QUASICRYSTALS: an introduction

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International School on Aperiodic Crystals

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1. Quasicrystal : general introduction
2. The Fibonnacci chain
3. Generalised 1D quasicrystals
4. Structure determination
5. Generalization to higher dimensions.

References can be found in the book:

Janssen T., Chapuis G. and de Boissieu M.: *Aperiodic Crystals. From modulated phases to quasicrystals,* Oxford University Press, Oxford 2007.

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What is a quasicrystal?

- Aperiodic crystals:

  Crystal: ‘Diffraction pattern is essentially discrete’

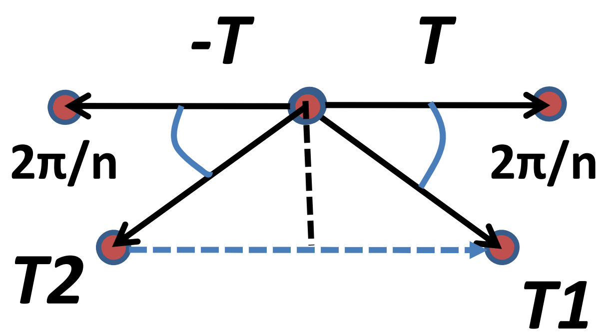
  Aperiodic crystal: Bragg peaks and indexing with more than 3 integers.

- Symmetry allowed by lattice translation:

  1, 2, 3, 4 and 6.

Periodicity and allowed symmetry

- Let us consider a periodic structure, with periodicity ***T*** and a n-fold rotation axis.



***T1-T2**=n**T** is also a lattice translation*

This implies that 2cos(2π/n)=integer

True only if n=1 , 2, 3, 4 and 6: 'allowed' symmetry with periodicity.

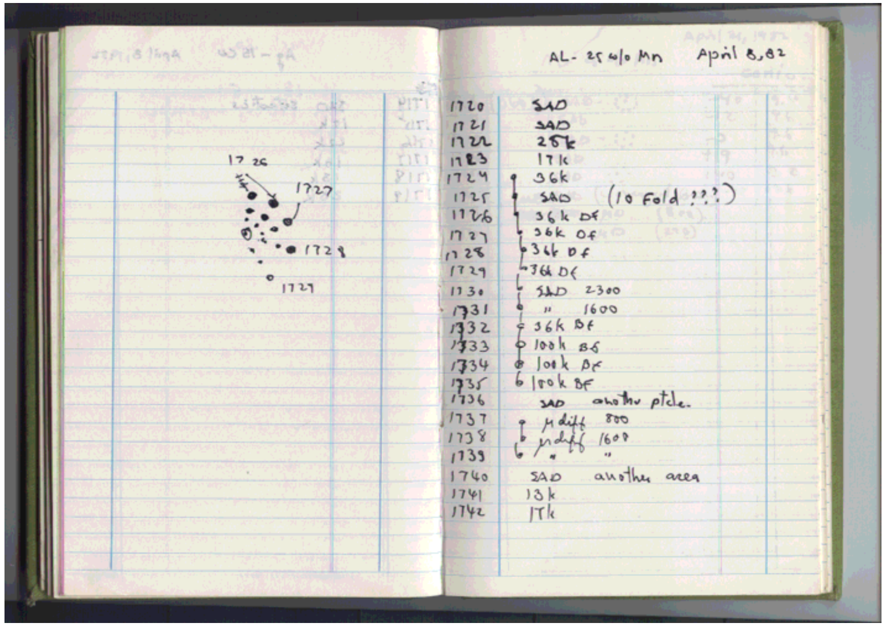
Quasicrystal

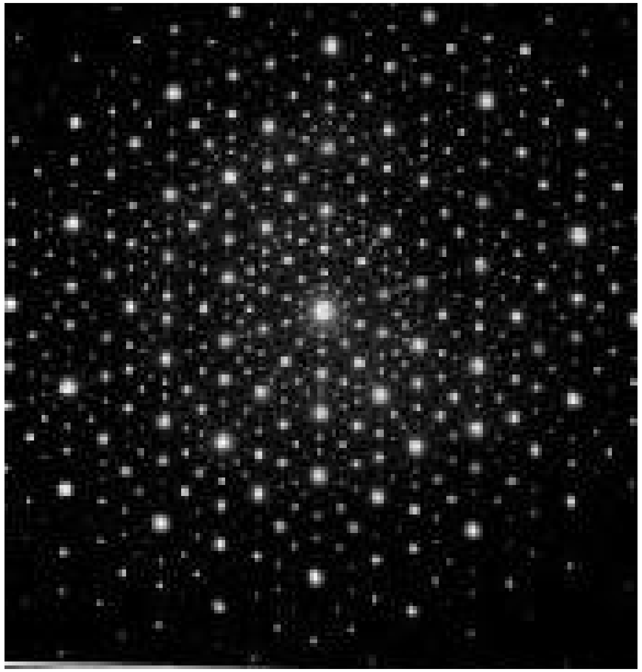
- Quasicrystal: diffraction pattern with sharp Bragg peaks and a symmetry incompatible with lattice translation.

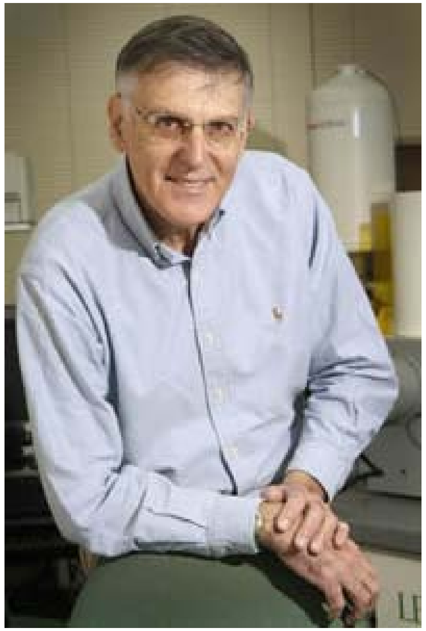
- Icosahedral symmetry and 5-fold rotation for instance.
- Other symmetry exists.

Quasicrystal discovery

- 1982: Shechtman observes the first icosahedral diffraction pattern in a rapidly quenched AlMn alloy.







VOLUME 53, NUMBER 20 PHYSICAL REVIEW LETTERS 12 NOVEMBER 1984

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

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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.

- Rapidly solidified Al-Mn alloy
- Electron diffraction pattern : icosahedral symmetry
- Single grain diffracting.

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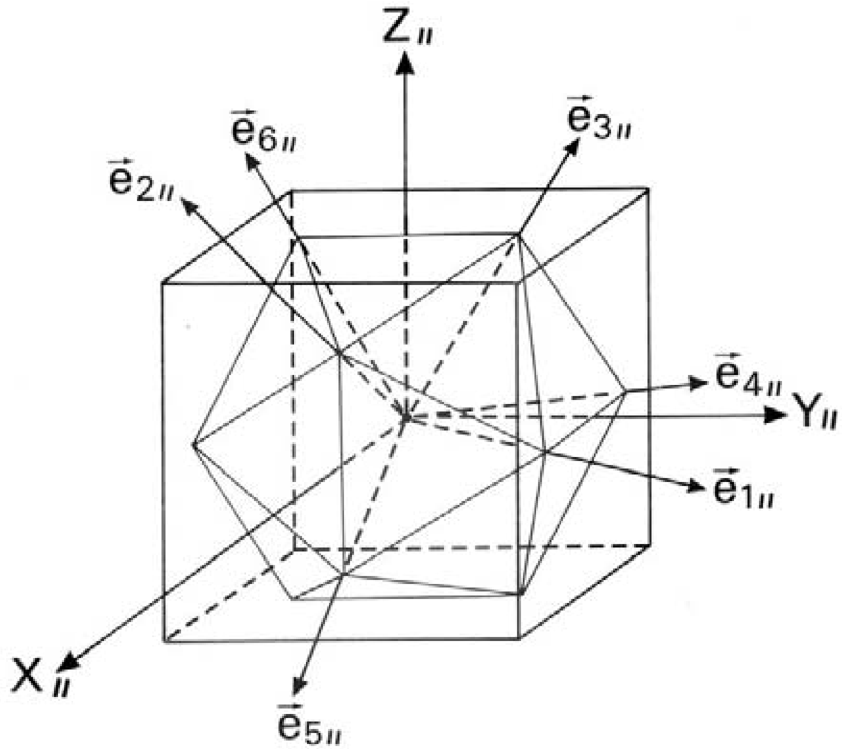
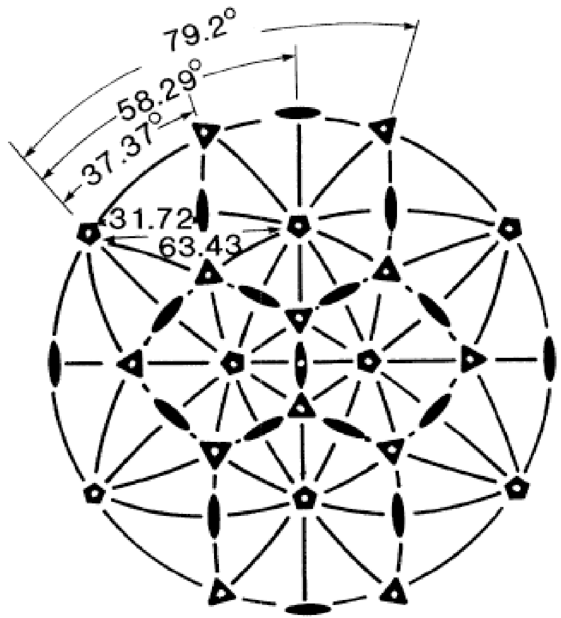
Quasicrystal discovery





- Icosahedral symmetry of the diffraction pattern
- 5-fold axis (6), 3-fold axis (20), 2-fold axis (30)

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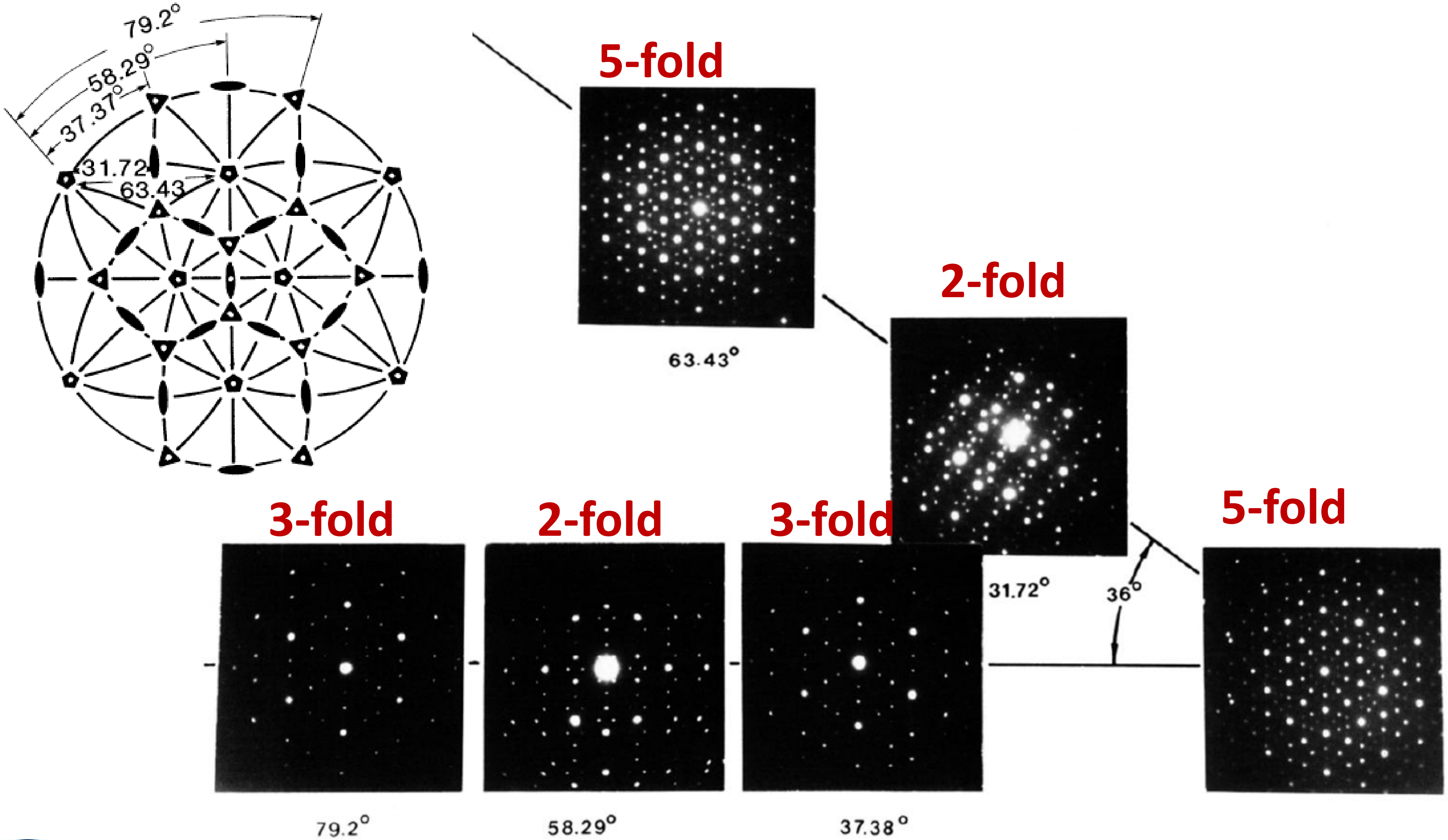
Metallic Phase with Long-Range Orientational Order and No Translational Symmetry



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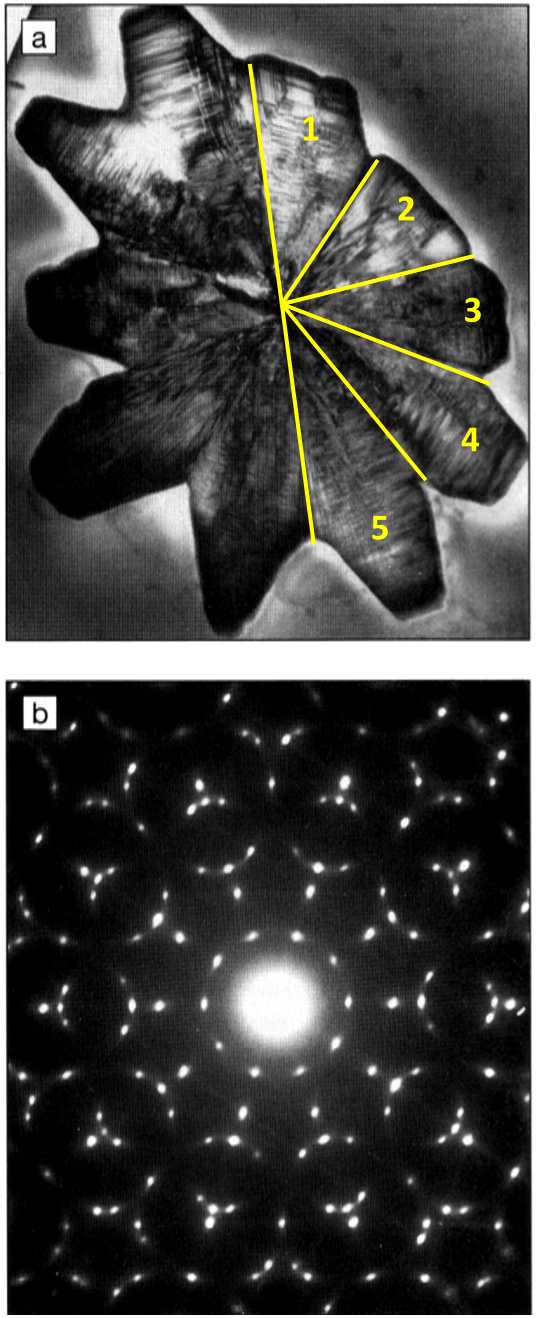
Quasicrystal discovery

- Bragg peaks and ‘forbidden’ symmetry.
- New long range order: quasicrystals

- Is it really a quasicrystal?
- Other explanations? Twinning?



Rapidly-solidified Al-Fe alloy

Apparent icosahedral symmetry is due to directed multiple twinning of cubic crystals

Linus Pauling

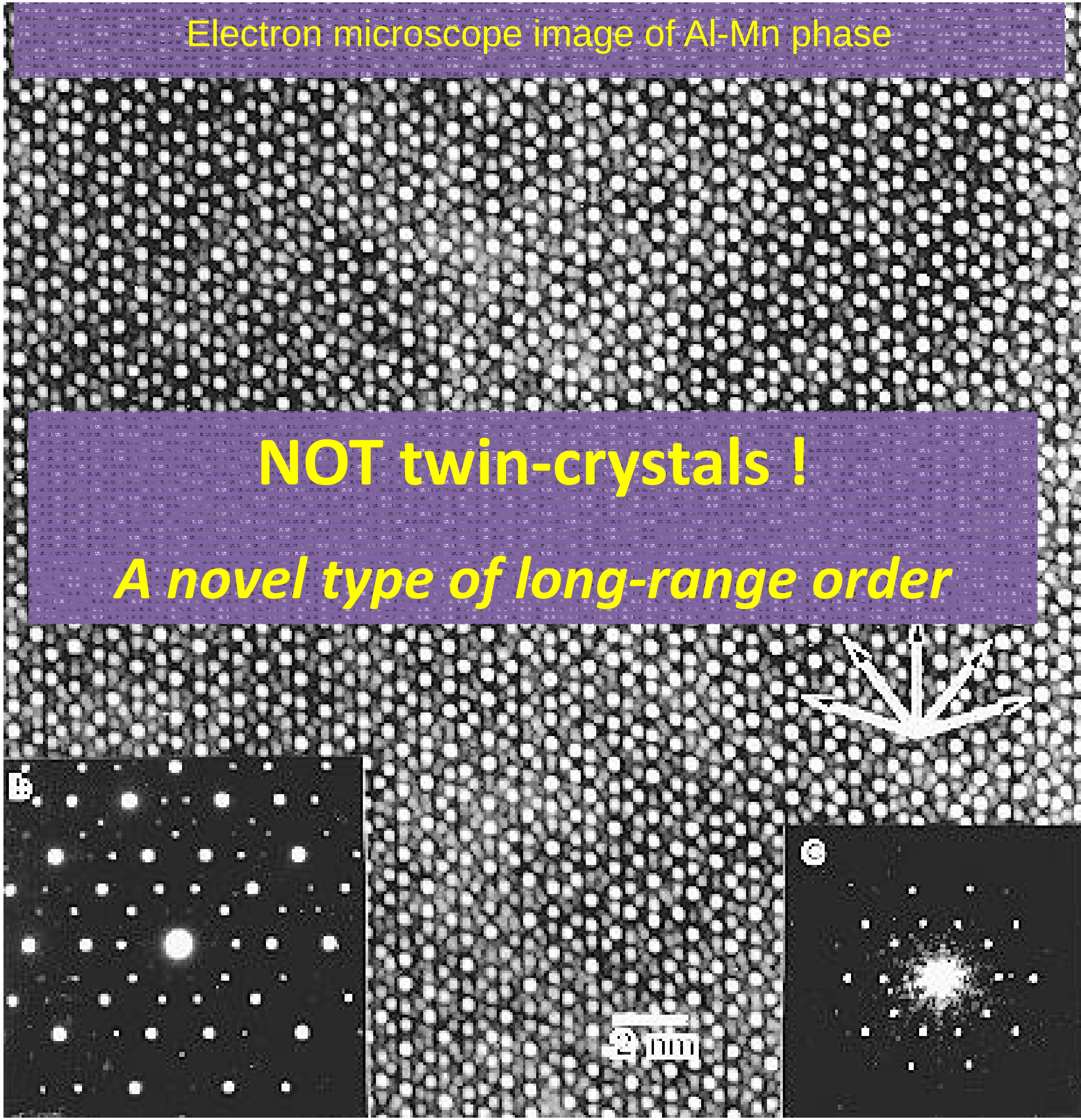
Linus Pauling Institute of Science and Medicine,
440 Page Mill Road, Palo Alto, California 94306, USA

Recently the announcement was made of the remarkable discovery of intermetallic compounds with approximate composition $MA1^6$ (M = Cr, Mn, Fe) that formed crystals or pseudocrystals with icosahedral symmetry, as shown by the shape of the small nodules and by their electron diffraction patterns[1]. I have found it hard to believe that any single crystal with 5-fold axes could give reasonably sharp diffraction patterns, resembling those given by crystals, and I have not been convinced to the contrary by the theoretical discussions of this possibility that have been published[2-7]. I therefore set myself the task of predicting how a molten alloy of Mn (or Cr or Fe) and A1 might react to sudden cooling. I have discovered that such an alloy on sudden cooling could form a metastable cubic crystal with a large cube edge, about 26,7±, with the unit cube containing about 1,120 atoms (possibly a few more), and that these crystals would show ordered multiple growth such that 20 of them, roughly tetrahedral in shape, grow out from a central seed in such a way as to produce an aggregate with approximately icosahedral symmetry.

From E. Abe

Nature vol 317 p 512 (1985)

Electron microscope image of Al-Mn phase



NOT twin-crystals !

A novel type of long-range order

From
E. Abe

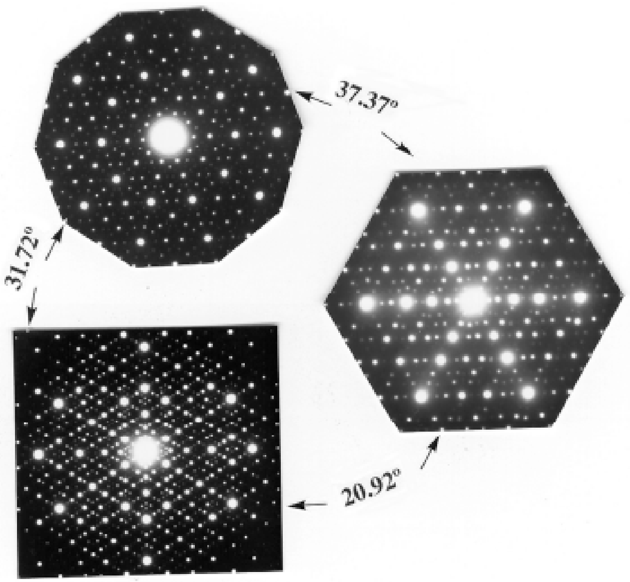
Quasicrystal symmetry

• Icosahedral:	'3D' quasicrystal.
• Decagonal quasicrystal:	2D QC + 1D periodic
• Dodecagonal	2D QC + 1D periodic
• Octagonal	2D QC + 1D periodic

Symmetry of quasicrystals

Three dimensional Qc

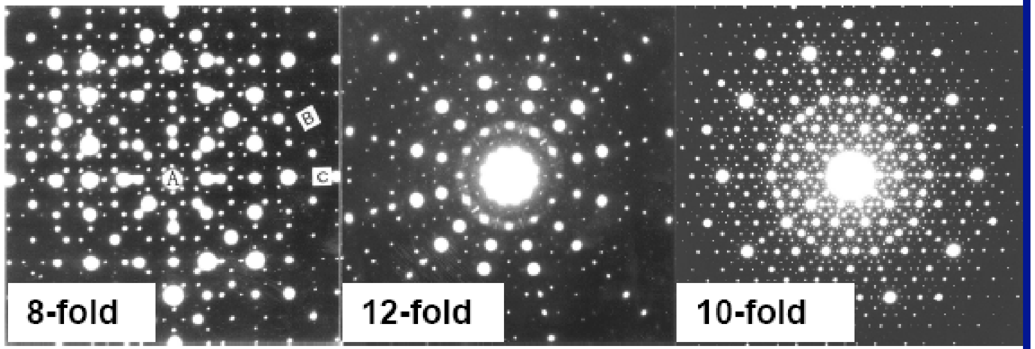
Icosahedral symmetry

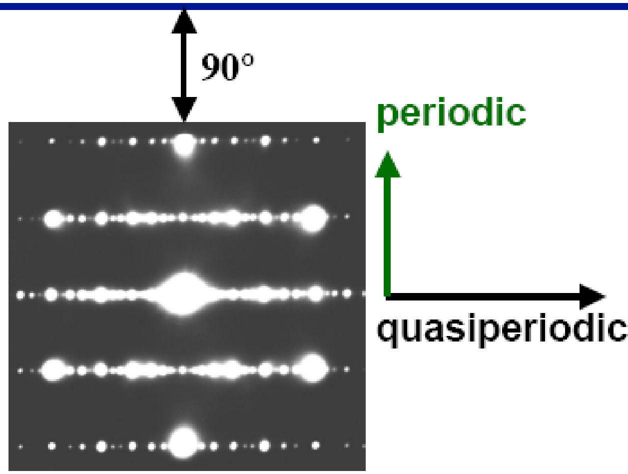


There is only one (icosahedral) *3-d Qc !!*

Two dimensional Qcs

Octagonal | Dodecagonal | Decagonal





Courtesy A.P. Tsai

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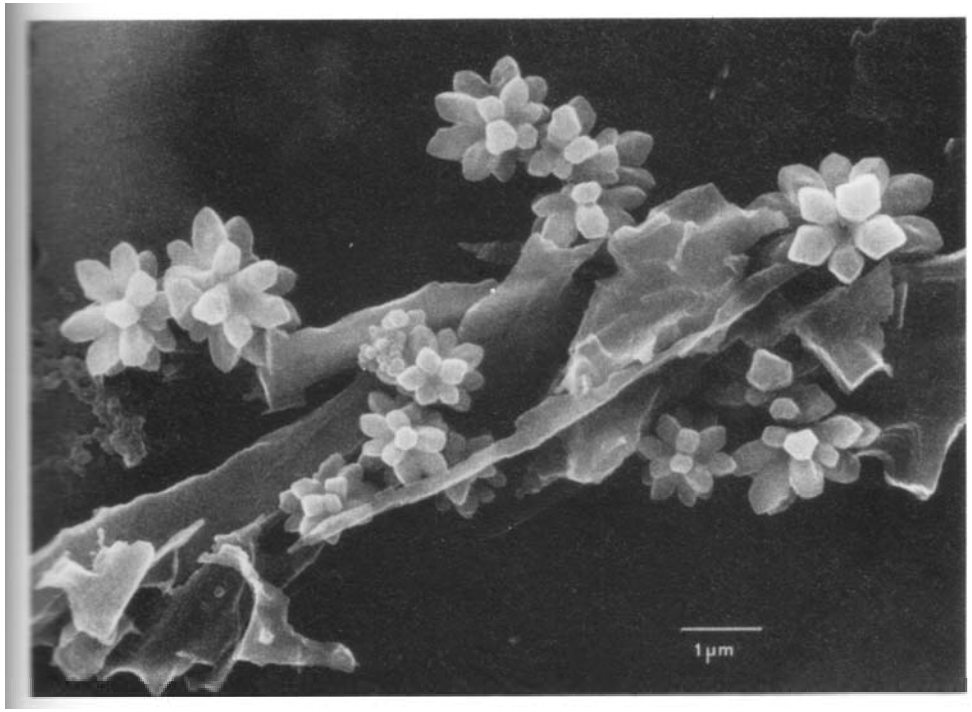
Which systems form quasicrystals?

- Mainly metallic alloys.
- First rapidly quenched Al-based alloy.
- Small grains (~ 1 µm)
- Defects, broad Bragg peaks.



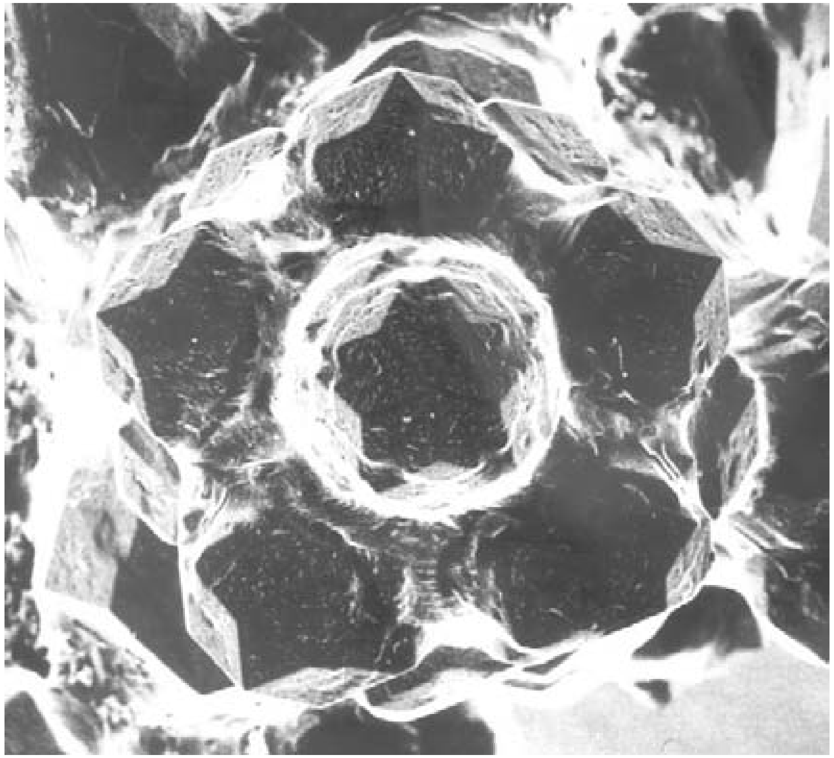
H.U. Nissen

Al alloys and others
Al-TM(TM=V, Cr, Mn, Ru…..) TM:15~20%
Al-(Mn,Cr, Fe)-(Si,Ge) Al: 60~70%, TM<20%
Al-(Cu, Pd)-TM(TM=Cr, Mo,)
$Ga_{70}Pd_{20}Mn_{10}$, $Cu_{40}Cd_{60}$
Zr-Ni-Ti

Zn and Cd alloys
Mg-Al-(Zn,Cu,Au,Pd,Ag)
Ga-Mg-Zn
Zn-Mg-RE(RE=rare earth metals)
Cd-Mg-RE

Which systems form quasicrystals?

- i-AlLiCu: first large single grain quasicrystal. But rather poor crystal quality (Dubost and Audier)

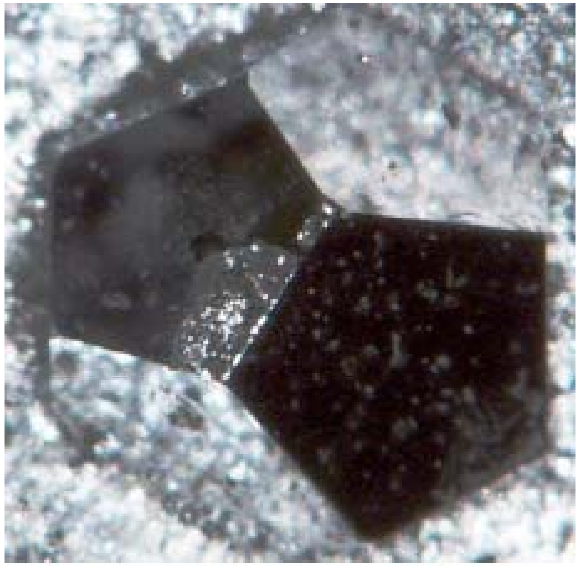


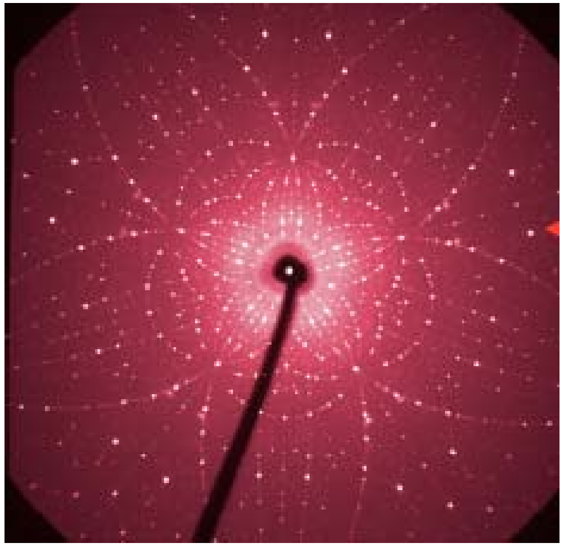
Diffraction pattern contains only a limited number of Bragg peaks.

But allowed the first X-ray and neutron study on a single crystal.

Stable quasicrystals

- A.P. Tsai has discovered the first stable i-AlCuFe quasicrystal of very good quality.
- Can be obtained by slow cooling from the melt
- Form large single grain, large number of reflections.





Stable quasicrystals

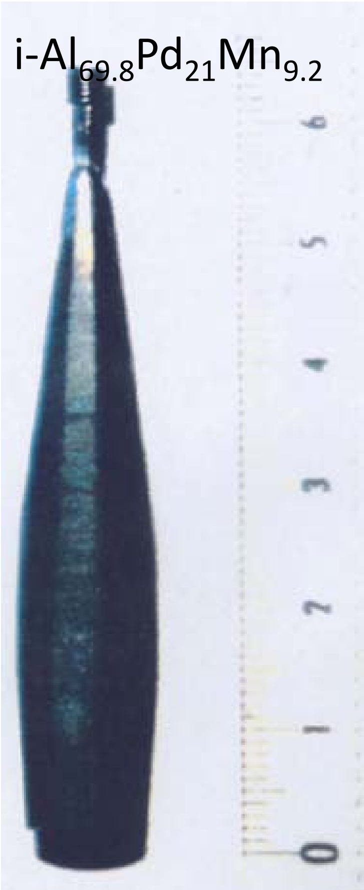
- Now a large number of examples
- Stabilised by a Hume-Rothery mechanism (e/a ratio)

List of stable icosahedral quasicrystals (from A. P. Tsai)

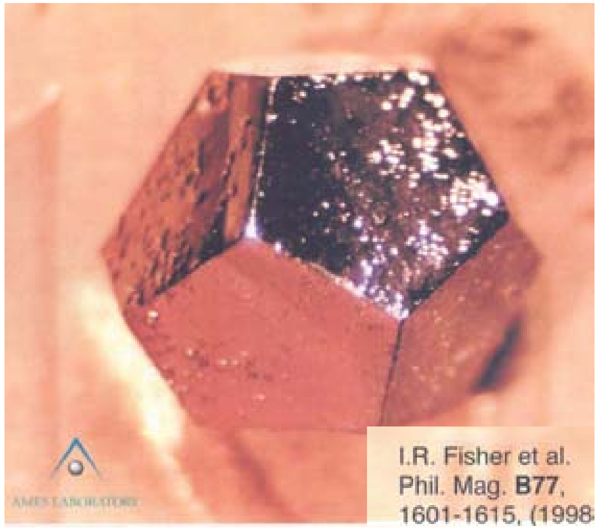
	P-type	F-type
Al-Mn-Si		$Al_{63}Cu_{25}TM_{12}$(TM:Fe Ru Os) $Al_{70}Pd_{20}TM_{10}$(TM:Mn Tc Re)
Zn-Mg-Al	Al_5Li_3Cu $Zn_{70}Mg_{20}RE_{10}$(RE:Er Ho)	$Zn_{60}Mg_{30}RE_{10}$(RE:Y Dy Ho Gd Er Tb) $Zn_{74}Mg_{19}TM_7$ (TM:Zr Hf)
Cd-Yb	$Cd_{5.7}M$ (M:Yb Ca) $Cd_{65}Mg_{20}M_{15}$ (M:Yb Ca Y Ho Gd Er Tb) $Zn_{80}Mg_5Sc_{15}$ $In_{42}Ag_{42}M_{16}$ (M:Yb Ca) $Zn_{74}Ag_{10}Sc_{16}$, $Zn_{75}Pd_9Sc_{16}$ $Zn_{77}Fe_7Sc_{16}$,$Zn_{78}Co_6Sc_{16}$ $Zn_{75}Ni_{10}Sc_{15}$	

A few examples of stable quasicrystals

$i\text{-}Al_{69.8}Pd_{21}Mn_{9.2}$

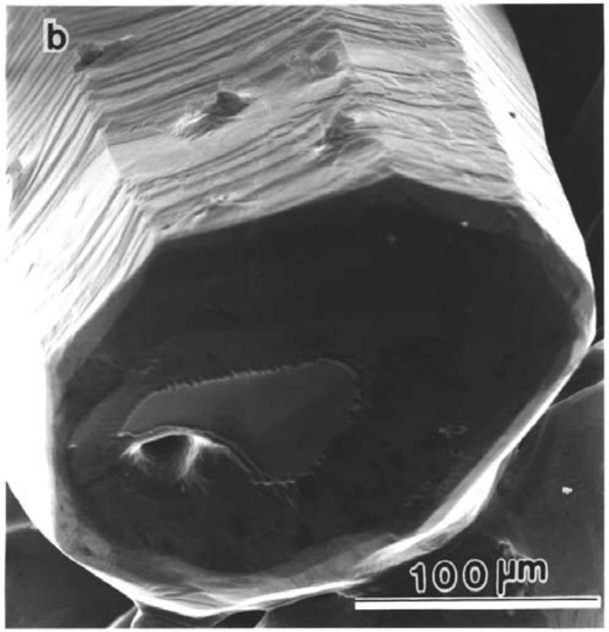


M. Boudard et al.



ZnMgY, I.R Fisher et al.

Icosahedral



A.P. Tsai et al.

Decagonal

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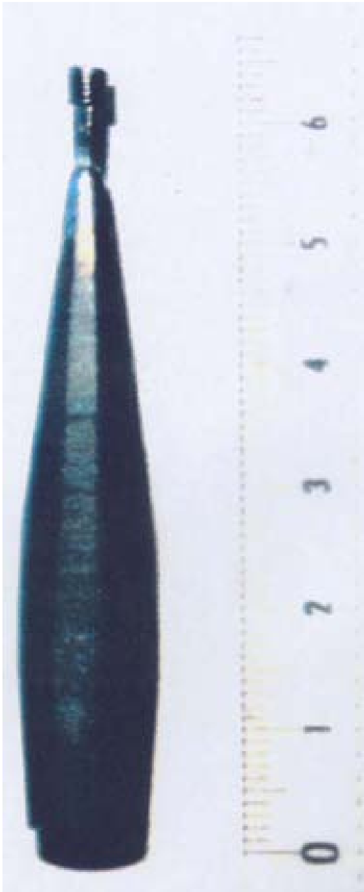
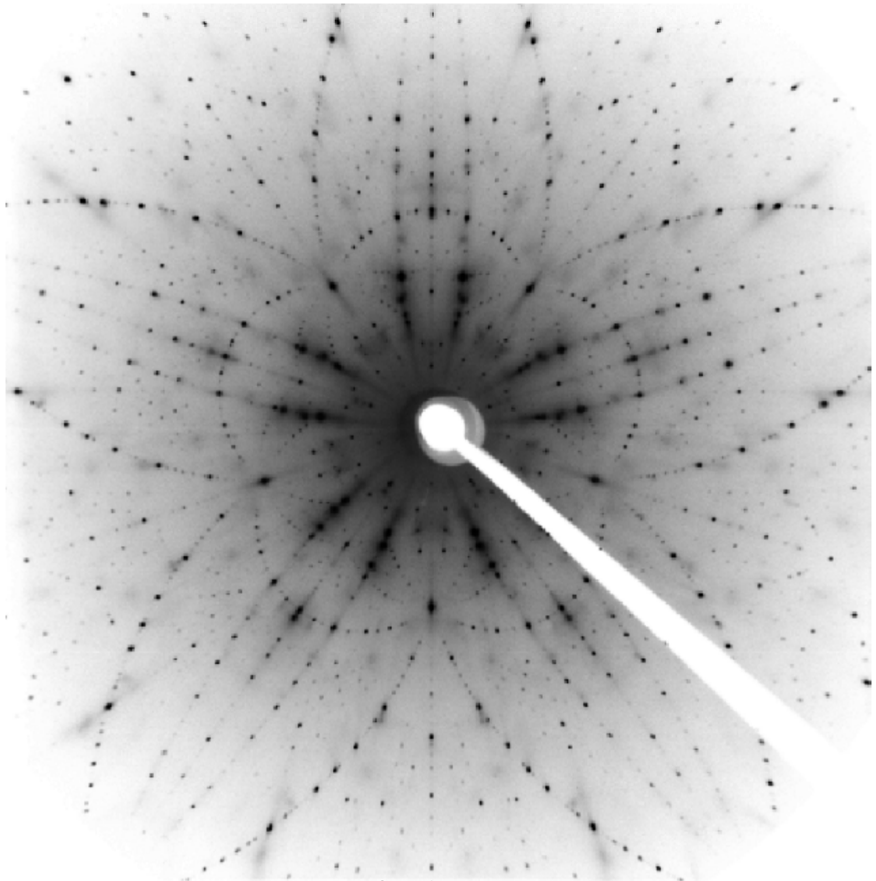
Stable quasicrystals

i-AlPdMn, growth of centimeter size single grains by Bridgman and Czokralski methods.



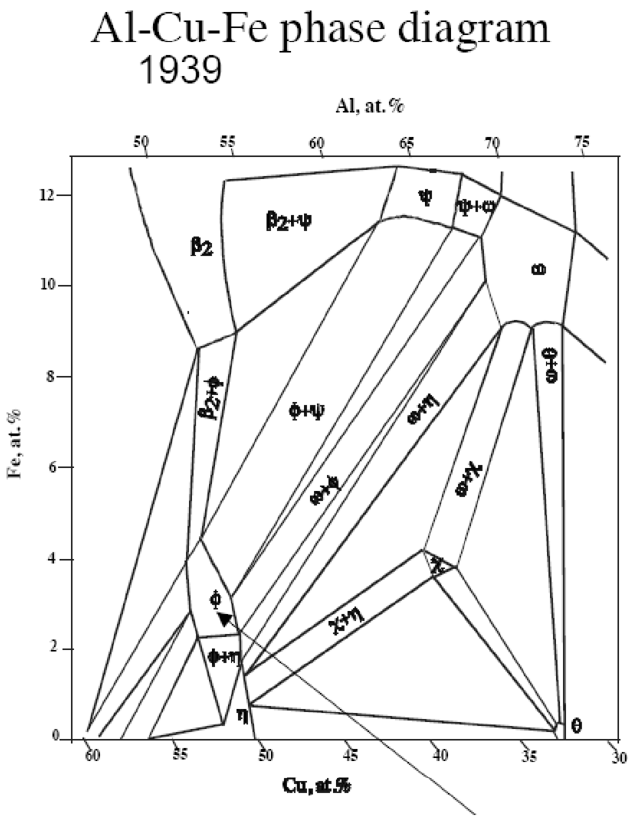
M. Boudard et al.

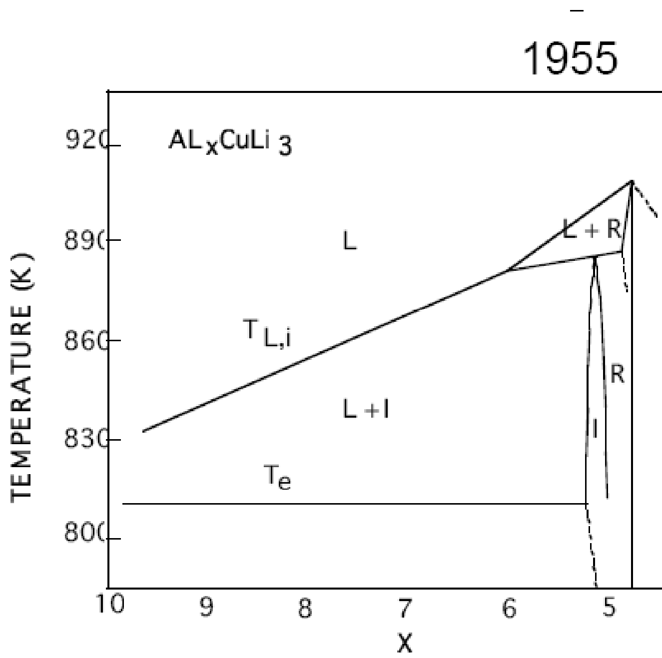


W. Steurer, i-AlPdMn Laue

Stable quasicrystals

- Quasicrystals were targeted has non-indexable phases long ago! Example of the AlCuFe phase diagram.





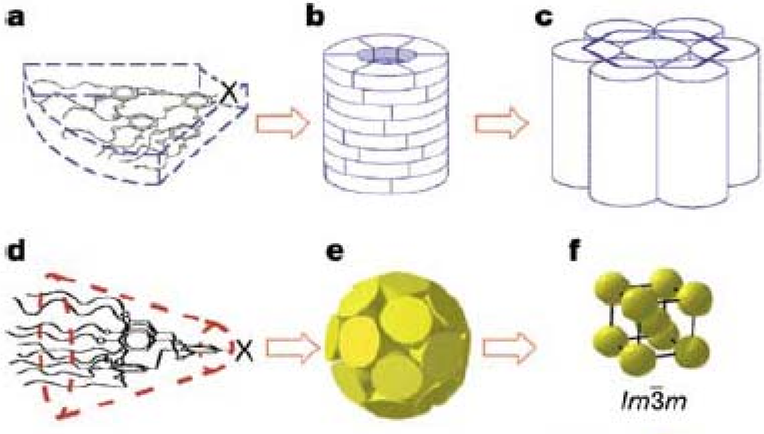
Soft condensed matter and QC

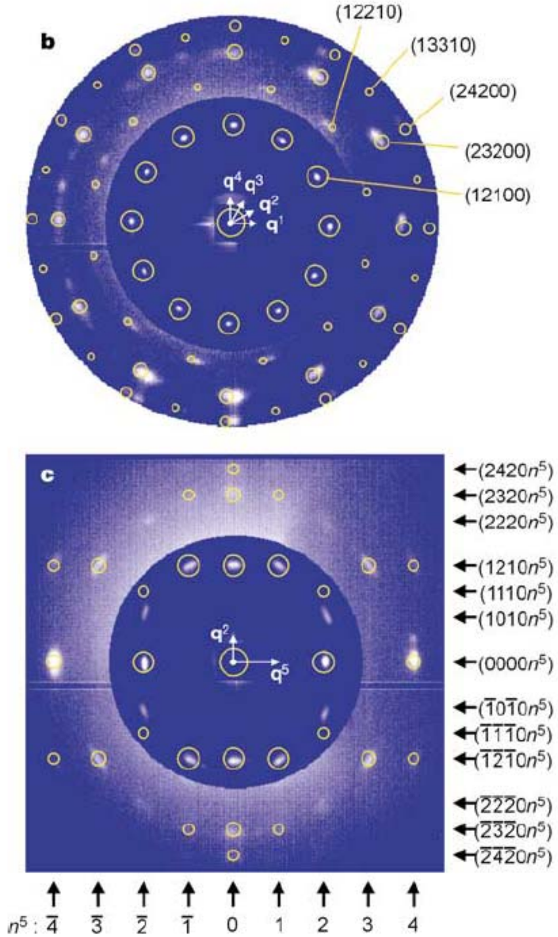
Recently, QC have been obtained in soft condensed matter: dodecagonal quasicrystals

Supramolecular dendritic liquid quasicrystals

Xiangbing Zeng[1], Goran Ungar[1], Yongsong Liu[1], Virgil Percec[2], Andrés E. Dulcey[2] & Jamie K. Hobbs[3]

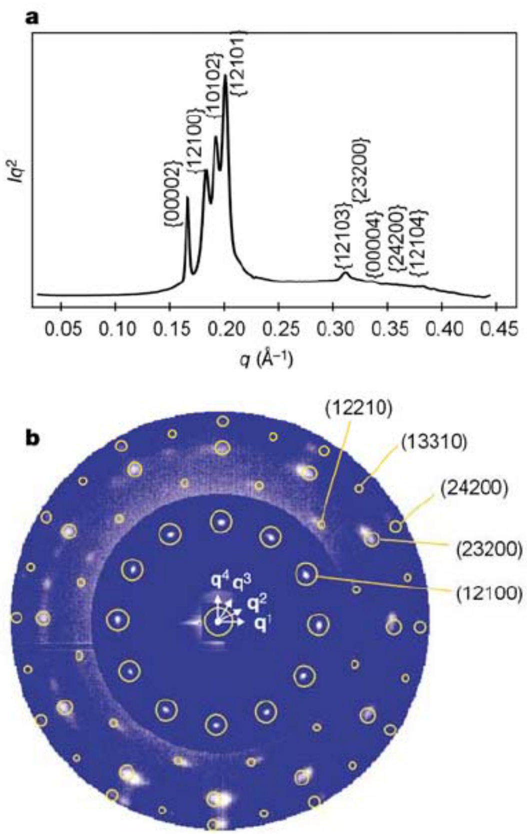
NATURE | VOL 428 | 11 MARCH 2004 |

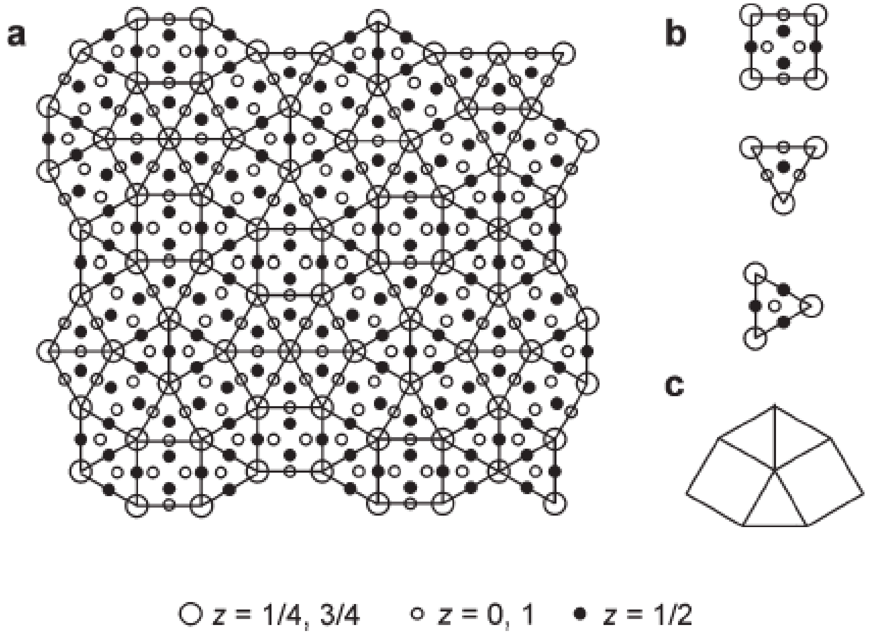




Liquid Quasicrystal

- Length scale: 8.1 nm , i.e 10 time metallic alloys



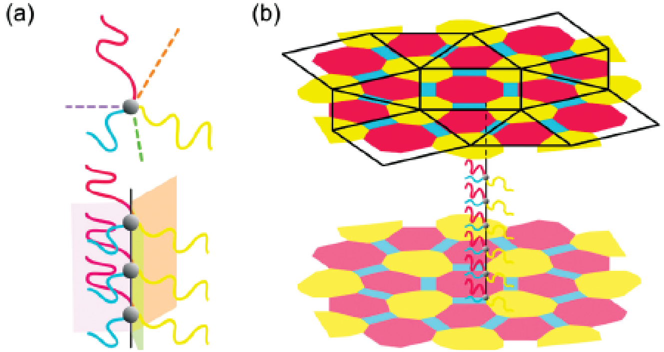


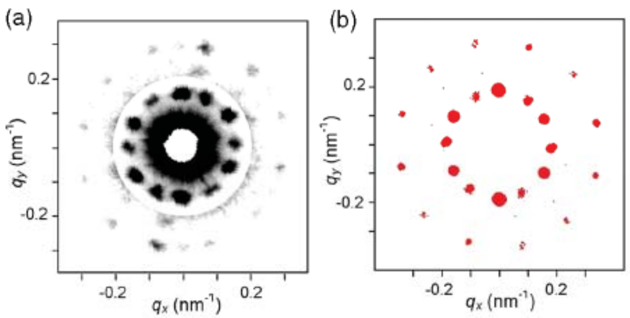
Polymeric quasicrystal

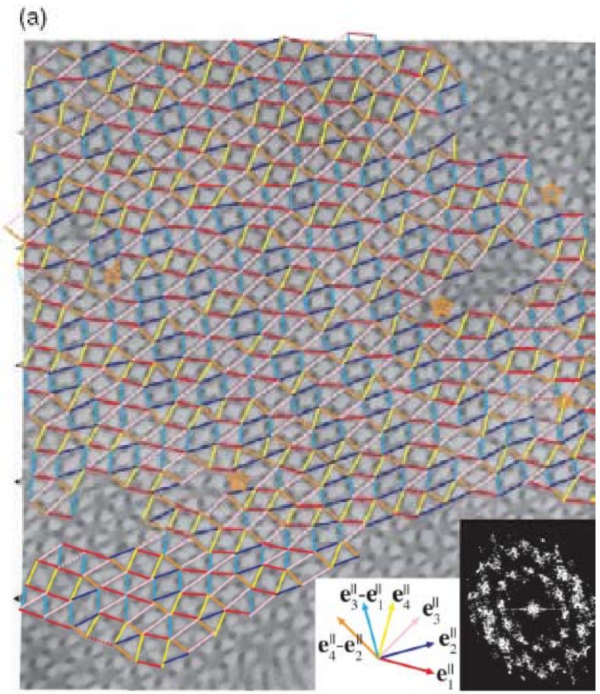
PRL **98,** 195502 (2007) PHYSICAL REVIEW LETTERS week ending 11 MAY 2007

Polymeric Quasicrystal: Mesoscopic Quasicrystalline Tiling in *ABC* Star Polymers

Kenichi Hayashida,[1] Tomonari Dotera,[2] Atsushi Takano,[1] and Yushu Matsushita[1]







Length scale: 50 nm

Summary

- Quasicrystal is really a new kind of long range order.
- Symmetry incompatible with translation and sharp Bragg peaks
- Found in intermetallic compounds but also in soft condensed matter.

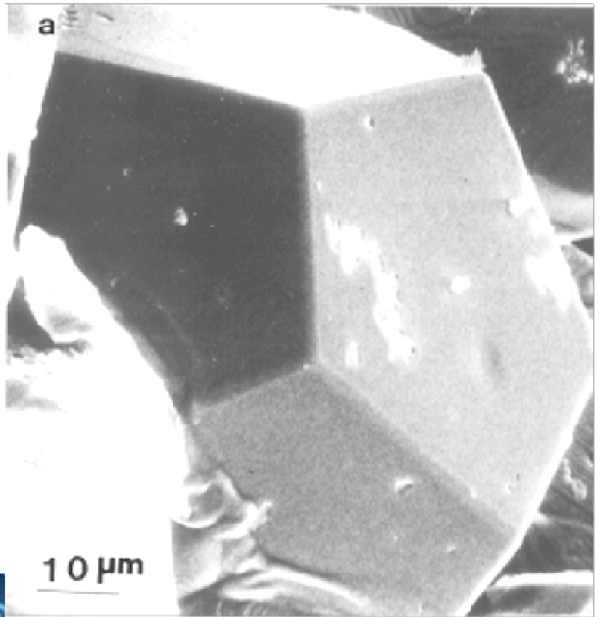
Diffraction pattern of quasicrystals

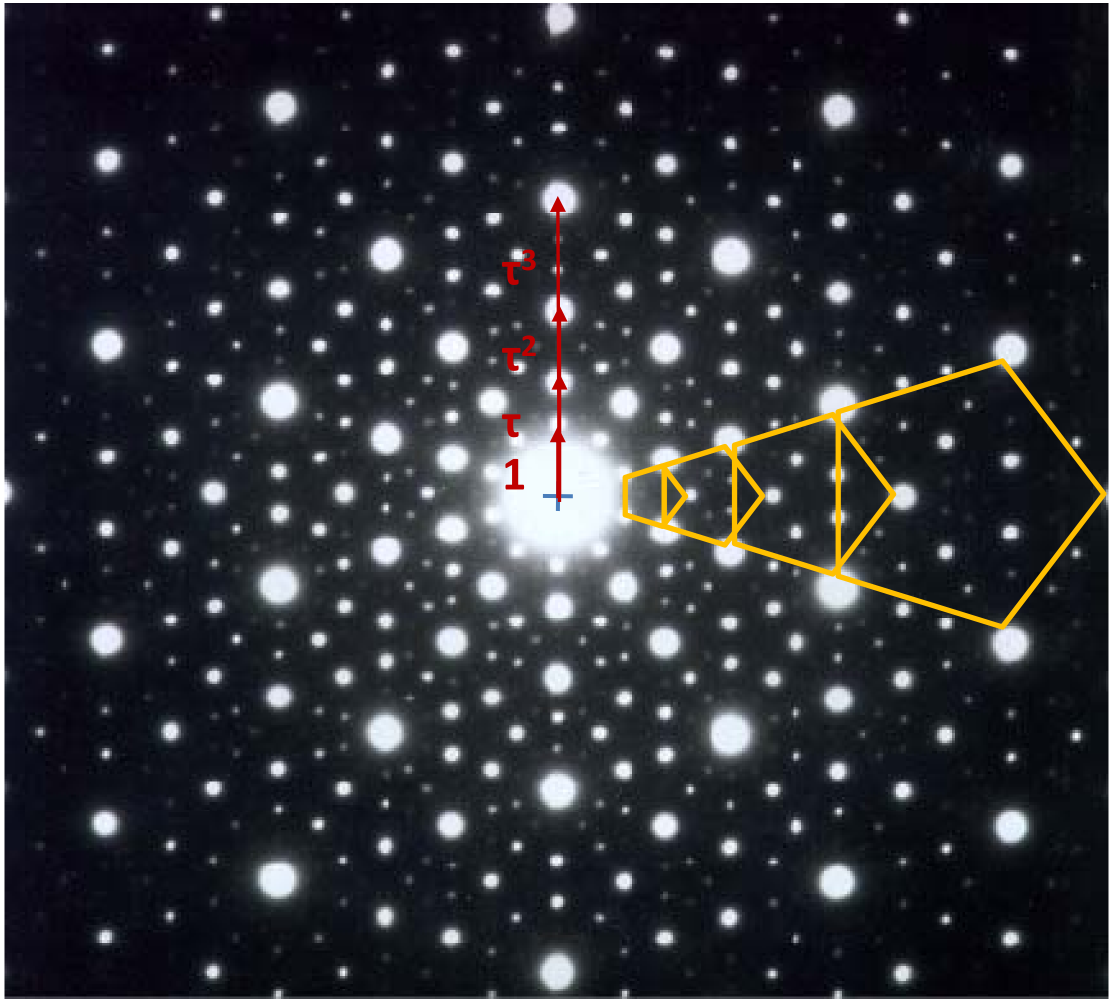
- Some general characteristics
- How ‘good’ is the quasicrystal ? True Bragg peak?

Diffraction pattern of quasicrystals

- i-AlCuFe
- Icosahedral symmetry
- τ inflation scaling
- Self-similarity

(from A.P. Tsai)





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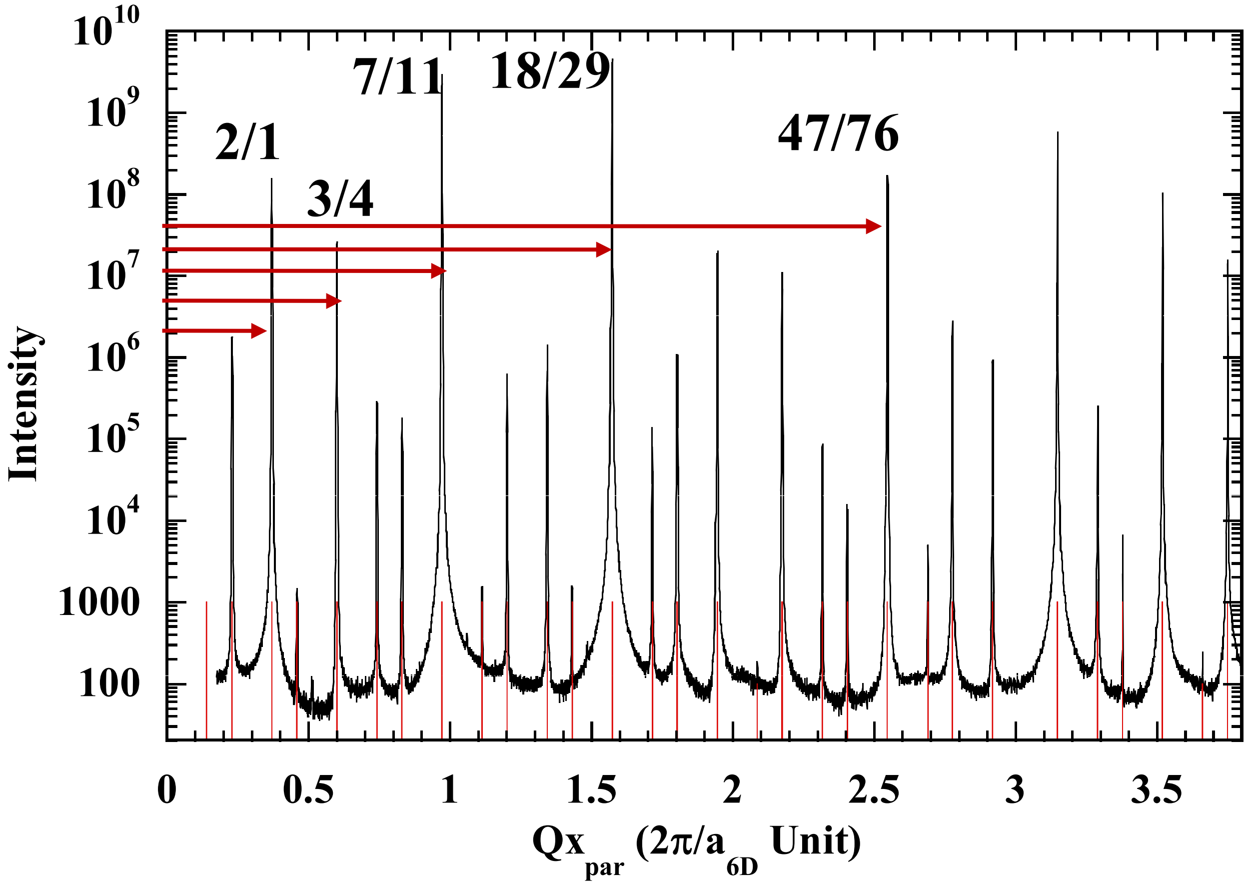
Diffraction pattern of quasicrystals

- X-ray diffraction along 5-fold axis. i-AlPdMn. ESRF. (Log I scale)
- Only few very strong Bragg. τ scaling of position (Fm35).

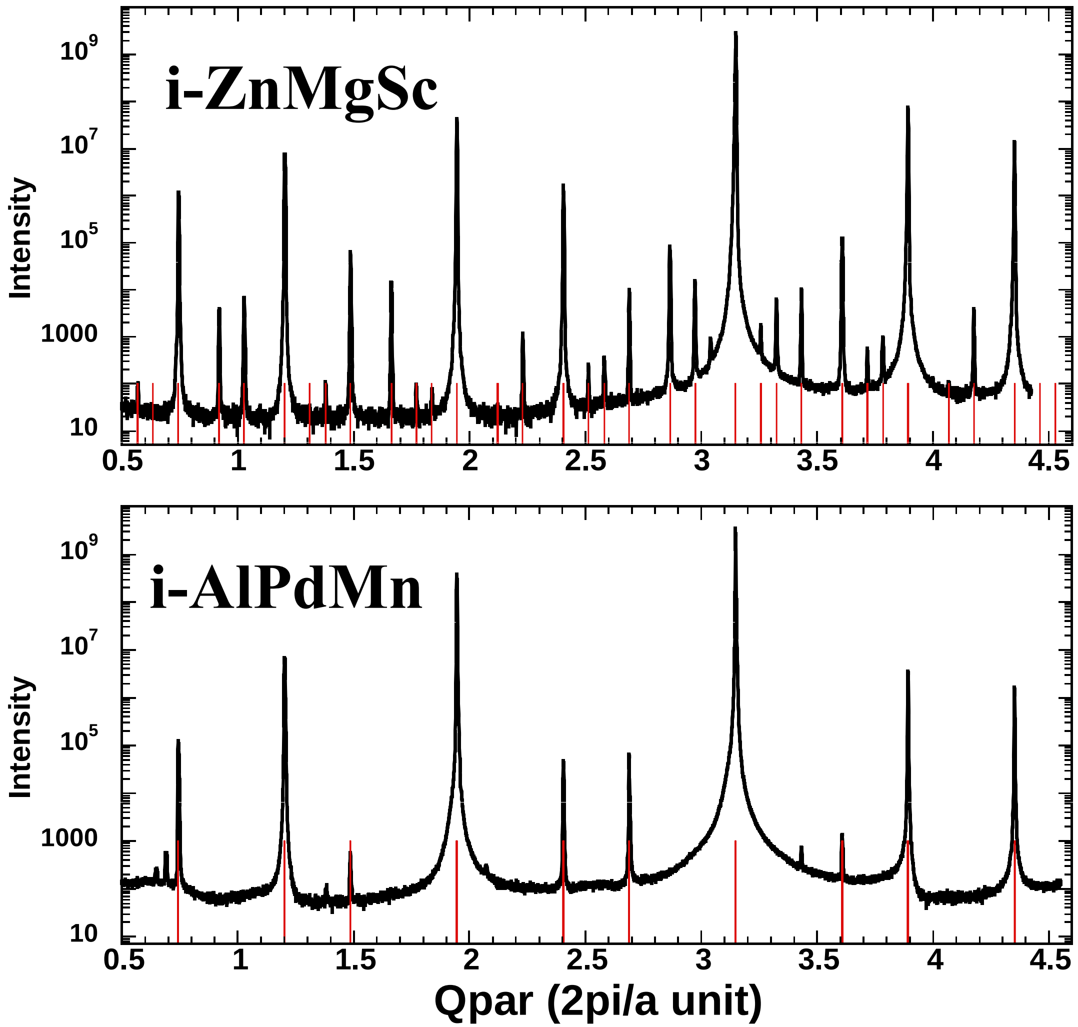
6 integer indices

N/M short hand notation (Gratias et al.)



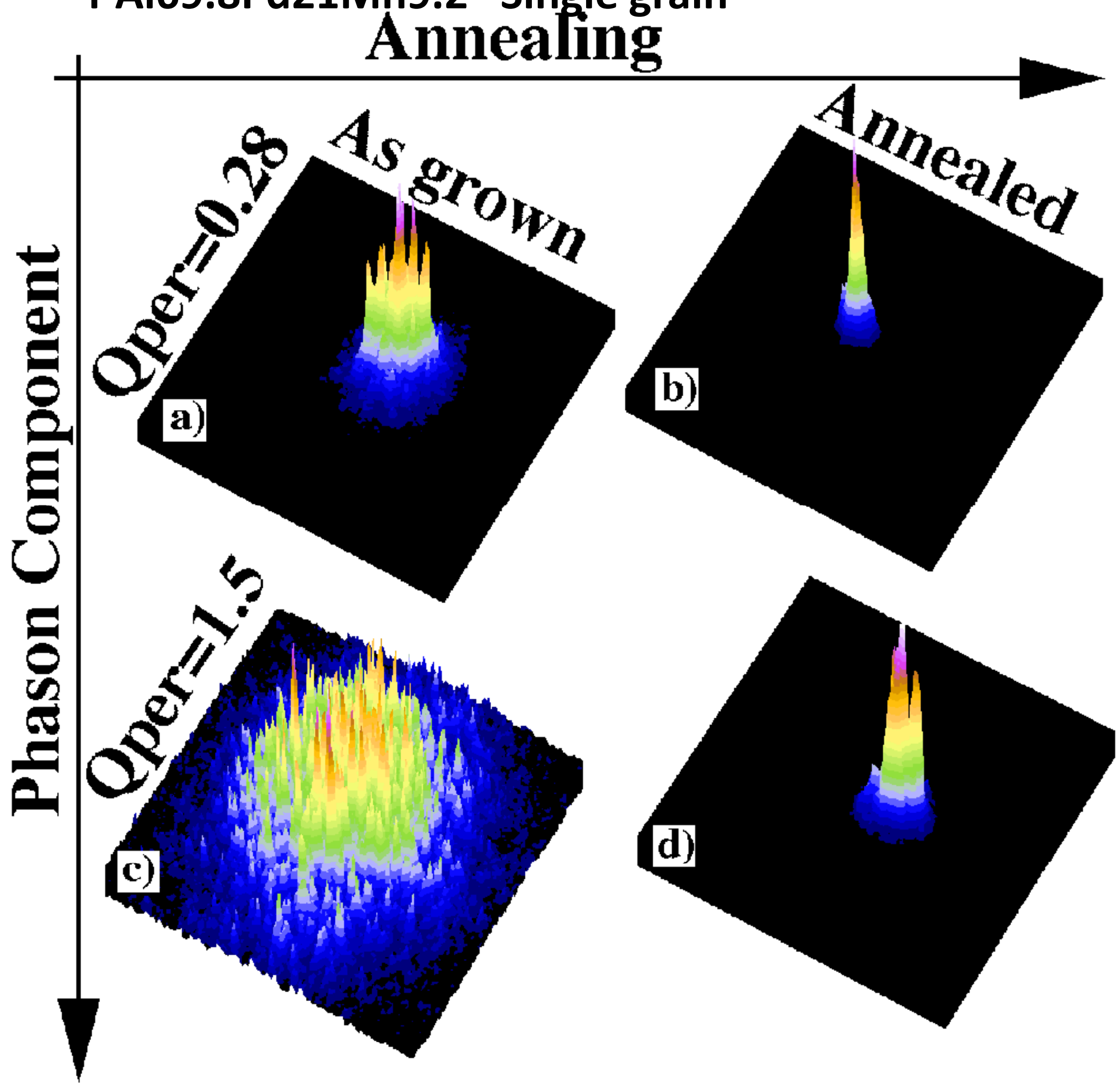
Diffraction pattern of quasicrystals

- The intensity distribution depends on the atomic structure and structural quality
- 2-fold scans of i-ZnMgSc and i-AlPdMn
- Very large number of reflexions in i-ZnMgSc (Ishimasa et al.)



Quasicrystal perfection: Bragg peak

i-Al69.8Pd21Mn9.2   Single grain



- High resolution, coherent setup (ID20, ESRF): one speckle

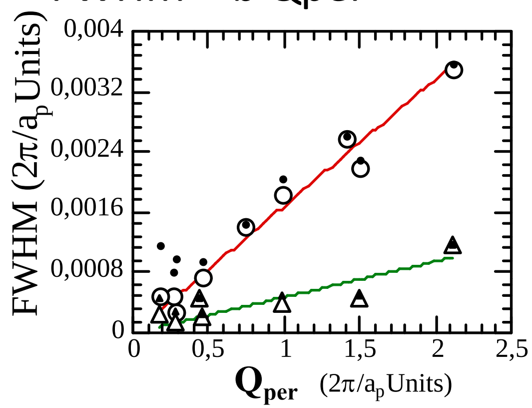
dQ=10^{-4} Å^{-1} ξ ~ 10µm

- Rocking curve:

0.005° FWHM

Unif phason strain:

FWHM = b Qper

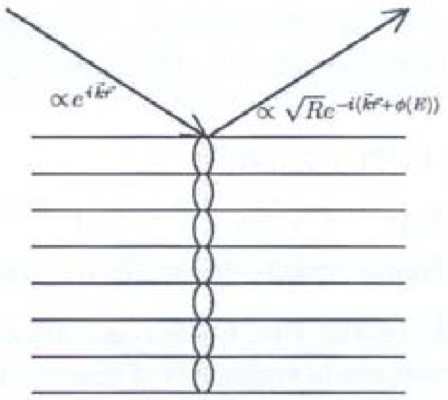


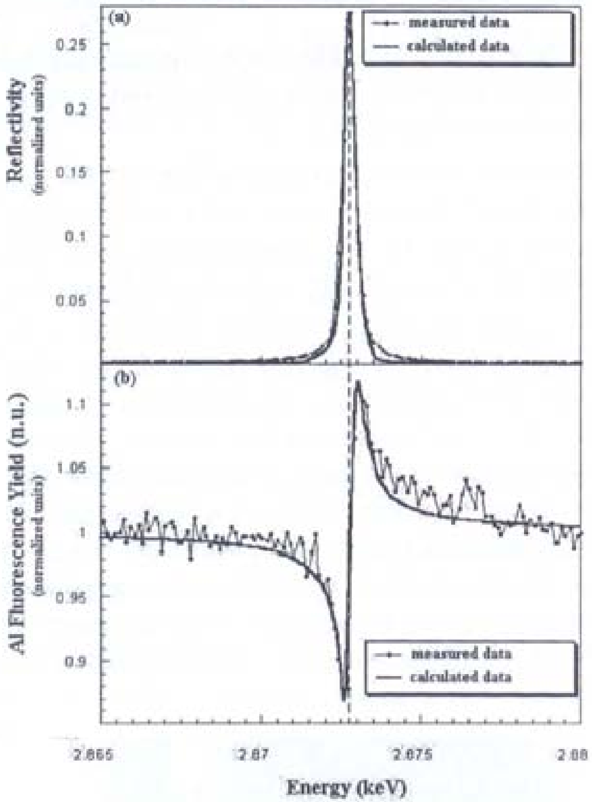
A. Létoublon et al.

Dynamical diffraction: standing waves

i-AlPdMn

Crystal





- Measurement in backscattering (ID32)
- Al fluorescence
- Modeling with a crude atomic model

T. Jachs et al, PRL, 82, 1999

F. Schmithusen, Phd thesis

See also J. Gastaldi, J. Hartwig, ID19, ESRF

Almost perfect quasiperiodic long range order

Summary

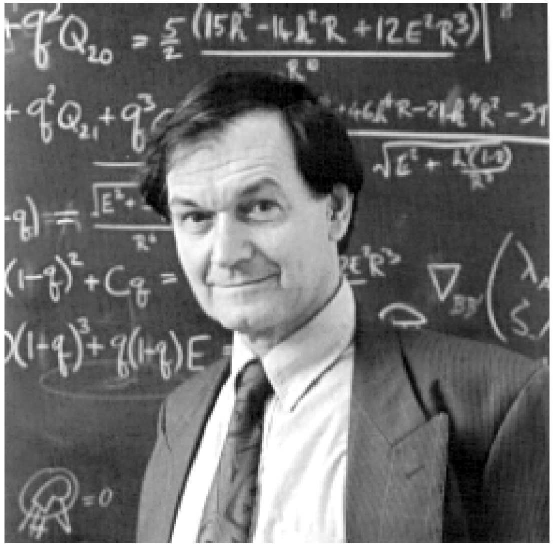
- The quasicrystal diffraction pattern displays inflation properties (tau scaling in the icosahedral case)
- A few very strong Bragg peaks and a large number of weak Bragg peaks
- The long range order is as good as in the best intermetallic alloys: extremely sharp Bragg peaks.

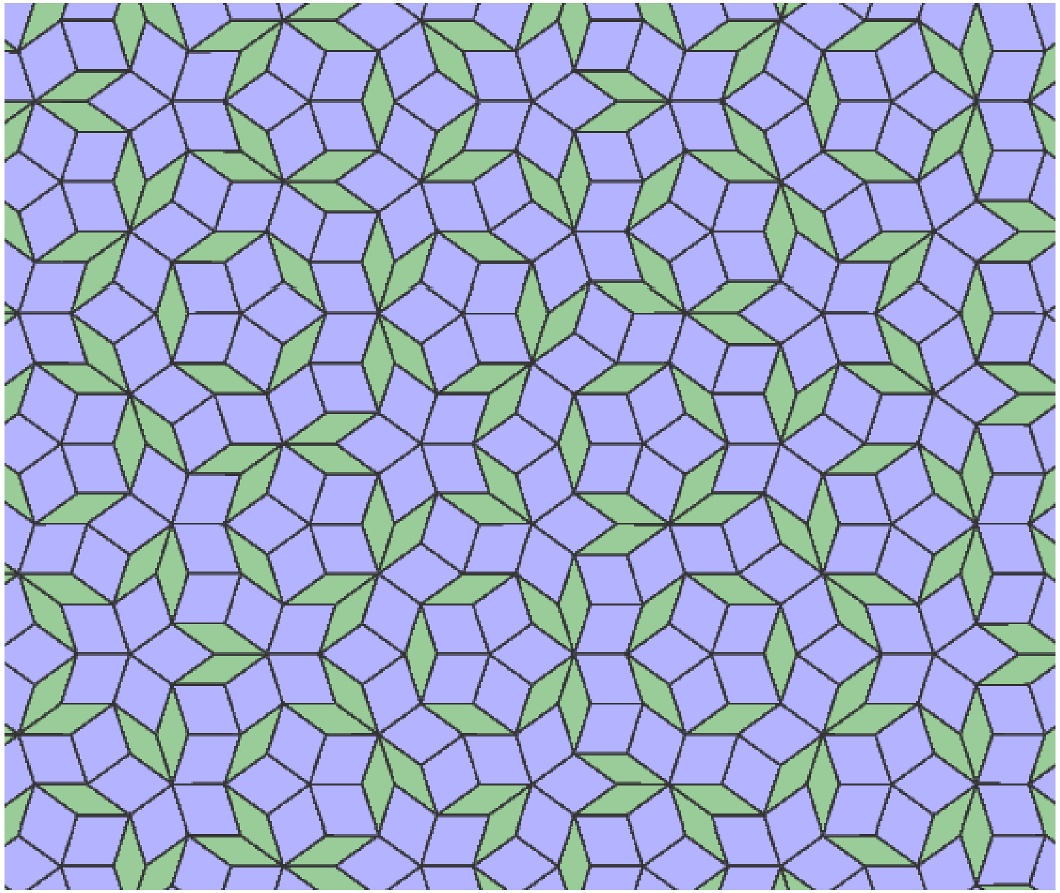
Atomic structure of quasicrystals

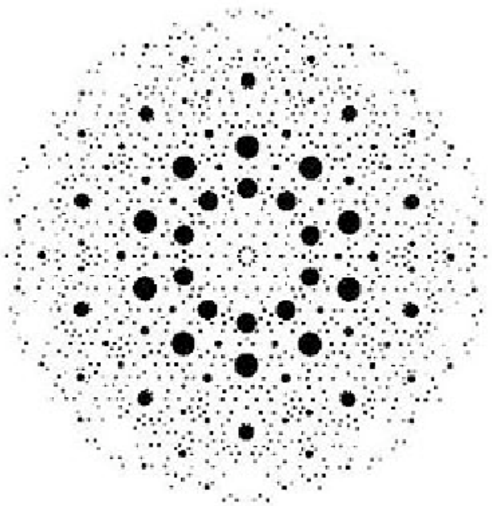
- Real space approach: tilings.
- High dimensional approach: atomic surfaces.
- Both methods have their advantage and drawback. The high dimensional approach is the most general one.

- Some characteristics in direct space: the Penrose tiling.

The Penrose tiling







2 tiles. Diffraction: sharp Bragg 5-fold symmetry

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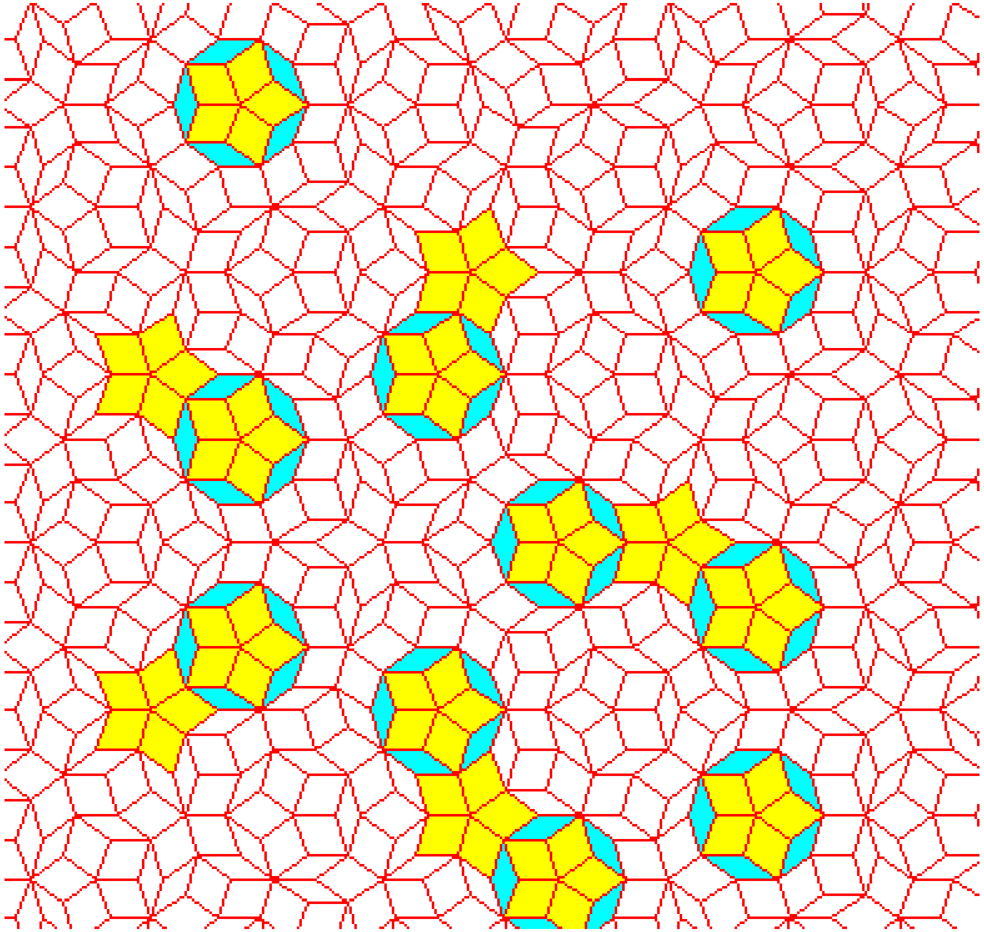
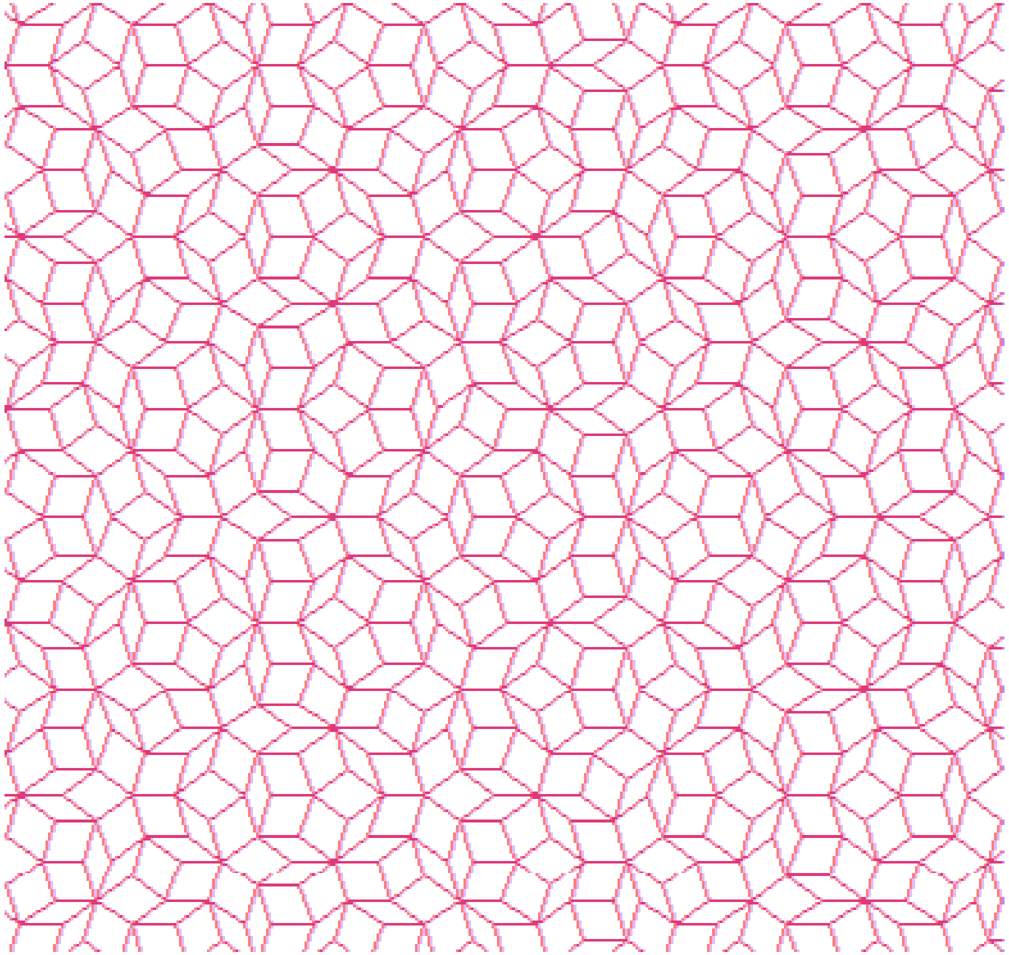
Penrose tiling



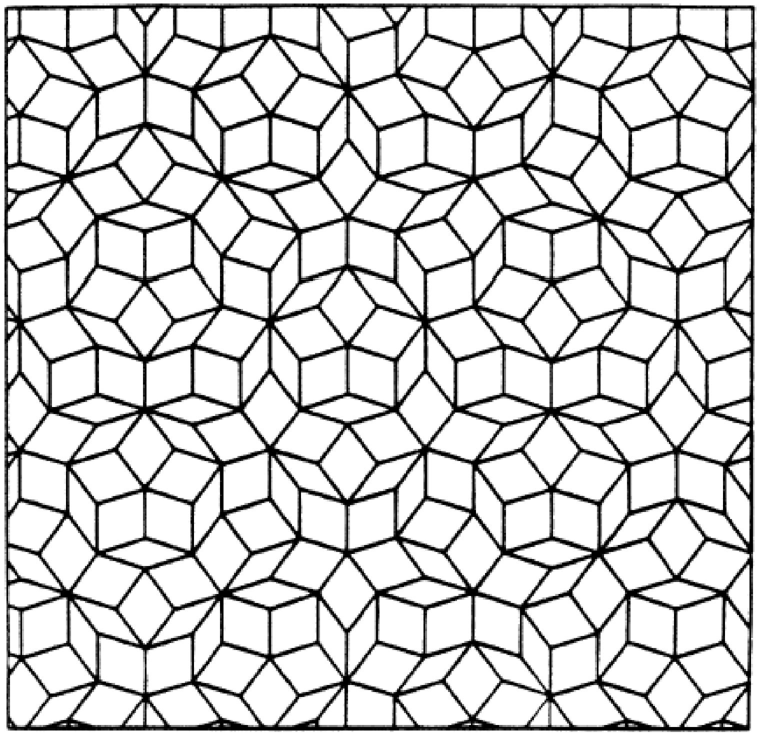
Same local environment found everywhere.

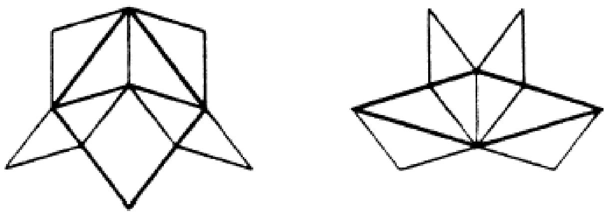
Penrose tiling



No true 5-fold symmetry in direct space; but almost perfect superposition with a translation. (Courtesy R. Lifshitz).

Penrose tiling

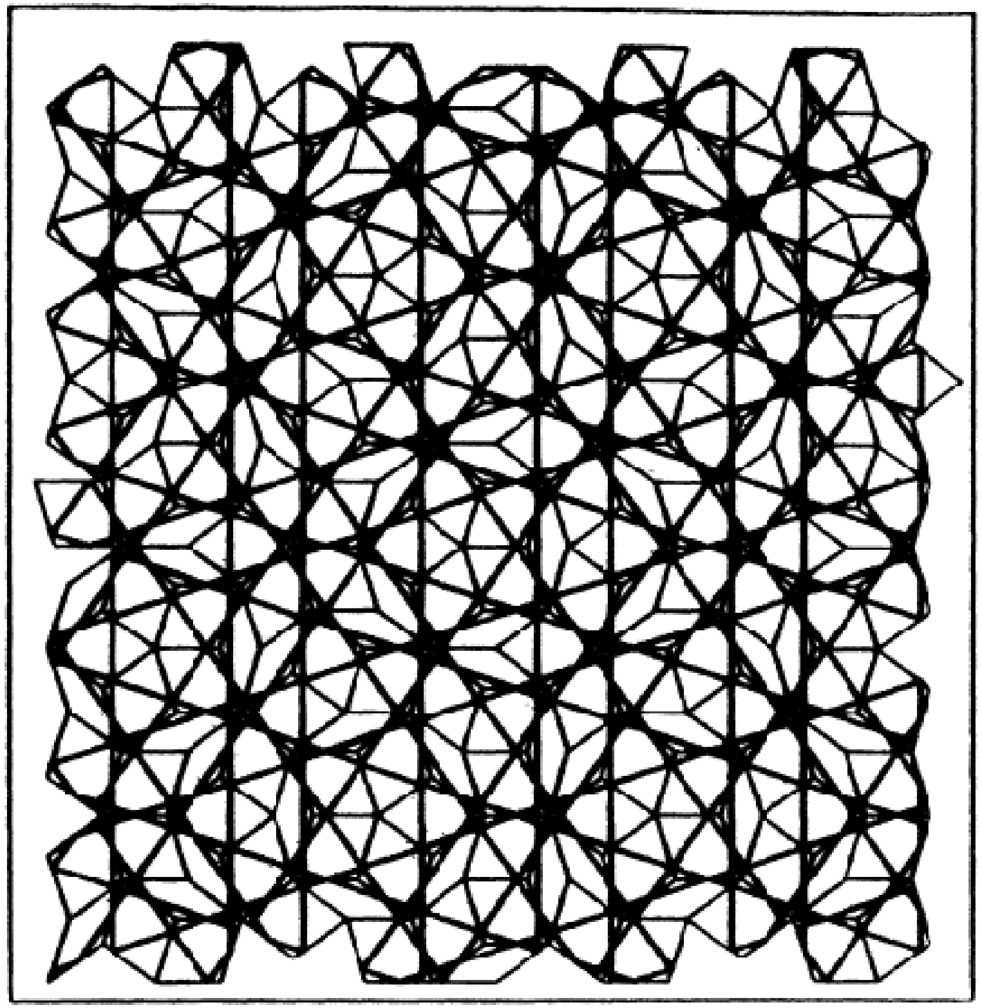


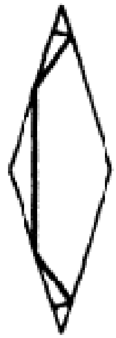


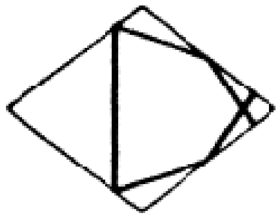
The Penrose tiling has a hierarchical structure

Inflation-deflation properties

Penrose tiling

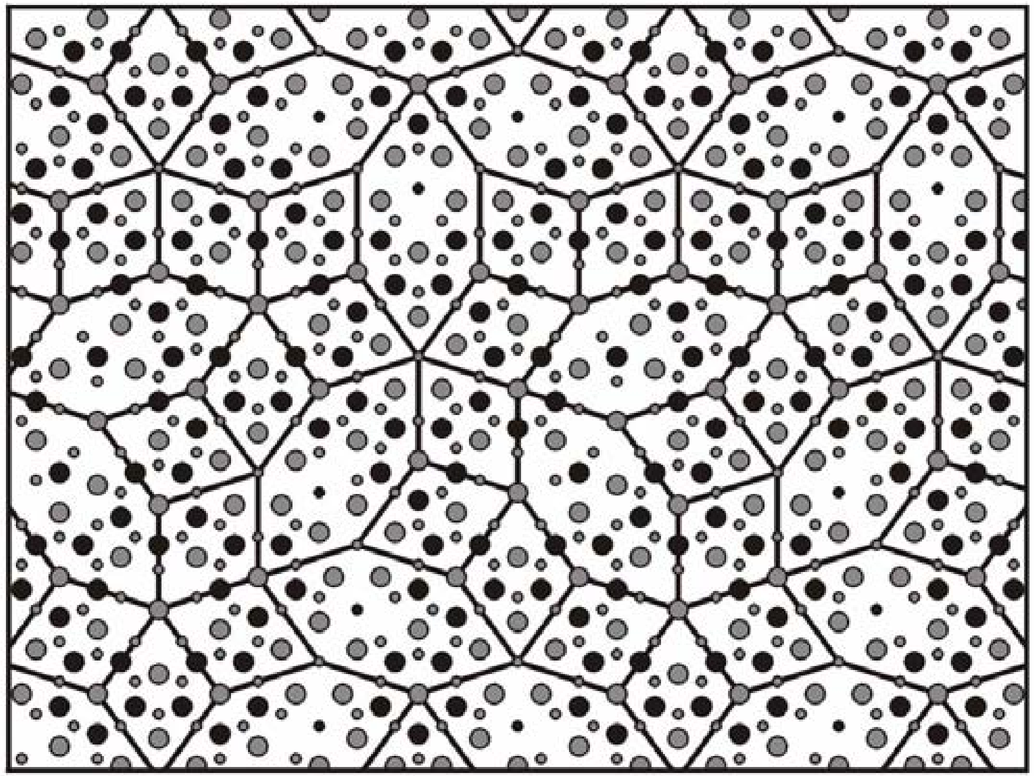






Structure as tiling

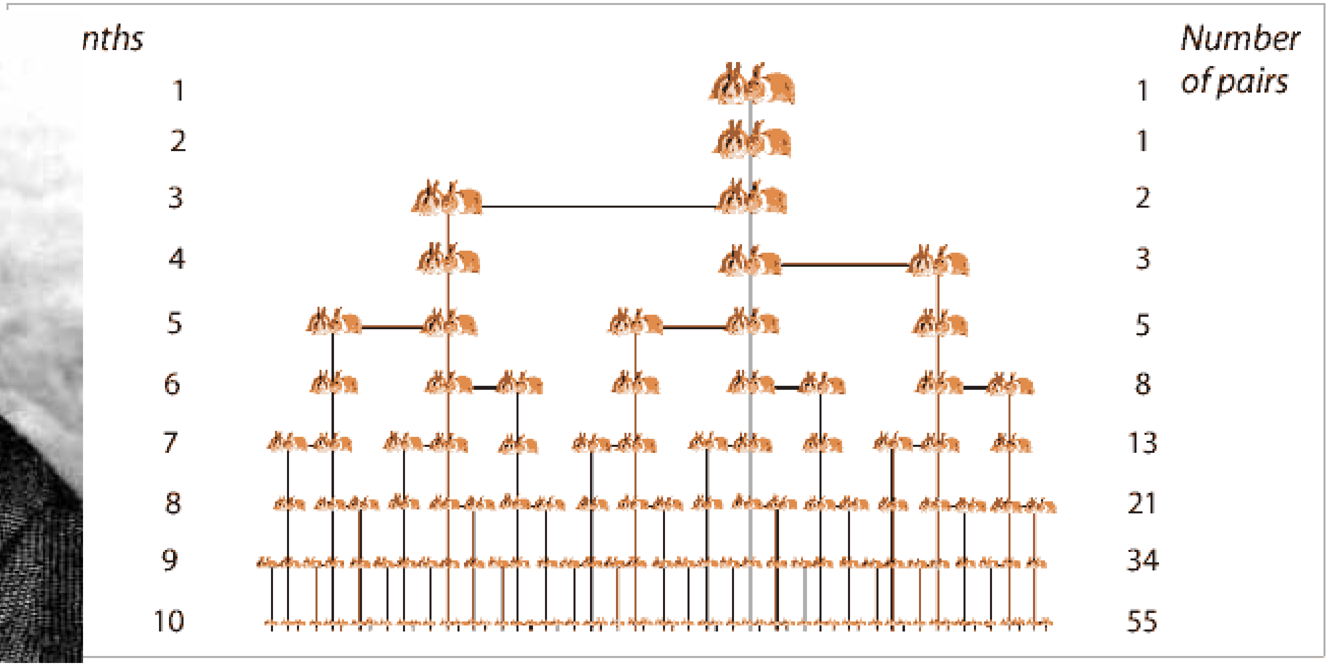
- Decorated tiling: example of decagonal AlNiCo (see H. Takakura and M. Mihalkovic lecture)



The Fibonnacci chain and 1D quasicrystals.

- 1D simple example
- Although there is no symmetry involved, this model has strong similarities with icosahedral quasicrystals.

Fibonacci



Form a series of numbers: 1, 1, 2, 3, 5, 8, 13….

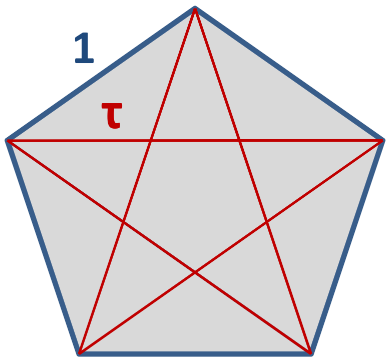
$U_n = U_{n-1} + U_{n-2}$

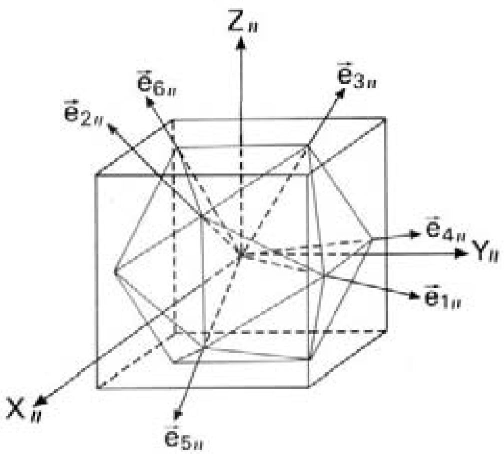
U_{n-1}/U_{n-2} -> τ the golden mean.

$\tau = 2\cos(36) = (1+)/2 = 1.618...$

The golden mean

- $\tau = (1+\sqrt{5})/2 = 1.618033....$
- Related to pentagonal and icosahedral symetry.





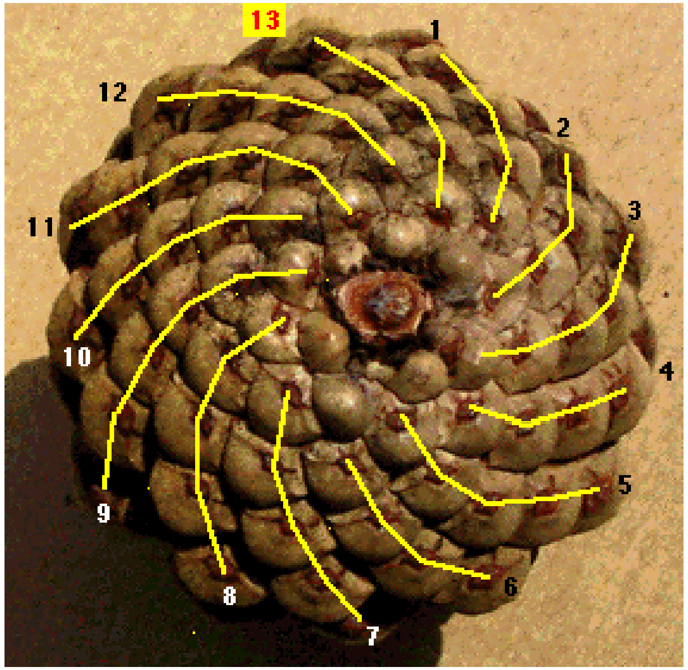
Coordinates of the 5-fold axis of the icosahedron in an orthonormal basis: $(1,\tau,0)$

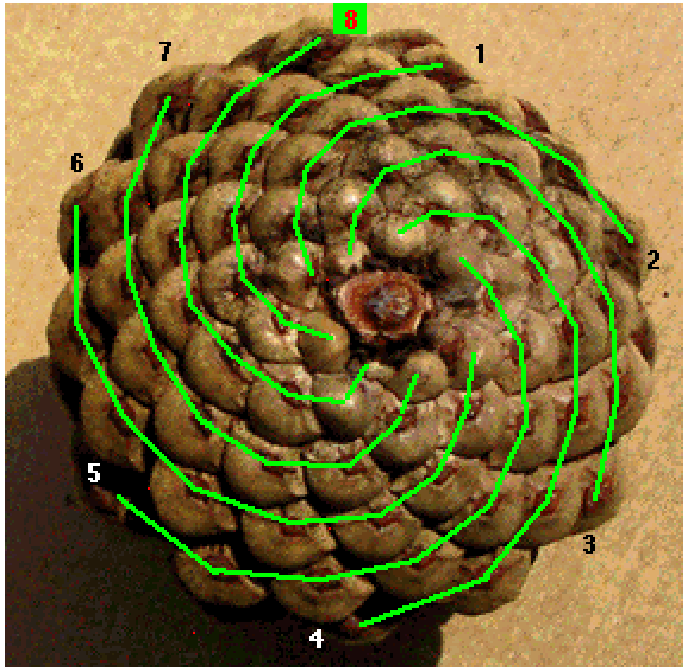
- τ is the solution of $x^2=x+1$; $\tau^2= \tau+1$
- The Fibonnacci series gives approximation to τ. **1, 1, 2, 3, 5, 8,13,21,34,55**. For instance 3/2=1.5 55/34=1.6176..
- The power of τ can be calculated with the Fibonnacci series: $\tau^n= U_n\tau+U_{n-1}$

For instance $\tau^4= 3\tau+2$ (this can be generalised to negative power of τ)

The golden mean

- Found in phyllotaxy : number of left and right spirals are two following Fibonnacci number. Related to seed packing efficiency.





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The golden mean

- Found in phyllotaxy : number of left and right spirals are two following Fibonnacci number. Related to seed packing efficiency.

The Fibonacci chain.

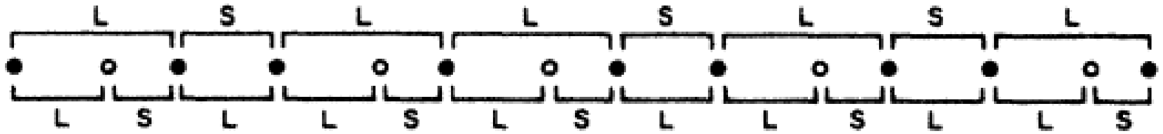
Two segments ('tiles') L and S, L/S=τ=1.618…

inflation construction S→L and L→LS

- ***S, L, LS, LSL, LSLLS, LSLLSLSL, LSLLSLSLLSLLS…***
- ***If L/S=*** τ , aperiodically ordered structure.
- ***$Fn=F_{n-1}F_{n-1}$*** Concatenation of two preceding 'words'
- Number of L (S) tiles NL (NS): NL/NS = τ
- Local order: no SS or LLL sequence for instance.

The Fibonacci chain.

- ***LSLLSLSLLSLLSLSLLSLSLLSLLSLSLLSLLS …***
- Self similarity and Inflation properties:
- If we multiply all vertices by τ one obtains *the same Fibonnacci chain. (True also for deflation by 1/τ)*



- Quasiperiodic order: take any portion of the chain another one is found nearby. True for any size.
- ***LSLLSLSLLSLLSLSLLSLSLLSLLSLSLLSLLS….***
- ***LSLLSLSLLSLLSLSLLSLSLLSLLSLSLLSLLS….***

The Fibonacci chain.

- ***LSLLSLSLLSLLSLSLLSLSLLSLLSLSLLSLLS …***
- Diffraction pattern: from the general expression:

Position of the nth point is given by:

$$L_n = na + \frac{a}{\tau}\left\lfloor \frac{n}{\tau} \right\rfloor \qquad \left\lfloor \frac{n}{\tau} \right\rfloor$$ *Is the Integer part*

- This gives two length scale: 1 and τ

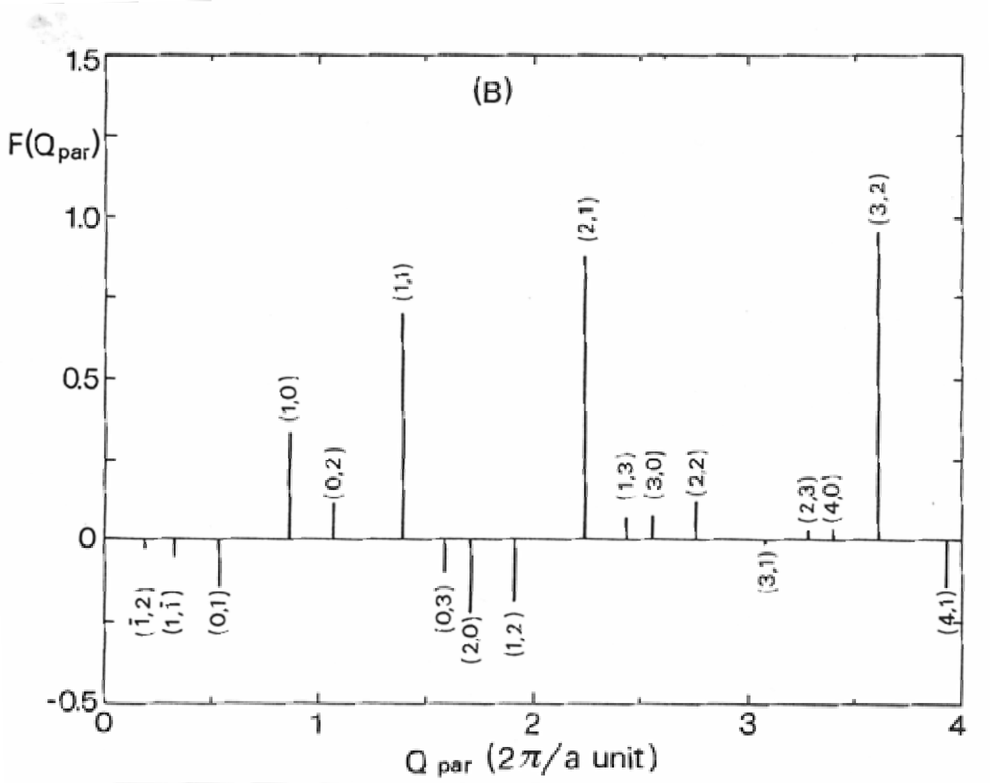
a and a+a/τ = a+a(τ-1) = a τ

- This definition can be used to compute de diffraction pattern: Bragg peaks and position defined by:

$$\mathbf{k}_{h,h'} = \frac{1}{a\sqrt{1+\tau^2}}(h + \tau h')$$

Fibonnacci chain diffraction pattern

$$\mathbf{k}_{h,h'} = \frac{1}{a\sqrt{1+\tau^2}}(h + \tau h')$$



- Two irrational length scale:

$$\frac{1}{\sqrt{1+\tau^2}} = 0.5257$$

$$\frac{\tau}{\sqrt{1+\tau^2}} = 0.8506$$

- 2-D embedding of the diffraction pattern

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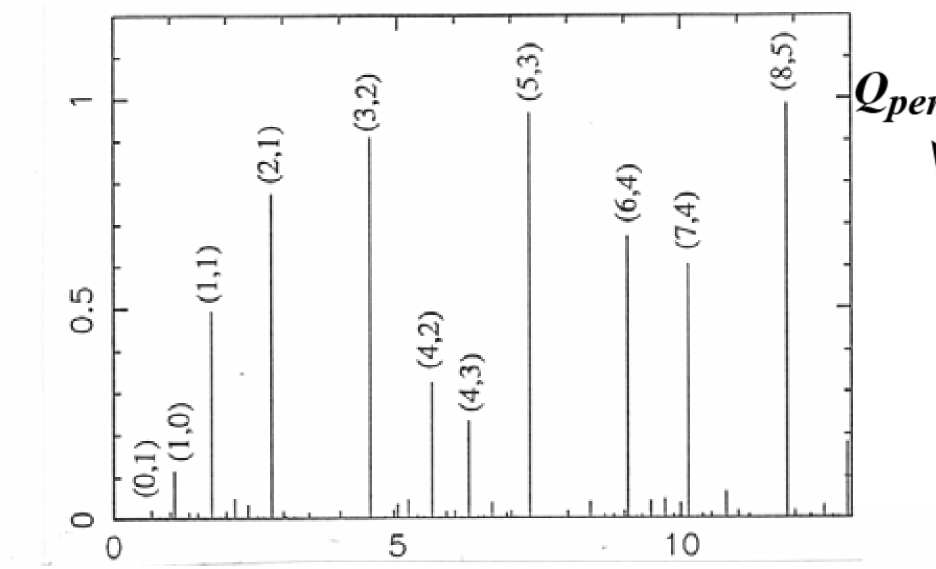
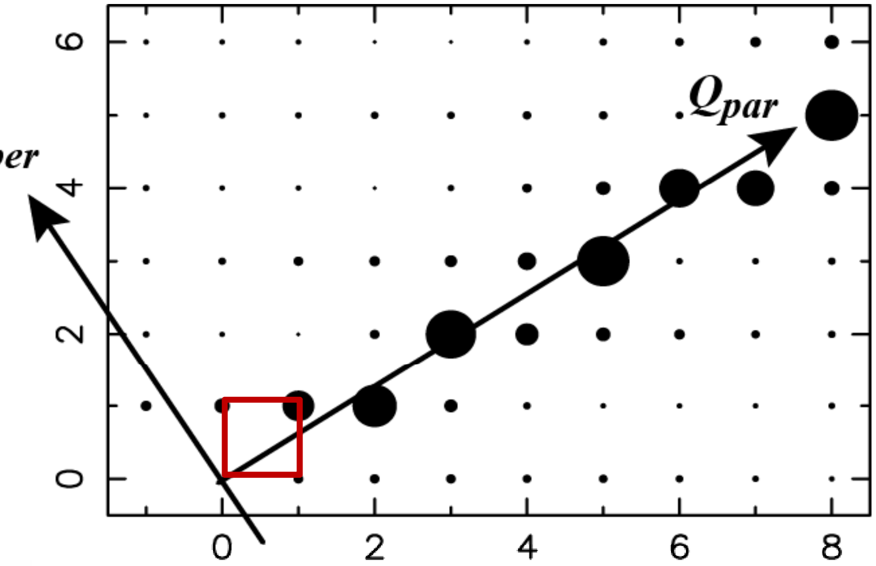
2D embedding of the diffraction pattern

$$\mathbf{k}_{h,h'} = \frac{1}{a\sqrt{1+\tau^2}}(h+\tau h')$$

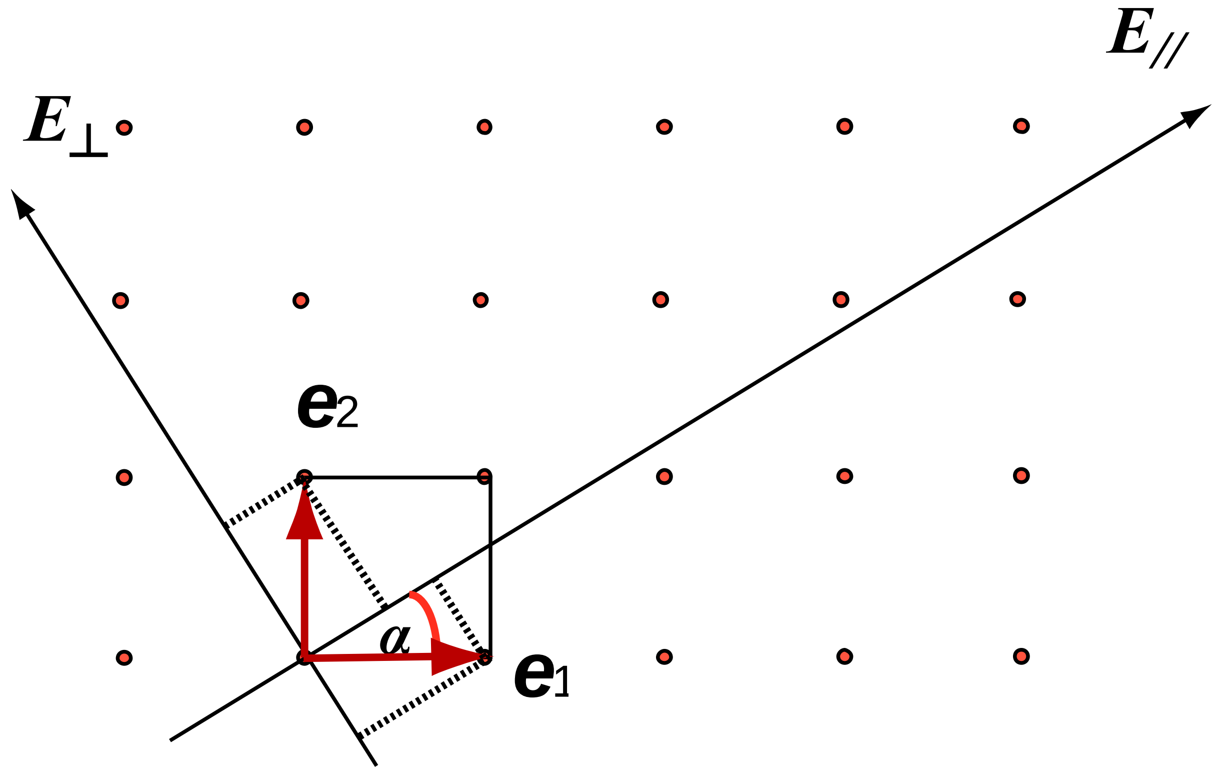




tgα = 1/τ α=31.7..°

$$\begin{pmatrix} \mathbf{H}_{par} \\ \mathbf{H}_{per} \end{pmatrix} = \frac{1}{a\sqrt{2+\tau}} \begin{pmatrix} \tau & 1 \\ \bar{1} & \tau \end{pmatrix} \begin{pmatrix} n1 \\ n2 \end{pmatrix}$$

2-D embedding of the Fibonacci chain

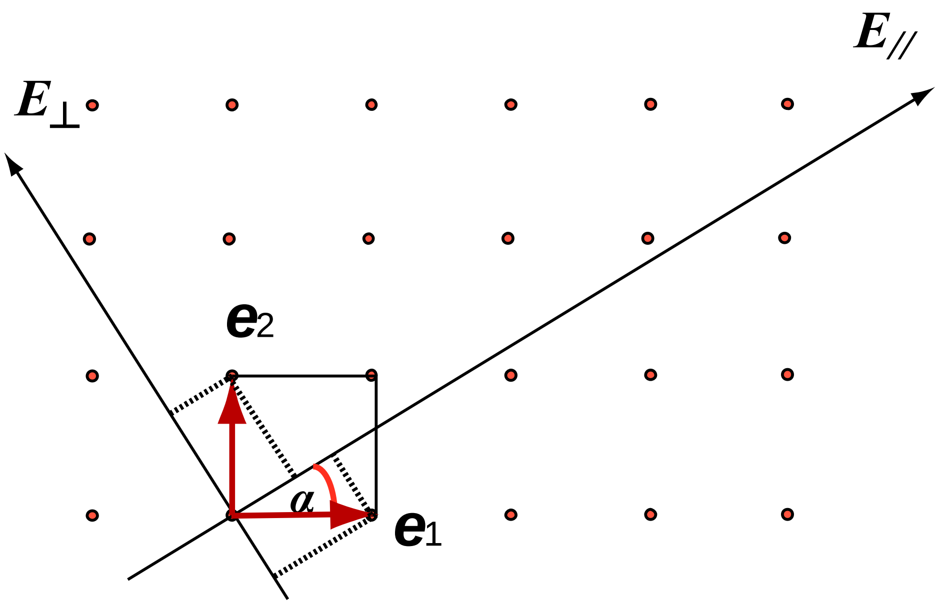


Square lattice: basis (**e**1,**e**2)

E_{par} (or external space), Physical space , with irrational slope 1/τ

E_{per} (or internal space)

2-D embedding



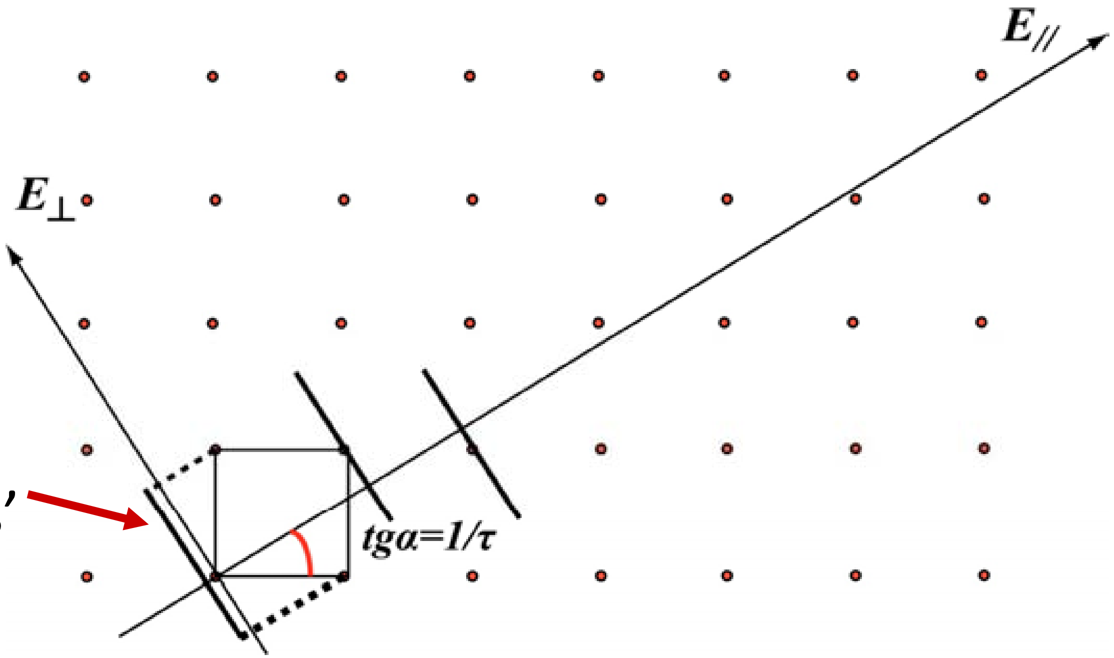
- ($\boldsymbol{e}_1$,$\boldsymbol{e}_2$) basis of the square lattice, parameter a.
- Projection on E_{par} and E_{per} (E_{int} and E_{ext}).
- tgα = 1/τ α=31.7..°
- *cos*(α) = τ/√(2+τ)=0.8506…
- *sin*(α) = 1/√(2+τ)=0.5257…
- $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ projects on two length τa*sin*(α) and a*sin*(α) on the parallel space.

$$\begin{pmatrix} X_{par} \\ X_{per} \end{pmatrix} = \frac{a}{\sqrt{2+\tau}} \begin{pmatrix} \tau & 1 \\ -1 & \tau \end{pmatrix} \begin{pmatrix} n_1 \\ n_2 \end{pmatrix}$$

2-D embedding of the Fibonacci chain

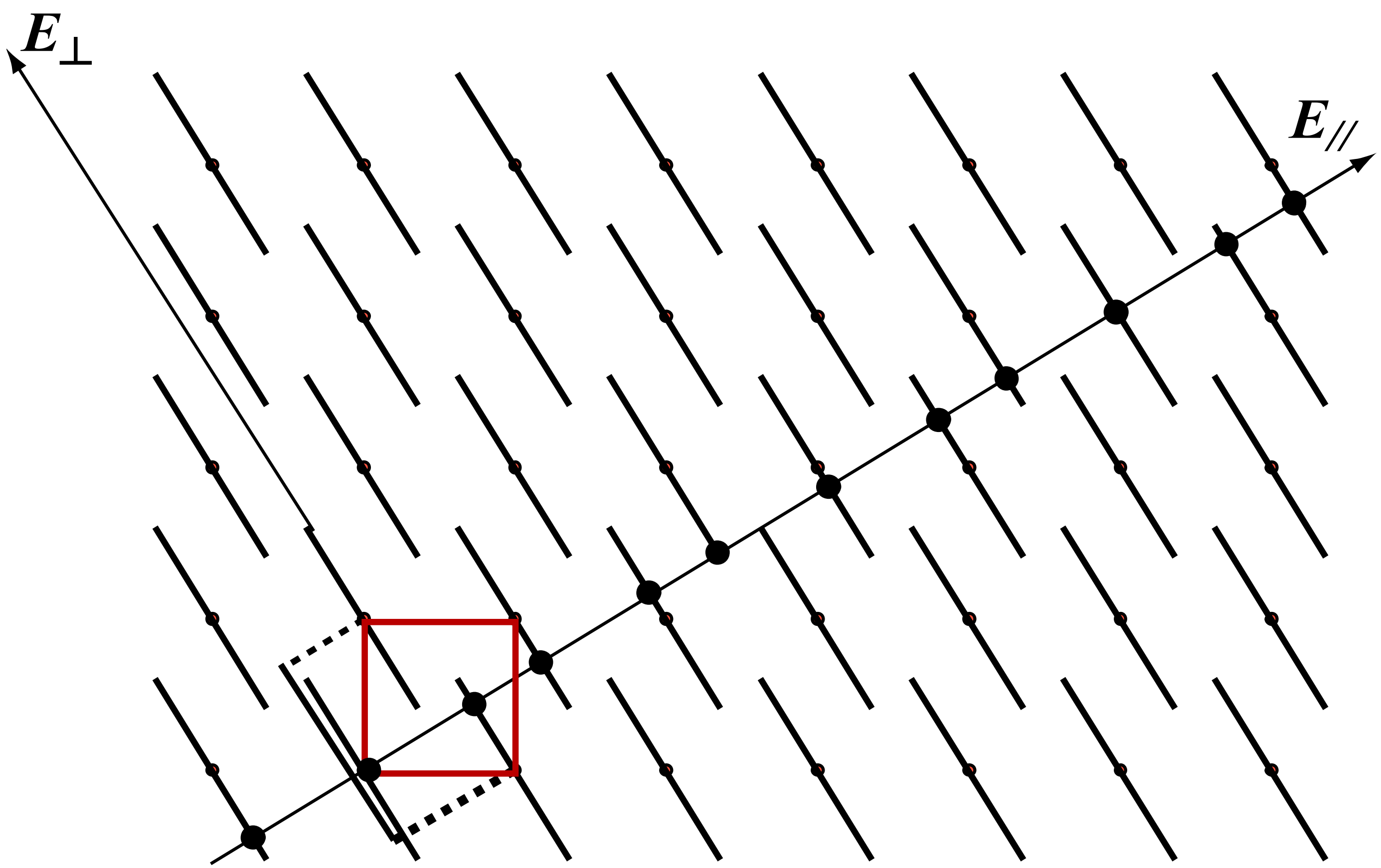
Atomic surfaces along E_{per} decorate the square lattice

‘Atomic surfaces’



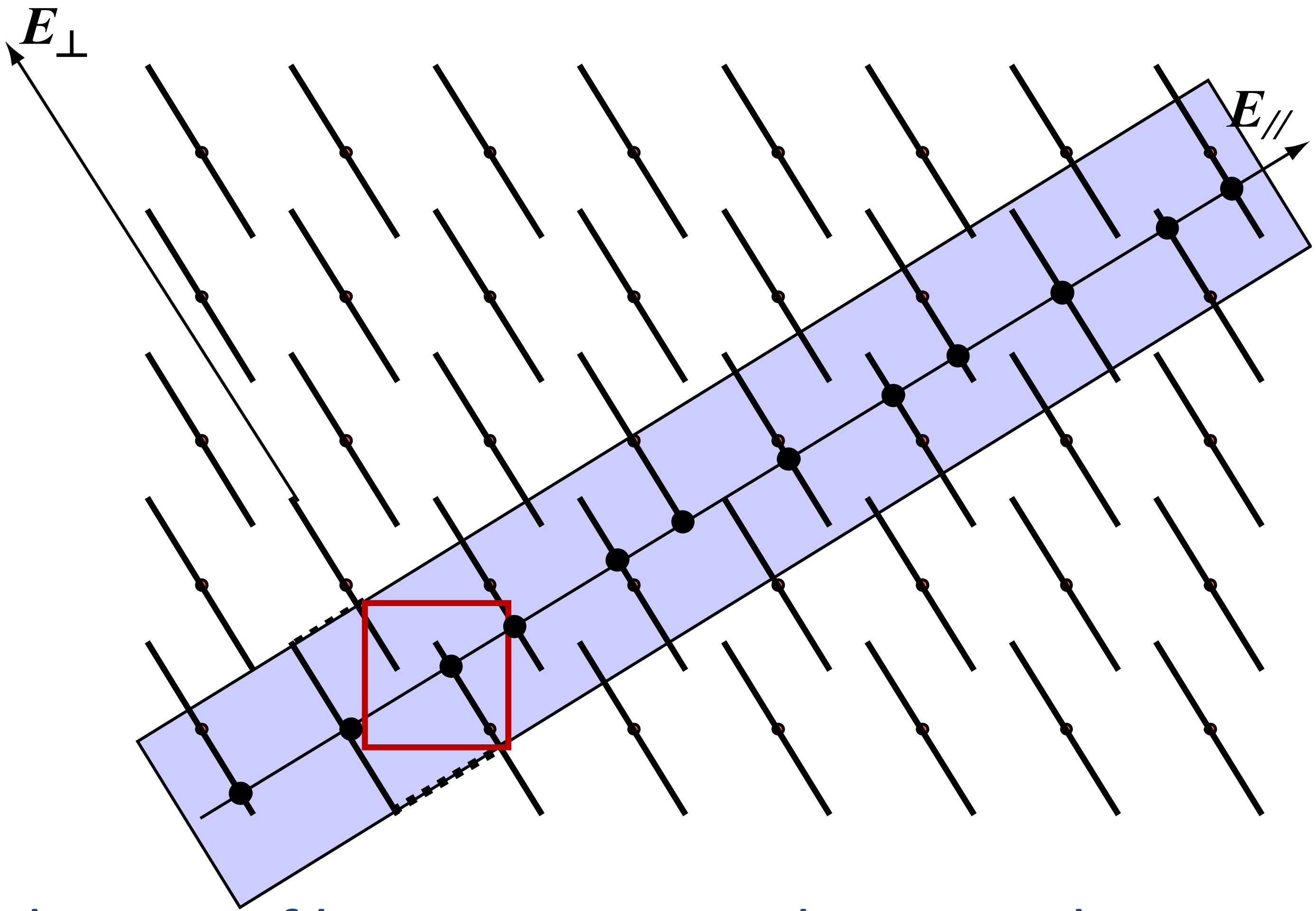
Length of the atomic surface: projection of the square lattice along E_{per}. : $L = a(1+\tau)/\sqrt{(2+\tau)} = a.1.376...$

2-D Embedding



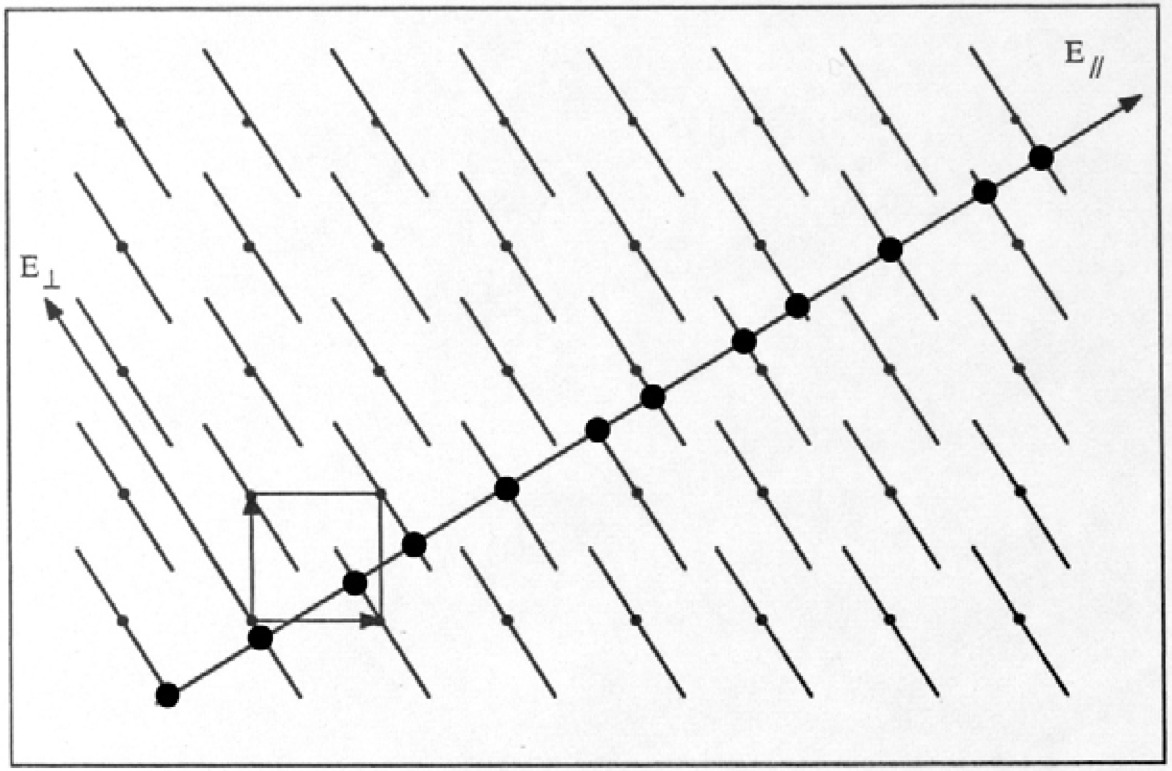
- 1D QC is obtained as a section of the 2D decorated QC

2-D Embedding: the ‘strip’ method



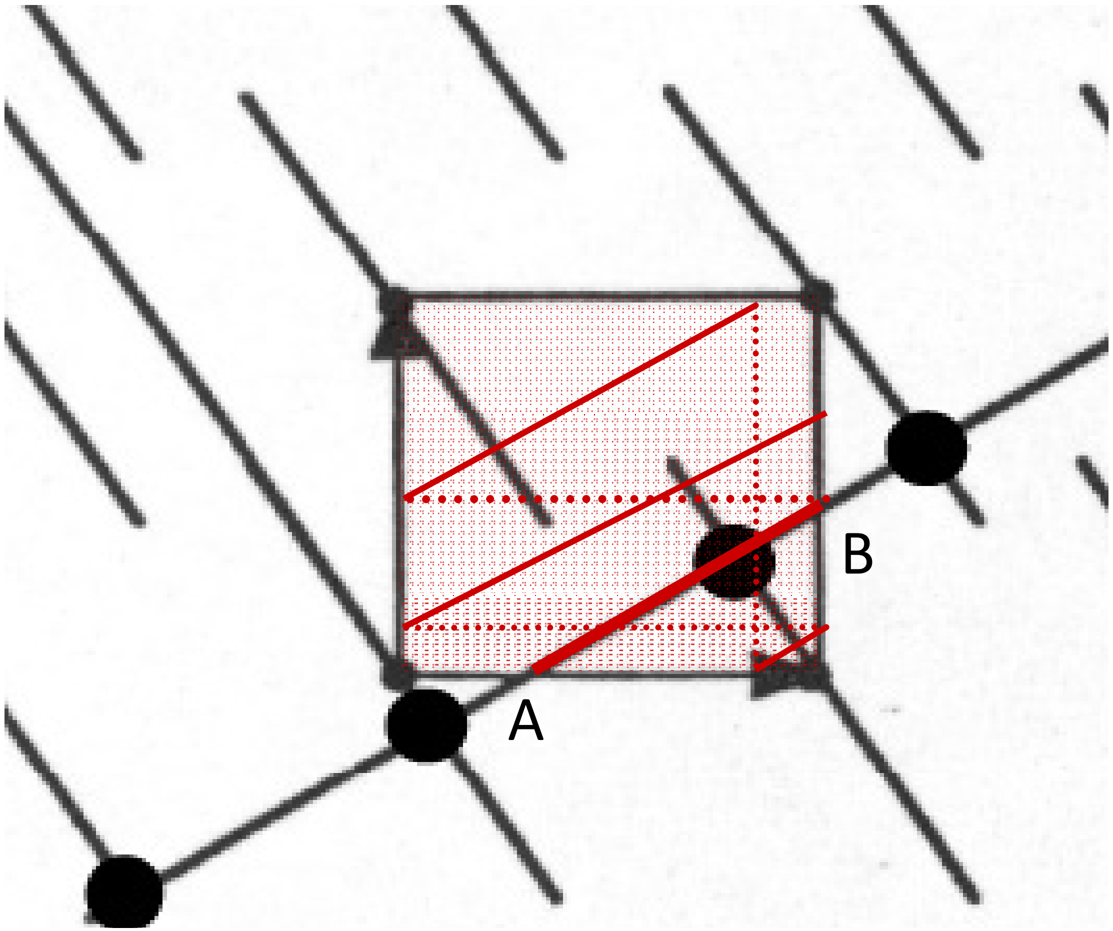
Selection of lattice points in the strip, then projection.

2-D embedding of the Fibonacci chain



1D   • L • L • S • L • L • S • L • S • L • L • S •

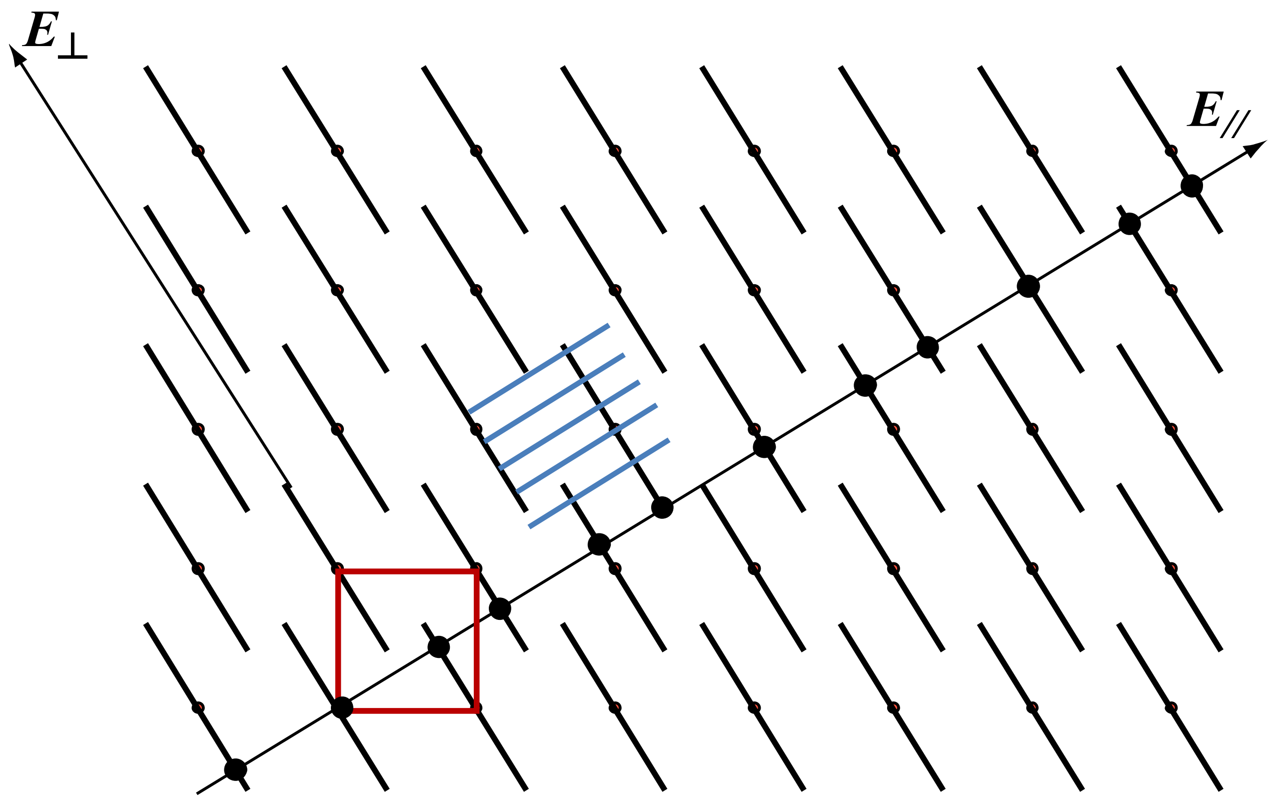
2-D embedding of the Fibonacci chain



The 2-D Unit cell contains all the information on local order.

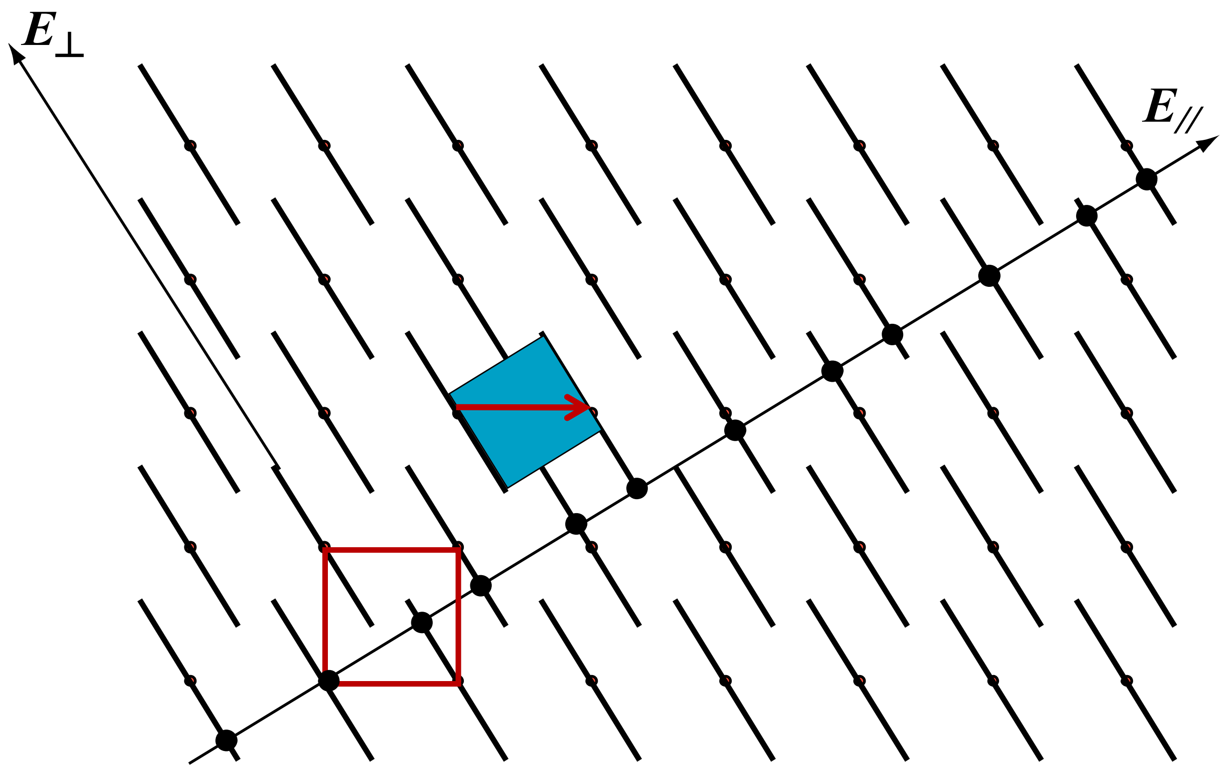
Point density = L_{per}/a^2

Local environments



When do we find a point followed by another one at a distance L on the right?

Local environments



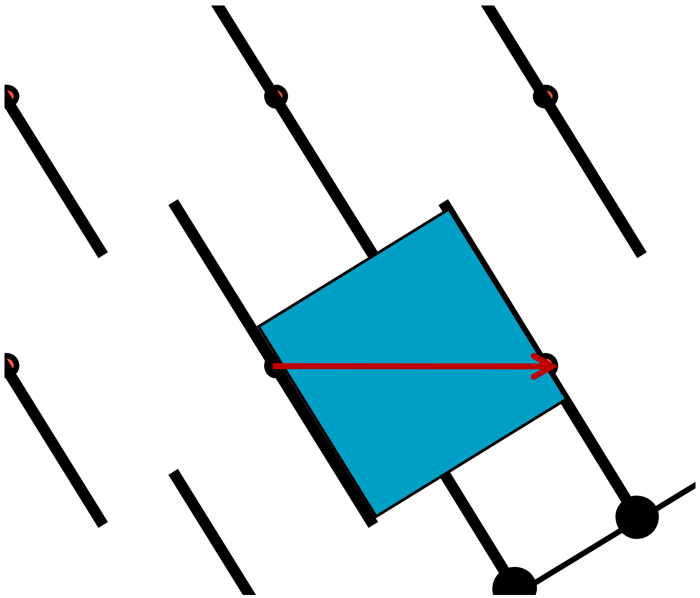
$$\begin{pmatrix} X_{par} \\ X_{per} \end{pmatrix} = \frac{a}{\sqrt{2+\tau}} \begin{pmatrix} \tau & 1 \\ -1 & \tau \end{pmatrix} \begin{pmatrix} n_1 \\ n_2 \end{pmatrix}$$

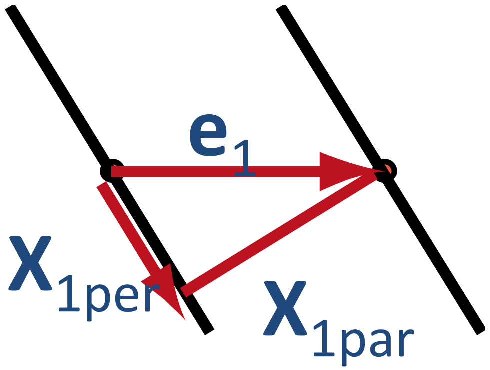
Point followed by L on the right

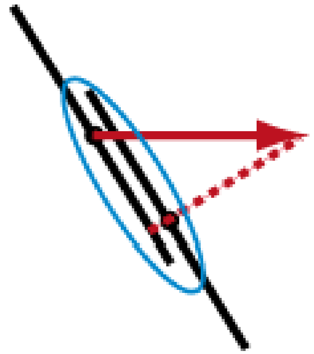
Displacement in 2D is $\mathbf{e}_1$

Projection is L in parallel space and S in perp space

Local environments





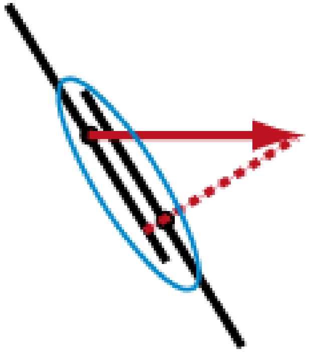


- $e_1 = (X_{1par}, X_{1per})$
- **Existence domain** of the configuration L:

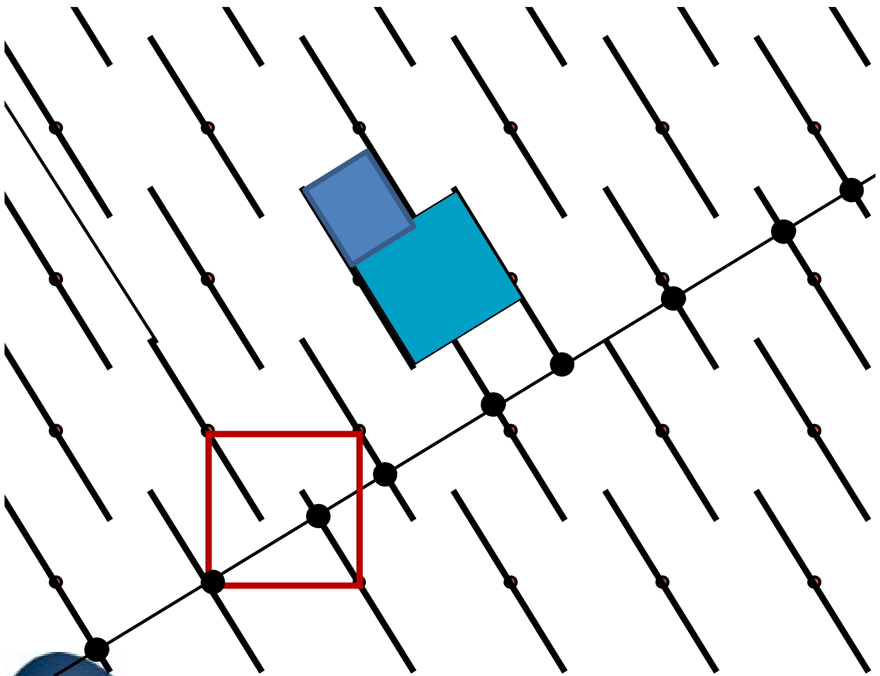
Intersection between the atomic surface and its copy translated by $\mathbf{X}_{1per}$.

$$\begin{pmatrix} X_{par} \\ X_{per} \end{pmatrix} = \frac{a}{\sqrt{2+\tau}} \begin{pmatrix} \tau & 1 \\ -1 & \tau \end{pmatrix} \begin{pmatrix} n_1 \\ n_2 \end{pmatrix}$$

Local environment.



- Existence domain: The size of the intersection is proportional to the frequency of the configuration in the infinite structure



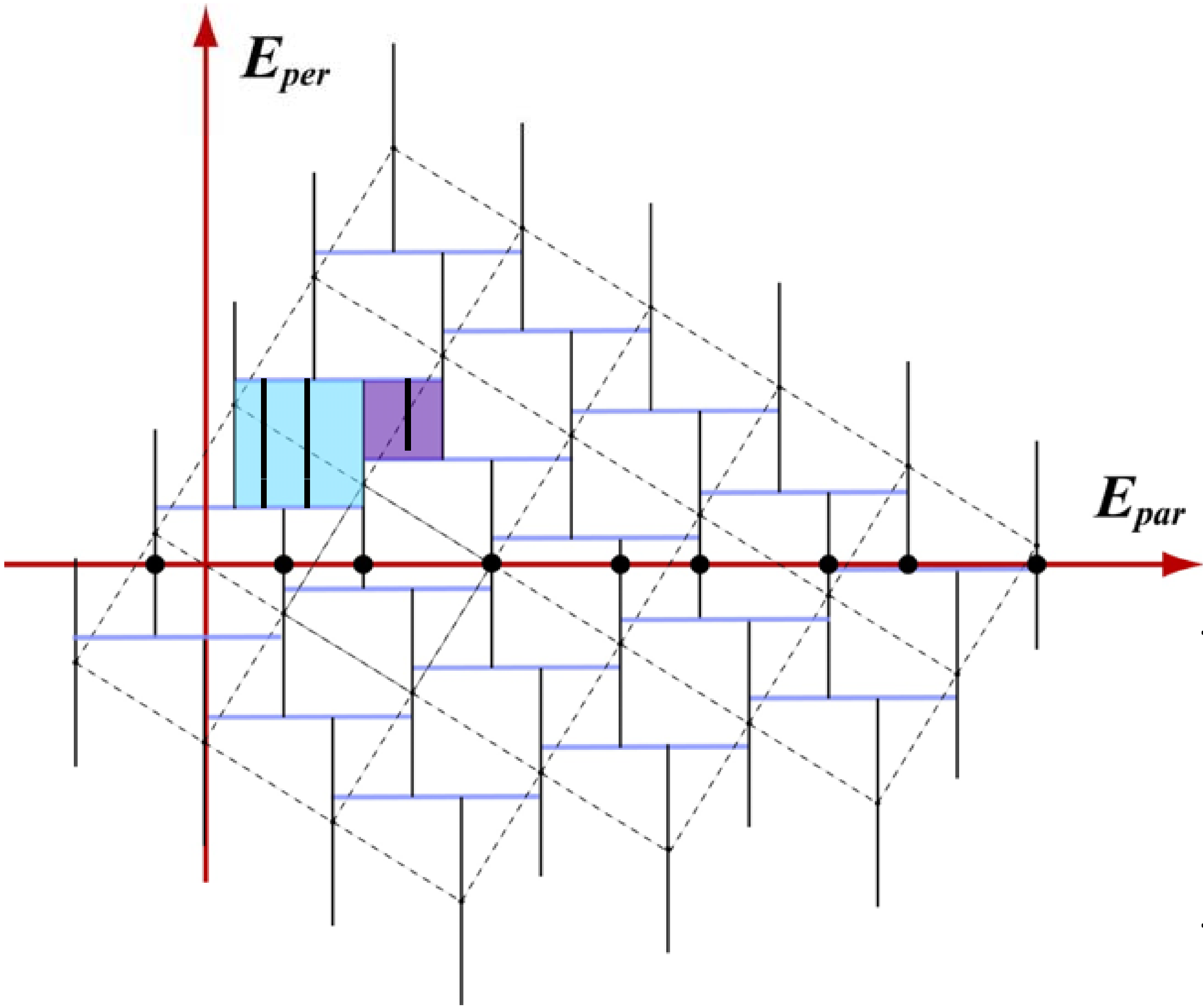
- Case of the configuration S

$\mathbf{e}_2 = (\mathbf{X}_{2par}, \mathbf{X}_{2per})$

The perp translation is now $\mathbf{X}_{2per}$

The existence domain is smaller of a factor τ

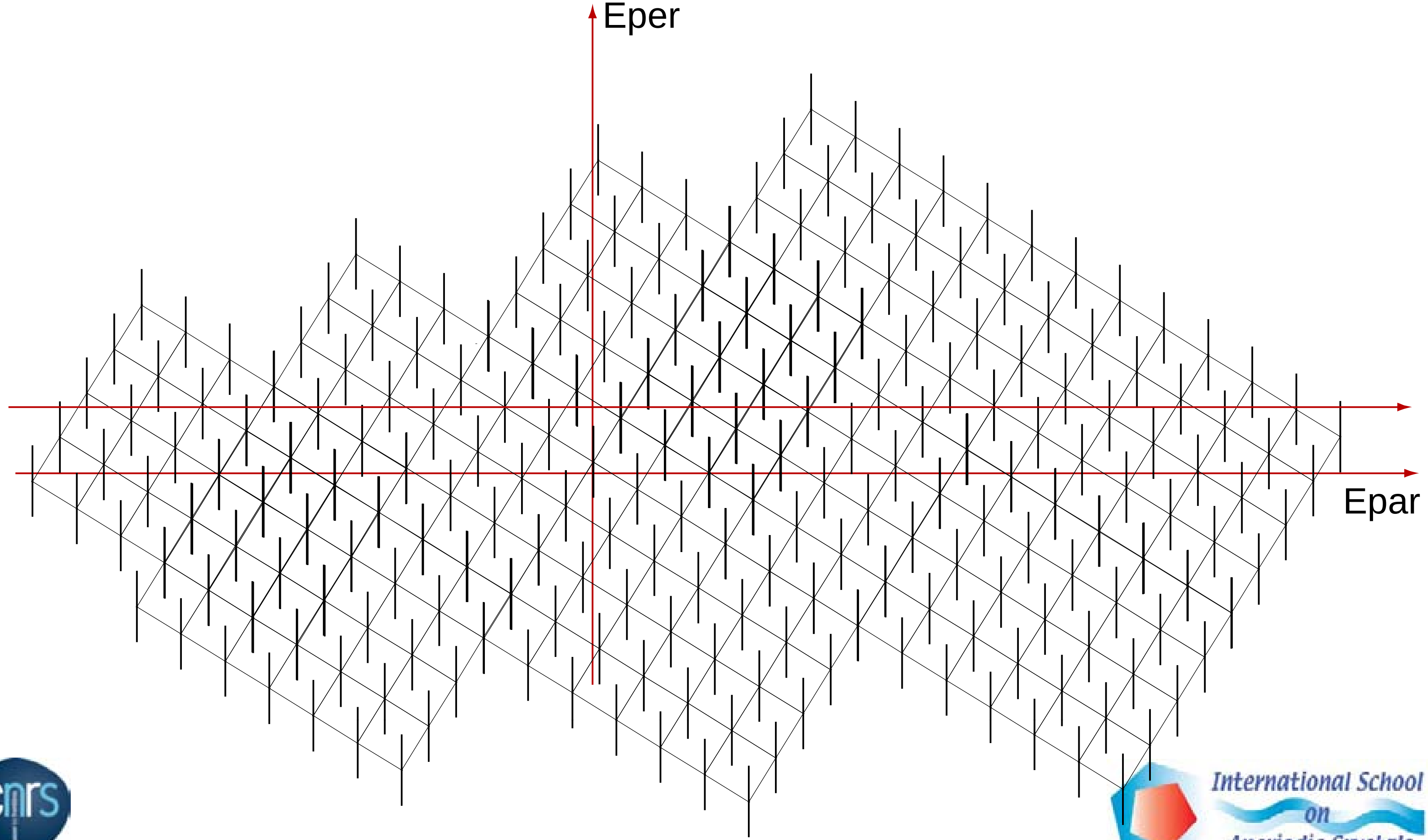
Local environment of the Fibonacci chain



- First distances either L or S
- Related to the 'connection' of atomic surfaces.
- Proportion of L and S is related to respective length of occupation domain here in the ration 1 and τ

Exercice

- Demonstrate, using the 2D representation, that the sequence LLL does not exists in the Fibonacci chain.



Exercice

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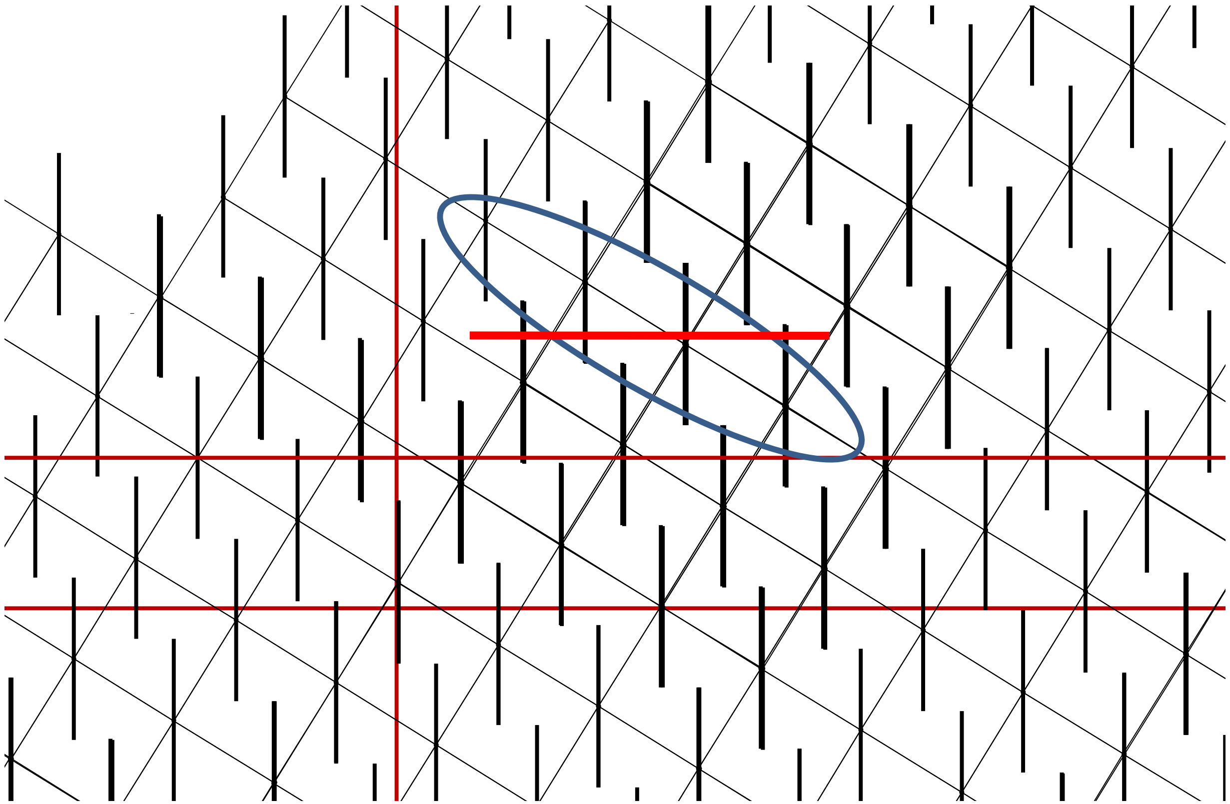
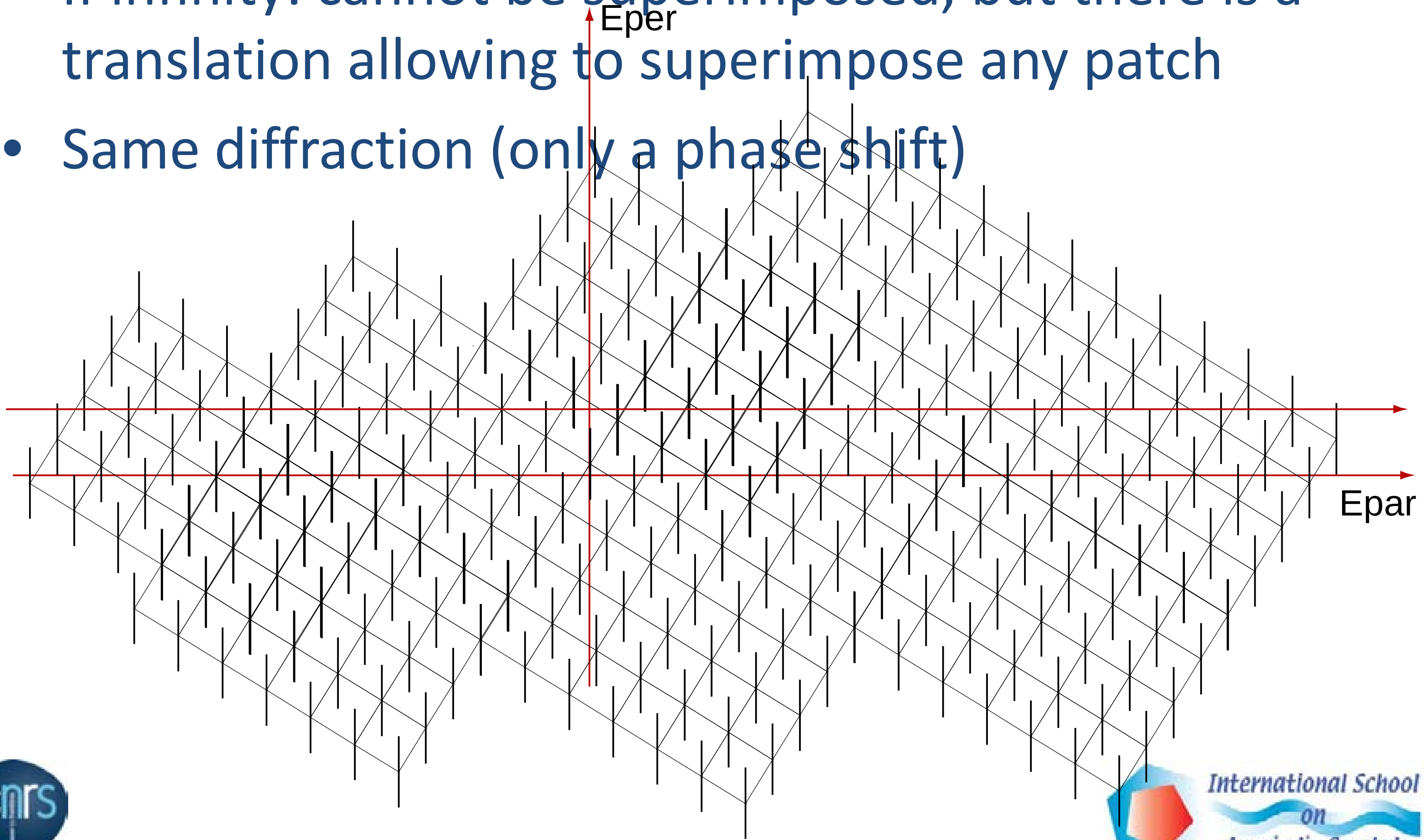
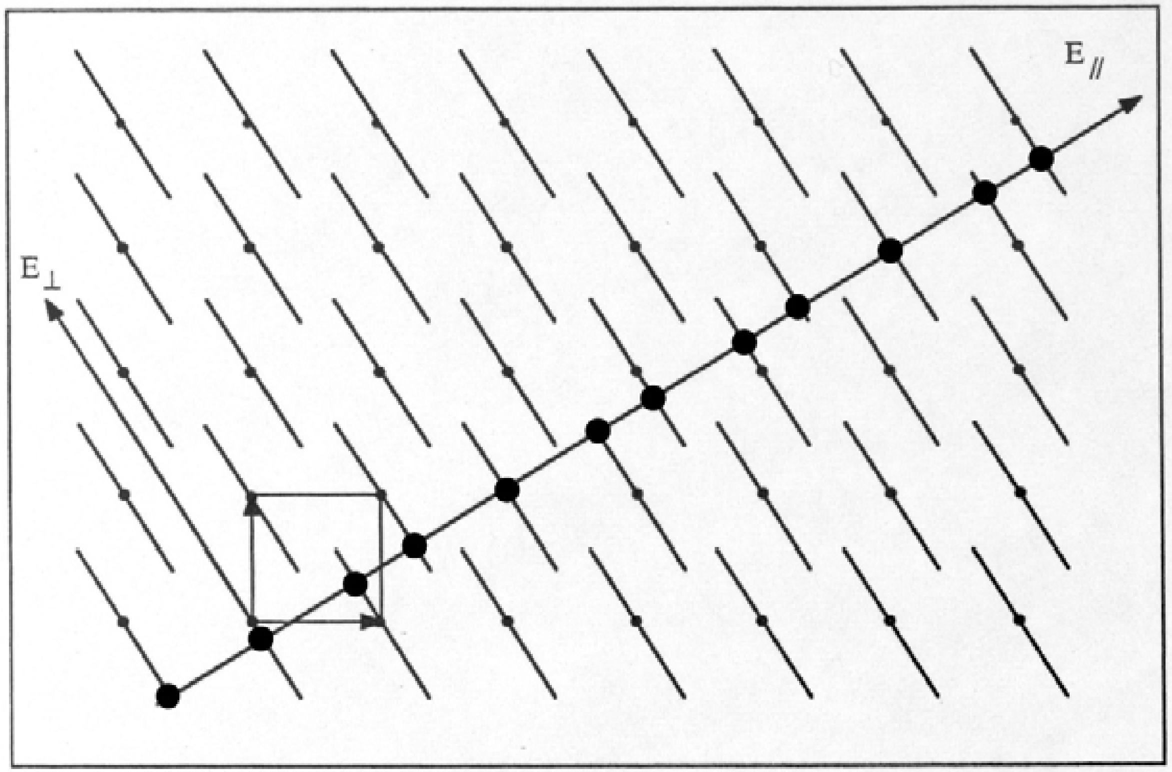


Exercice

- Compare the 2 generated QC
- If infinity: cannot be superimposed, but there is a translation allowing to superimpose any patch
- Same diffraction (only a phase shift)



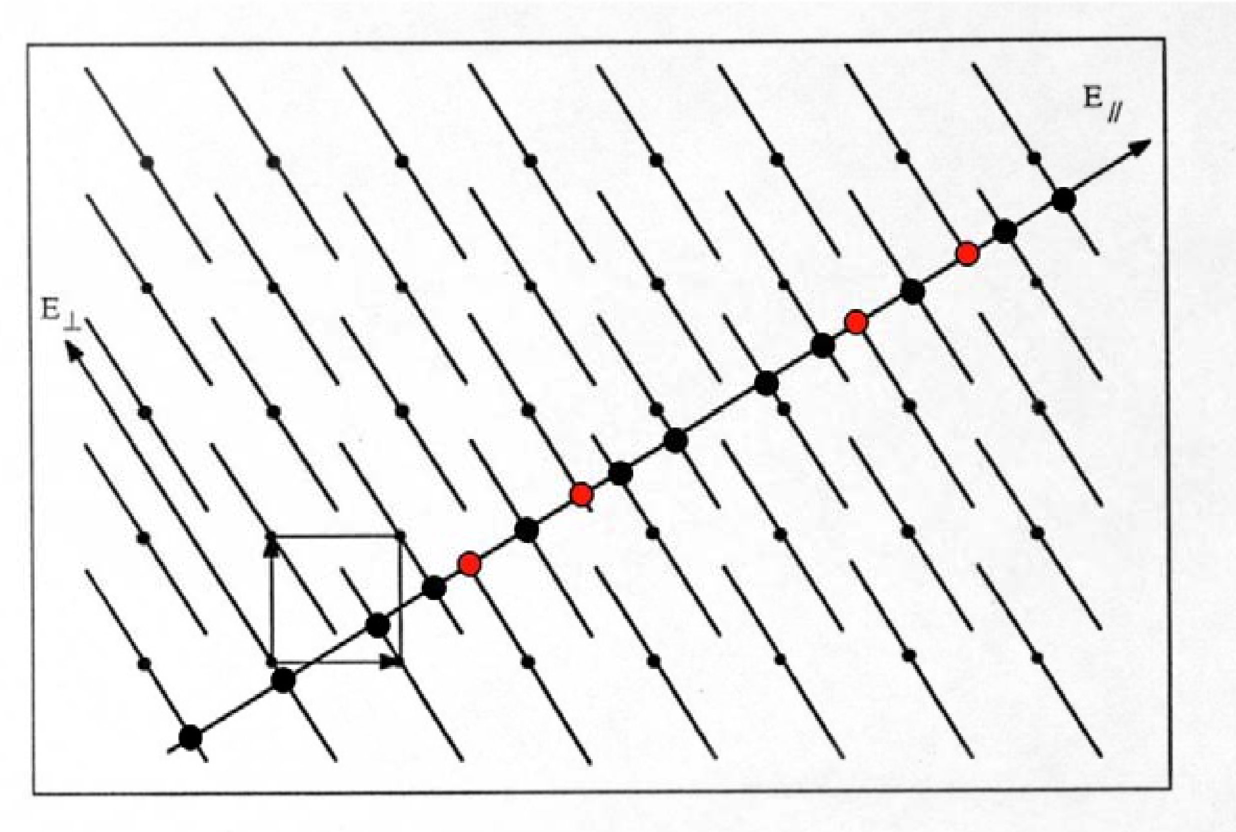
General 1D quasiperiodic structure



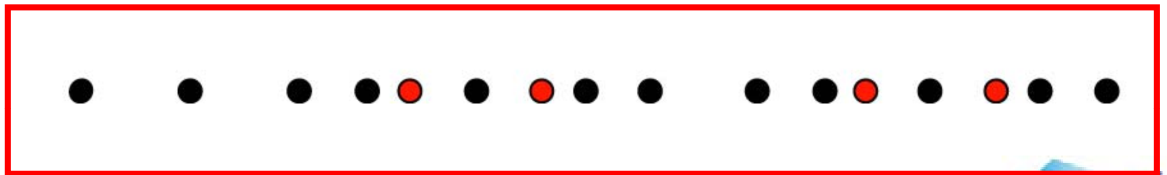
1D • L • L • S • L • L • S • L • S • L • L • S •

General 1D quasiperiodic structure

Length (shape) of the AS.

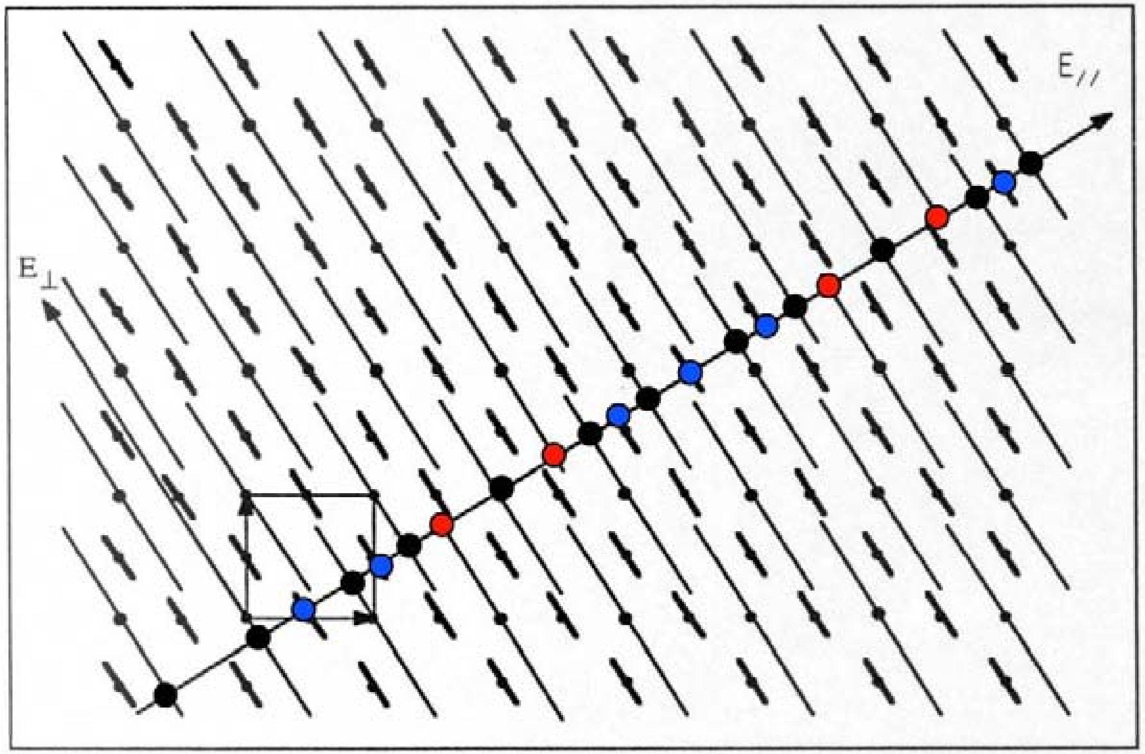


1D

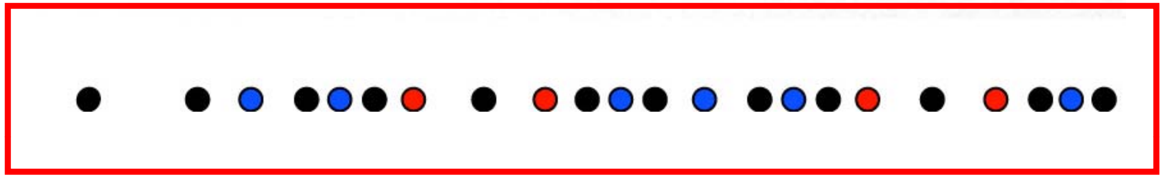


General 1D quasiperiodic structure

Length (shape) of the AS. Decoration of unit cell

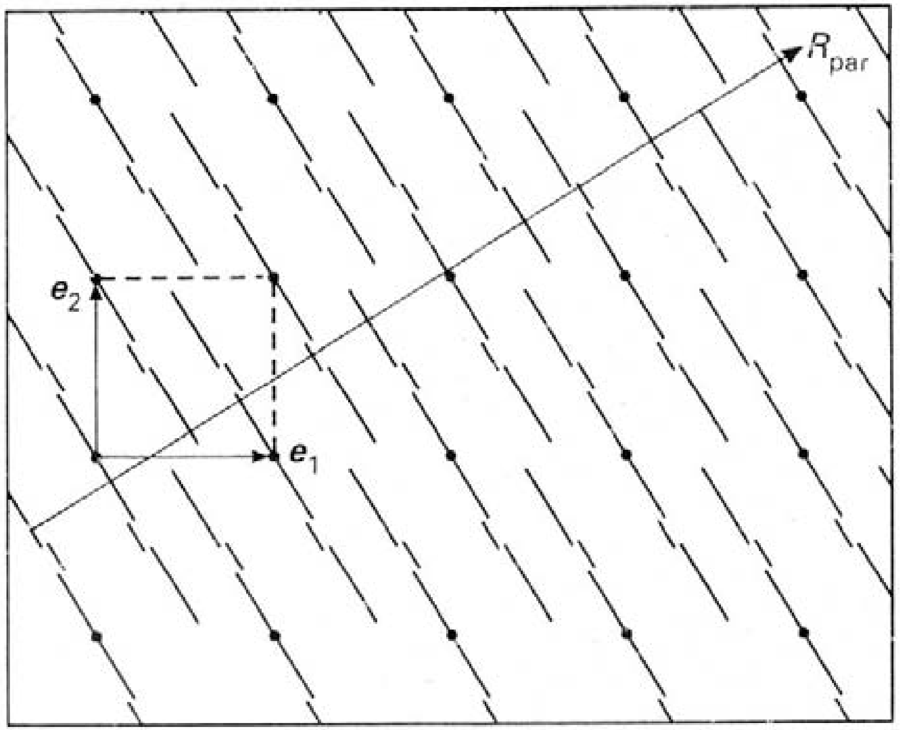


1D



General 1D quasiperiodic structure

Parallel component of the AS



Relaxation of local environment

Can be a continuous or discontinuous displacement.

Relaxation can be associated with local environments and used in the further refinement..

Summary

- The 1D quasicrystal is obtained by a section of a decorated square lattice.
- Decoration by atomic surfaces lying in the perpendicular space.
- 2D image of the 1D quasicrystal allows to understand its local environment: distances and frequencies
- Frequency given by the size of the existence domain obtained by geometric Xperp translation.
- QC characterized by: position and shape of the atomic surfaces. Their chemical decoration. Parallel component related to structure relaxation

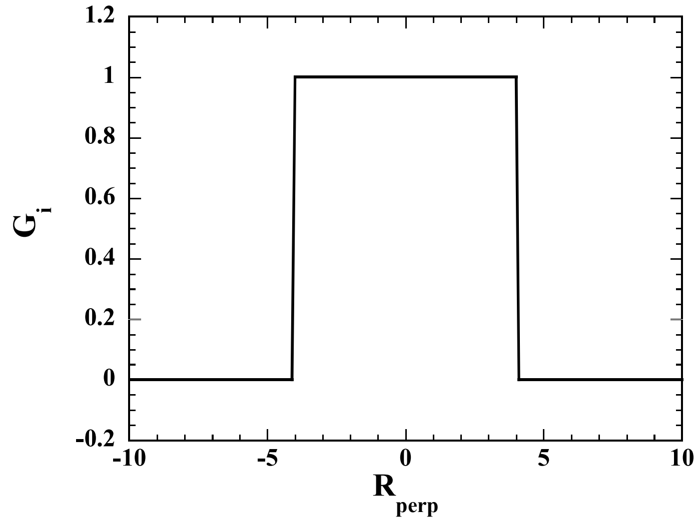
Diffraction pattern of the 1D QC

1- *Diffraction pattern of the 2D decorated lattice*:

There are i atomic surfaces (AS) at positions **R**i which decorate the 2D square lattice.

The electron or atomic density can be expressed as the convolution product between the lattice and the decoration. $G_i(\mathbf{R}_{per})$ represents the shape function of the AS

$$\rho(\mathbf{R}) = \delta(\mathbf{R} - \mathbf{R}_{n1,n2}) * \sum_i G_i(\mathbf{R}_{per})\mathbf{R}_i$$



Diffraction Pattern

FT= FT(lattice).FT(decoration)

Reciprocal space: $G(H_{per})$ is the FT of the atomic surface or occupation domain.

$$F(\mathbf{K}) = \delta(\mathbf{K} - \mathbf{H}_{n1,n2}).\frac{1}{V}\sum_i G_i(\mathbf{H}_{per})exp(2\pi i \mathbf{H}_{n1,n2}.\mathbf{R}_i)$$

FT(lattice) is a square lattice parameter 1/a

Reciprocal space also decomposes in two sunspaces: parallel and perpendicular space.

$$\begin{pmatrix} \mathbf{H}_{par} \\ \mathbf{H}_{per} \end{pmatrix} = \frac{1}{a\sqrt{2+\tau}} \begin{pmatrix} \tau & 1 \\ \bar{1} & \tau \end{pmatrix} \begin{pmatrix} n1 \\ n2 \end{pmatrix}$$

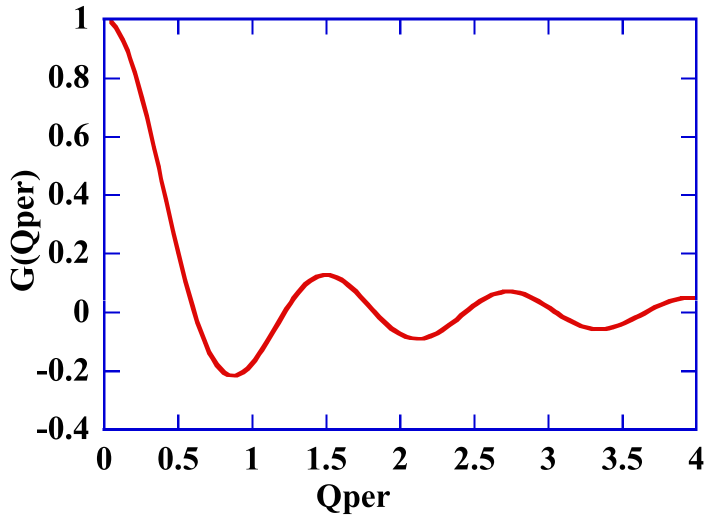
Diffraction Pattern: Fibonacci chain

$$\begin{pmatrix} \mathbf{H}_{par} \\ \mathbf{H}_{per} \end{pmatrix} = \frac{1}{a\sqrt{2+\tau}} \begin{pmatrix} \tau & 1 \\ \bar{1} & \tau \end{pmatrix} \begin{pmatrix} n1 \\ n2 \end{pmatrix}$$

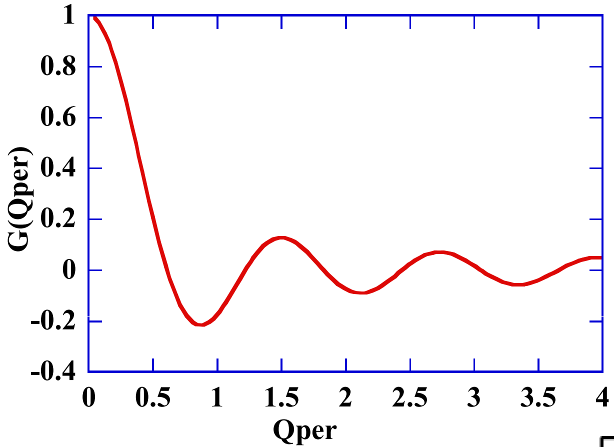
$$F(\mathbf{K}) = \delta(\mathbf{K} - \mathbf{H}_{n1,n2}) \frac{1}{a^2} G(\mathbf{H}_{per})$$

$$G(H_{per}) = L \frac{\sin(\pi Q_{per} L)}{\pi Q_{per} L}$$

L is the length of the AS



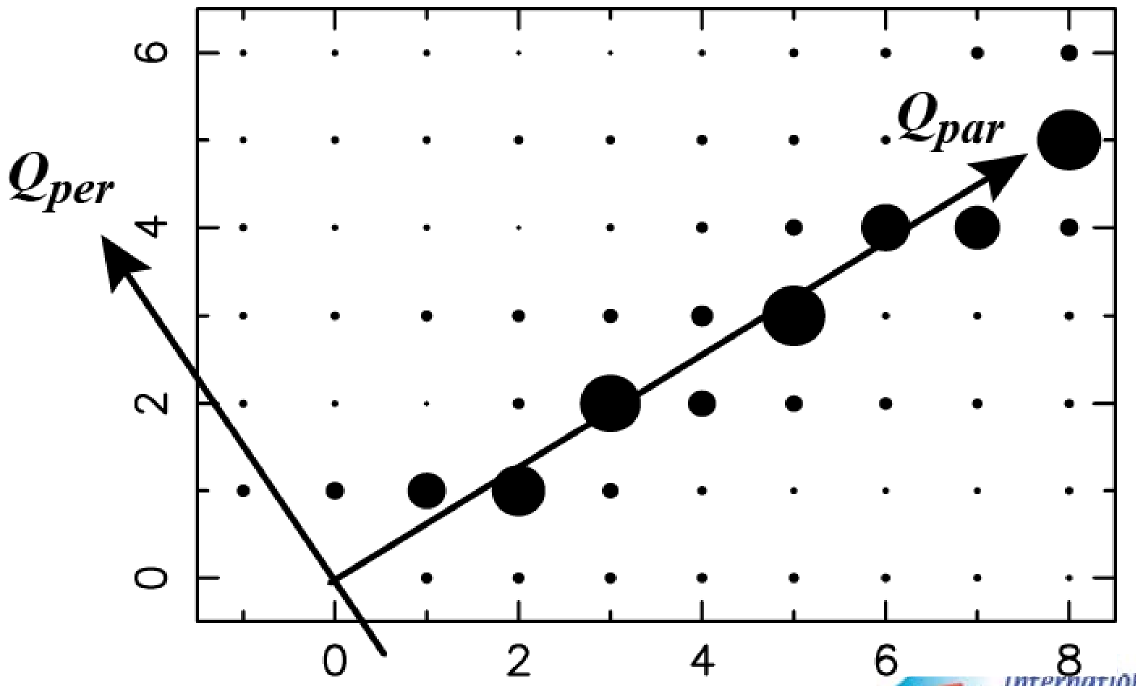
Diffraction Pattern: Fibonacci chain



Intensity is given by G(Qper)

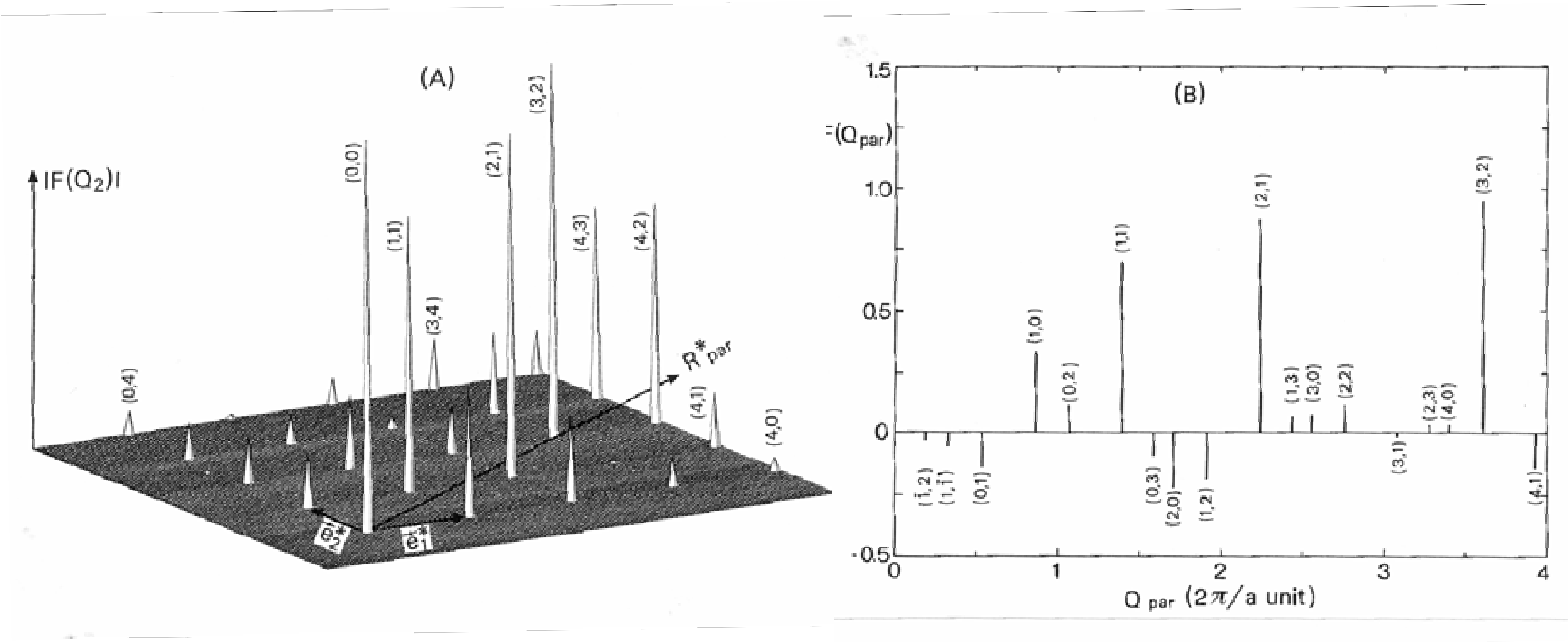
Strong intensity for small values of Q_{perp}

n1,n2 Fibonacci numbers

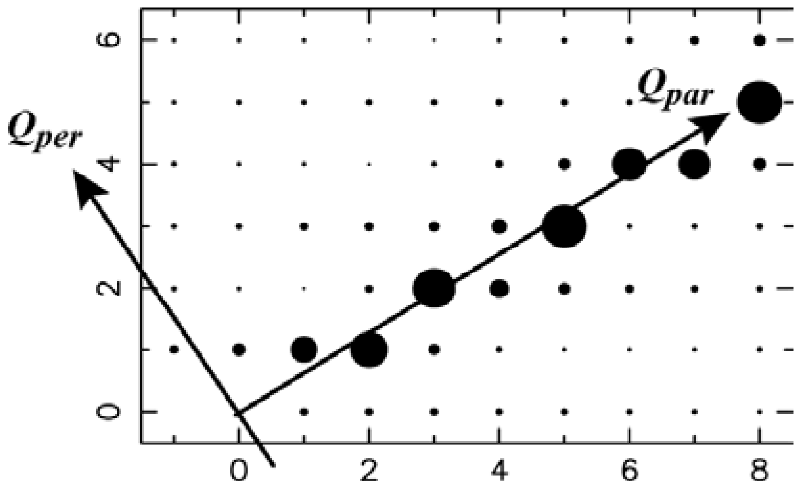


Diffraction pattern

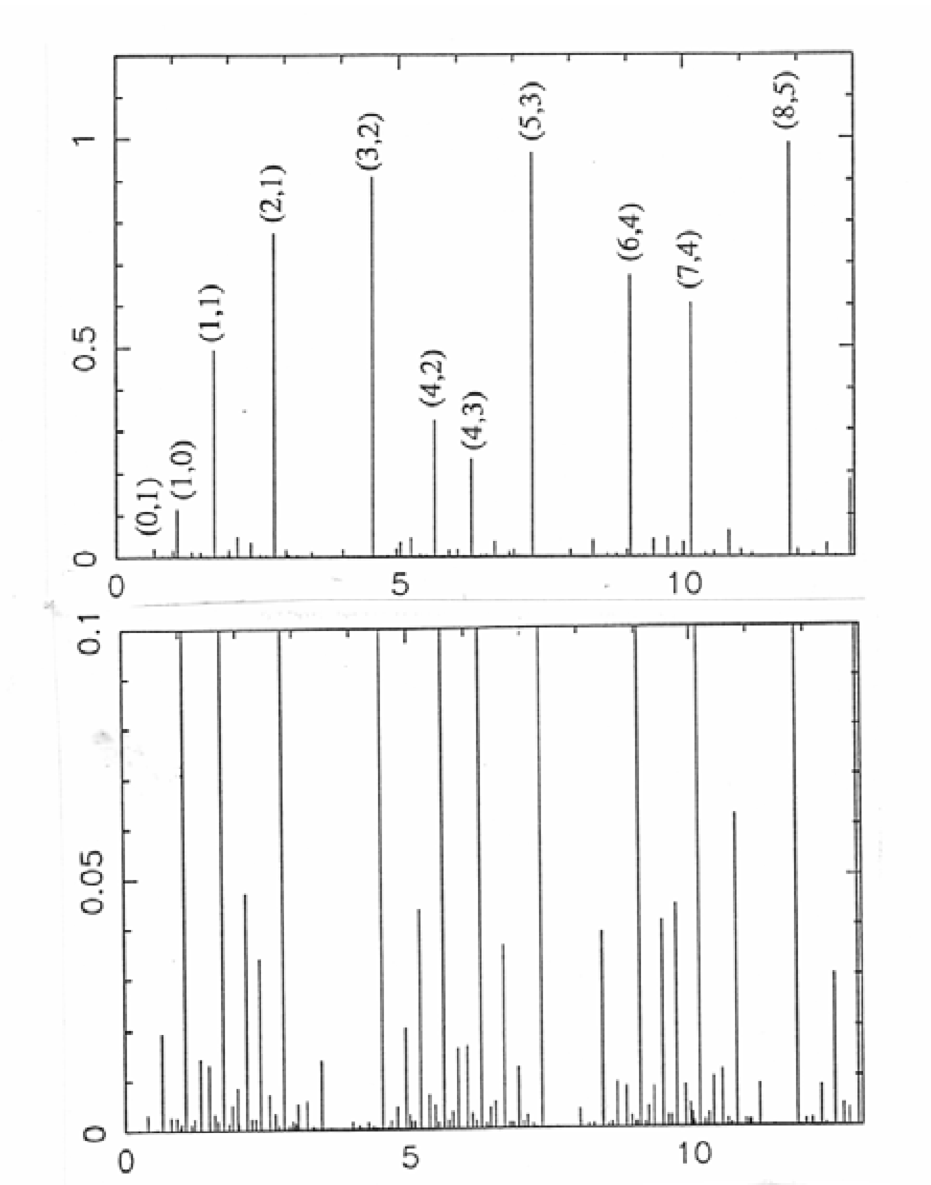
2- Projection of the diffraction pattern to 1D.



2-D Diffraction pattern



Fibonacci Diffraction pattern



- The 1D diffraction pattern is dense. Infinite number of Braggs
- But above a certain threshold only a finite number of Bragg peaks in a given Q range
- τ scaling of the position and intensities: (1, 1), (2,1), (3,2)…

Diffraction pattern

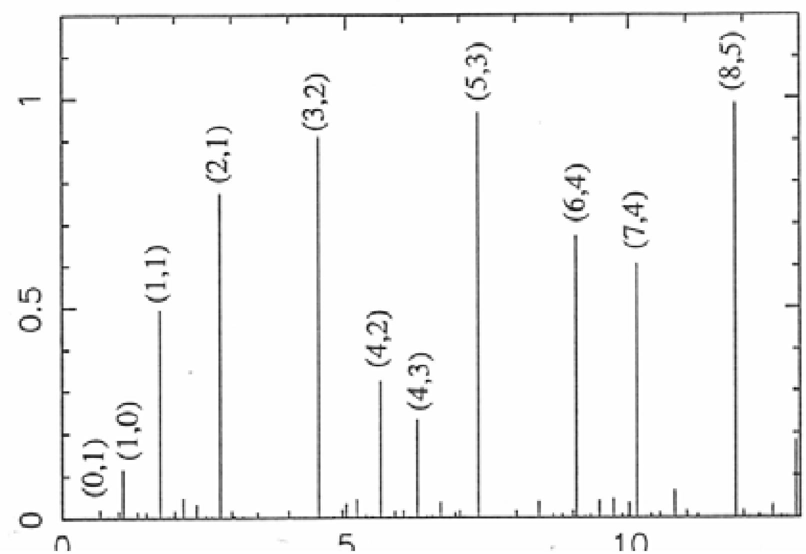
$$\begin{pmatrix} \mathbf{H}_{par} \\ \mathbf{H}_{per} \end{pmatrix} = \frac{1}{a\sqrt{2+\tau}} \begin{pmatrix} \tau & 1 \\ \bar{1} & \tau \end{pmatrix} \begin{pmatrix} n1 \\ n2 \end{pmatrix}$$

- Compare the parallel and perpendicular component of (1,1) and (2,1)
- Par: τ+1 and 2τ+1= τ(τ+1)

Per: -1+τ and -2+τ=-(-1+τ)/τ

τ scaling in par and -1/τ in perp

Inflation matrice $\begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}$



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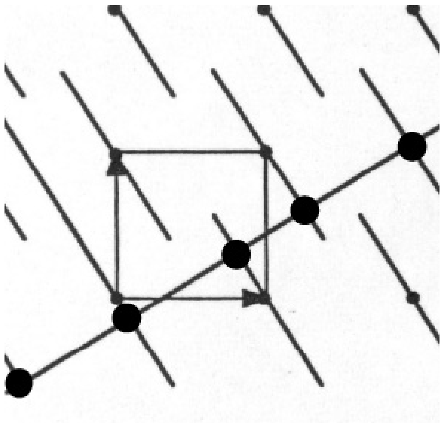
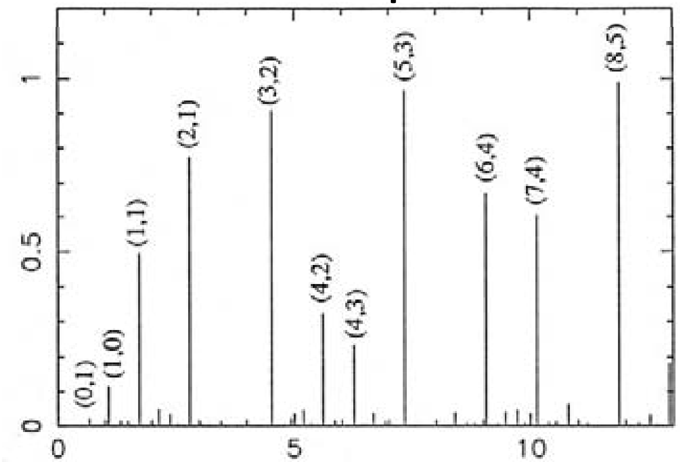
Fibonacci



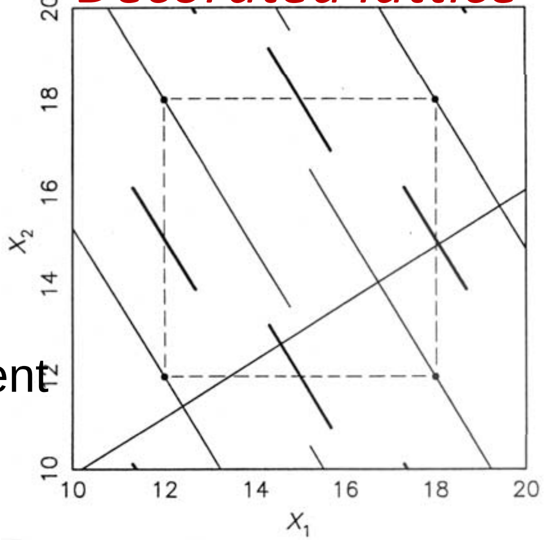
Diffraction pattern

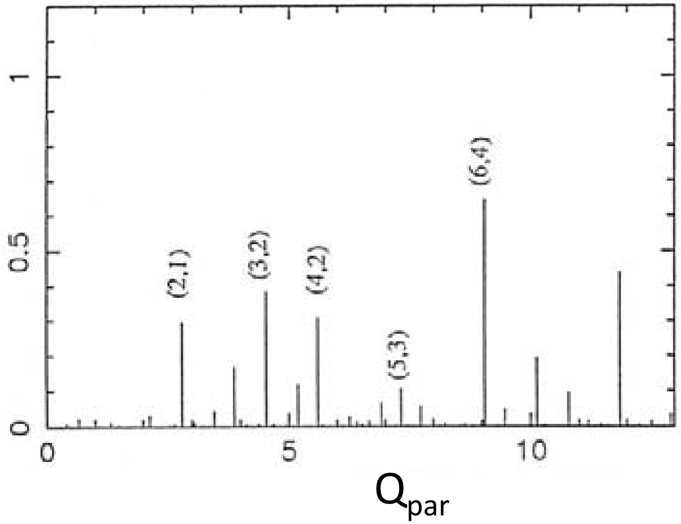


$$F(\mathbf{K}) = \delta(\mathbf{K} - \mathbf{H}_{n1,n2}).\frac{1}{V}\sum_i G_i(\mathbf{H}_{per})exp(2\pi i\mathbf{H}_{n1,n2}.\mathbf{R}_i)$$

Decorated lattice

Interferences between the different FT of the AS Scaling different





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Summary

- 1D diffraction pattern is the projection of the 2D one
- Indexing($n_{1,}n_2$) and ($\mathbf{H}_{par}$, $\mathbf{H}_{per}$).
- FT contains two terms: FT of the AS + interferences

$$F(\mathbf{K}) = \delta(\mathbf{K} - \mathbf{H}_{n1,n2}).\frac{1}{V}\sum_i G_i(\mathbf{H}_{per})exp(2\pi i\mathbf{H}_{n1,n2}.\mathbf{R}_i)$$

- Large intensity for small H_{per} component
- The 1D diffraction pattern is densely filled by Bragg peaks, but only a finite number above a threshold.
- τ scaling

Structure determination

- From diffraction data to a structural model. 1D example.

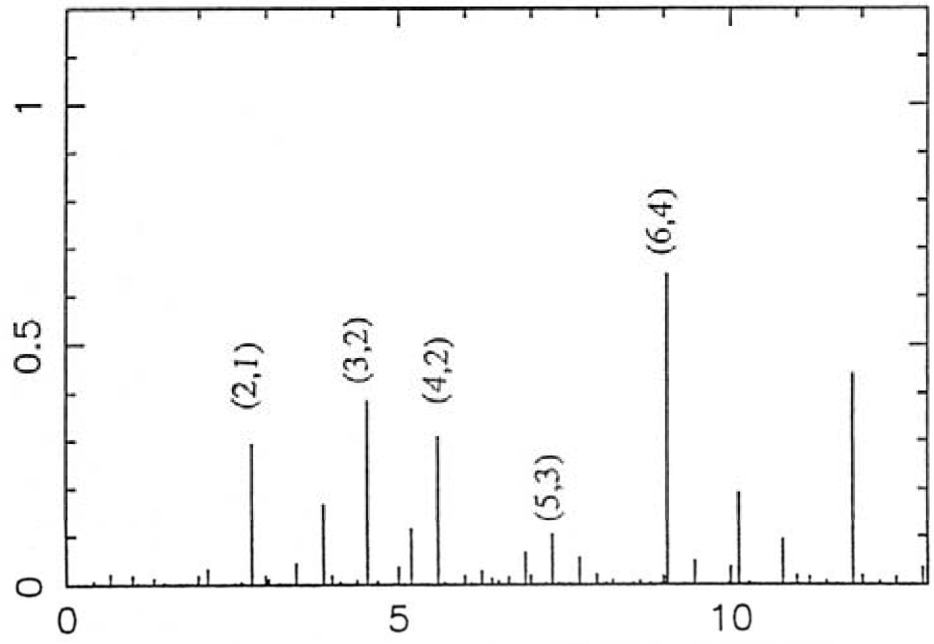
1- Indexing the diffraction pattern.

How to chose the lattice parameter and indices ?

- Strong Bragg peaks should have a small H_{per} component.
- List of indices to be compared to the diffraction pattern
- Problem of the τ scaling.

Indexing

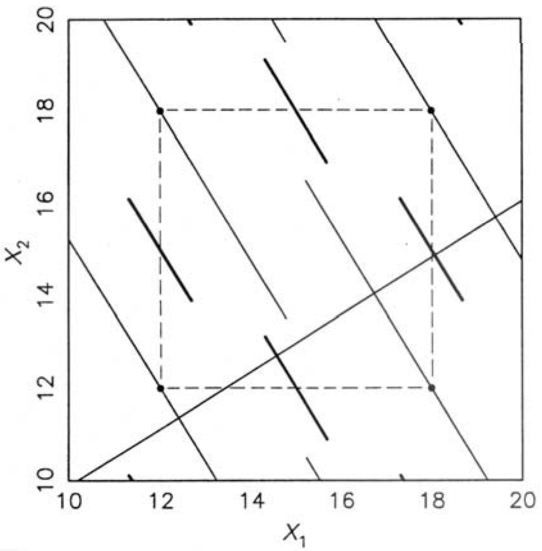
- Lattice parameter ambiguity within tau
- Choice from local order configuration (pseudo tile, distances …)

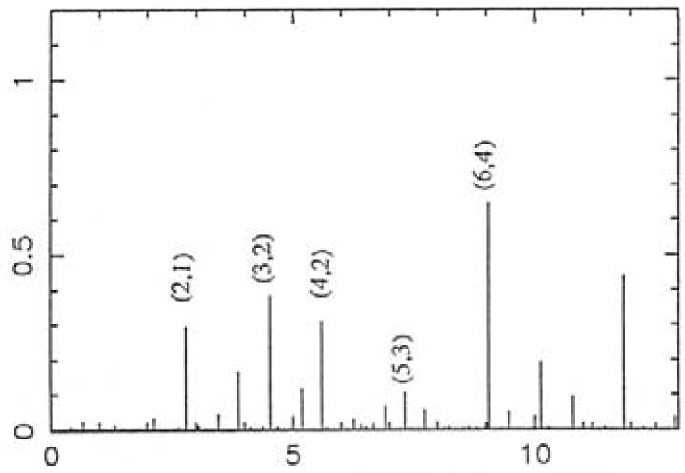


Fourier map

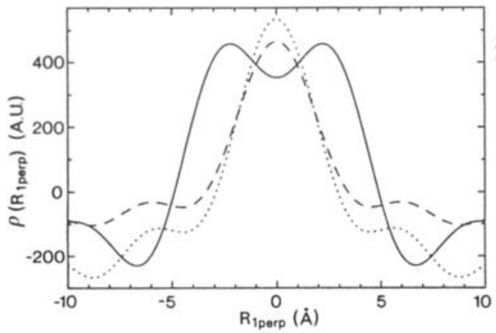
- ***2- Phasing structure factors***
- 2D Patterson analysis : gives the position and rough shape of the AS: first phasing
- Phase reconstruction: maximum charge density (V. Elser), low density elimination (H. Takakura), charge flipping (L. Palatinus). Allows to compute a density map, much easier to interpret than the Patterson

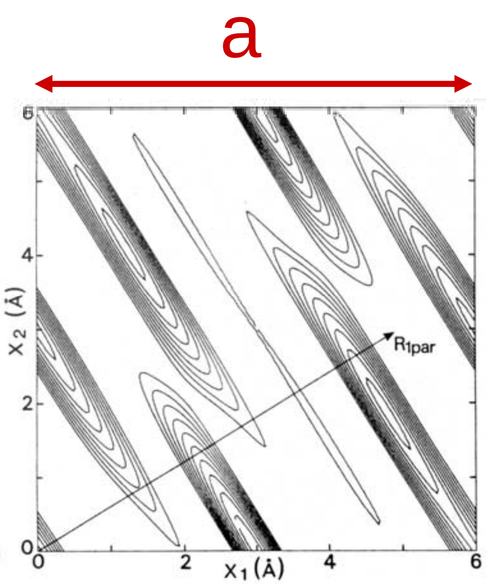
Example of 1D QC



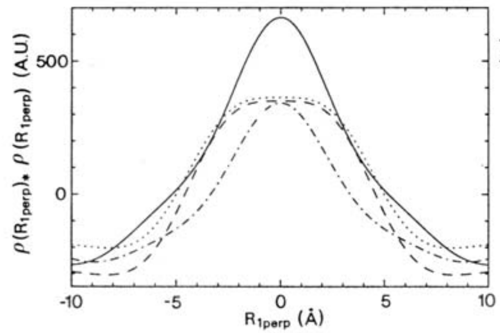


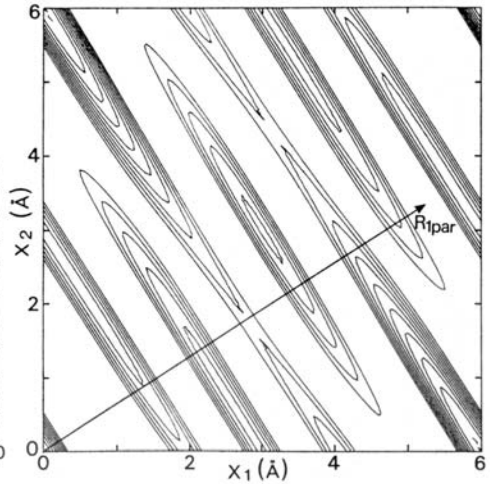
2D Density



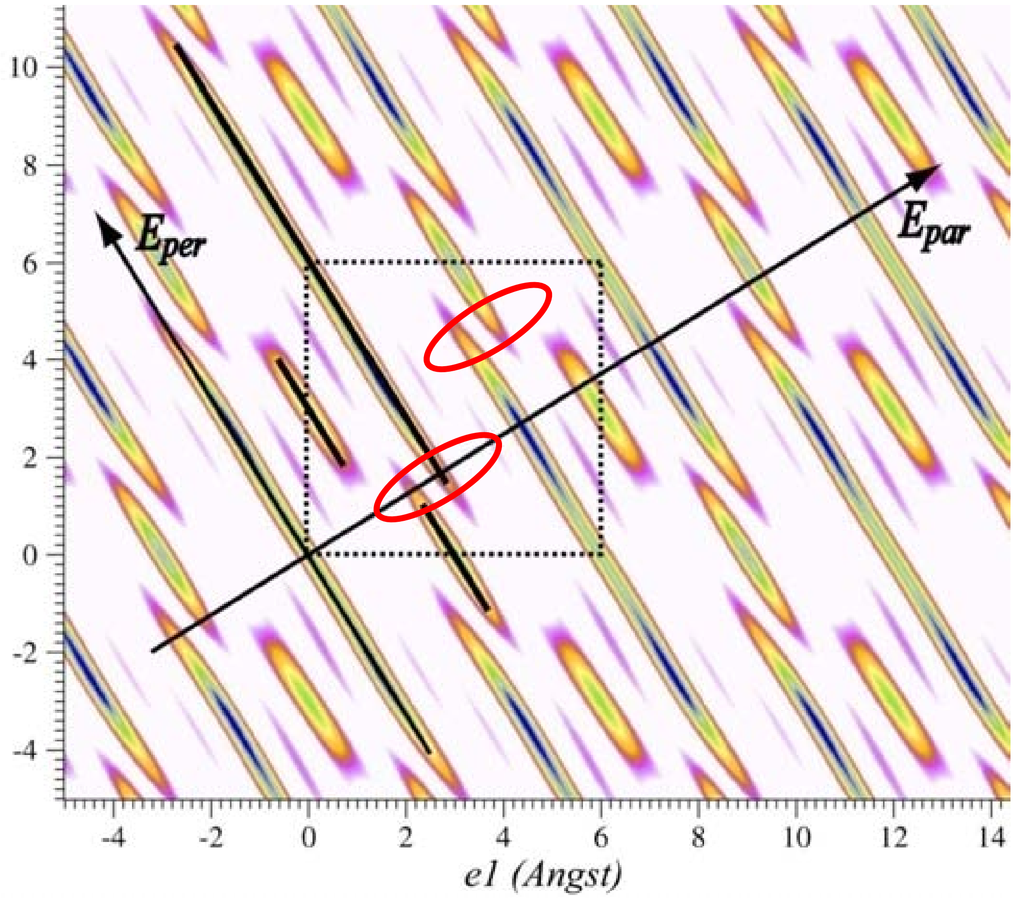


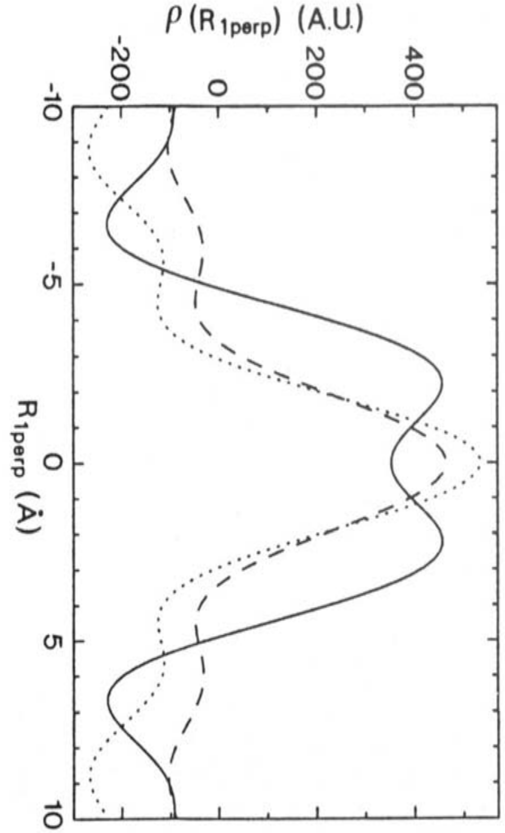
2D Patterson





Fourier Transform of phased Amplitudes: Density





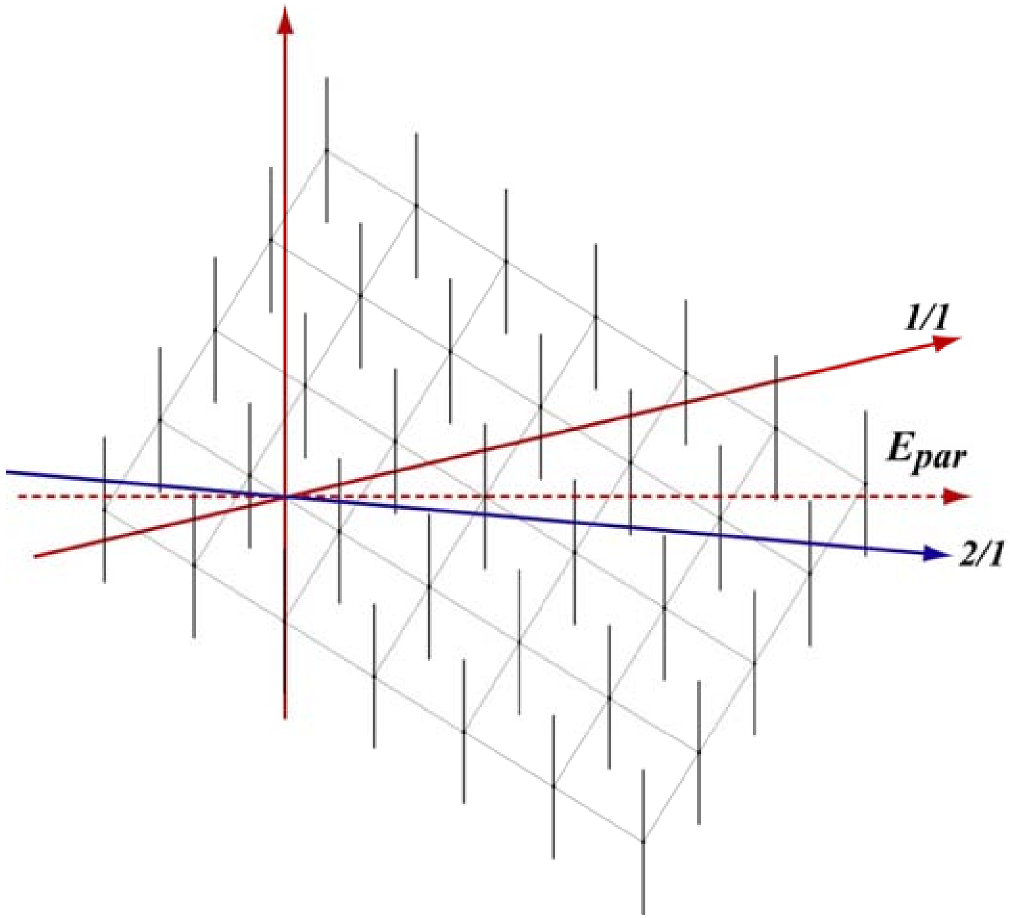
'Split positions' due to Fourier truncation effect: two sites with partial occupancy and short distance

Modeling

- Modeling is necessary
- Unlike modulated and composites phase there is no general procedure.
- ‘Hand made’ building of the model
- Some general rules:

- Chemistry, density and chemical composition
- Short distances and local environment
- Periodic approximant structure

Quasicrystal and approximant



1/1 LSLSLS $a_{1/1}=\tau+1$

2/1 LSLLSL $a_{2/1}=2\tau+1=?\ a_{1/1}$

- Rational tilt of Epar generates a periodic approximant : slope 1/1, 2/1, 3/2… instead of τ=1.618…
- Approximant and QC share the same local envt or clusters
- Series of approximant with larger and larger unit cells
- CdYb system: 1/1 and 2/1 approximant

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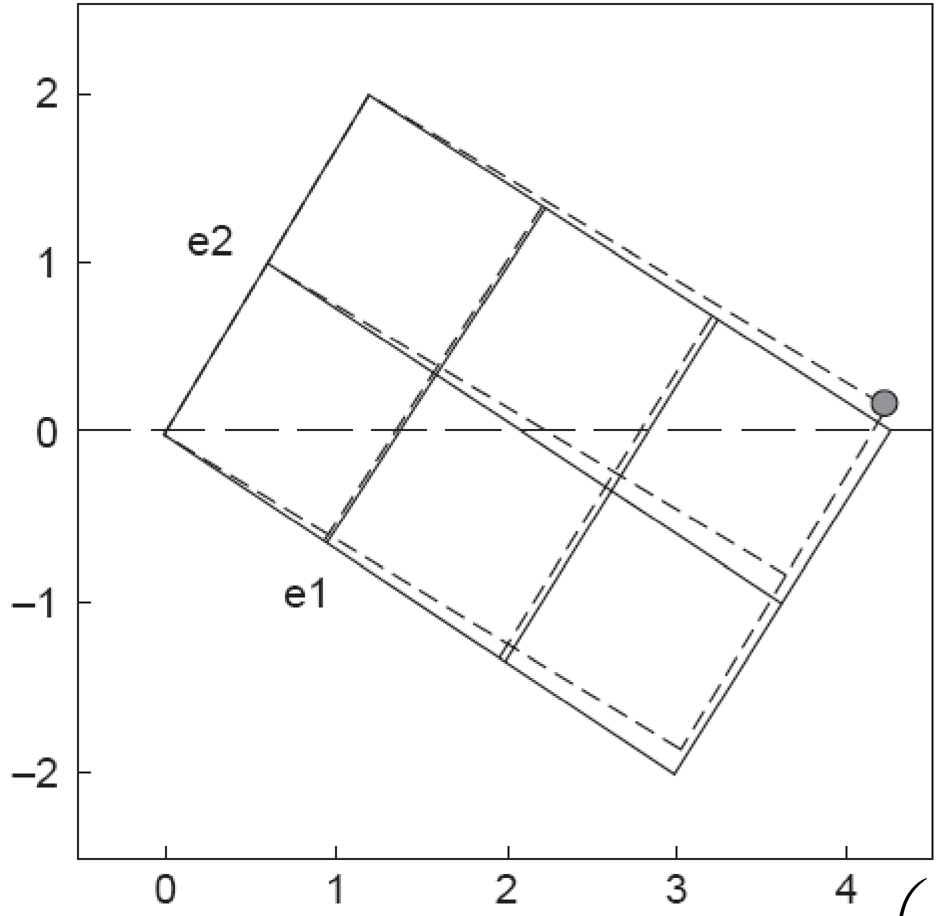
Quasicrystal and approximant

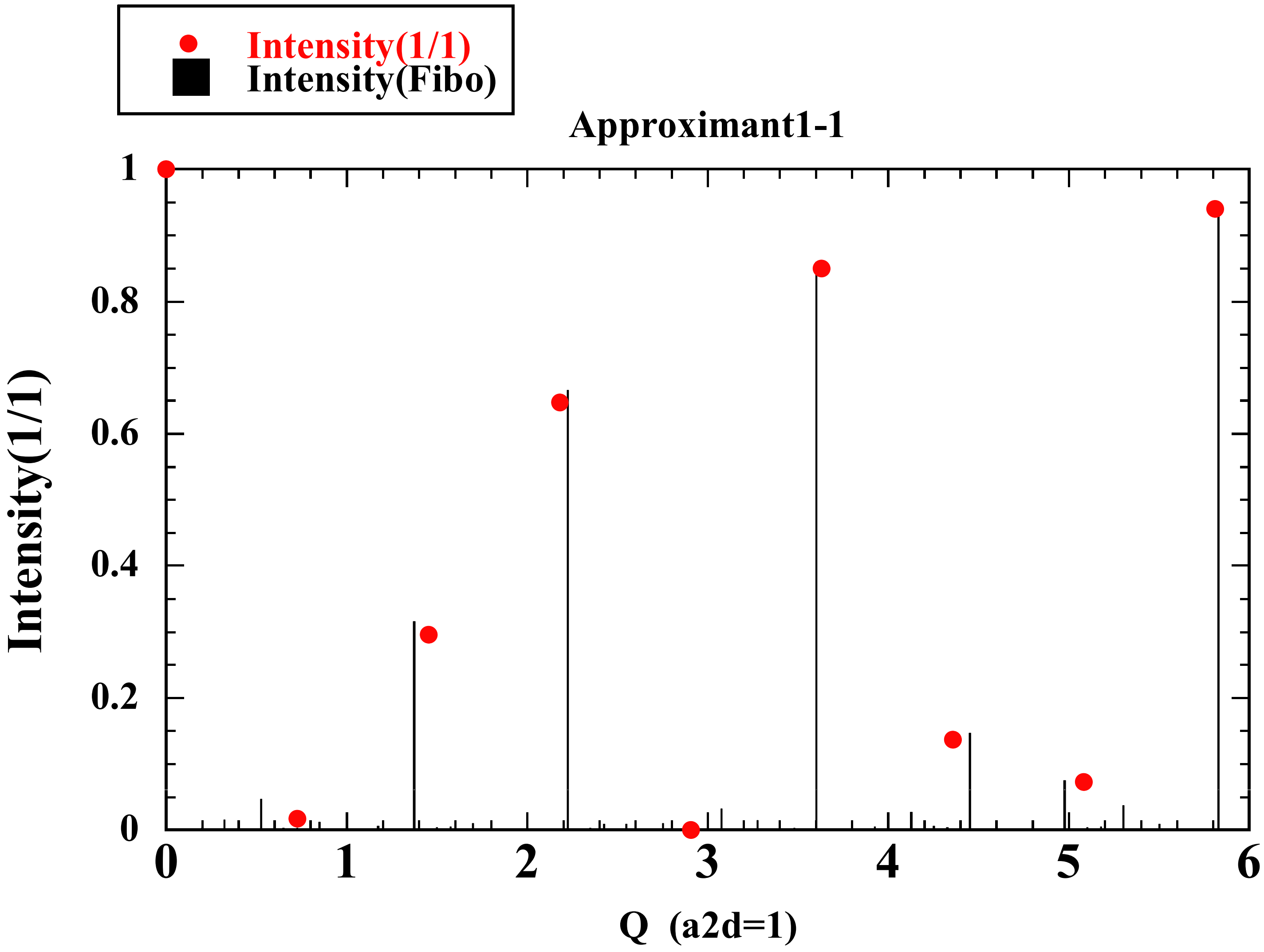


3/2 approximant

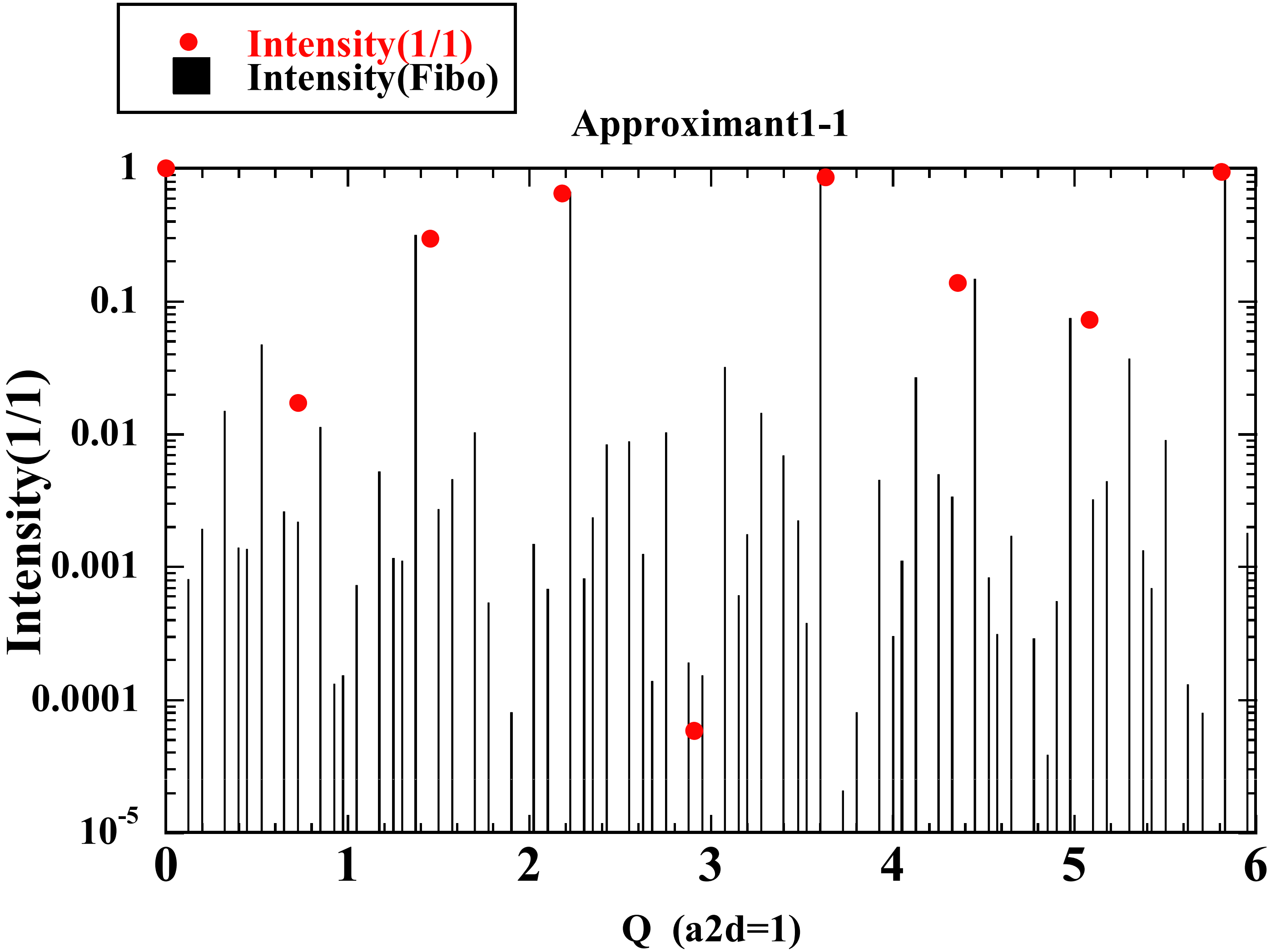
- The correct formulation is actually a shear strain of the periodic lattice.
- Strain along the perpendicular space: phason strain
- τ is replaced by a Fibbonacci approximant: 1/1, 2/1, 3/2

$$\begin{pmatrix} X_{par} \\ X_{per} \end{pmatrix} = \frac{a}{\sqrt{2+\tau}} \begin{pmatrix} \tau & 1 \\ -1 & \tau \end{pmatrix} \begin{pmatrix} n_1 \\ n_2 \end{pmatrix}$$

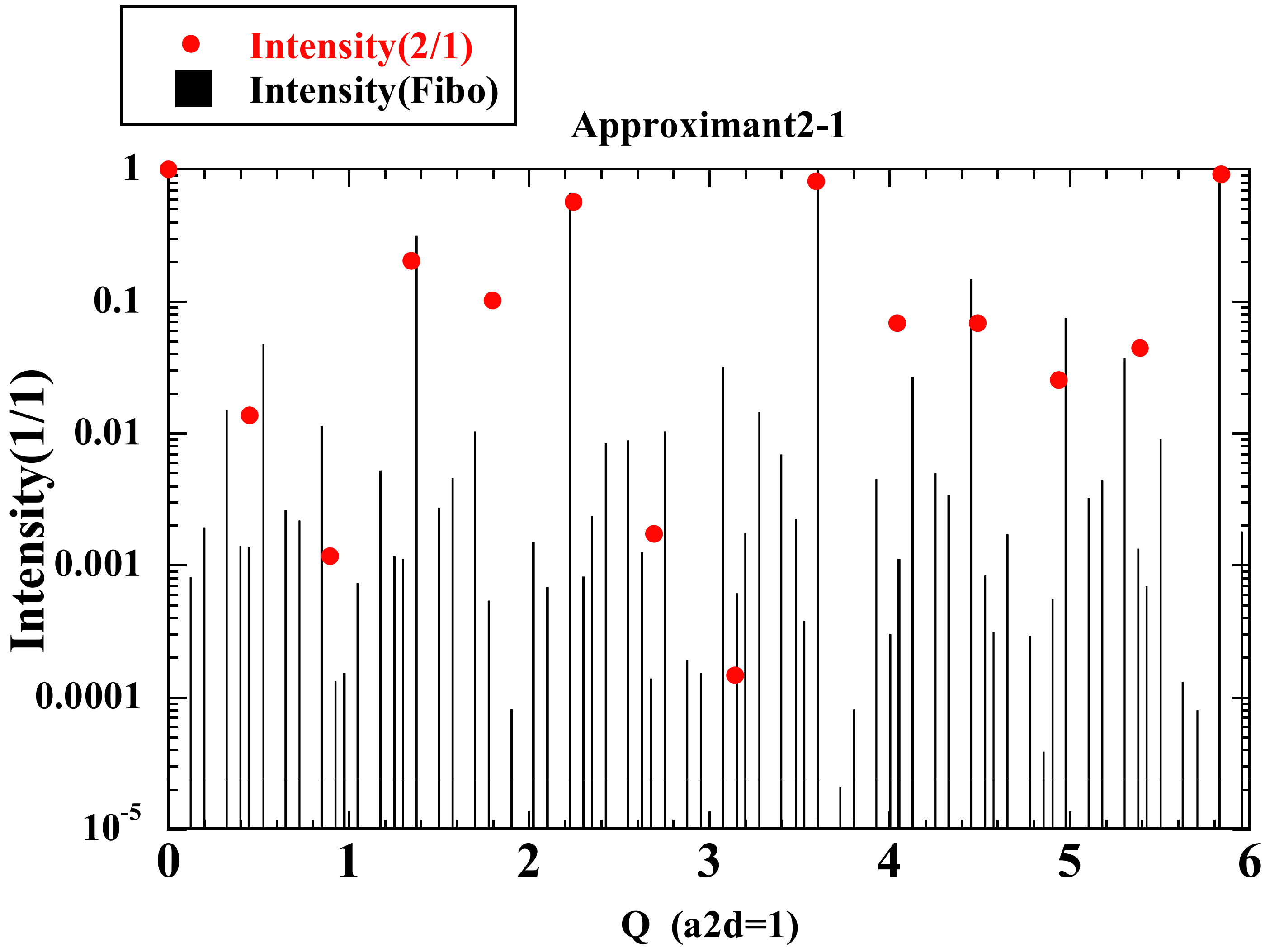
Similar diffraction pattern



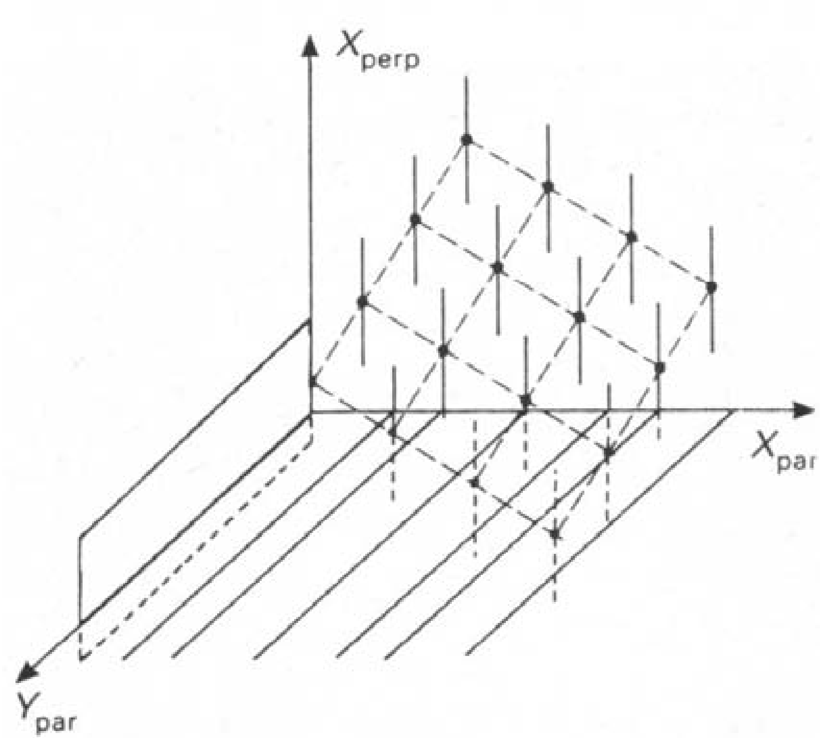
Similar diffraction pattern



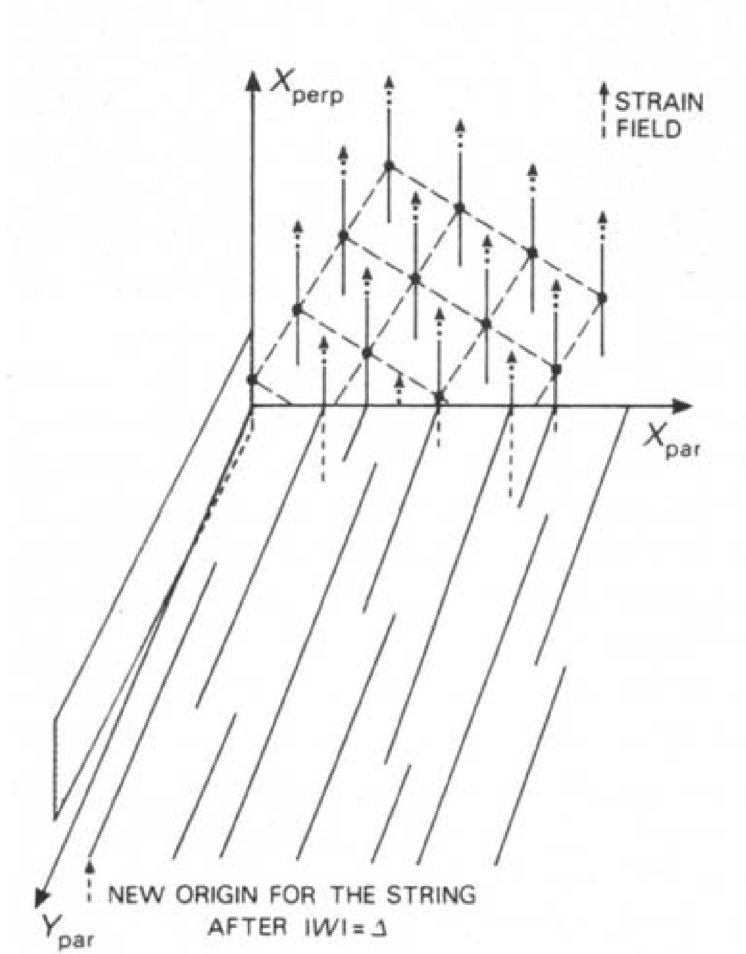
Similar diffraction pattern



Phason strain

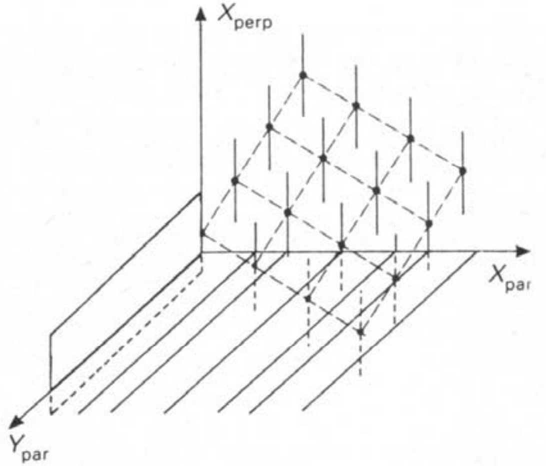


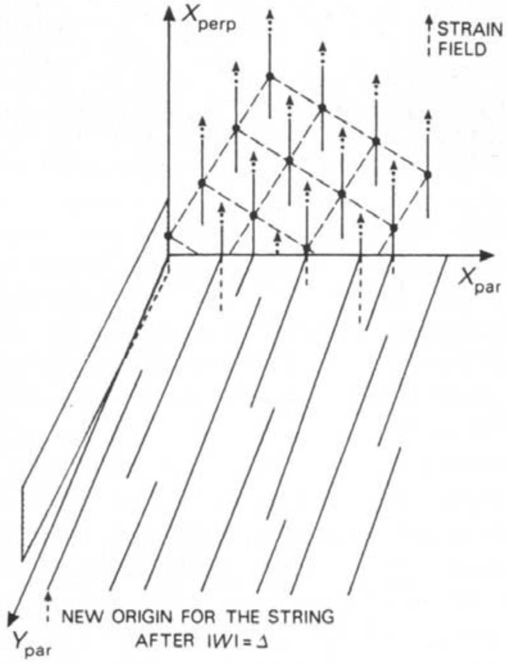
Fibonacci planes

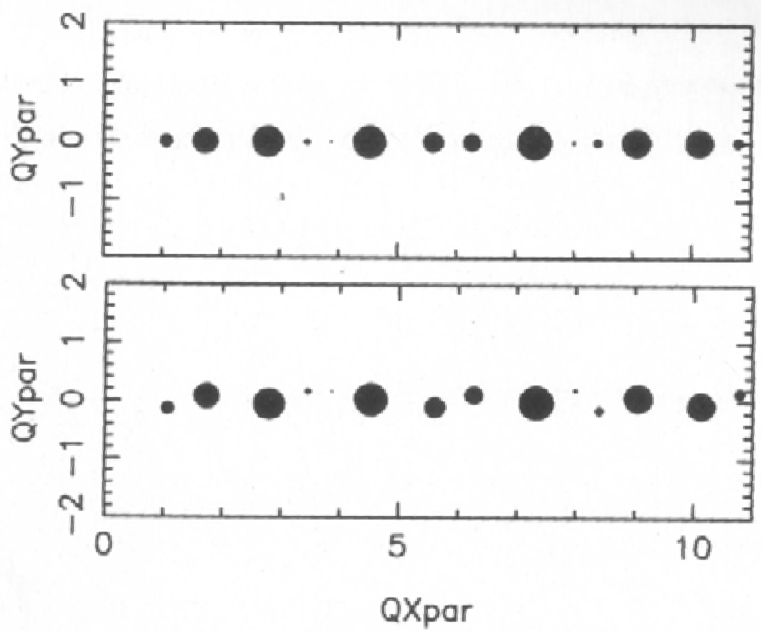


$$R_{per}=R^0_{per} + \alpha Y_{par}$$

Phason strain







$\mathbf{R}_{per}=\mathbf{R}^{0}_{per} + \alpha\mathbf{Y}_{par}$

$\mathbf{H}_{par}=\mathbf{Hx}_{par} + \Delta\mathbf{Hy}_{par}$

· $\Delta Hy_{par} = -\alpha H_{xper}$

shift larger for large H_{xper}

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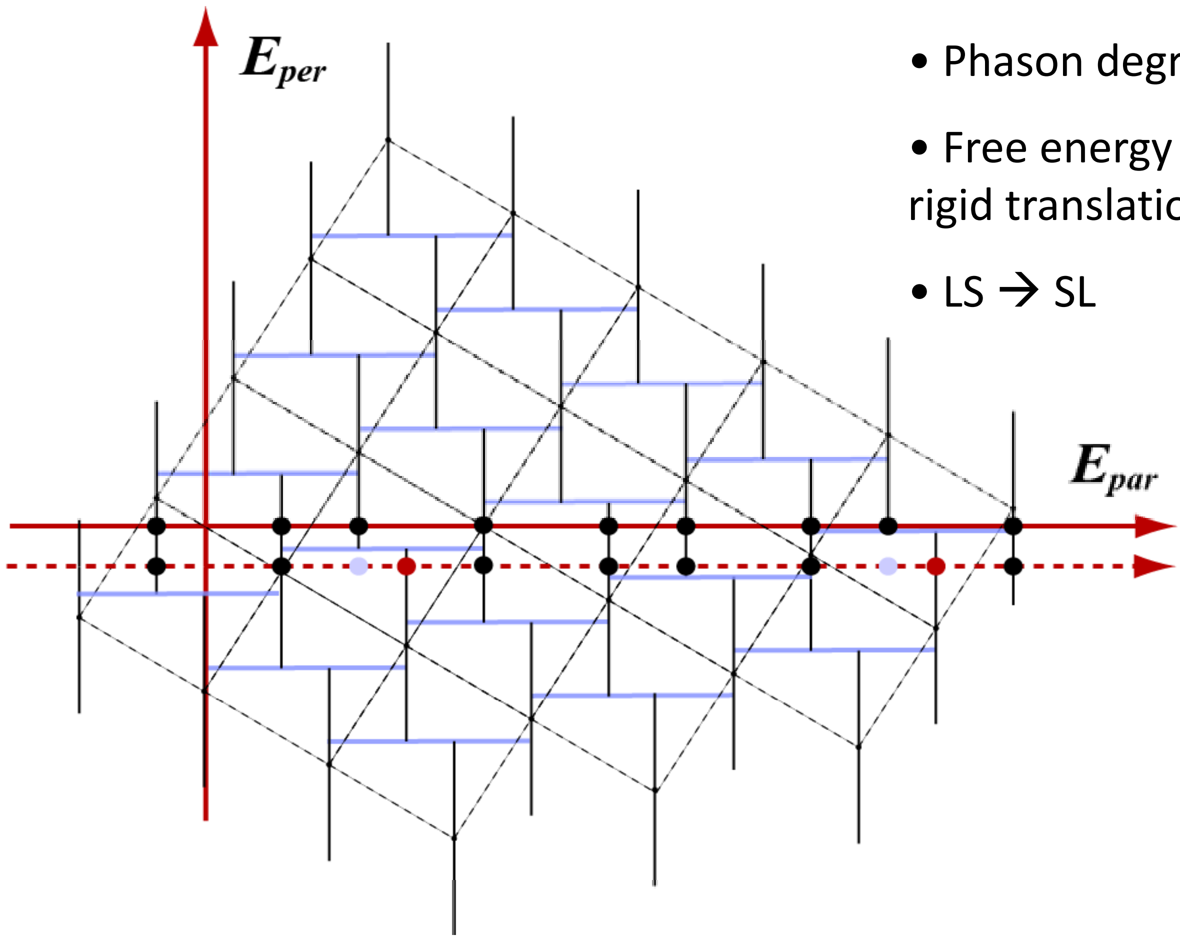
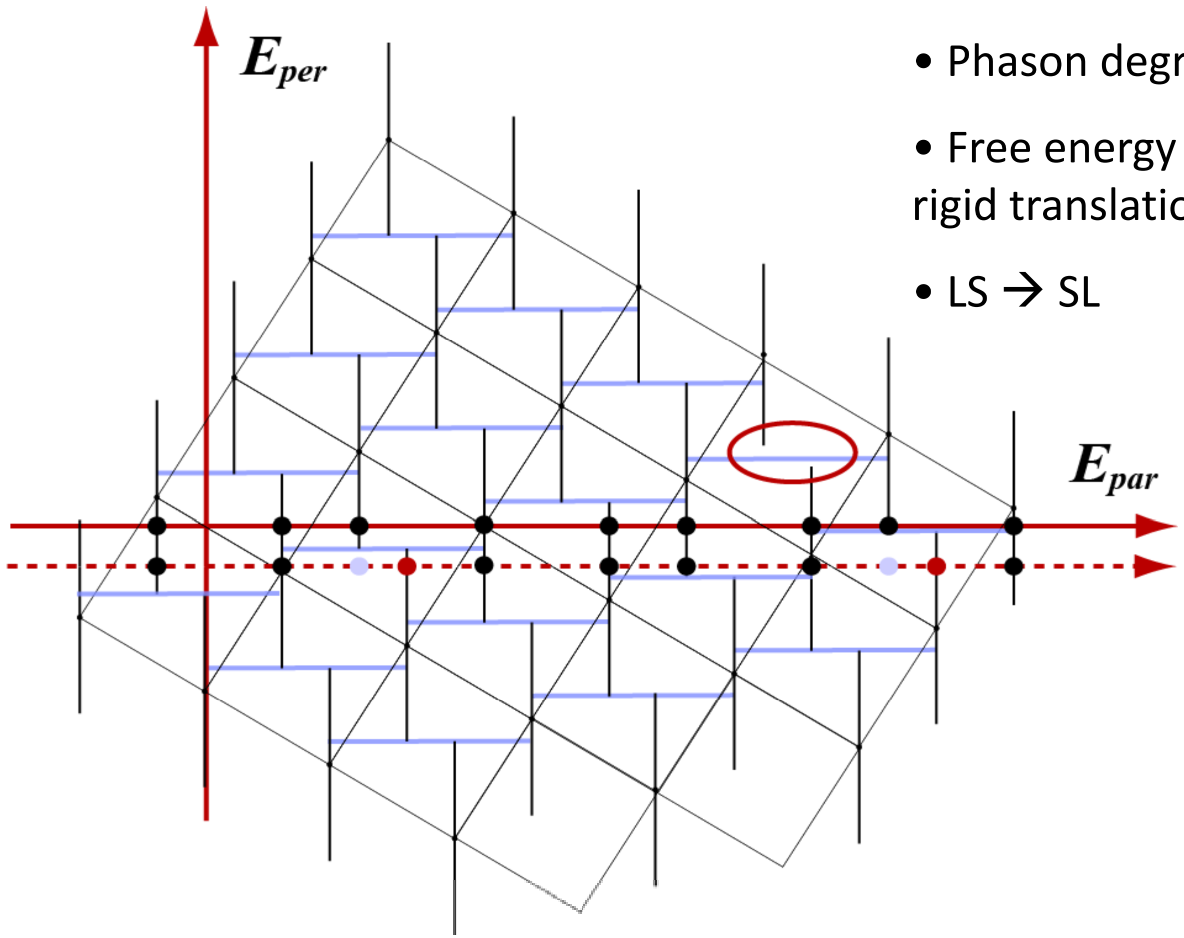
Closeness condition



- Phason degree of freedom
- Free energy is invariant under a rigid translation along Eper
- LS → SL

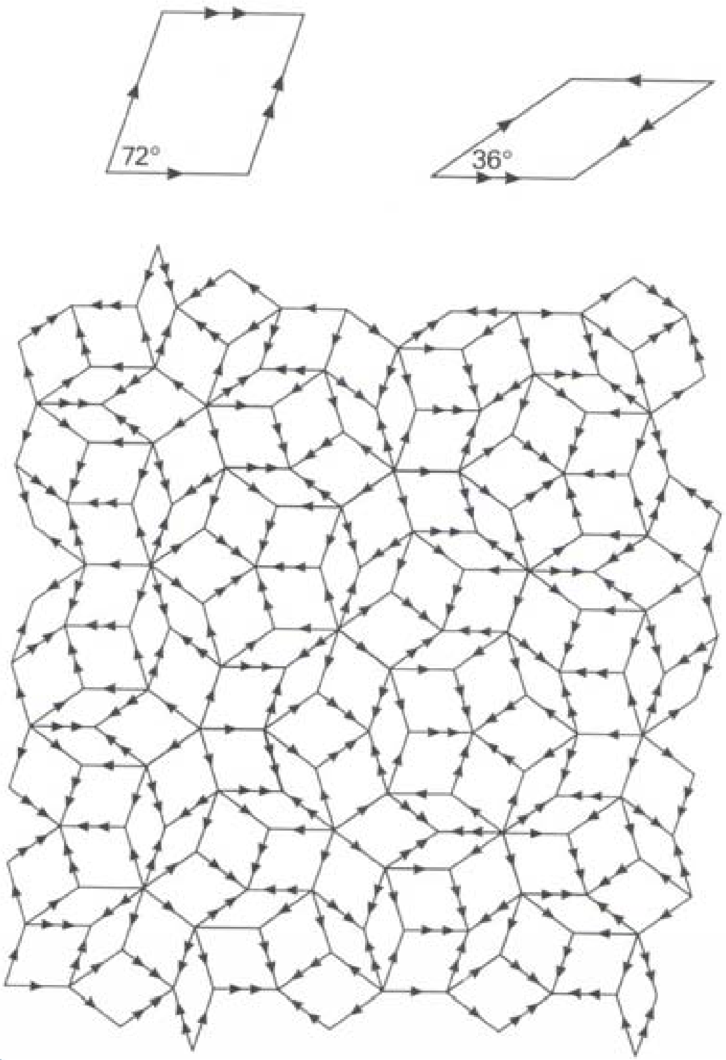
Closeness condition

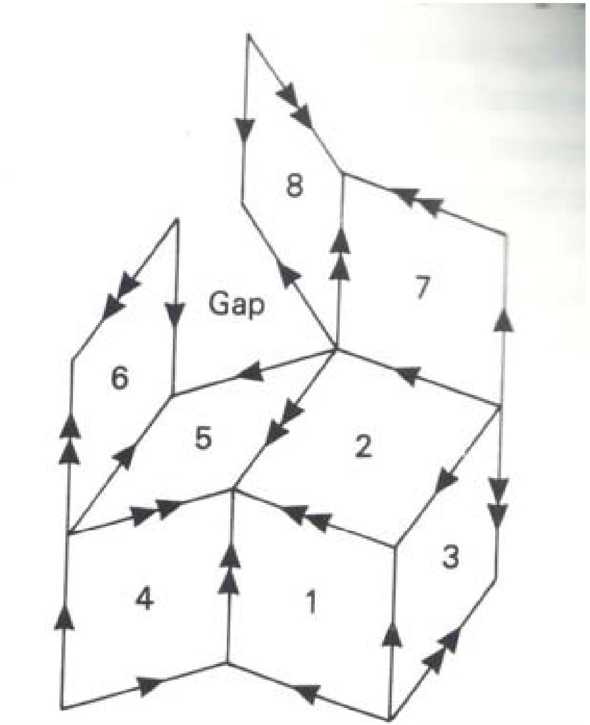


- Phason degree of freedom
- Free energy is invariant under a rigid translation along Eper
- LS → SL

- Atomic surfaces are connected (no ‘creation or anhinilation of atom).
- Constraint very difficult to fulfill in general cases.

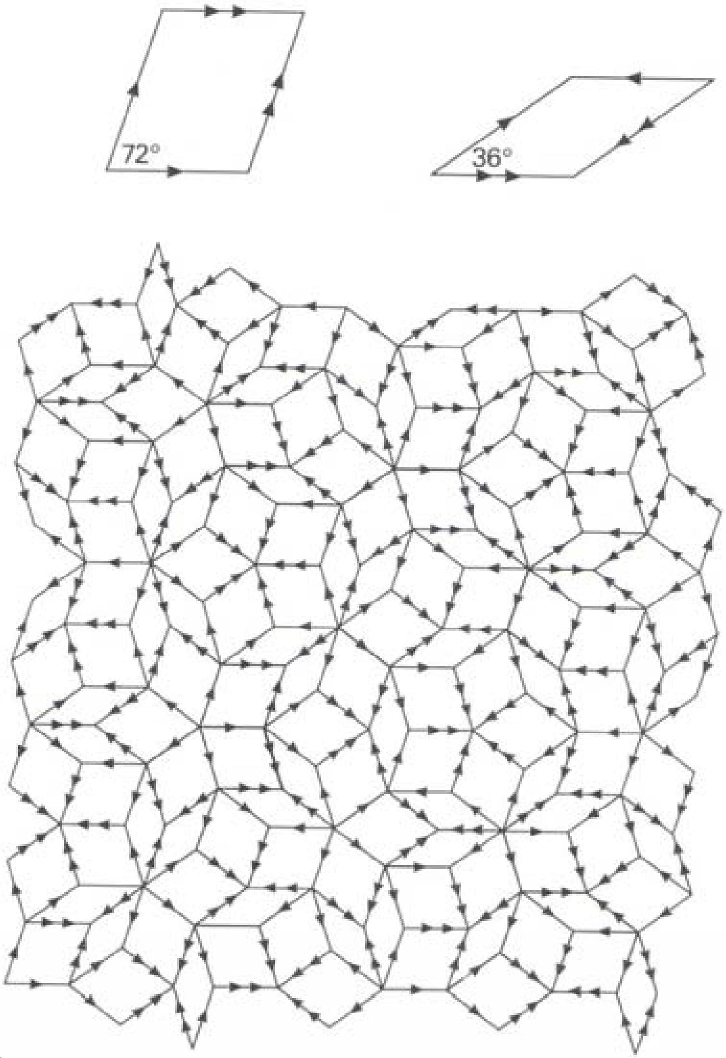
Can quasiperiodic long range order propagates with local rules?

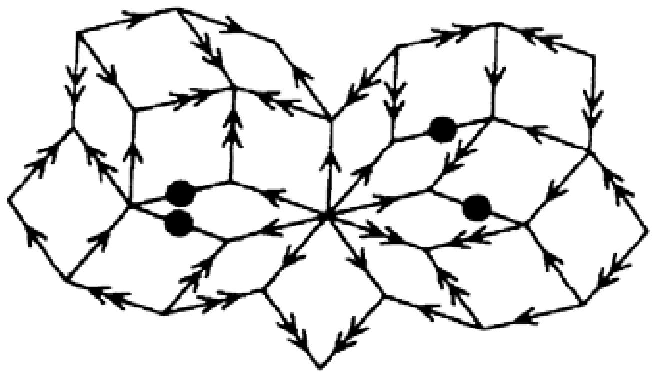




- Matching rules are not growing rules

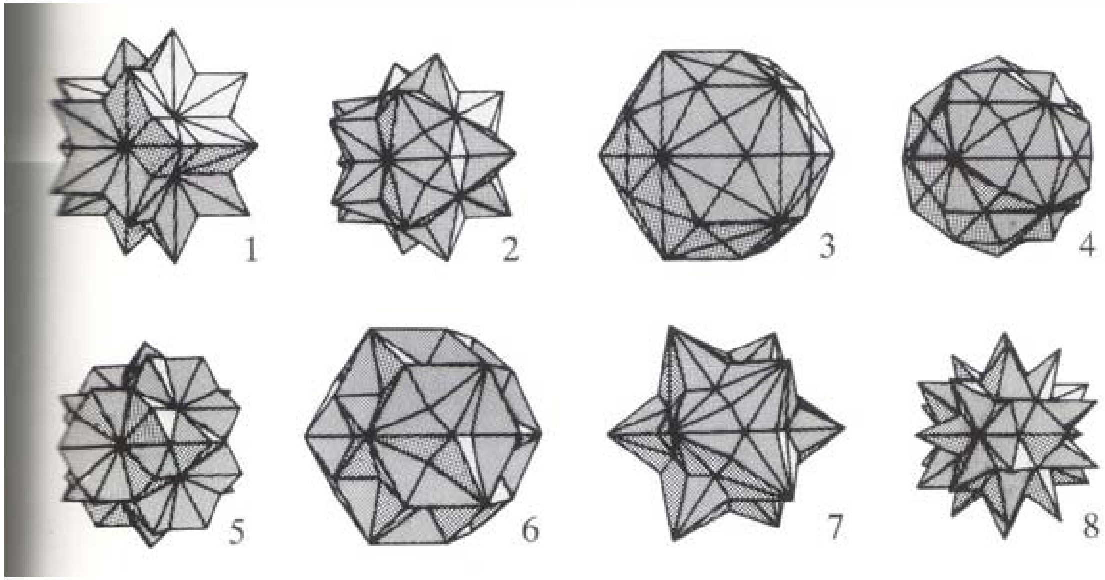
Can quasiperiodic long range order propagates with local rules?



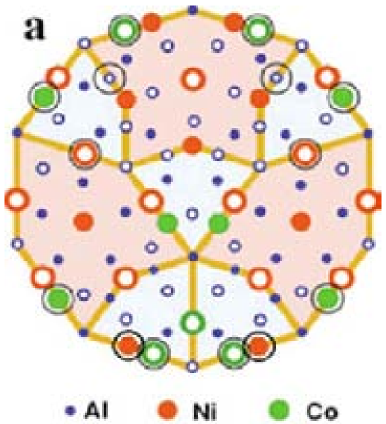


- But ‘local’ growth possible around a seed defect

Can quasiperiodic long range order propagates with local rules?



•Which atomic surfaces for matching rules?? Icosahedral bounded by 2-fold planes (Katz and Gratias). Set of polyhedra to be used.

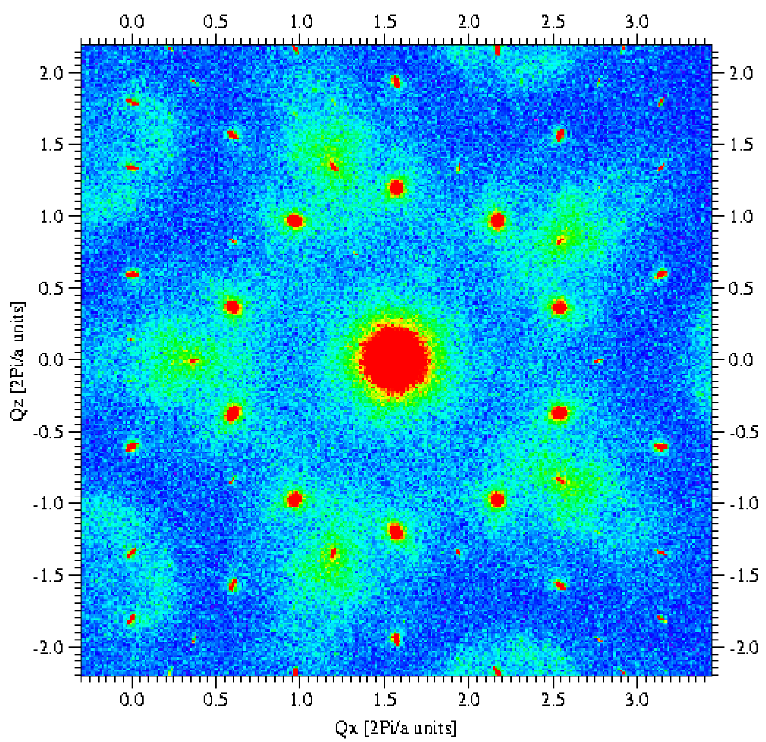


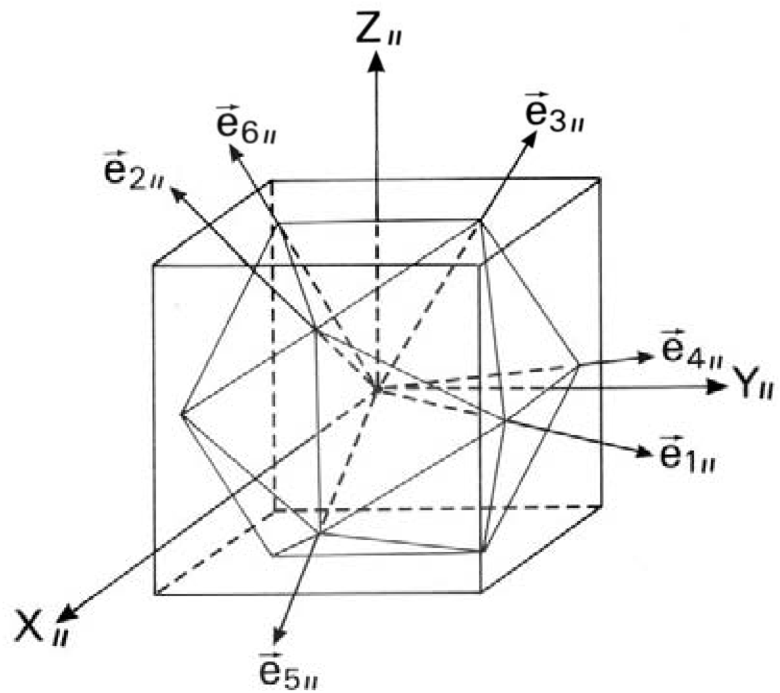
• Decagonal Cluster covering (Gummelt, Steinhardt) is a rephrasing of matching rules. Deca phase (Abe et al)

Summary

- Structural solution:
- Indexing and space group
- Phasing (or Patterson analysis)
- Fourier map: position and rough shape of the AS
- Modeling and refinement

Icosahedral symmetry

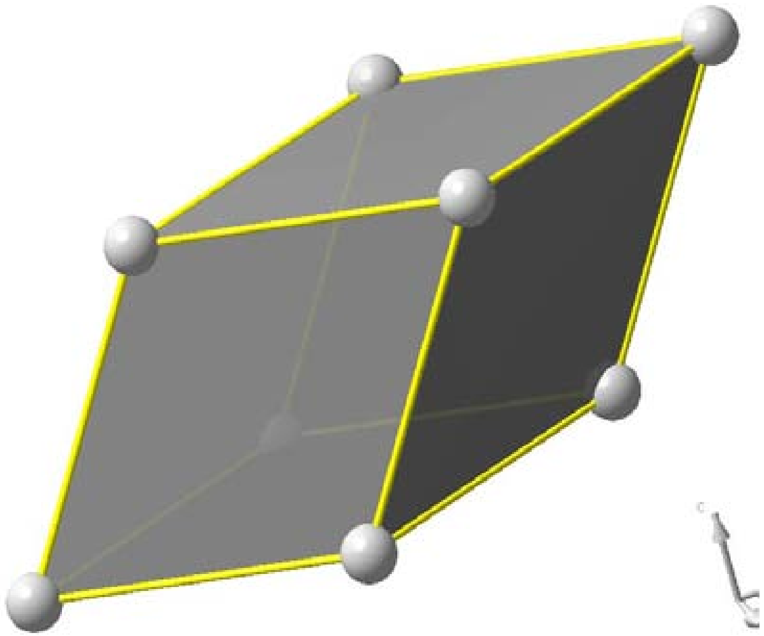




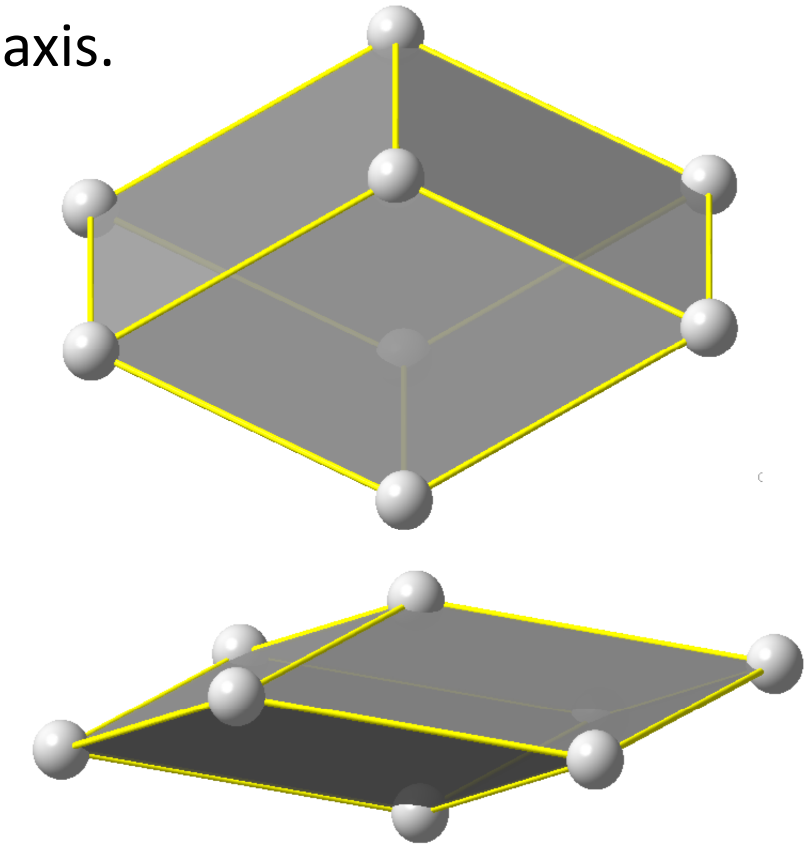
- Diffraction pattern indexed with a linear combination of 6 Vectors (5-fold axis of the icosahedron)
- Periodicity in 6D space: 6D cube
- Decomposed in two 3D spaces: paralell (or physical space) and perpendicular space

3-D Penrose tiling

- 3D tiling with icosahedral symmetry.
- 2 tiles, with edges // to a 5-fold axis.



Prolate

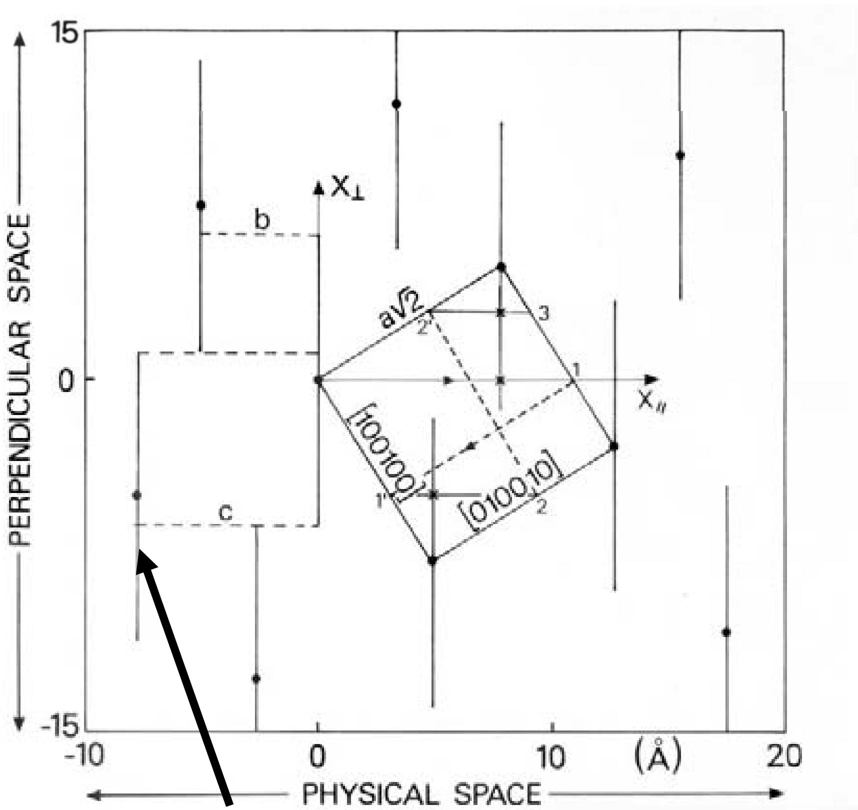


Oblate

3D Penrose tiling
Section of a 6D cube decorated by a triacontahedron (Atomic surface) in perp space

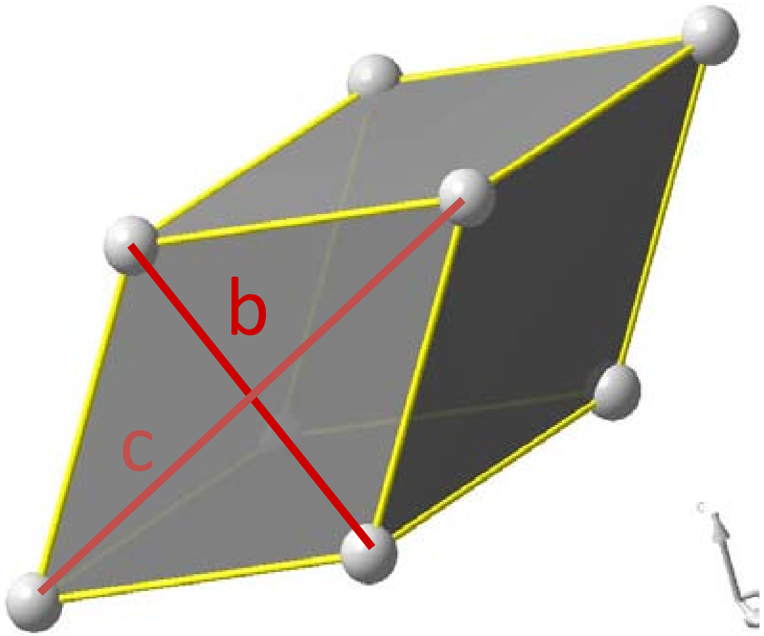
Triacontahedron lying in Perpendicular space

2-fold section of the 6D cube



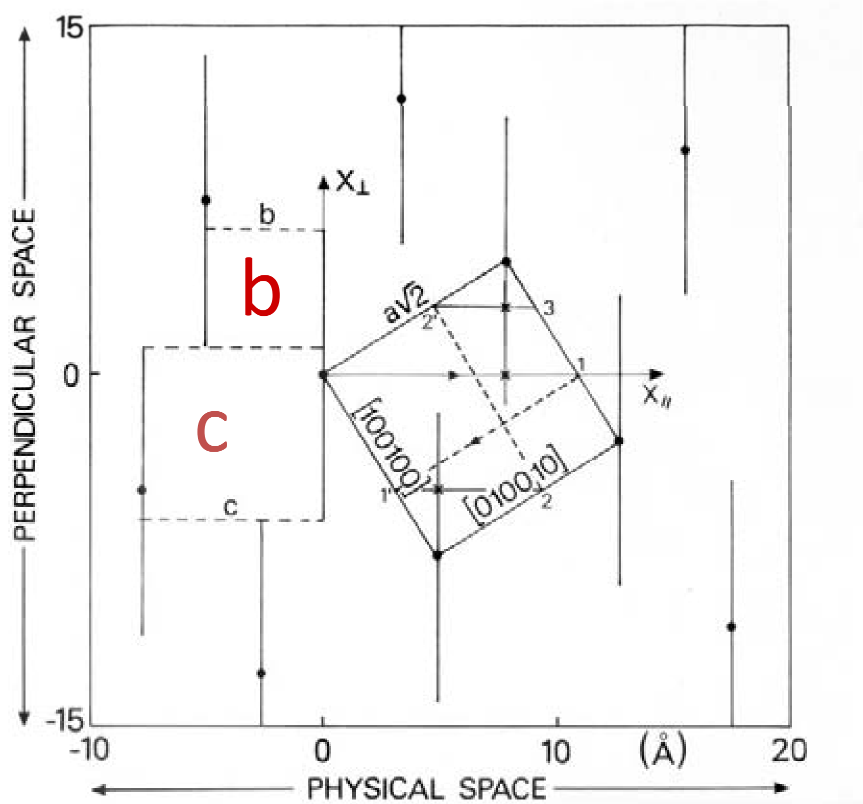
2-fold trace of the Triaconta

3D Penrose tiling
Section of a 6D cube decorated by a triacontahedron (Atomic surface)



Prolate (physical space)

2-fold section of the 6D cube

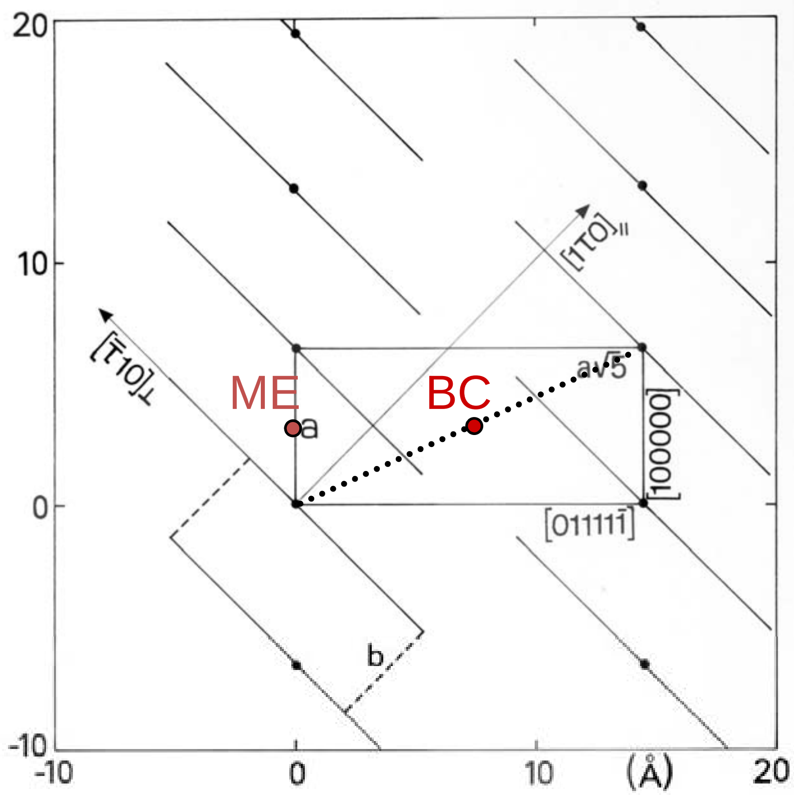


5-fold section of the 6D cube

- 5-fold rational section
- Information on 5-fold axis.
- Allows to visualise three Wickoff position of the 6D cube, possible for the decoration:

Origin: (000000)
Body center: 0.5(111111)
Mide edge: 0.5(100000)

5-fold section of the 6D cube



Icosahedral space groups

- There are different space group, related to the icosahedral Bravais lattice
- This give extinction conditions.

- Structure solution is following the same process as the 1D example
- Complex shape of atomic surfaces but related to local environments
- Real space modeling is also complementary

Conclusion

- The high dimensional space description is a powerful tool for the structure analysis of QC
- No general algorithm, but strong connection between the high dim space and the local environment
- Position, shape, chemical nature and local relaxation of the atomic surfaces : refinement is possible.