\boldsymbol{k}) = |F| \exp(\mathrm{i}\phi) \qquad I \propto |F|^2$$

The phase ϕ cannot be obtained by ordinary diffraction experiment.

Principle of the density modification method

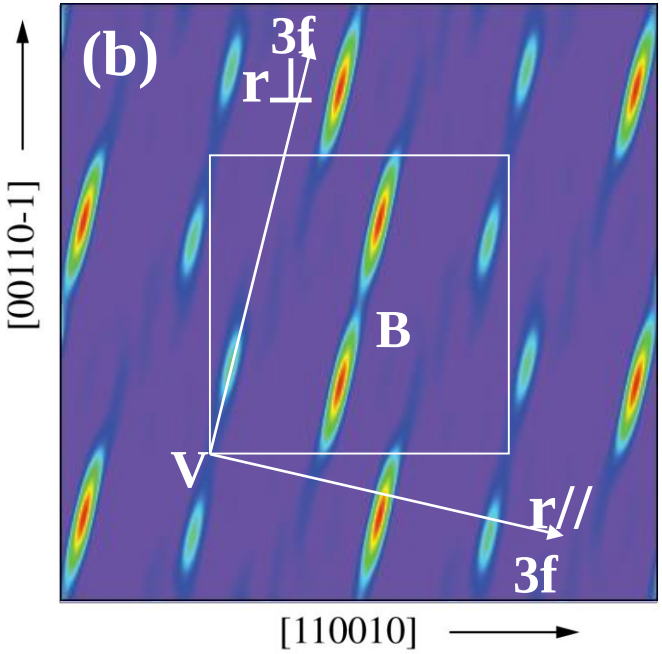


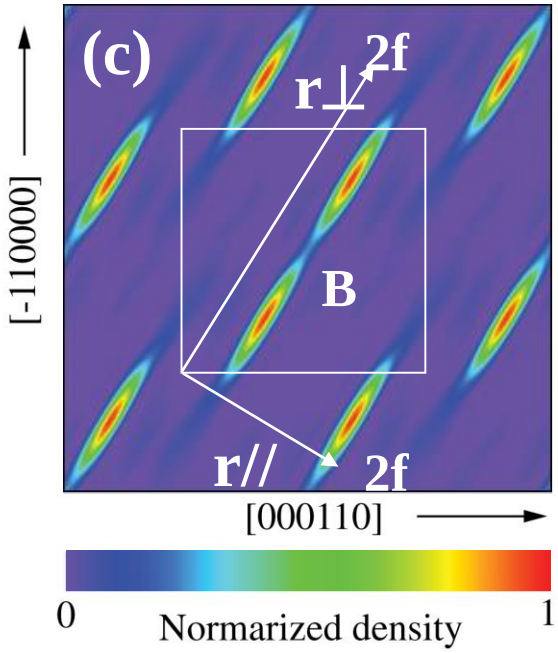
Structure solution of P-type i-Zn-Mg-Ho QC



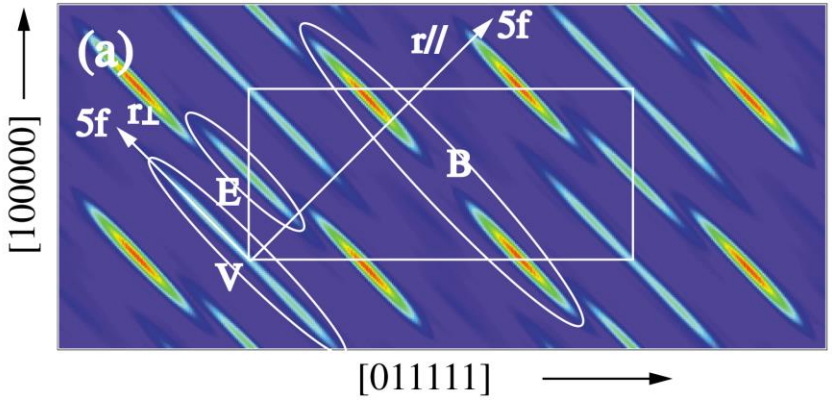
space group $Pm\bar{3}5$

V: (0,0,0,0,0,0)
B: (1,1,1,1,1,1)/2
E: (1,0,0,0,0,0)/2
***a* = 0.5137 nm**





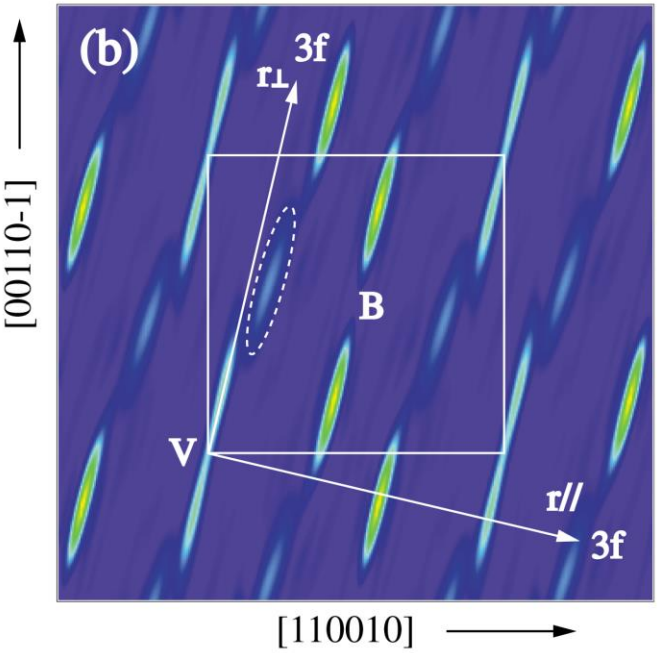
Structure solution of i-Yb-Cd QC

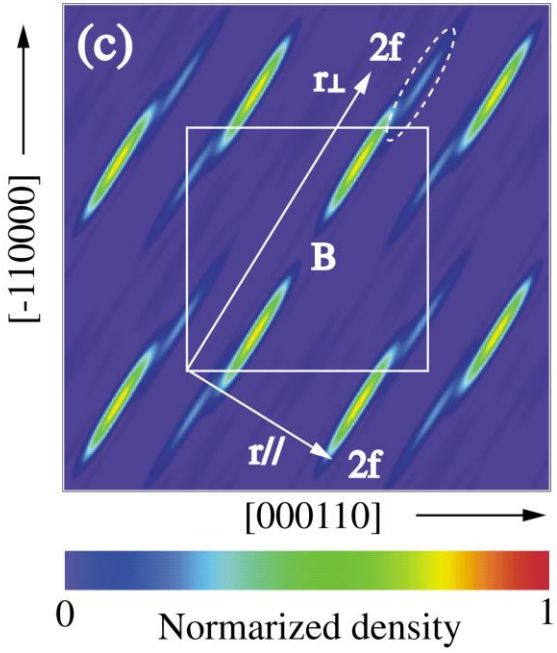


space group $Pm\bar{3}5$

V: (0,0,0,0,0,0)
B: (1,1,1,1,1,1)/2
E: (1,0,0,0,0,0)/2

***a* = 0.5689 nm**

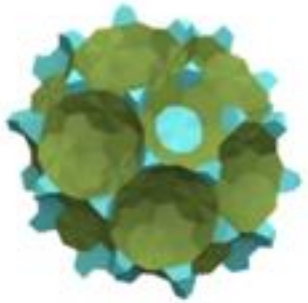




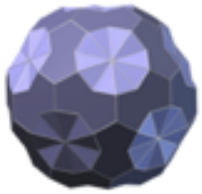
Occupation domains for i-Yb-Cd QC

V:(000000)

B:(111111)/2



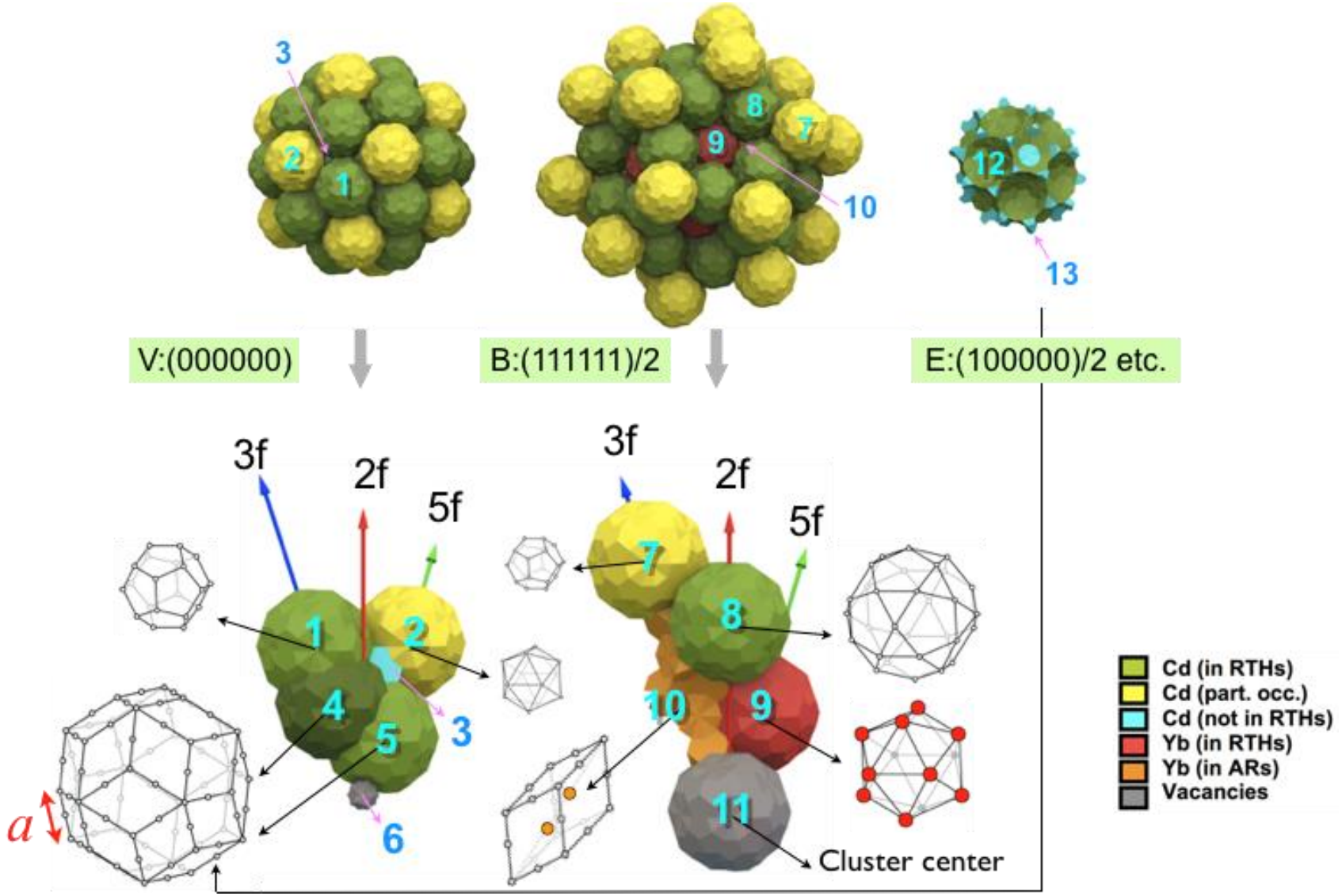
E:(100000)/2

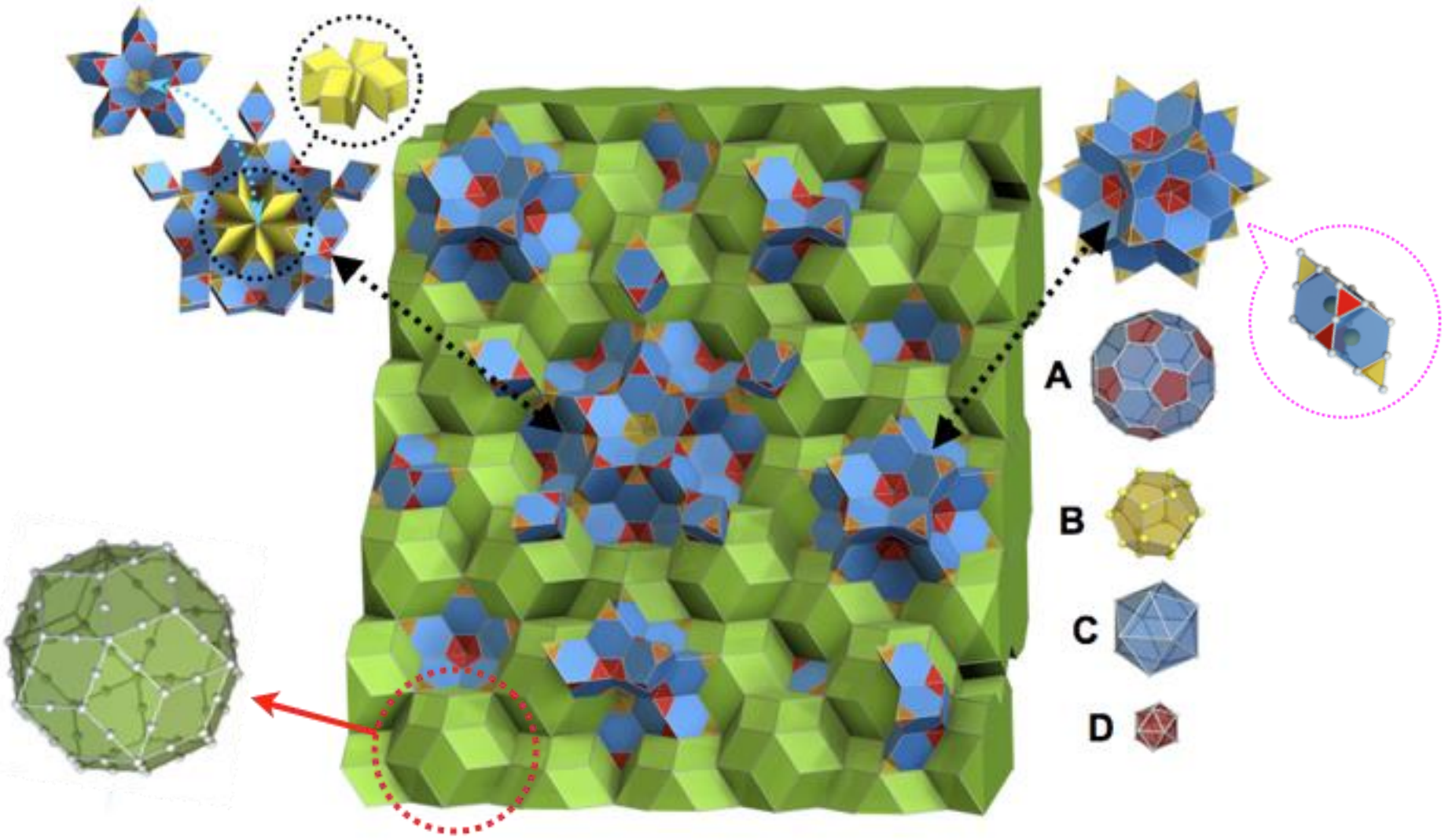


: OD for the 12-fold vertices of 3D AKN tiling

Cd (in RTHs)
Cd (part. occ.)
Cd (not in RTHs)
Yb (in RTHs)
Yb (in ARs)
Vacancies

Constitution of the ODs for i-YbCd QC





H.Takakura, C.P.Gomez, A.Yamamoto, M.deBoissue, A.P.Tsai, Nat. Mater. 2007, 6, 58.

Summary

- The 6D structure of iQCs can be known by the 6D electron densities obtained through a phase retrieval of diffraction data.
- Respective iQCs have different 6D crystal structures.
- Result of phase retrieval is a starting point of structure analysis of iQCs.
- The purpose of the structure analysis of QCs is to determine the 3D atomic structure, which means that to determine the detailed shape of occupation, to specify its location and to reveal the distribution of constituent elements in it.