Structure Analysis of Quasicrystals

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Tokyo University of Science

2020/05/28

Yamamoto, Akiji, *Acta Cryst. A* **52**, 4, 509-560, (1996)

Lecture by H. Takakura in 1st International School on Aperiodic Crystals, France, (2010)

Outline

Part 1, Fibonacci Chain

- Section Method
- Diffraction Pattern
- Linear Phason Strain (Approximant of Fibonacci Chain)
- Diffraction Pattern and Phason distortion

Part 2, Icosahedral Quasicrystals (iQCs)

- Unit vector
- Symmetry, Brave lattice
- 3D Penrose Tilling
- Simple Decoration on 3D Penrose Tilling
- Cluster-based Model
- Tsai-type iQC

Part 3, Structure Analysis

- Structure Factor Formula
- Diffraction Intensities Measurement
- Useful Softwares

Exercise

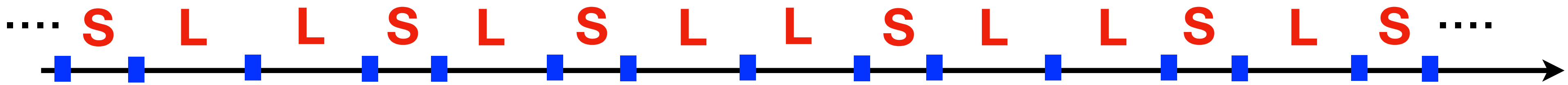
Part 1,
Fibonacci Chain

Section Method

Fibonacci Chain

Aperiodic sequence of two segments, S and L.

L/S=τ=1.618...



- Inflation construction, S → L and L → LS

  S, LS, LSL, LSLLS, LSLLSLSL, LSLLSLSLLSLLS, ...

- 1D Section of 2D periodic structure (Section Method)

  ....

Fibonacci Chain by Section Method

2D space :

Unit vector:

$\mathbf{a}_1 \quad \mathbf{a}_2$

Fibonacci Chain by Section Method

2D space :

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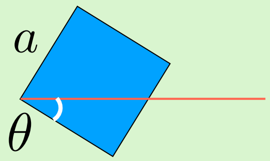
2D lattice :

Lattice const. = a



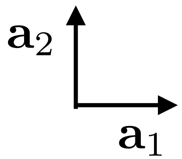
$$\tan\theta = \frac{1}{\tau}$$

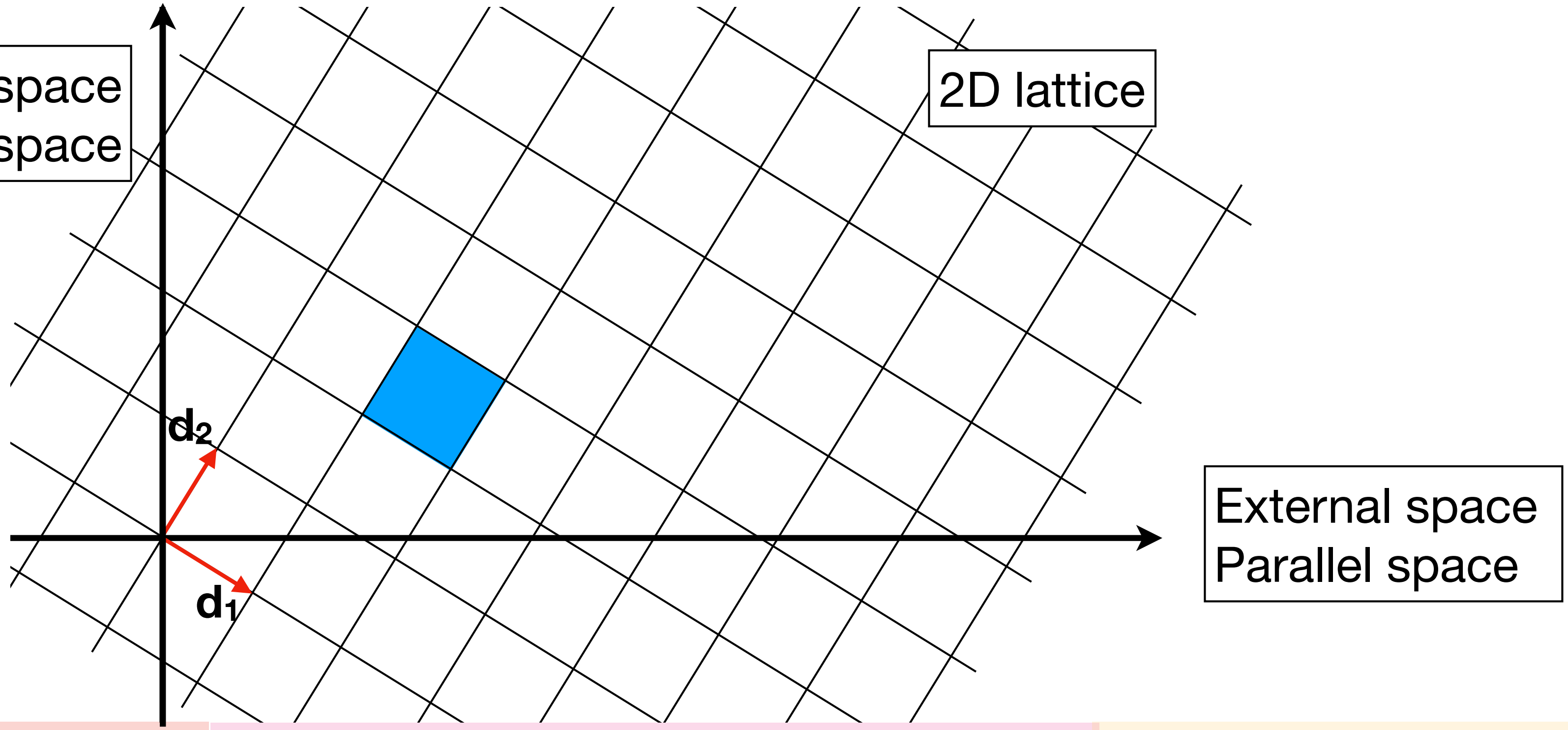
$$\tau = \frac{1+\sqrt{5}}{2} = 1.61803...$$

2D lattice vector : $\mathbf{d}_i (i = 1, 2)$

$$\mathbf{d}_i = \sum_{i=1}^{m} Q_{ij}\mathbf{a}_j$$

$$\begin{pmatrix} \mathbf{d_1} \\ \mathbf{d_2} \end{pmatrix} = \frac{a_{2D}}{\sqrt{\tau^2+1}} \begin{pmatrix} \tau & -1 \\ 1 & \tau \end{pmatrix} \begin{pmatrix} \mathbf{a_1} \\ \mathbf{a_2} \end{pmatrix}$$





2D lattice vector : $\mathrm{d}_i (i = 1, 2)$

$$\mathbf{d}_i = \mathbf{d}_i^e + \mathbf{d}_i^i$$

External Internal

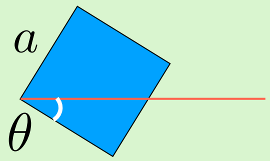
Fibonacci Chain by Section Method

2D space :

Unit vector:

$\mathbf{a}_1 \quad \mathbf{a}_2$

2D lattice :



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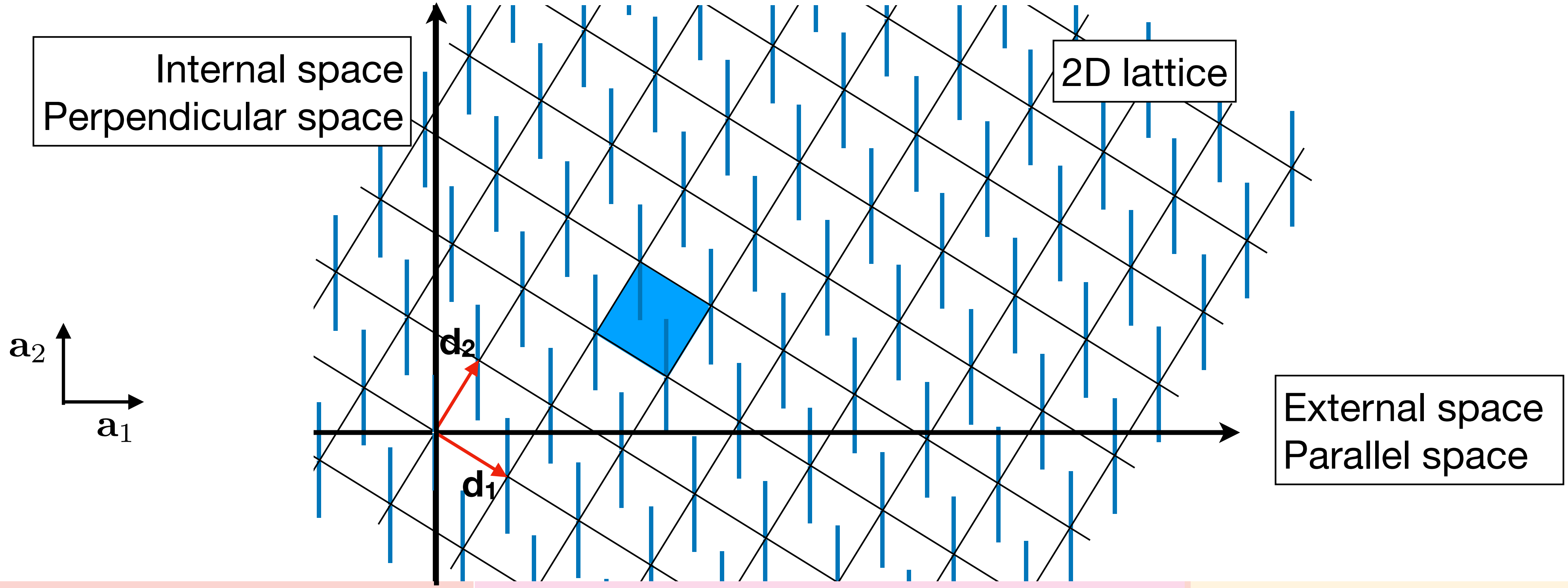

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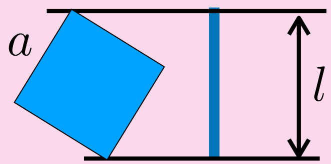
External Internal

Occupation domain :



$$l = \frac{\tau^2}{\sqrt{1+\tau^2}}a$$

Fibonacci Chain by Section Method

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$\mathbf{a}_1 \quad \mathbf{a}_2$

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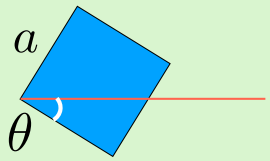

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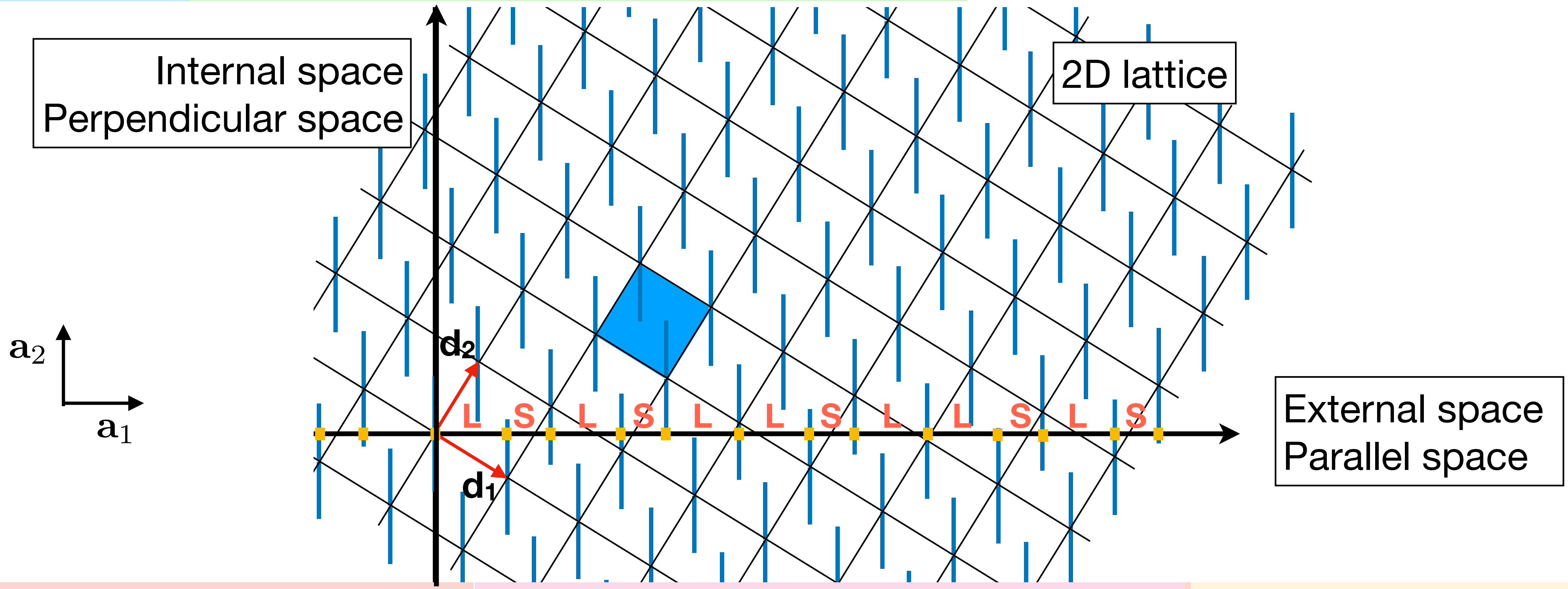

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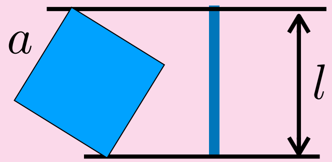
External　　Internal

Occupation domain :



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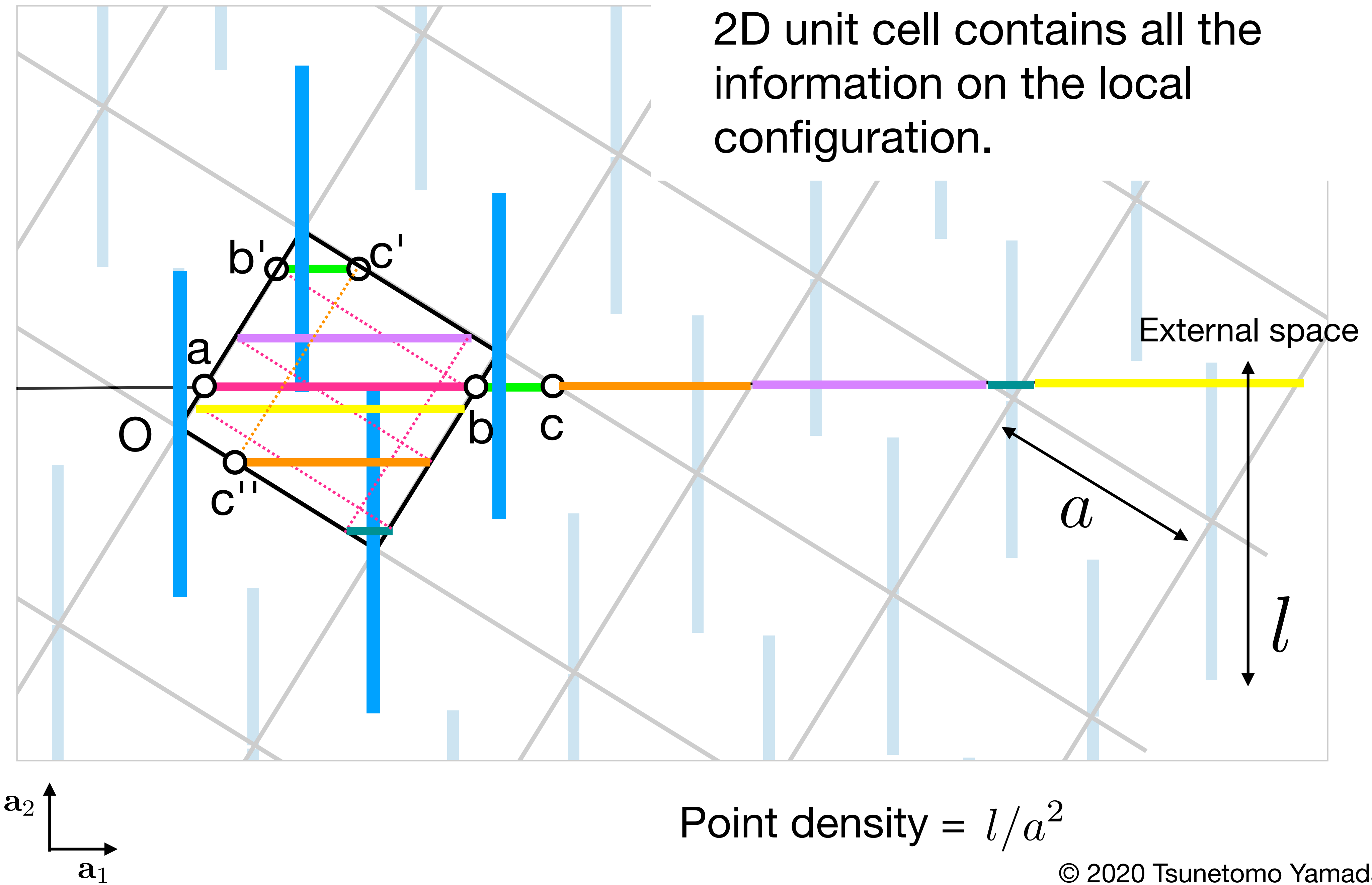
Fibonacci chain

- Aperiodic

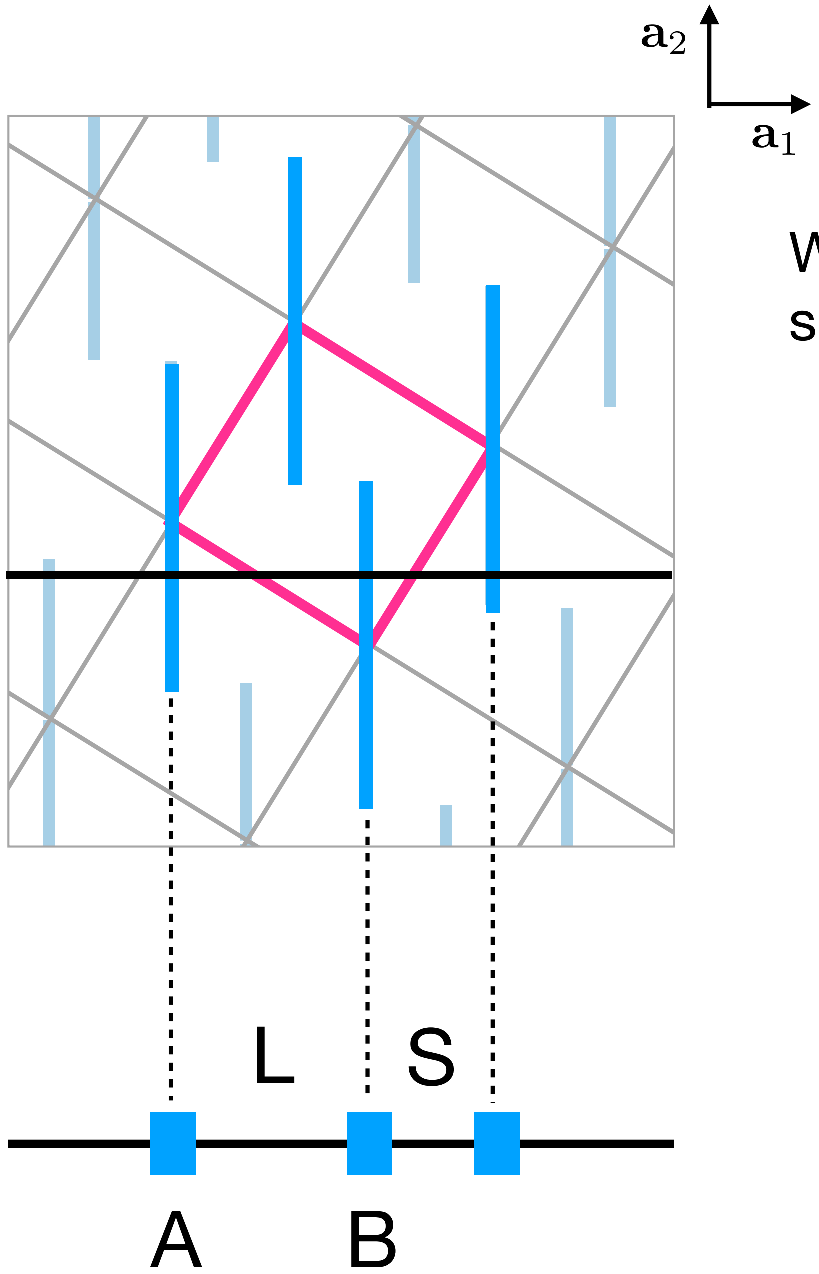
Fibonacci Chain by Section Method



2D unit cell contains all the information on the local configuration.

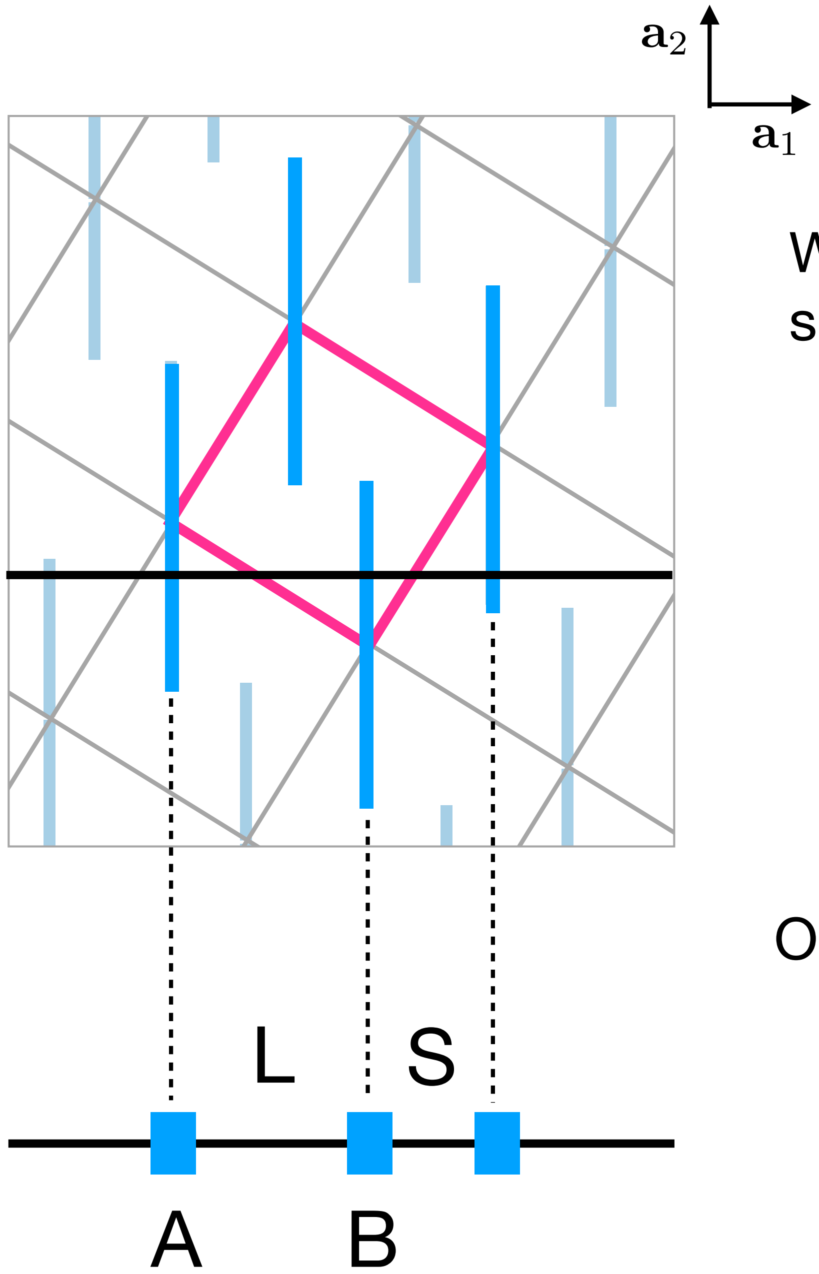
Point density = l/a^2

Fibonacci Chain by Section Method



When do we have a point "B" on the right side of a point "A" at a distance L?

Fibonacci Chain by Section Method



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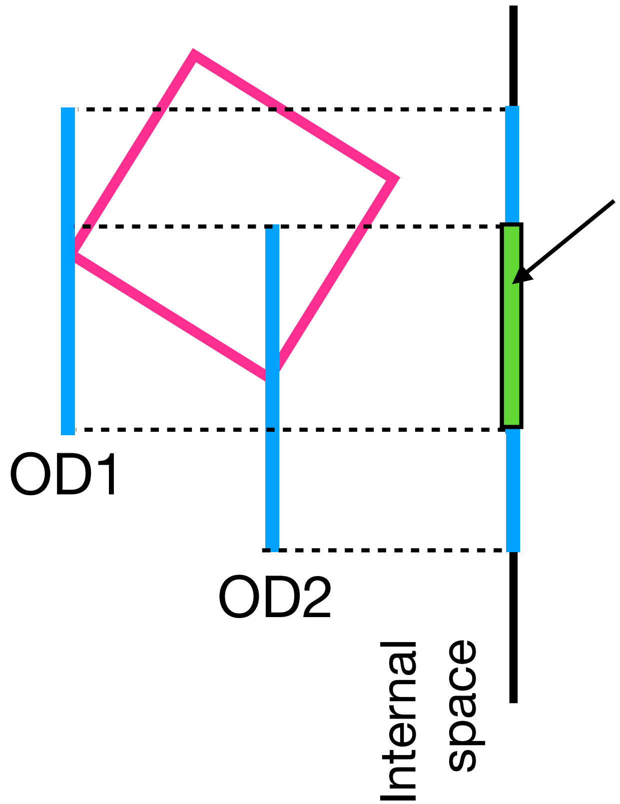
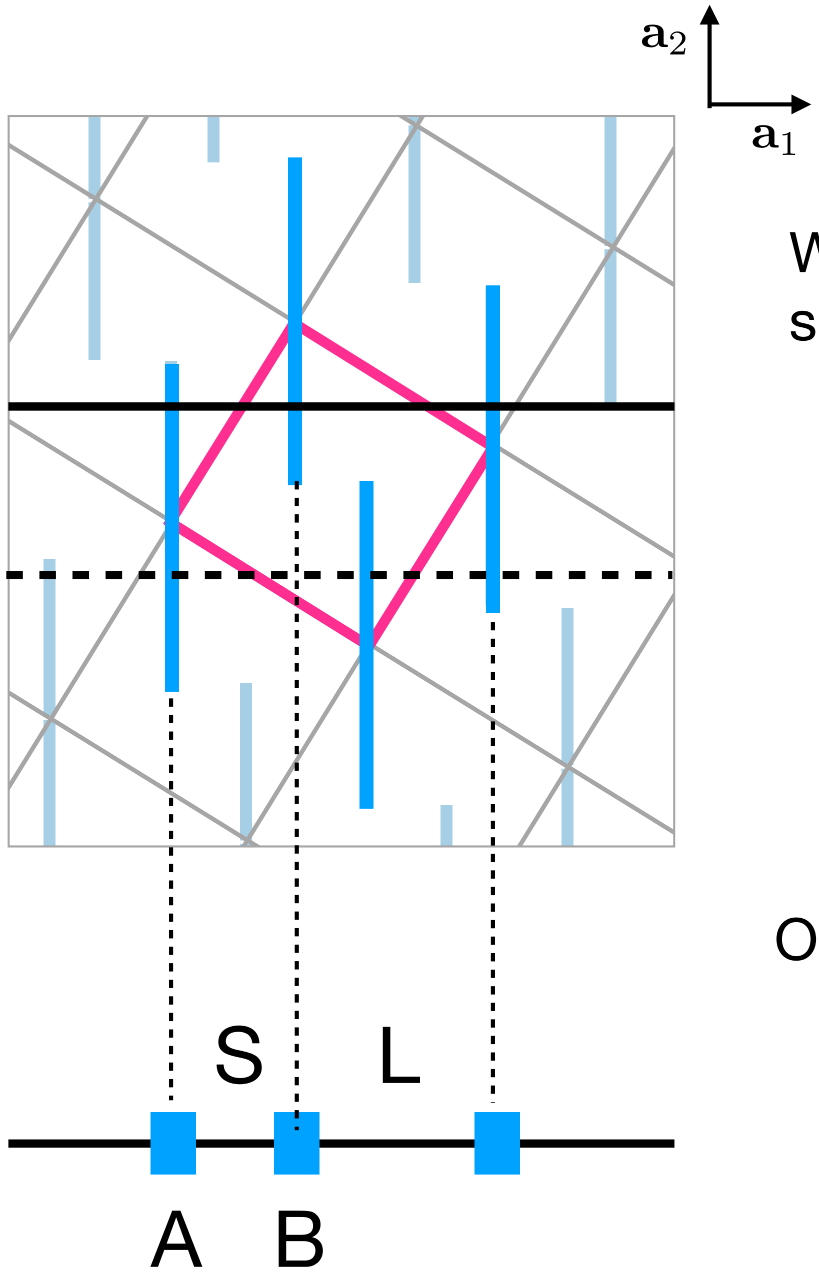


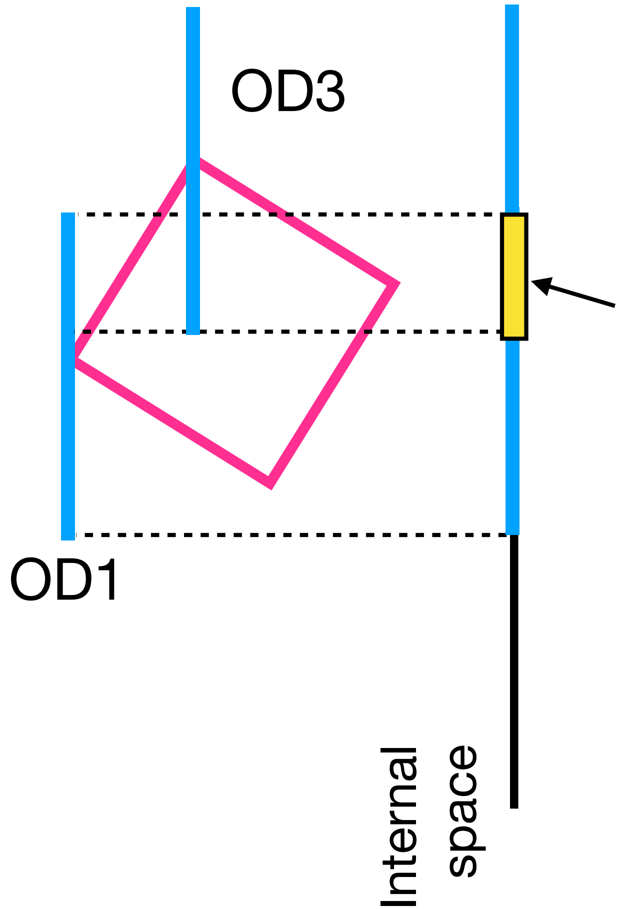
Existence domain of the configuration L:

Intersection between the projections of OD1 and 2 onto internal space.

Fibonacci Chain by Section Method



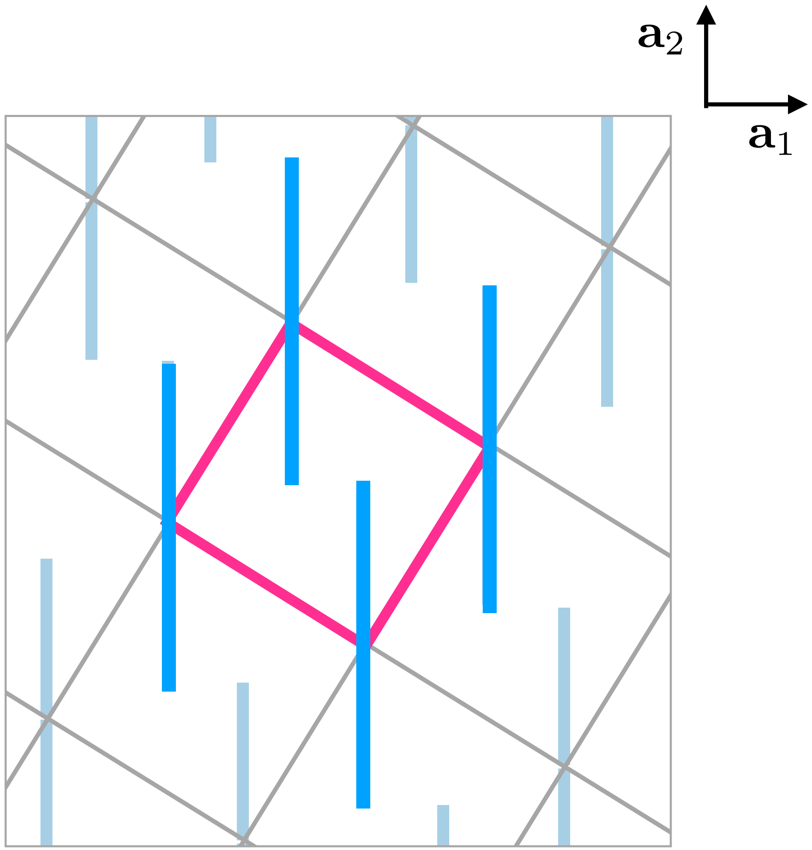
When do we have a point "B" on the right side of a point "A" at a distance S?



Existence domain of the configuration S:

Intersection between the projections of OD1 and 3 onto internal space.

Fibonacci Chain by Section Method



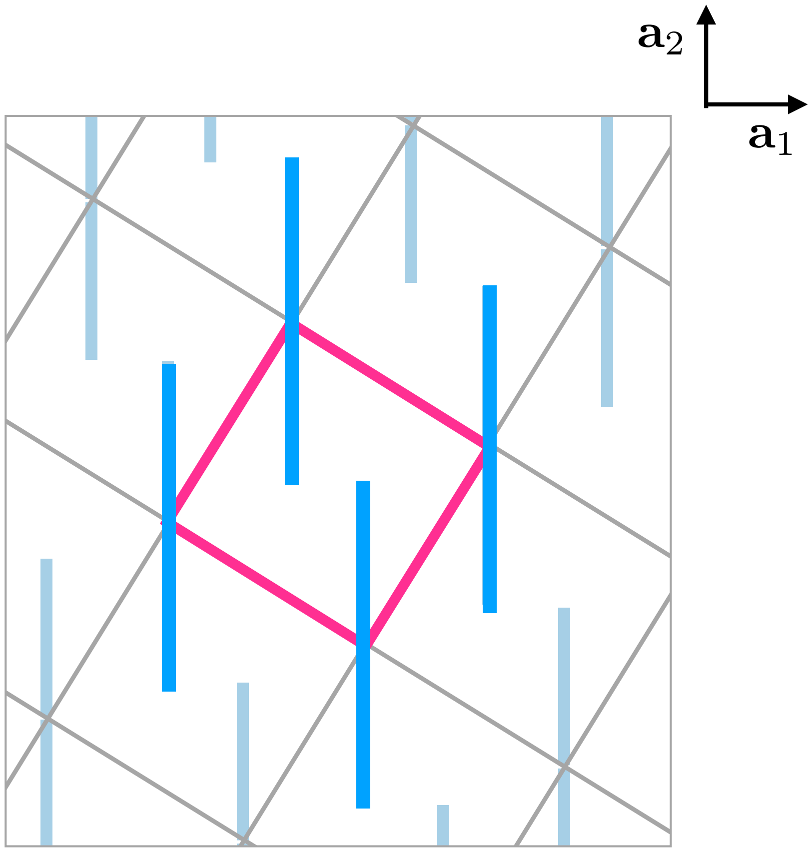
Existence domain of the configuration L:

Existence domain of the configuration S:

The frequency of the configuration in the finite structure is proportional to the size of intersection.

$$L : S = \tau : 1$$

Fibonacci Chain by Section Method



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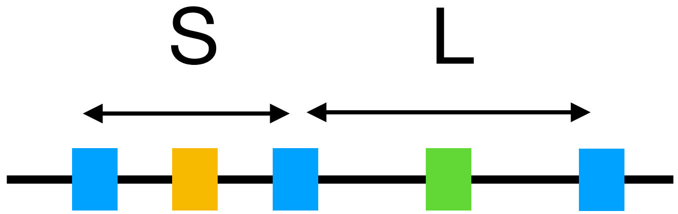
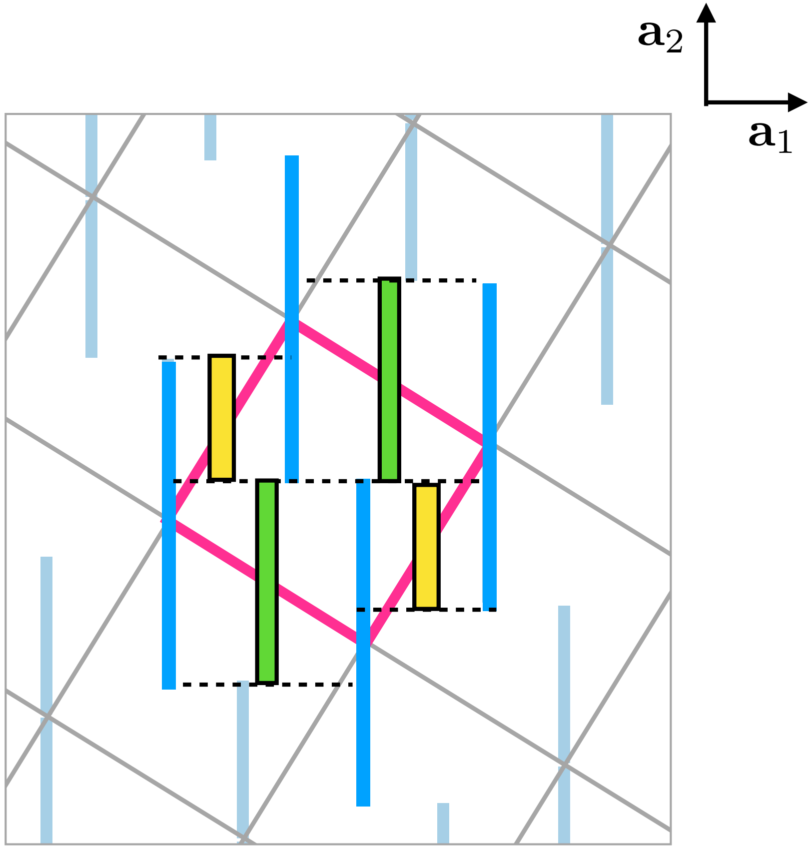
Decoration of Fibonacci chain



Fibonacci Chain by Section Method



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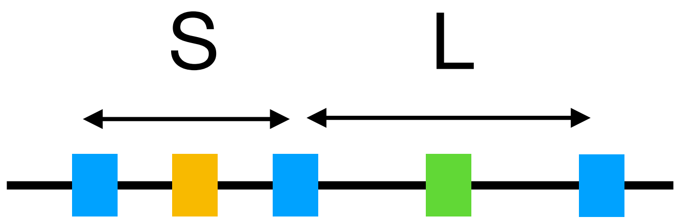

Diffraction Pattern of Fibonacci Chain

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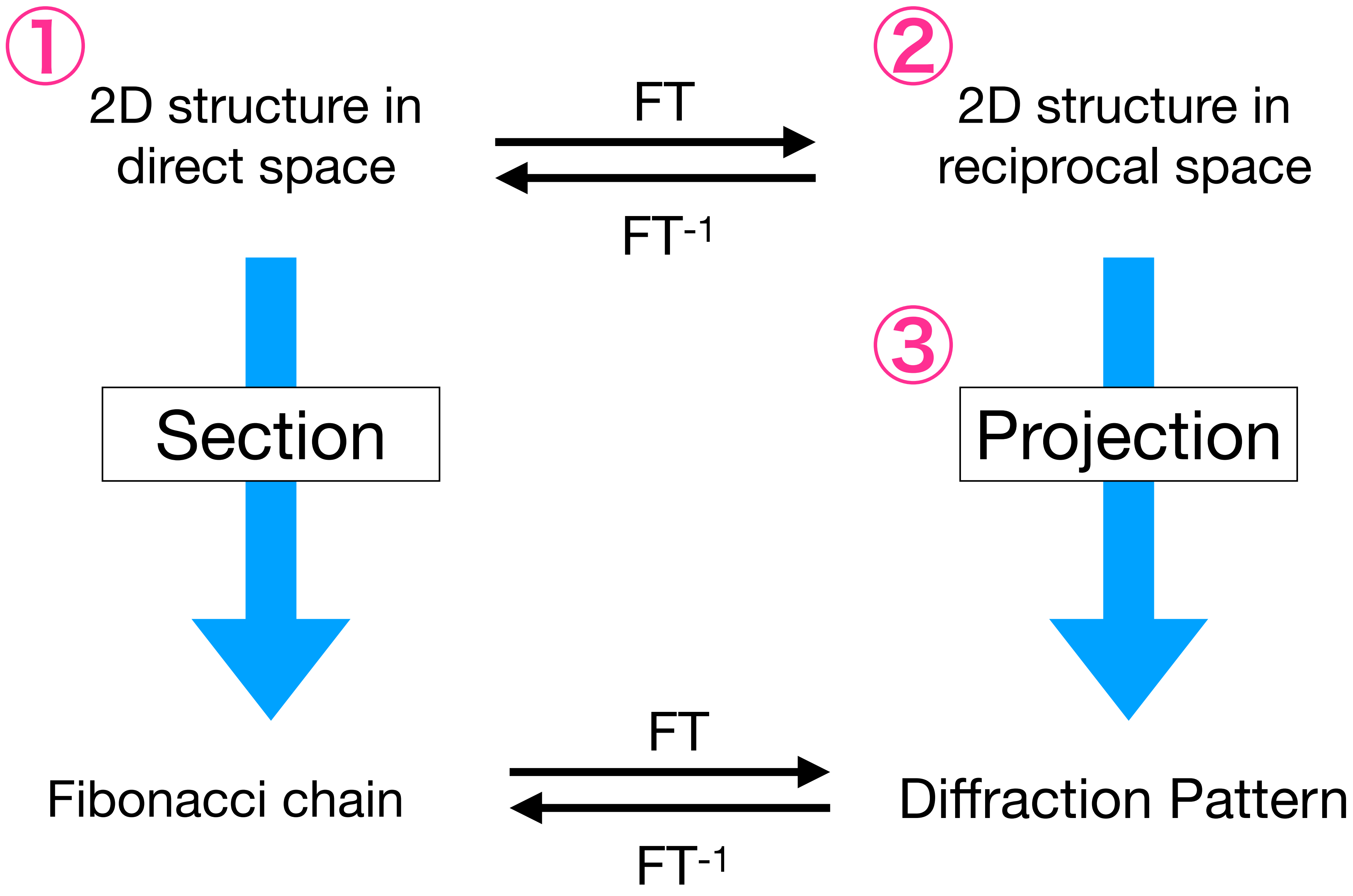


Diffraction Pattern

① 2D decorated structure:

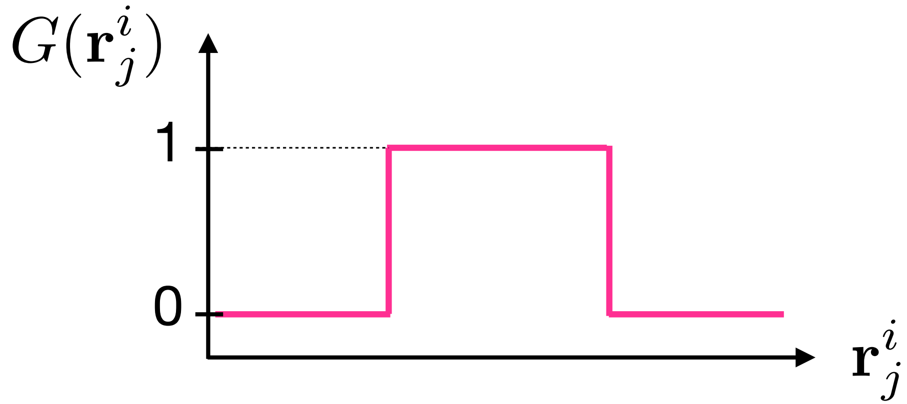
Atomic (or electron) density distribution cab be expressed as a convolution product between the lattice and the occupation domain (OD).

Structure = Lattice ∗ OD

$$\rho(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_{n1,n2}) * \sum_j G_j(\mathbf{r}_j^i)\mathbf{r}_j$$

$\mathbf{r}_j$: Position of j-th OD

$G_j(\mathbf{r}_j^i)$: Shape function that represents j-th OD



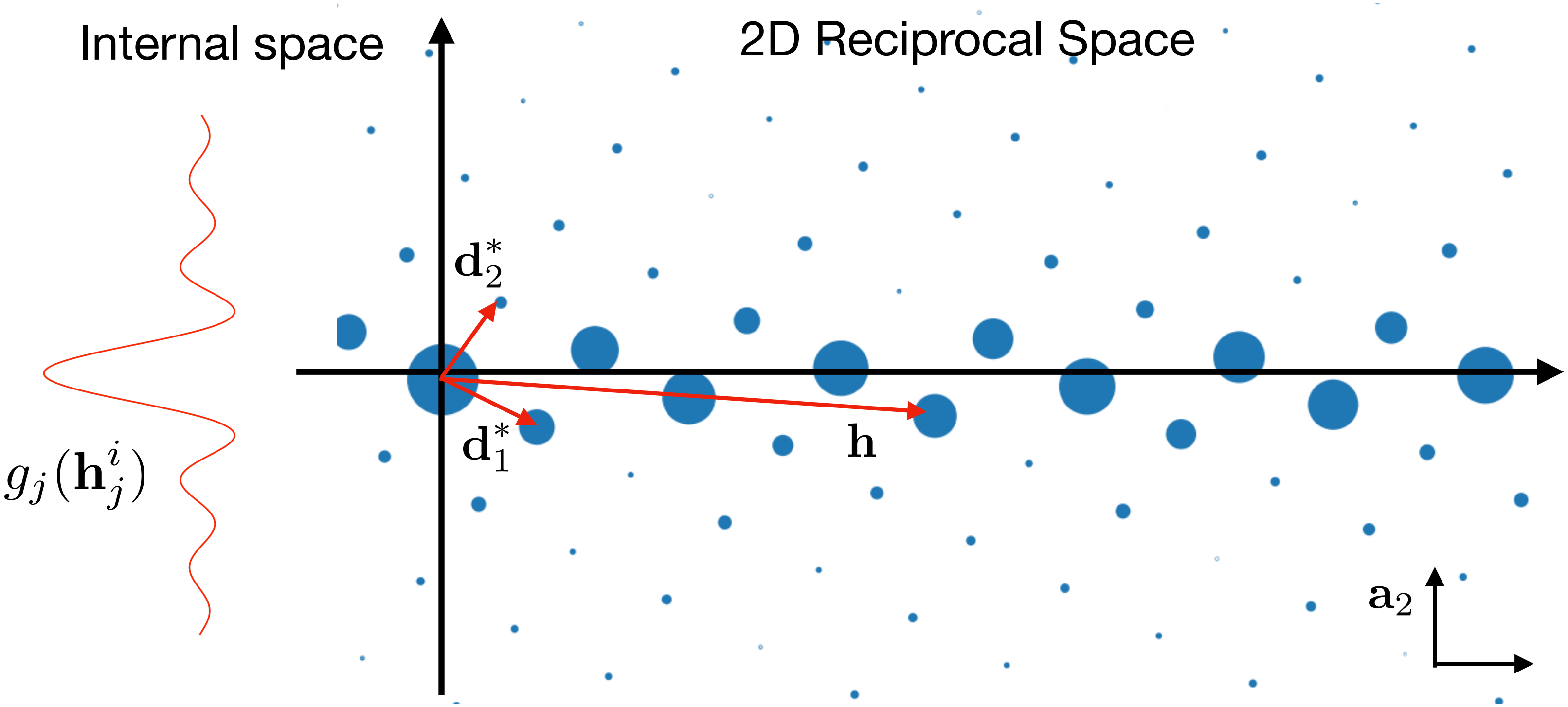
Diffraction Pattern

② Fourier transformation of 2D decorated structure:

FT(Lattice ∗ OD) = FT(Lattice) · FT (OD)

$$F(\mathbf{k}) = \delta(\mathbf{k} - \mathbf{h}_{h,k}) \frac{1}{V} \sum_j g_j(\mathbf{h}_j^i) \exp(2\pi i \mathbf{h}_{h,k} \cdot \mathbf{r}_j)$$

$$g_j(\mathbf{h}_j^i) = l \sin(\pi l \mathrm{h}^i)/(\pi l \mathrm{h}^i)$$



$$\mathbf{d}_1^* = \mathbf{d}_1^{*e} + \mathbf{d}_1^{*i}$$

$$\mathbf{d}_2^* = \mathbf{d}_2^{*e} + \mathbf{d}_2^{*i}$$

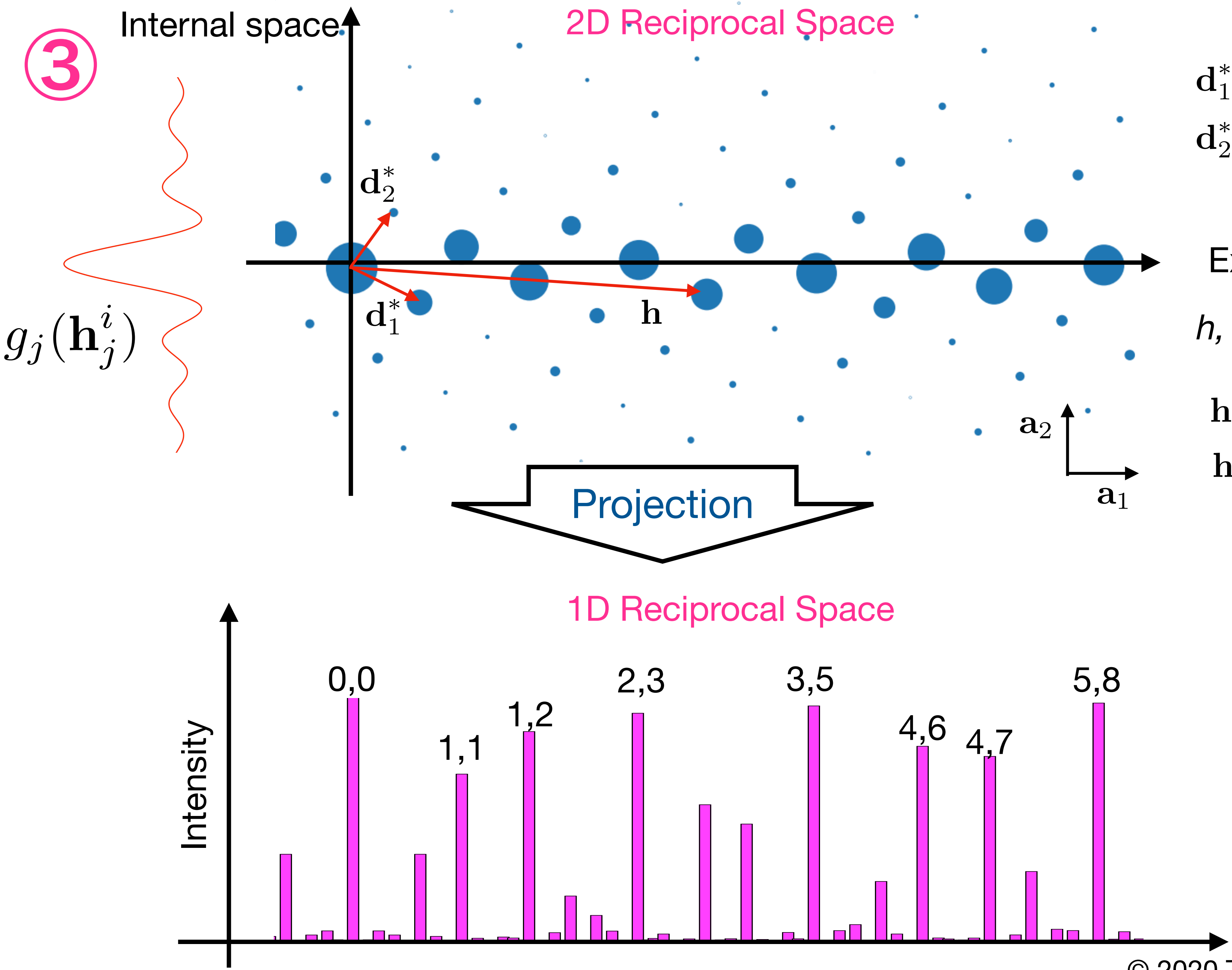
$$\mathbf{d}_i \cdot \mathbf{d}_j^* = \begin{cases} 1 (i = j) \\ 0 (i \neq j) \end{cases}$$

h, *k*: Miller Index

$$\mathbf{h} = h\mathbf{d}_1^* + k\mathbf{d}_2^*$$

$$\mathbf{h} = \mathbf{h}^e + \mathbf{h}^i$$

Diffraction Pattern



$$\mathbf{d}_1^* = \mathbf{d}_1^{*e} + \mathbf{d}_1^{*i}$$
$$\mathbf{d}_2^* = \mathbf{d}_2^{*e} + \mathbf{d}_2^{*i}$$

External space

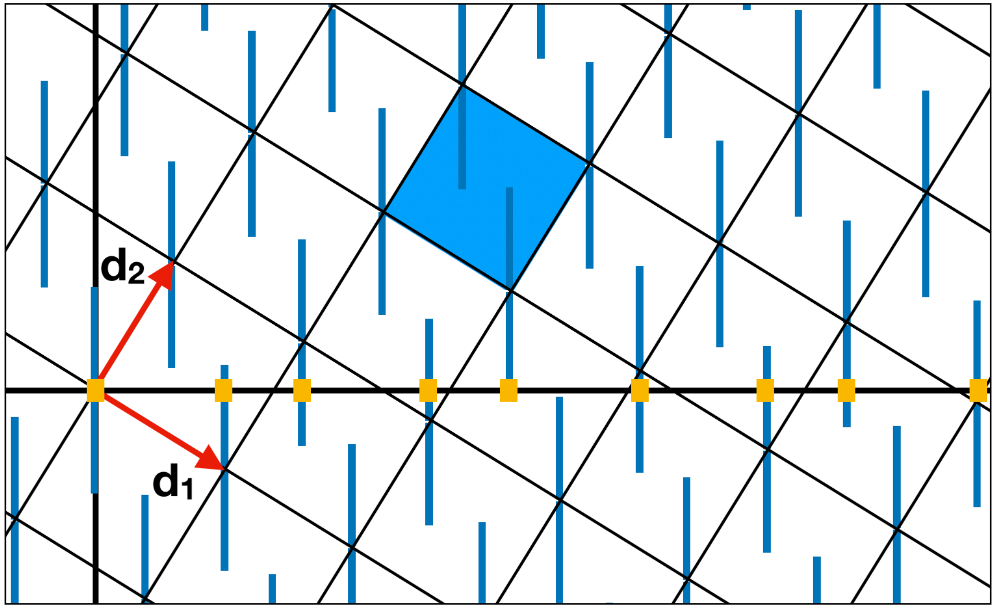
h, *k*: Miller Index

$$\mathbf{h} = h\mathbf{d}_1^* + k\mathbf{d}_2^*$$
$$\mathbf{h} = \mathbf{h}^e + \mathbf{h}^i$$

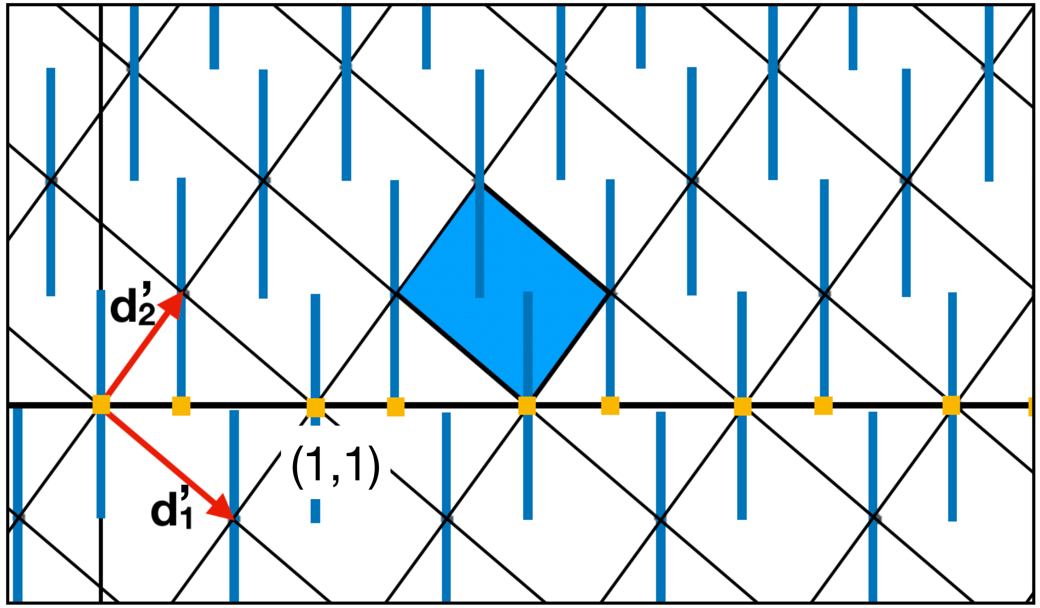
Phason Strain and its Consequences on Diffraction Pattern

Fibonacci Chain under Phason Strain

Fibonacci lattice

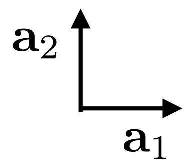


1/1 Approximant



Linear phason strain

Phason matrix : U^i



$$\mathbf{d}'_i = \sum_{i=1}^{m} Q_{ij}\mathbf{a}'_j = \sum_{i=1}^{m} (QT^i)_{ij}\mathbf{a}_j \qquad T^i = \begin{pmatrix} I_d & U^i \\ 0 & I_d \end{pmatrix}$$

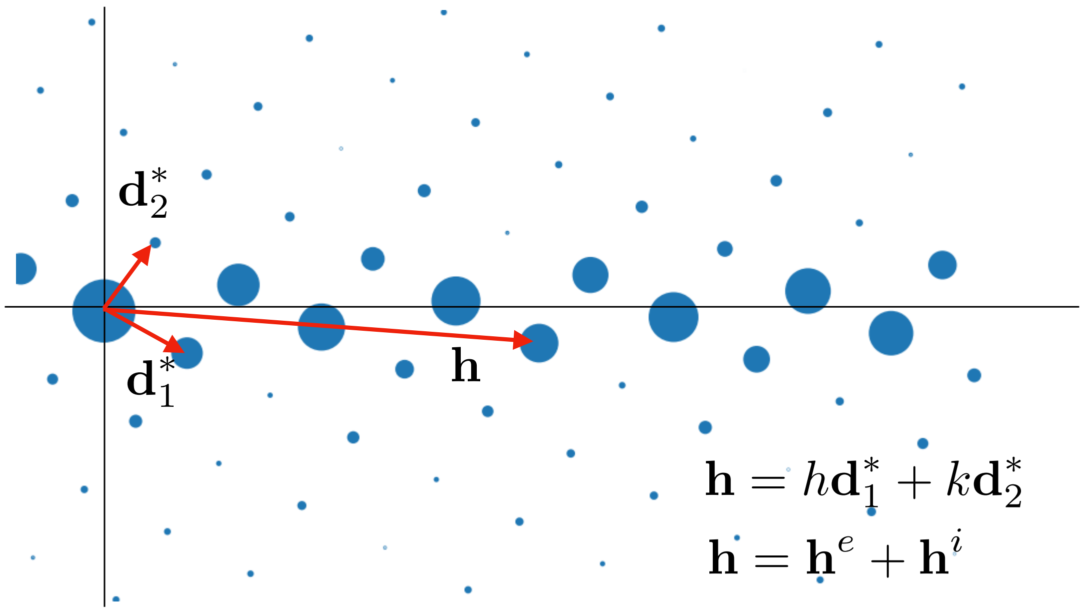
Unit vectors under phason strain

$$\begin{pmatrix} \mathbf{d'_1} \\ \mathbf{d'_2} \end{pmatrix} = \frac{a_{2D}}{\sqrt{\tau^2+1}} \begin{pmatrix} \tau & \bar{1} \\ 1 & \tau \end{pmatrix} \begin{pmatrix} 1 & u \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a_1} \\ \mathbf{a_2} \end{pmatrix}$$

Q1 Determine the phason matrix for q/p approximant.

Diffraction Pattern under Phason Strain

Fibonacci chain



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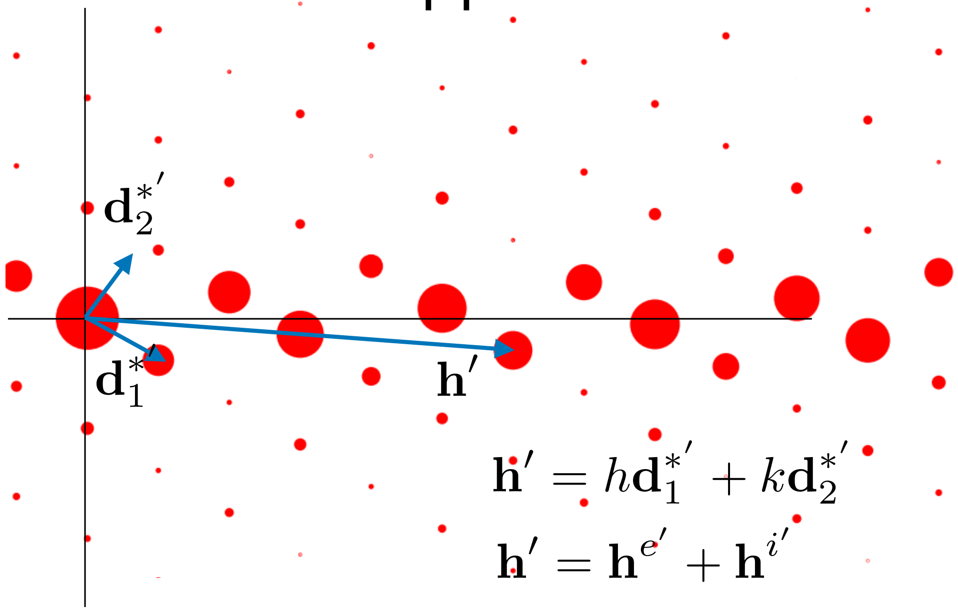


Linear phason strain

Phason matrix : U^i

$$\mathbf{d}_i^{*\prime} = \sum_{i=1}^{m} (MT^e)_{ij}\mathbf{a}_j \qquad T^e = \begin{pmatrix} I_d & 0 \\ -\tilde{U}^i & I_d \end{pmatrix}$$

Unit vectors under phason strain

$$\begin{pmatrix} \mathbf{d}_1^{*\prime} \\ \mathbf{d}_2^{*\prime} \end{pmatrix} = \frac{a^*}{\sqrt{\tau^2+1}} \begin{pmatrix} \tau & \bar{1} \\ 1 & \tau \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -u & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \end{pmatrix}$$

Q2 By the phason strain, how the external and internal components of a reflection HK changes?

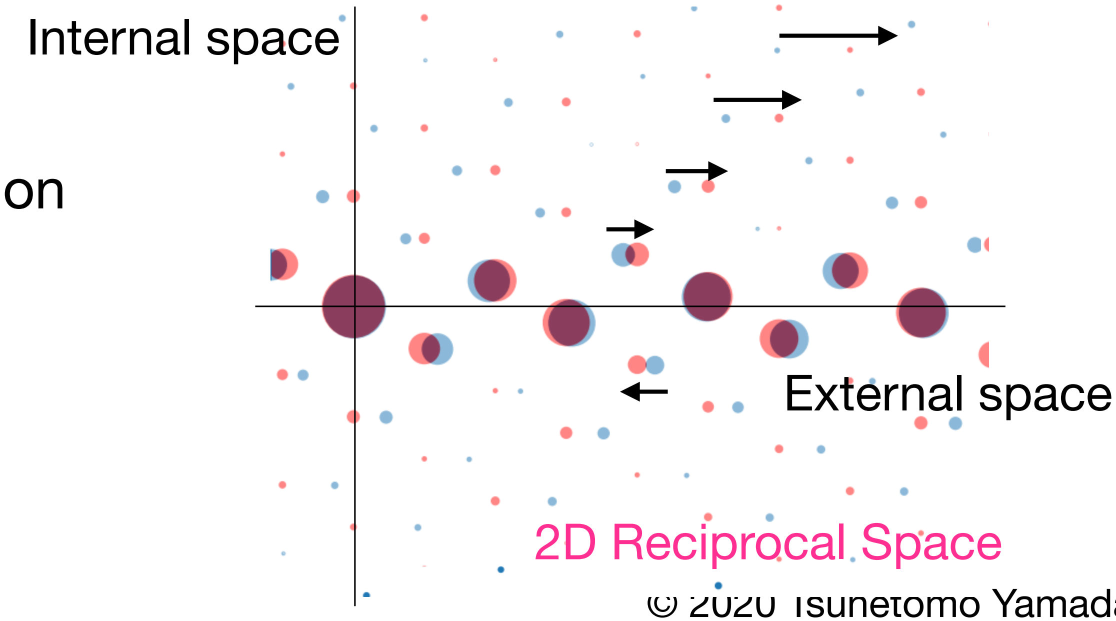
Diffraction Pattern under Phason Strain

Q2 By the phason strain, how the external and internal components of a reflection HK change?

HK reflection	Finbonacci lattice	Finonacci lattice under phason strain
External component		
Internal component		

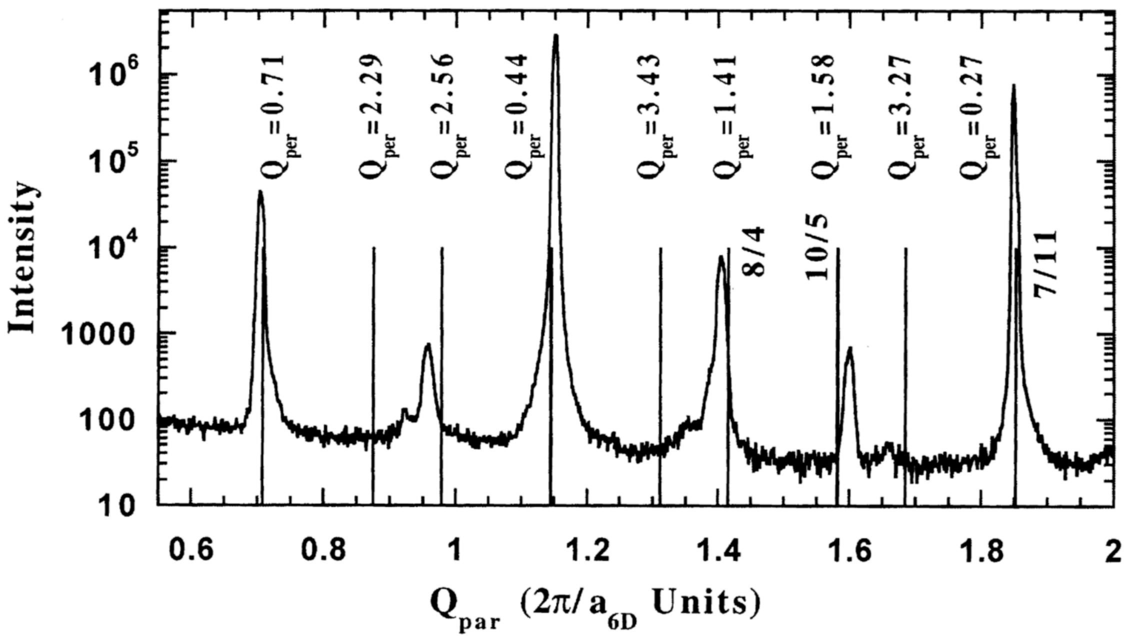
Phason strain leads to shift of reflection positions from their deal positions.

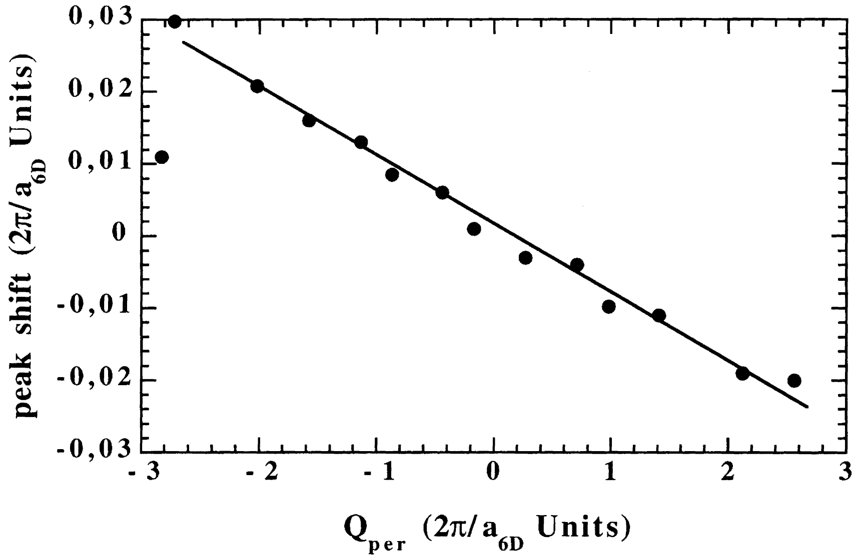
$$\Delta \mathbf{h} = \mathbf{h}^{e'} - \mathbf{h}^{e} = -u\mathbf{h}^{i}$$



Diffraction Pattern under Phason Strain

e.g. Zn-Mg-Y Quasicrystal



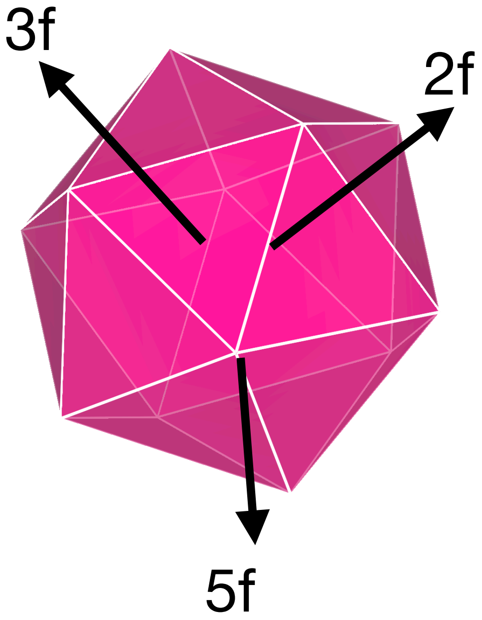


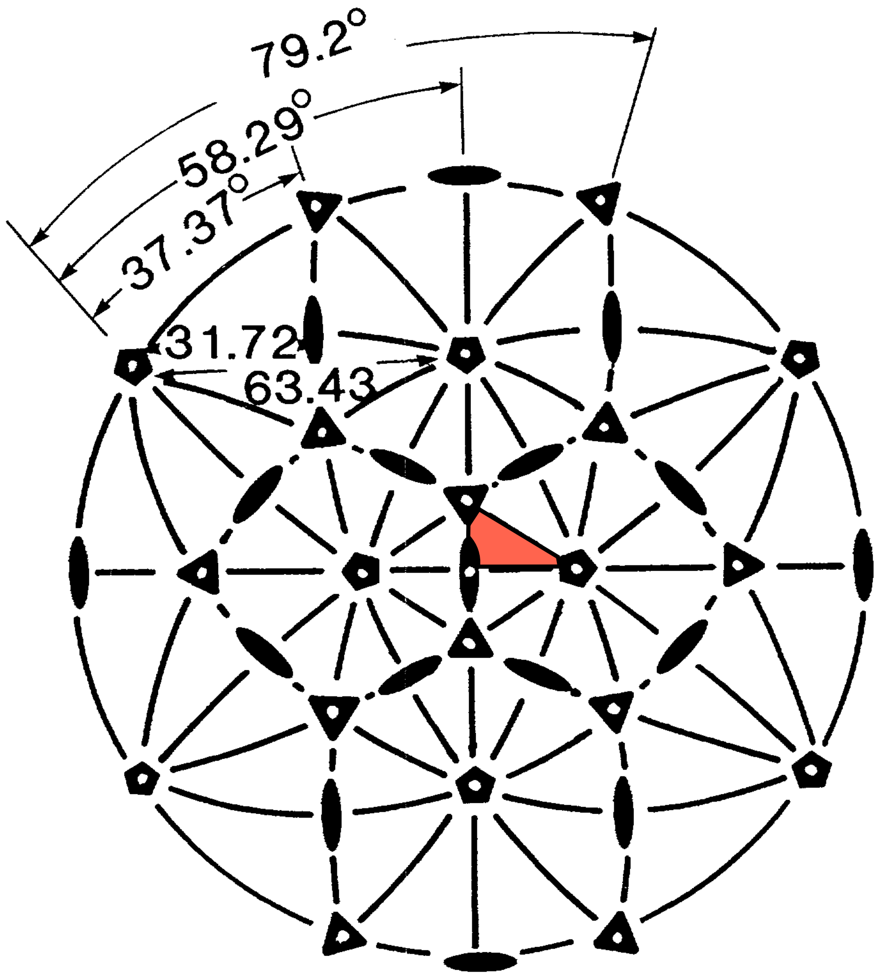
Létoublon, A., I. et al. *Materials Science and Engineering: A* 294 (2000): 127-130.

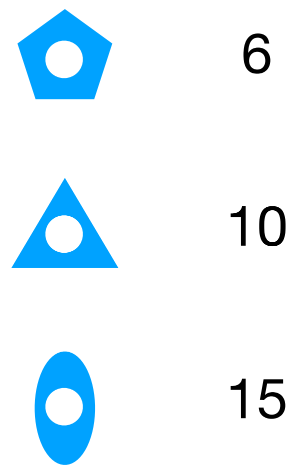
Part 2,
Icosahedral Quasicrystals (iQCs)

Icosahedral Symmetry

Point Group $m\bar{3}\bar{5}$ Number of symmetry operation, 120







Mirror

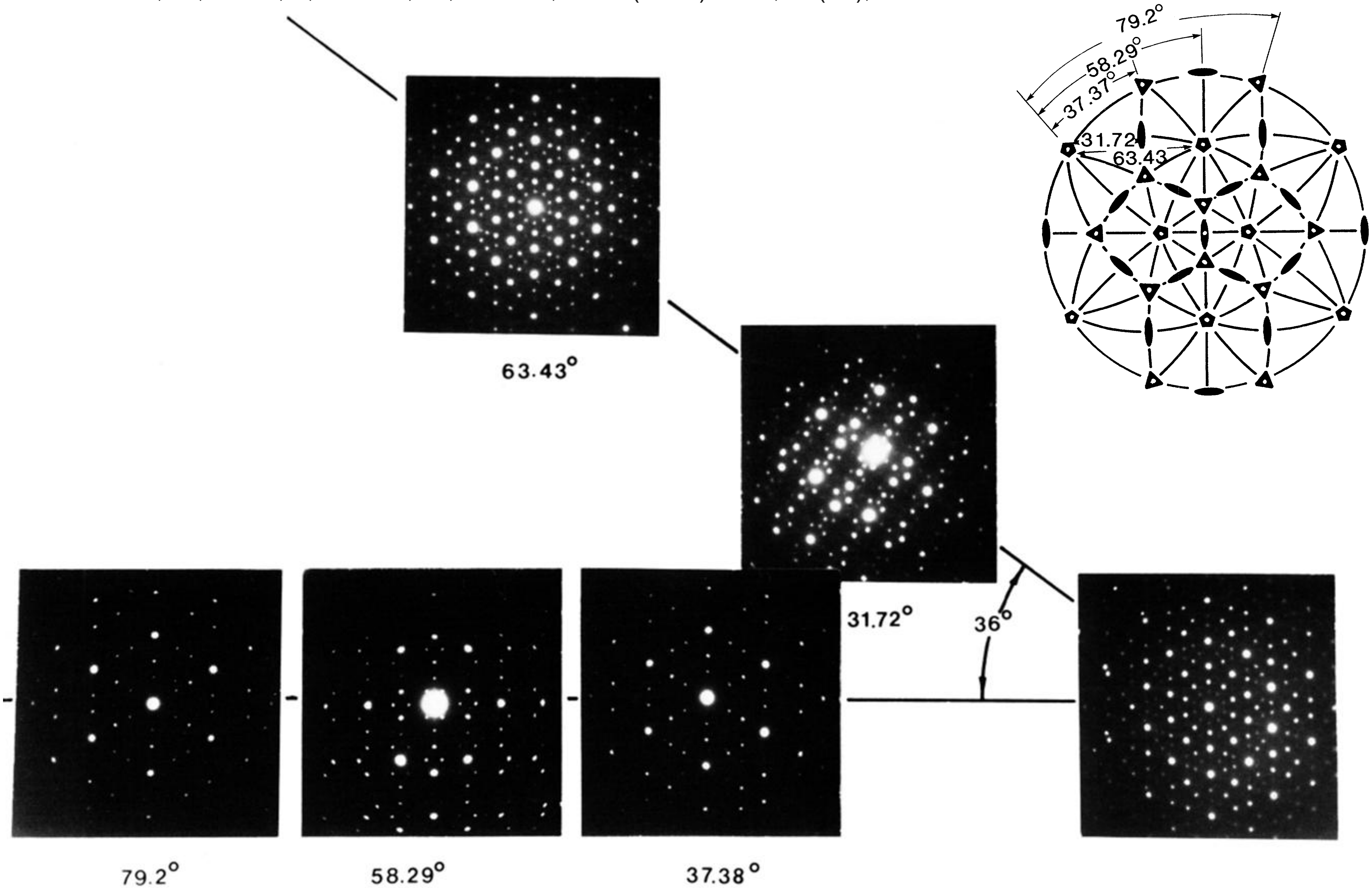
Inversion

Identity

Shechtman, D., Blech, I., Gratias, D., & Cahn, J. W. (1984). *PRL*, *53*(20), 1951.

Diffraction from iQCs

Shechtman, D., Blech, I., Gratias, D., & Cahn, J. W. (1984). *PRL*, *53*(20), 1951.



6D lattice of iQCs

Lattice type		Reflection condition
Primitive	$Pm\bar{3}\bar{5}$	all
Body-centered	$Im\bar{3}\bar{5}$	$\sum_{i=1}^{6} h_i = 2n$ for $h_1h_2h_3h_4h_5h_6$
Face-centered	$Fm\bar{3}\bar{5}$	all even for all odd for $h_1h_2h_3h_4h_5h_6$

F and *I* lattices

Face-centered (*F*) lattice

32 centering translations:

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

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

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

...

Body-centered (*I*) lattice

2 centering translations:

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

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

How to determine lattice vectors of iQCs

Indexing of diffraction pattern

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

Choice of $\mathbf{d}_i^{*e}$ is not unique.

Miller index $\quad h_1h_2h_3h_4h_5h_6$

Lattice constant $\quad a^*$

↓

6D reciprocal lattice

Reflection condition
Lattice type; *P*, *F* or *I*

↓

6D reciprocal lattice vector $\quad \mathbf{d}_i^* = \sum_{j=1}^{6} M_{ij}\mathbf{a}_j$

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

External ↕ Internal

$$a = \frac{1}{2a^*}$$

↓

6D lattice vectors $\quad \mathbf{d}_i = \sum_{j=1}^{6} Q_{ij}\mathbf{a}_j$

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

6D reciprocal lattice vectors $\mathbf{d}_i^*$

$\mathbf{d}_i^* (i = 1, 2, ..., 6)$: Reciprocal lattice vector

$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{a}_4, \mathbf{a}_5, \mathbf{a}_6$: orthogonal base vector

$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ expand external space

$\mathbf{a}_4, \mathbf{a}_5, \mathbf{a}_6$ expand internal space

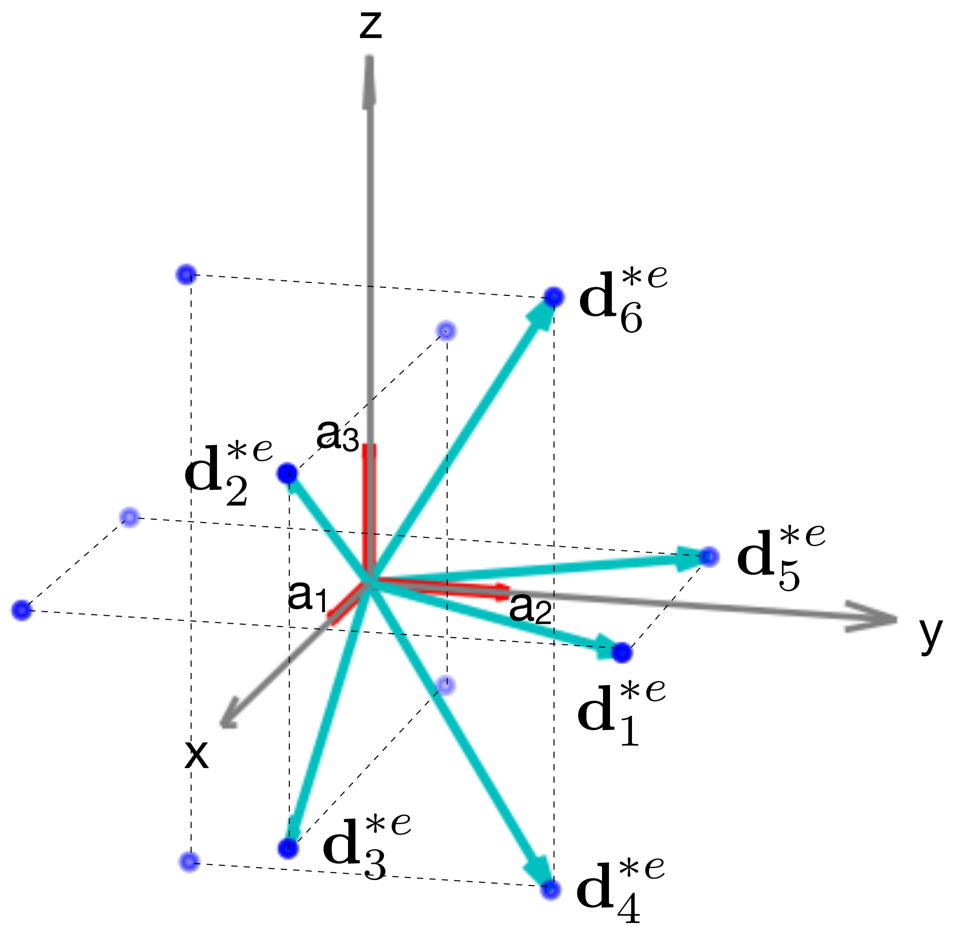
$$\begin{pmatrix} \mathbf{d}_1^* \\ \mathbf{d}_2^* \\ \mathbf{d}_3^* \\ \mathbf{d}_4^* \\ \mathbf{d}_5^* \\ \mathbf{d}_6^* \end{pmatrix} = \frac{a^*}{\sqrt{\tau^2+1}} \underbrace{\begin{pmatrix} 1 & \tau & 0 & \tau & -1 & 0 \\ \tau & 0 & 1 & -1 & 0 & \tau \\ \tau & 0 & 1 & -1 & 0 & -\tau \\ 0 & 1 & -\tau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

a^* : lattice constant of reciprocal lattice

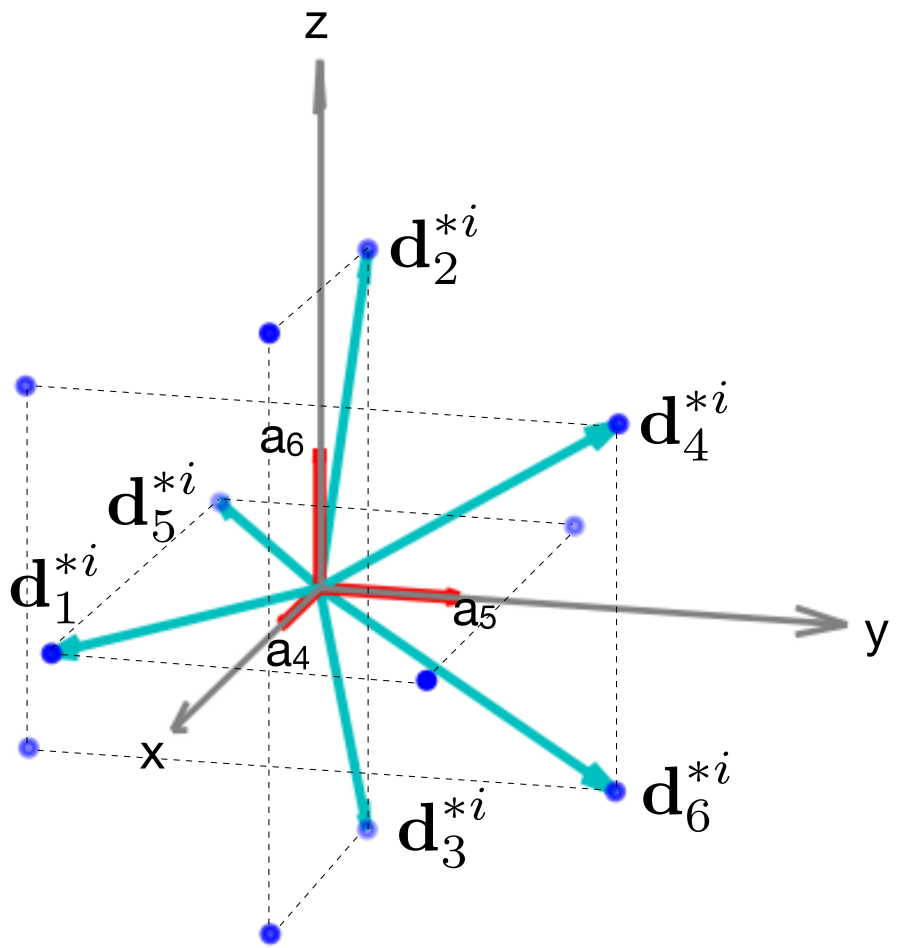
Yamamoto, Akiji, "Crystallography of quasiperiodic crystals."Acta Cryst. A 52, 4, 509-560, (1996)

Projection of $\mathbf{d}_i^*$

External space



Internal space



6D Lattice vectors $\mathbf{d}_i$

Reciprocal lattice vectors

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

$$\mathbf{d}_i^* = \sum_{j=1}^{6} M_{ij}\mathbf{a}_j$$

$$\mathbf{d}_i \cdot \mathbf{d}_j^* = \begin{cases} 1(i=j) \\ 0(i \neq j) \end{cases}$$

Direct lattice vectors

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

$$\mathbf{d}_i = \sum_{j=1}^{6} Q_{ij}\mathbf{a}_j$$

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

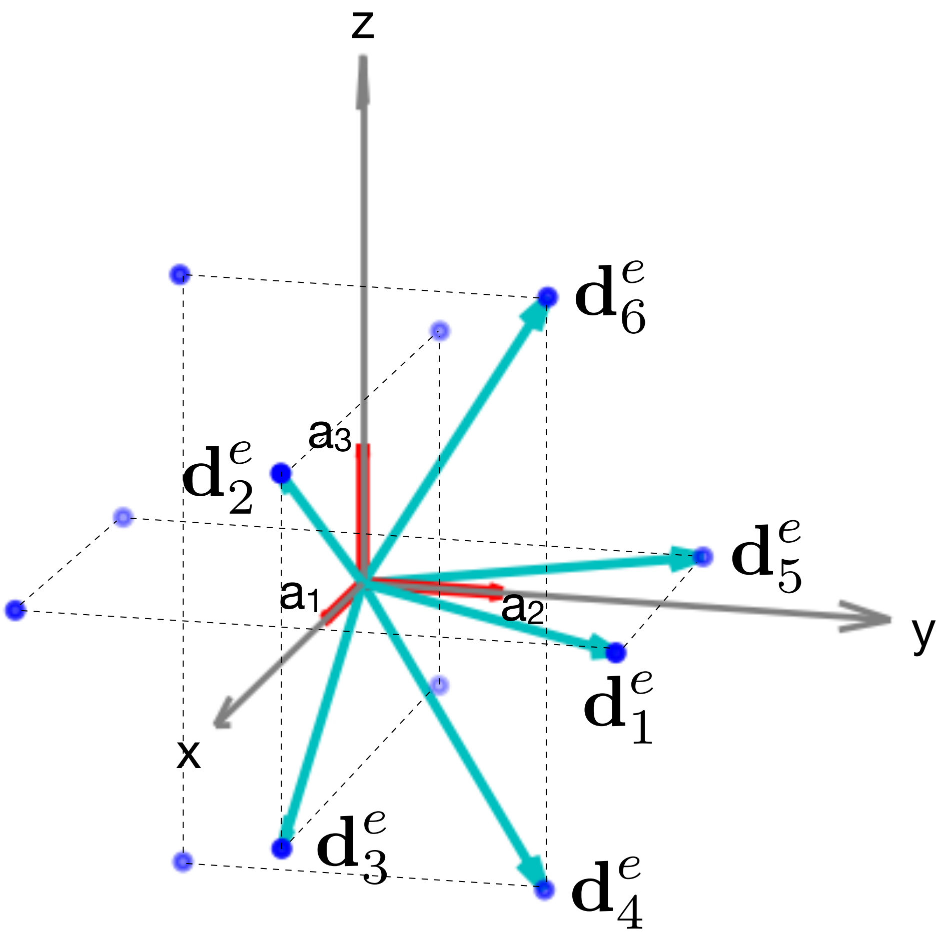
$$Q = \tilde{M}^{-1}$$

$$a = \frac{1}{2a^*}$$

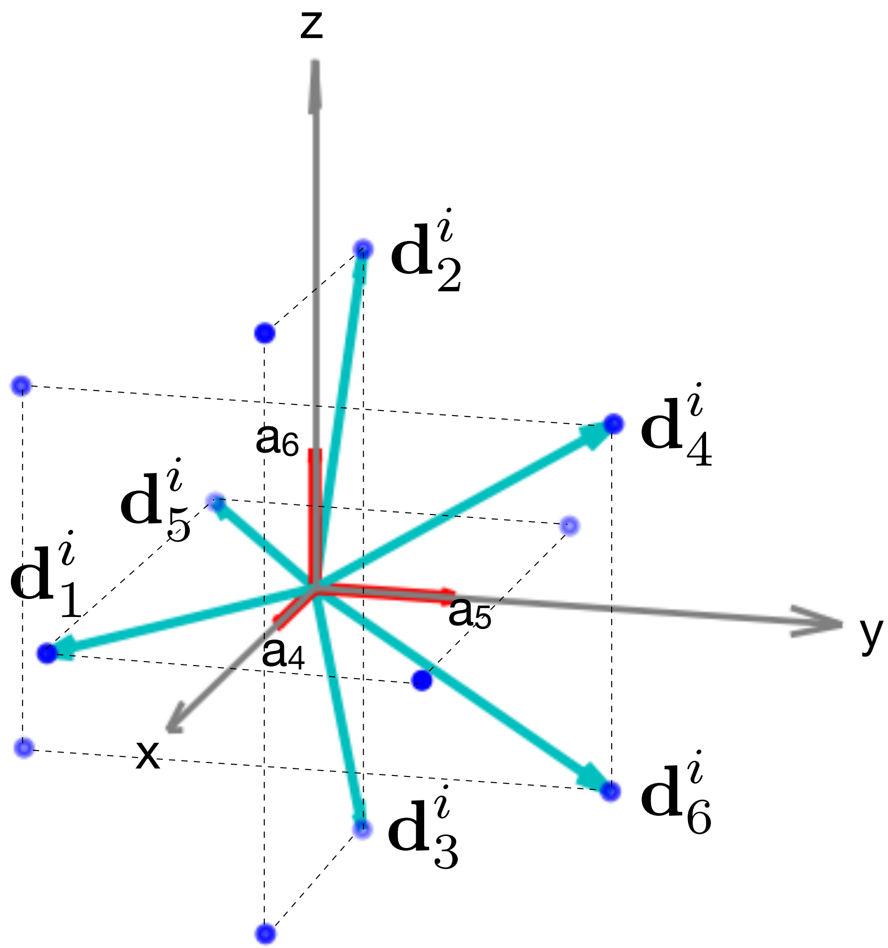
Yamamoto, Akiji, "Crystallography of quasiperiodic crystals."Acta Cryst. A 52, 4, 509-560, (1996)

Projection of $\mathbf{d}_i$

External space



Internal space

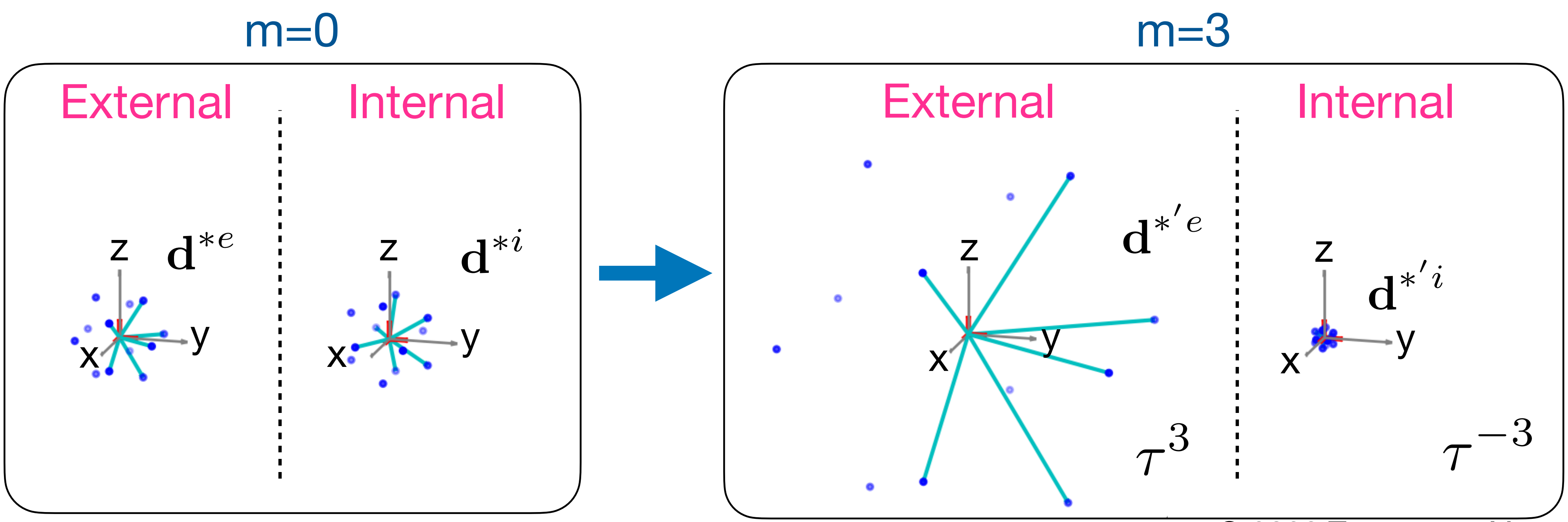


Similarity transformation

Choice of $\mathbf{d}_i^{*e}$ is not unique for indexing the diffraction peaks.

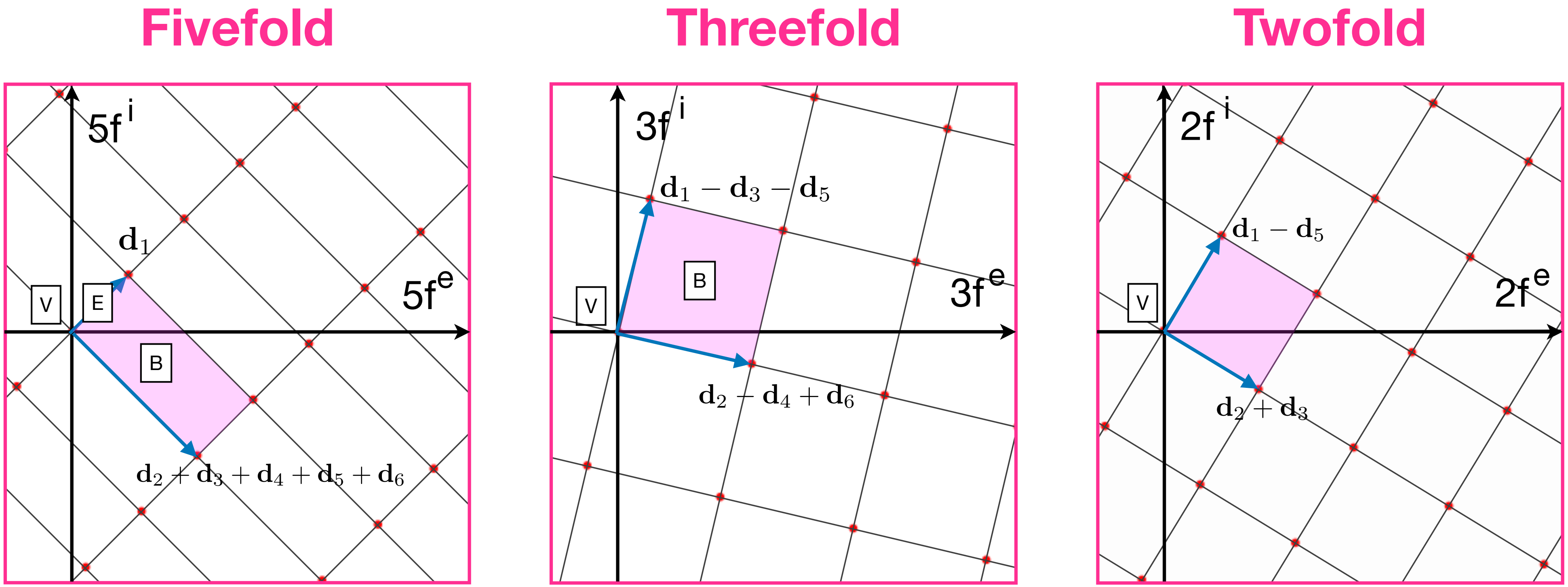
$$\mathbf{d}_i^{*'} = \sum_{j=1}^{6} (\tilde{S})_{ij}^{m} \mathbf{d}_j^{*} \quad \text{with} \quad S = \frac{1}{2}\begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & -1 & 1 \\ 1 & 1 & 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & 1 & 1 & -1 \\ 1 & -1 & -1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 & 1 & 1 \end{bmatrix}$$

m=3 for *P*-type, m=1 for *F*- and *I*-types



Yamamoto, Akiji, "Crystallography of quasiperiodic crystals."Acta Cryst. A 52, 4, 509-560, (1996)

2D sections of 6D direct lattice



High symmetrical positions:

V	$(0,0,0,0,0,0)$	$m\bar{3}\bar{5}$
C	$(\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2})$	$m\bar{3}\bar{5}$
E	$(\frac{1}{2},0,0,0,0,0)$ ...	$m\bar{5}$

for Wyckoff positions of quasicrystal space groups
visit https://wcp2-ap.eng.hokudai.ac.jp/yamamoto/

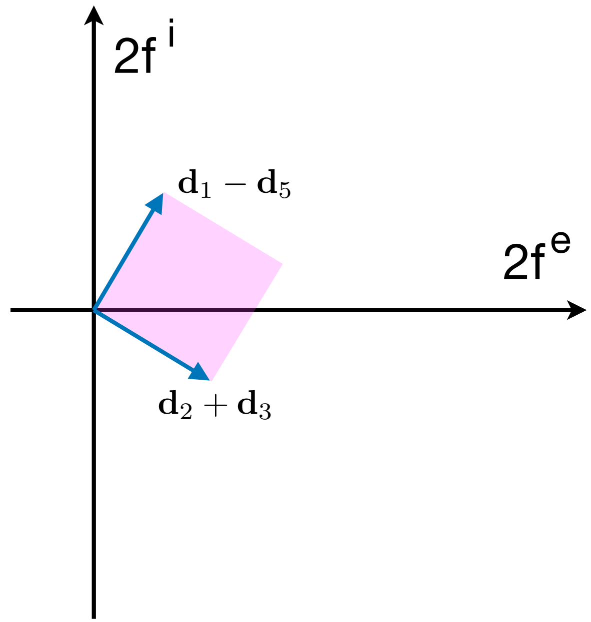
Q3 **Determine the phason matrix for 1/1 cubic approximant.**

Linier Phason Matrix

Phason Matrix U^i (3×3)

$$\mathbf{d}_i' = \sum_{i=1}^{m} Q_{ij}\mathbf{a}_j' = \sum_{i=1}^{m} (QT^i)_{ij}\mathbf{a}_j \qquad T^i = \begin{pmatrix} I_d & U^i \\ 0 & I_d \end{pmatrix}$$

Twofold



In the case of 1/1 approximant、internal component of

[ ] becomes [ ].