

reciprocals workshop on twins

a Z – module approach
hidden symmetries

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the concept of great space and \mathbb{Z} -module was used for the description of quasicrystals, objects ordered at great distances but without the property of translation invariance

this concept can be used when the atoms of a crystal, beyond being periodically spaced, are located on an ordered subset of a \mathbb{Z} -module

« pedagogical » approach with a 1-D physical space and a 2-D great space

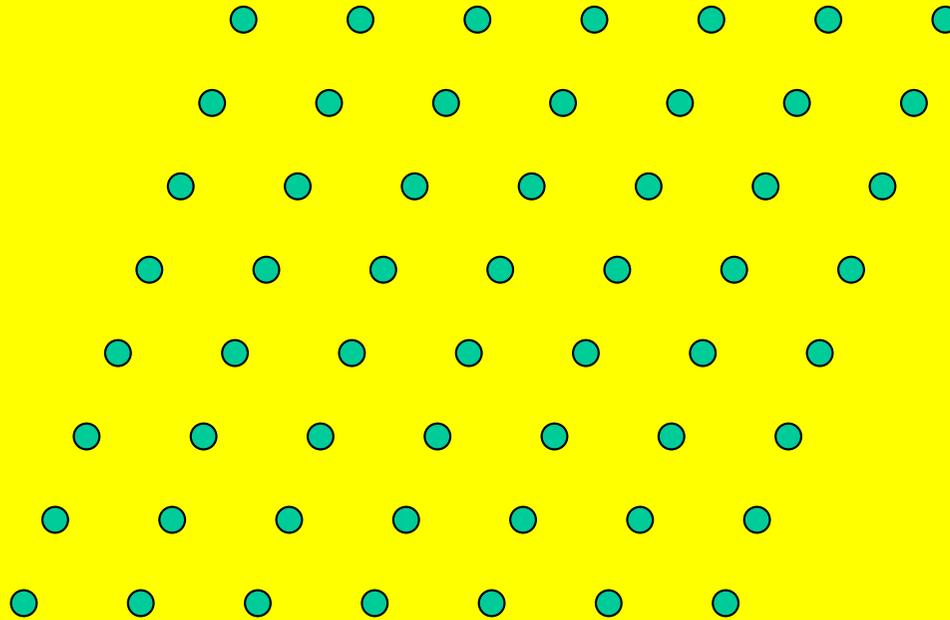
then, with a 2-D physical space and a 5-D great space

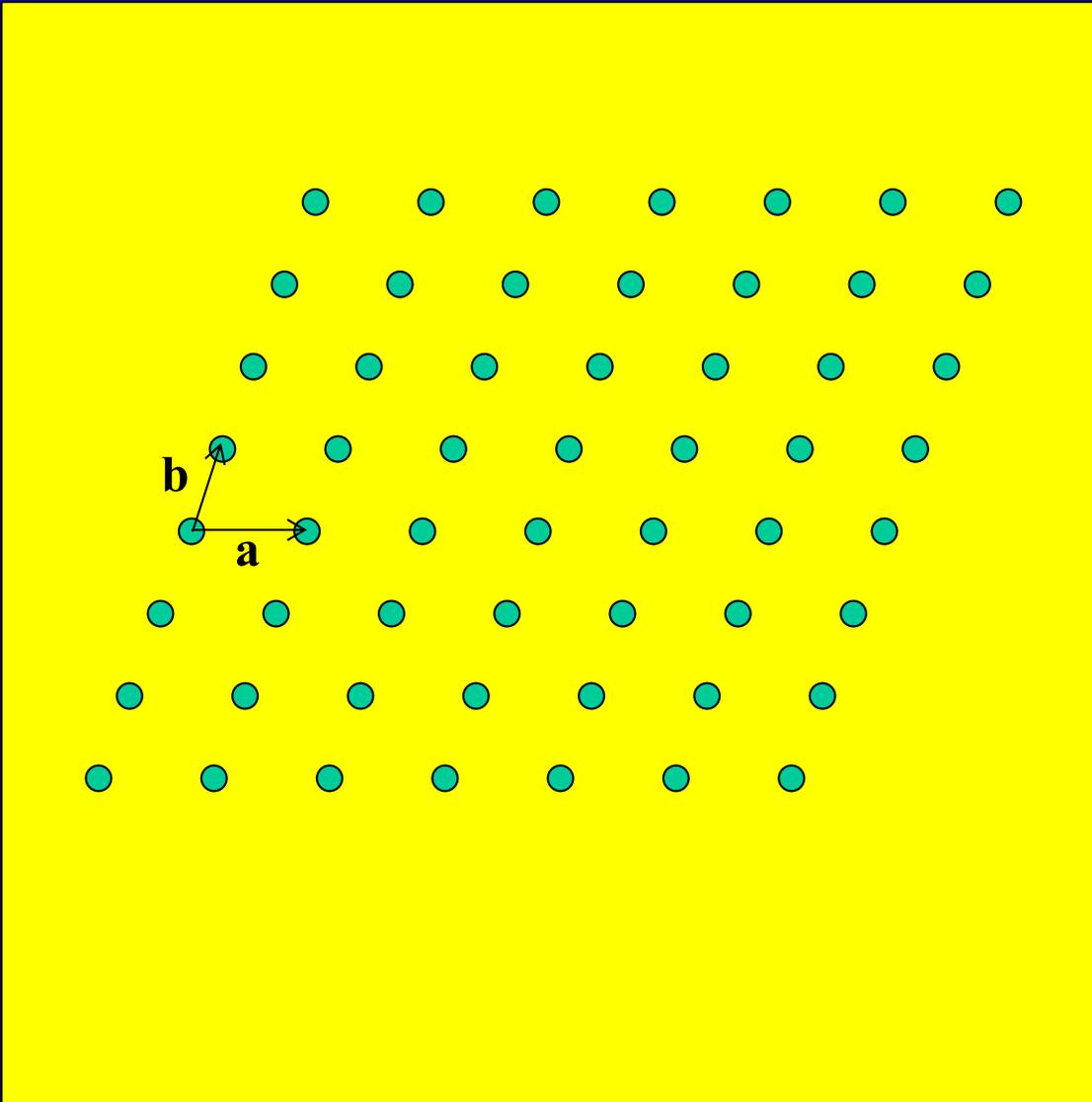
lattices

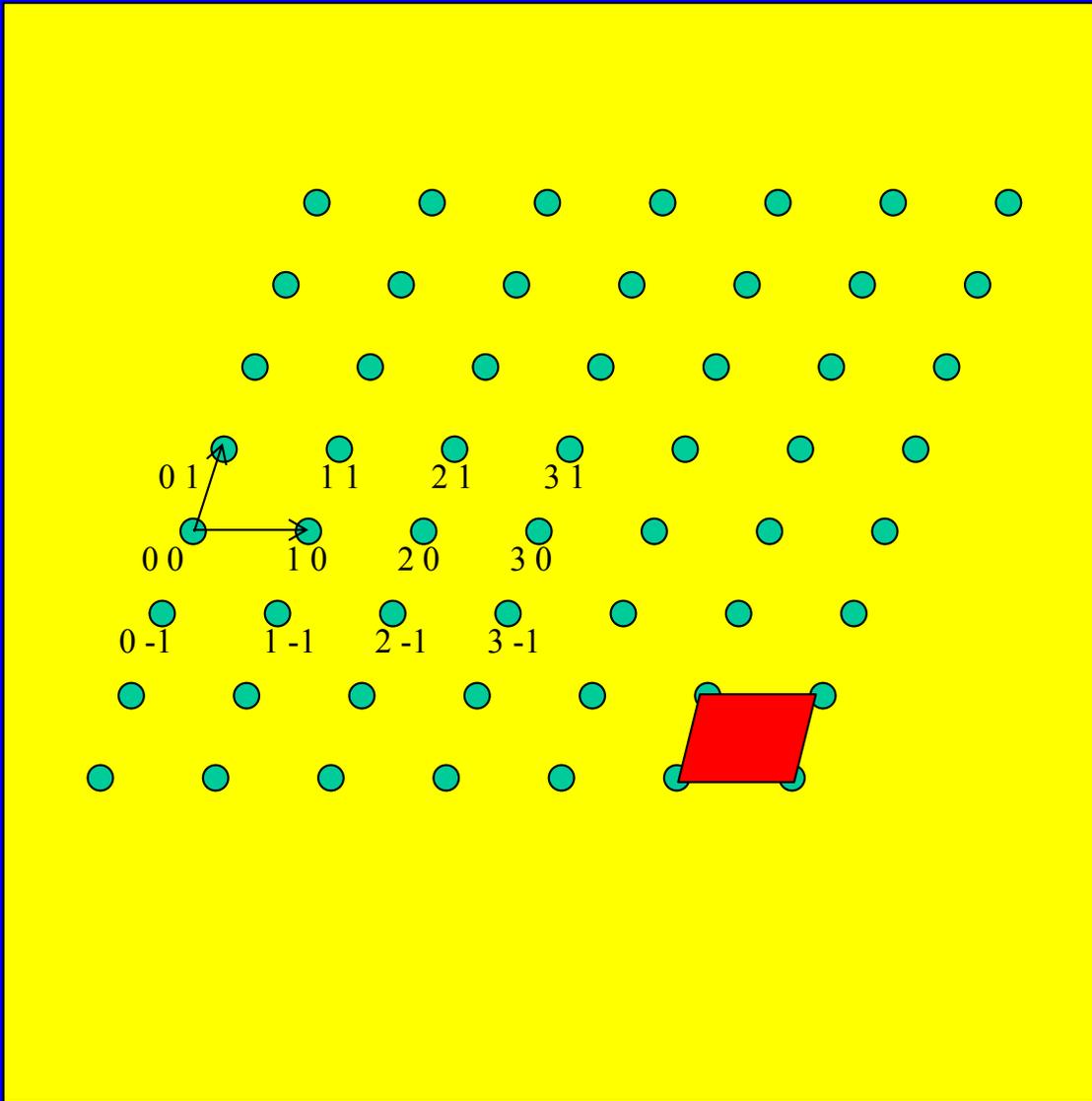
2-D space



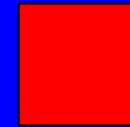
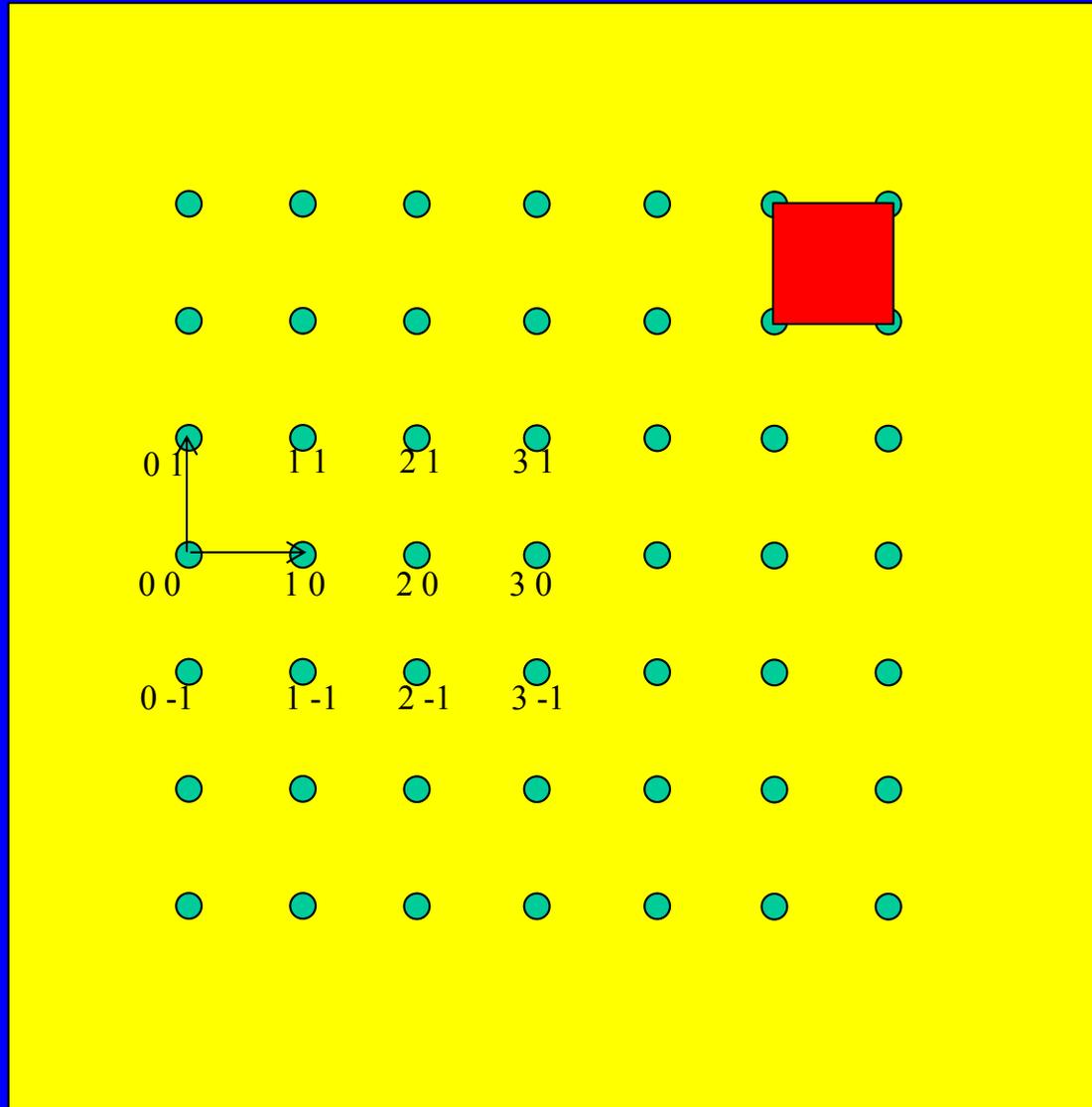
unit cell







each node : two integers



square cell

[4]

rotation axis θ

matrix representation

$$\begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix}$$

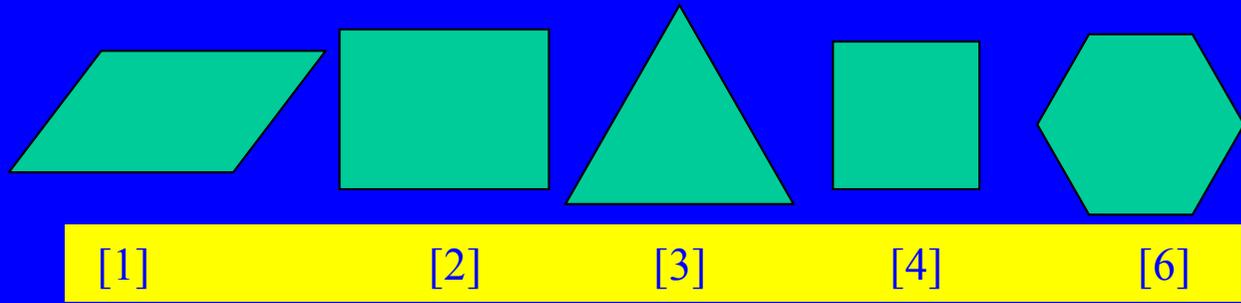
$$\theta = \pi/2 \quad [4] \quad \begin{pmatrix} \cos \pi/2 & -\sin \pi/2 \\ \sin \pi/2 & \cos \pi/2 \end{pmatrix} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \longrightarrow \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} n \\ p \end{pmatrix} = \begin{pmatrix} -p \\ n \end{pmatrix}$$

2-D : polygons

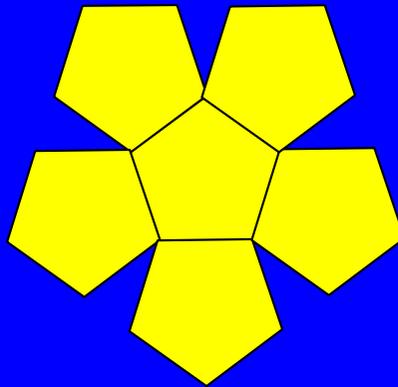
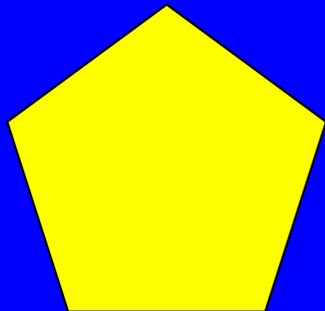
invariance by translation



discrete Fourier spectrum
↕
translation invariance



crystallographic symmetries

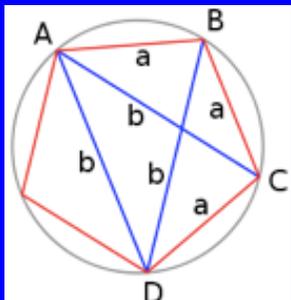


[5]
non crystallographic symmetries

no translation invariance



no discrete Fourier spectrum !!!



$$b / a = \tau$$

τ : the golden mean

aperiodic tiling (2-D)

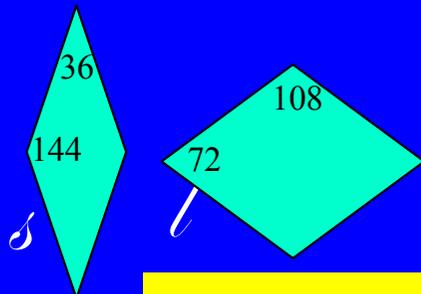
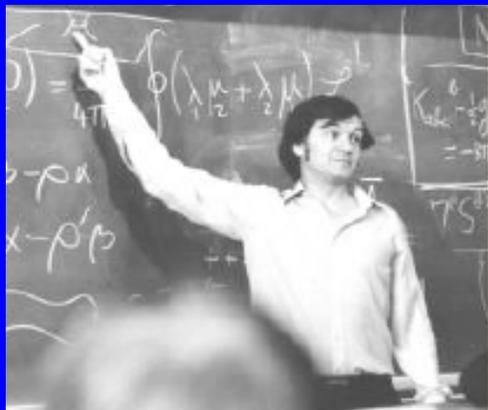
isomorphisme local

Sir Roger Penrose

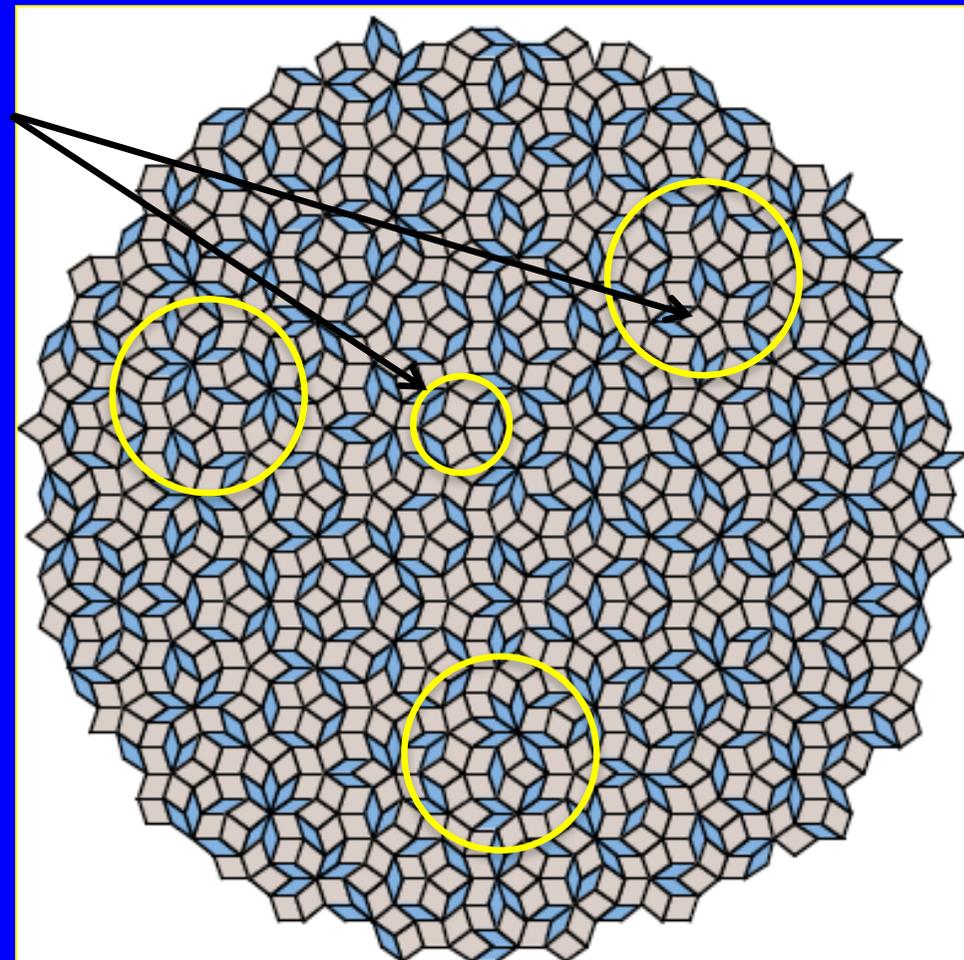
2 prototiles

2 rhombus

→ 1974 Penrose



Penrose tiling



aperiodic

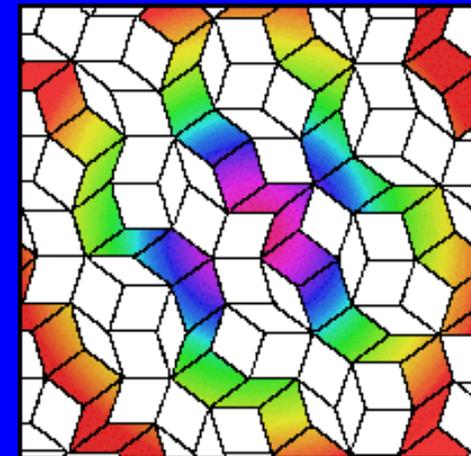
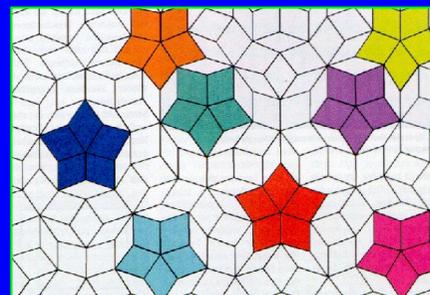
$$\frac{N}{N'} \rightarrow \tau$$

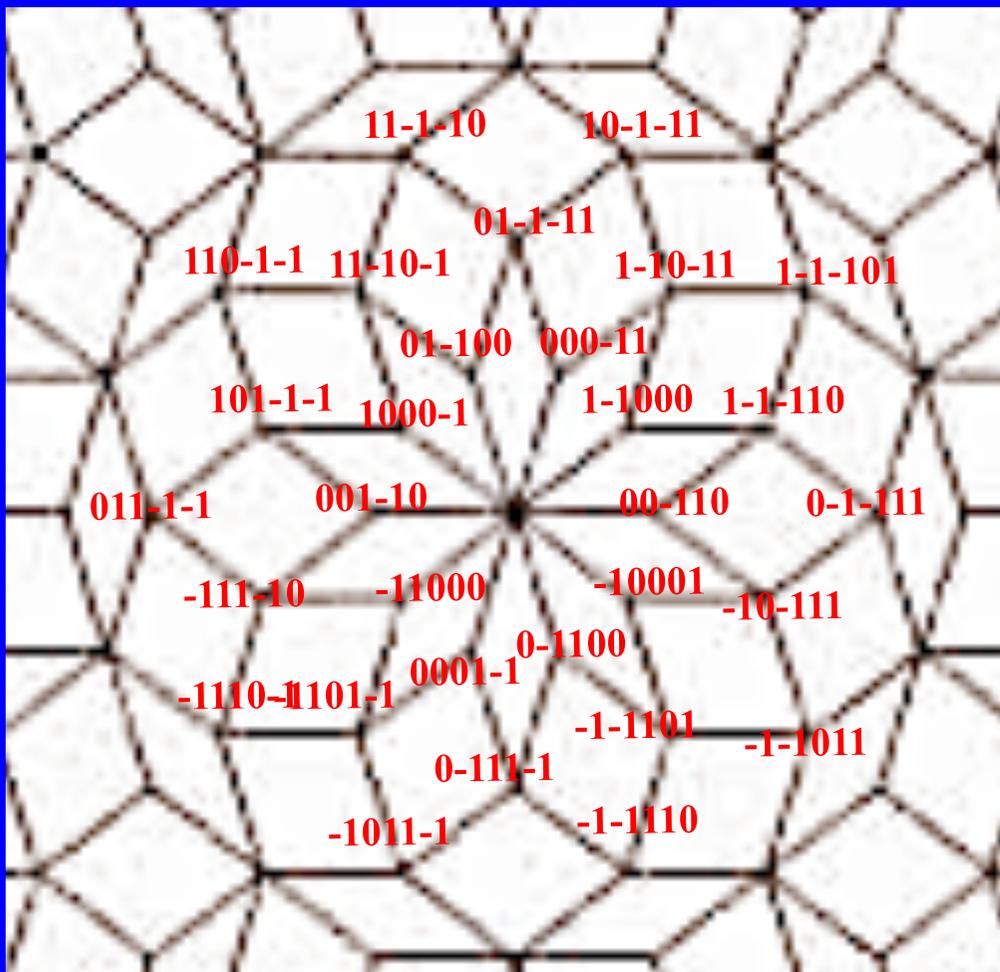
but also possible periodicity



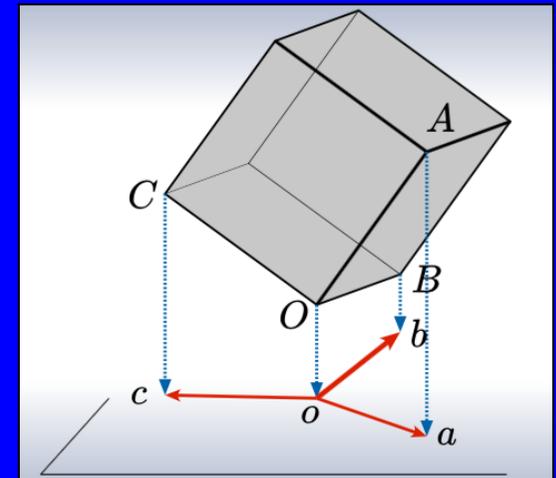
symmetry [5]
local

support for the description of structures whose construction is based on the pentagon





→
cut and projection
method



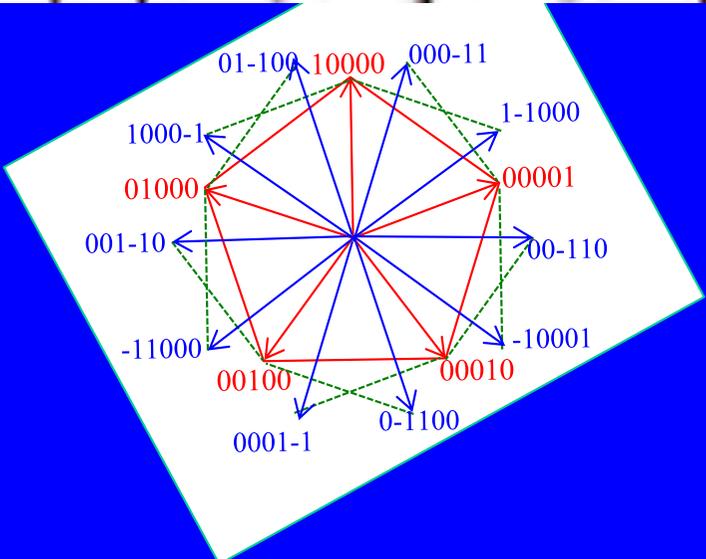
a \mathbb{Z} -module of rank p in \mathbb{R}^d of dimension d , ($d < p$) is the set of points x defined by

$$x = \sum_{i=1}^p n_i e_i$$

where the basic vectors e_i are arithmetically independent

it is isomorphic to an irrational projection in d -dimensional space of an N -dimensional lattice, with $N > d$.

for $d = p$, the \mathbb{Z} -module is a lattice.



quasicrystals

the cut and projection method

a **3-dim** aperiodic icosahedral lattice can be generated by projection along an irrational hyperspace of the nodes of a periodic-cubic lattice in a **6-dim** space

great space

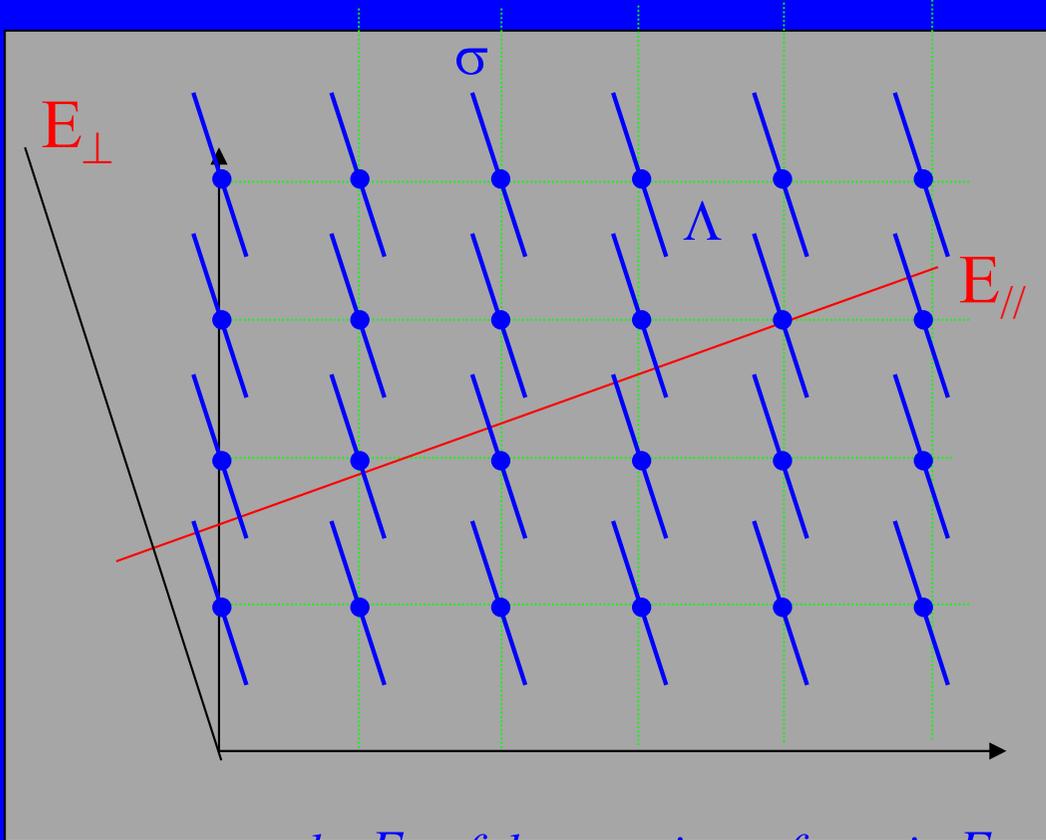
[5] : ~~symmetry~~ operation

[5] : indiscernability operation

Penrose and some periodic structures described in a 2-D space

physical space : 2-D

great space : 5-D



a quasiperiodic crystal in a d-dim space can be viewed as a d-dim cut of a N (> d)-dim periodic crystal, irrationally oriented with respect to the N-dim space

(Bak 1985)

Λ = N-dim periodic lattice

σ = (N - d)-dim atomic surface (volume)

$E_{//}$ = d-dim physical space which cut the hyperspace

$$QC = (\sigma * \Lambda) \cdot E_{//}$$

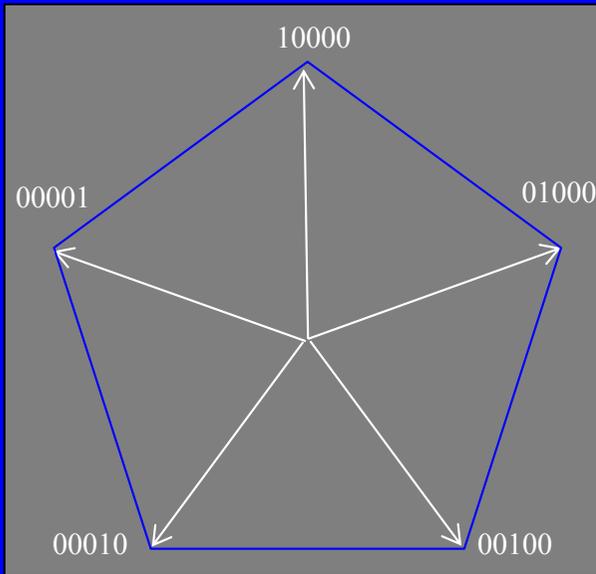
local [5] symmetry

Z-module rank 5

$\{e_1, e_2, e_3, e_4, e_5\}$

- isomorphous with a periodic lattice in a great space of dimension 5

- generated by irrational projection in the 2-dim physical space



$$\sum e_i = 0$$

$$\begin{matrix} \mathbb{R}^2 \\ \dots \\ \mathbb{R}^3 \end{matrix} \begin{pmatrix} x_{//} \\ y_{//} \\ x_{\perp} \\ y_{\perp} \\ z_{\perp} \end{pmatrix} = \frac{\sqrt{2}}{\sqrt{5}} \begin{pmatrix} |1\rangle & |2\rangle & |3\rangle & |4\rangle & |5\rangle \\ 1 & \cos \phi & \cos 2\phi & \cos 2\phi & \cos \phi \\ 0 & \sin \phi & \sin 2\phi & -\sin 2\phi & -\sin \phi \\ \dots \\ 1 & \cos 2\phi & \cos \phi & \cos \phi & \cos 2\phi \\ 0 & \sin 2\phi & -\sin \phi & \sin \phi & -\sin 2\phi \\ 1/\sqrt{2} & 1/\sqrt{2} & 1/\sqrt{2} & 1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} \begin{pmatrix} n_1 \\ n_2 \\ \dots \\ n_4 \\ n_5 \end{pmatrix}$$

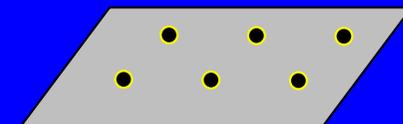
E_{\perp}

perpendicular space $(x_{\perp}, y_{\perp}, z_{\perp})$
selection of the 5-dim nodes

5-dim great space $(n_1, n_2, n_3, n_4, n_5)$

$E_{//}$

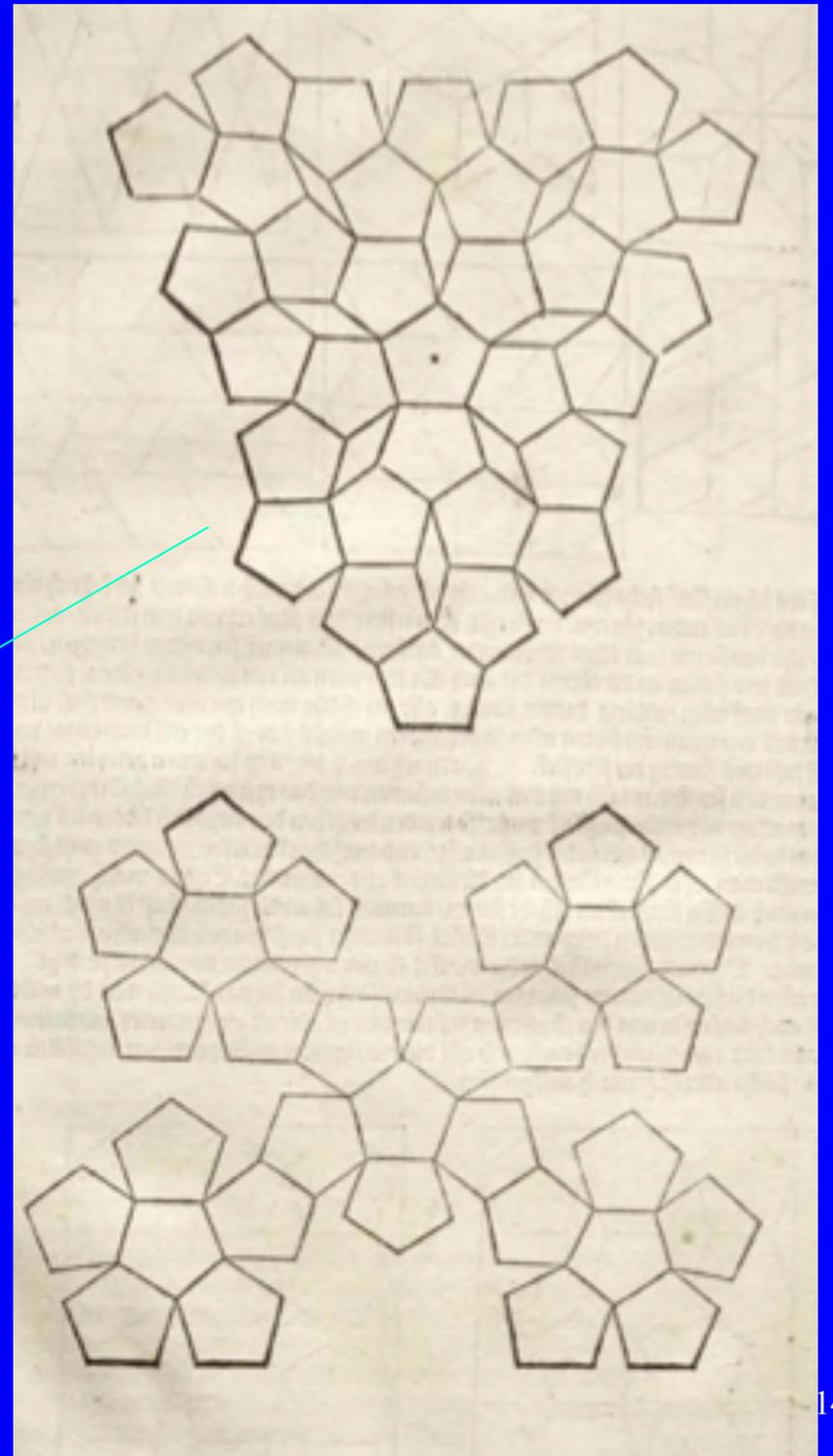
parallel space $(x_{//}, y_{//}) =$ physical space
selected nodes are projected



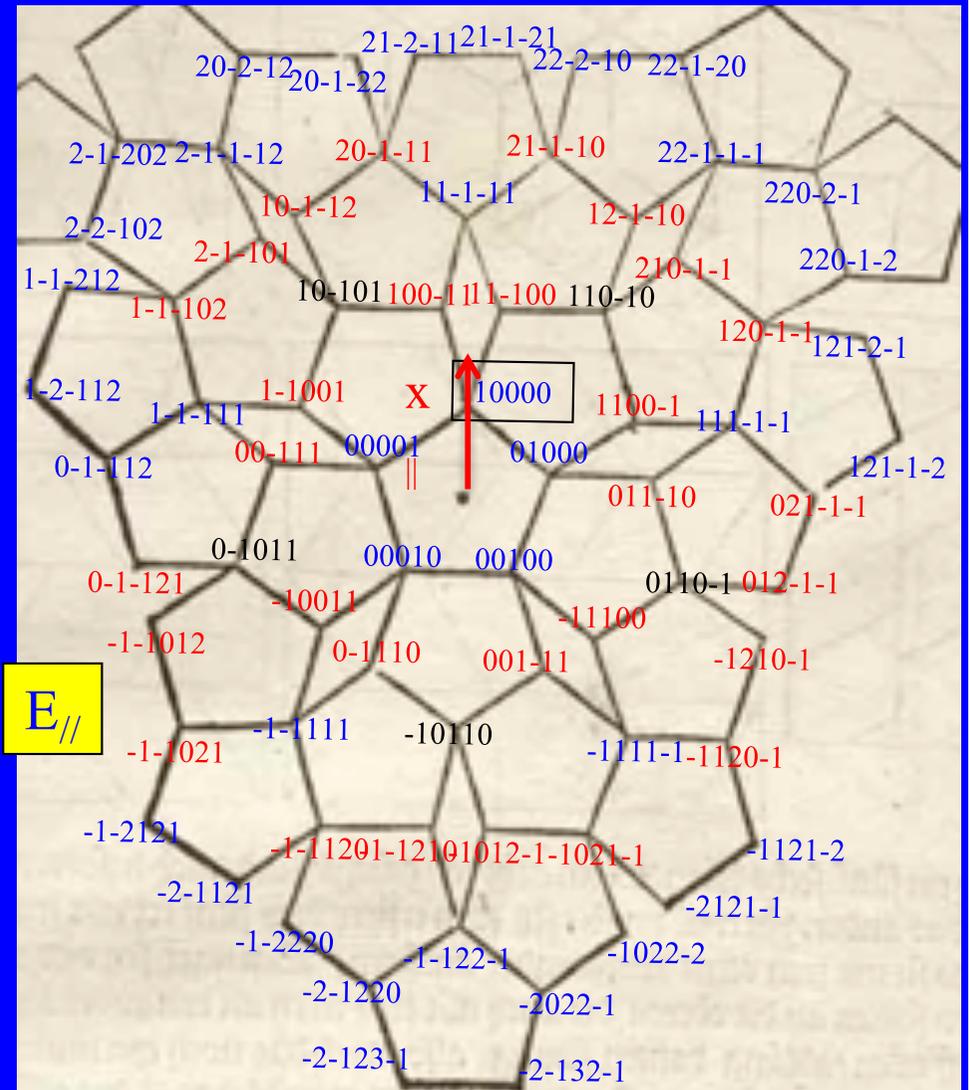
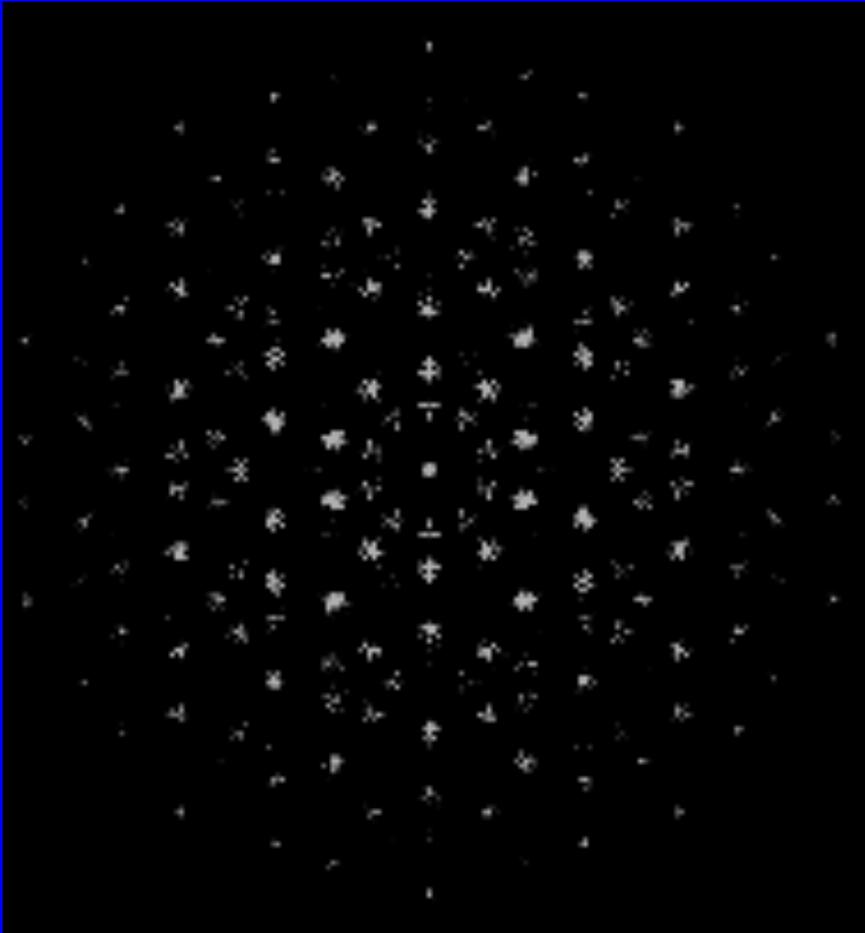
apply for any structure whose description involves pentagons (icosaedrons)
= decoration of a penrose type pattern

Dürer tiling (1525)

Albrecht Dürer
De Symmetria ... Humanorum Corporum
and *Underweysung der Messung*



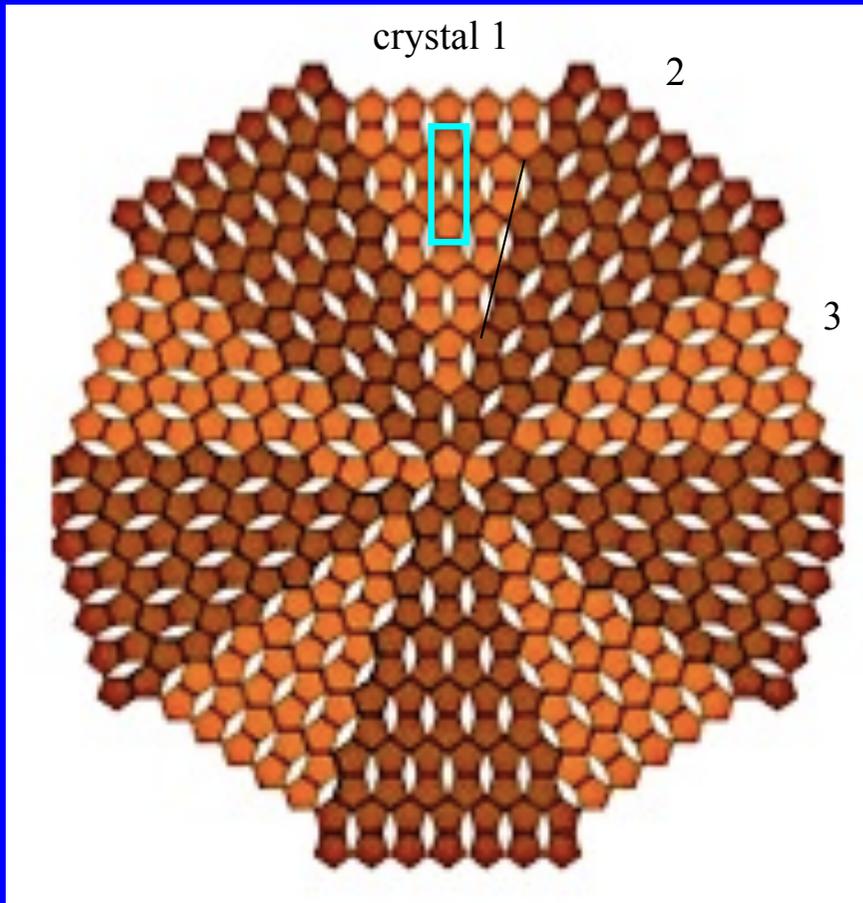
- the whole pattern as a tiling of pentagons
- a multiple twinned periodic crystal



same \mathbb{Z} -module
built with a pentagon

(indices Σ !)

Dürer tiling: twin description



$$A = (2+\tau)^{1/2}$$

$$B = 3\tau+1$$

C2mm

Origine en Ω

Maille 2D $\begin{cases} A = (0, \bar{1}, 0, 0, 1) \\ B = (2, 1, \bar{2}, \bar{2}, 1) \end{cases}$

Groupe 5D d'éléments générateurs

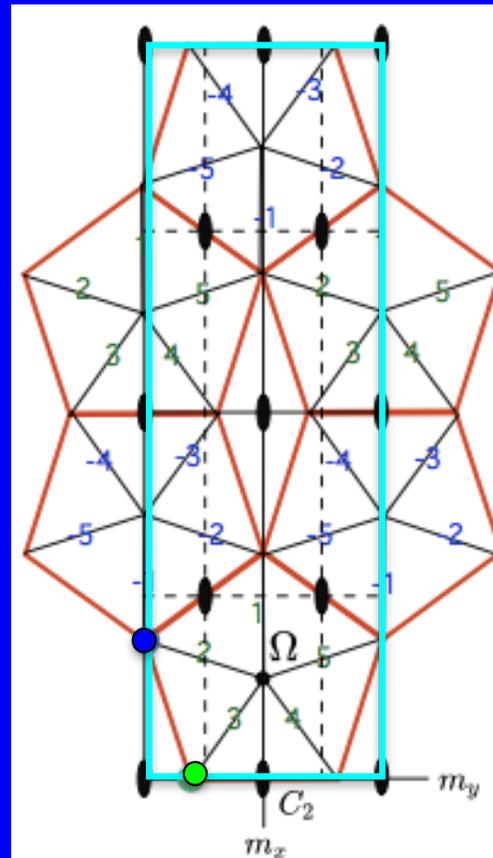
$$C_2 = (\{-1, -2, -3, -4, -5\} | 0, 0, 1, 1, 0)$$

$$m_x = (\{1, 5, 4, 3, 2\} | 0, 0, 0, 0, 0)$$

$$m_y = (\{-1, -5, -4, -3, -2\} | 0, 0, 1, 1, 0)$$

Positions de Wyckoff

- (0, 0, 1, 0, 0)
 - (0, 1, 0, 0, 0)
- Ω origine

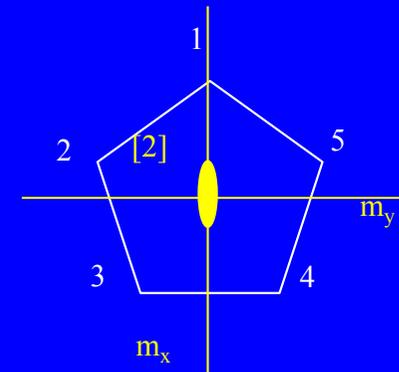


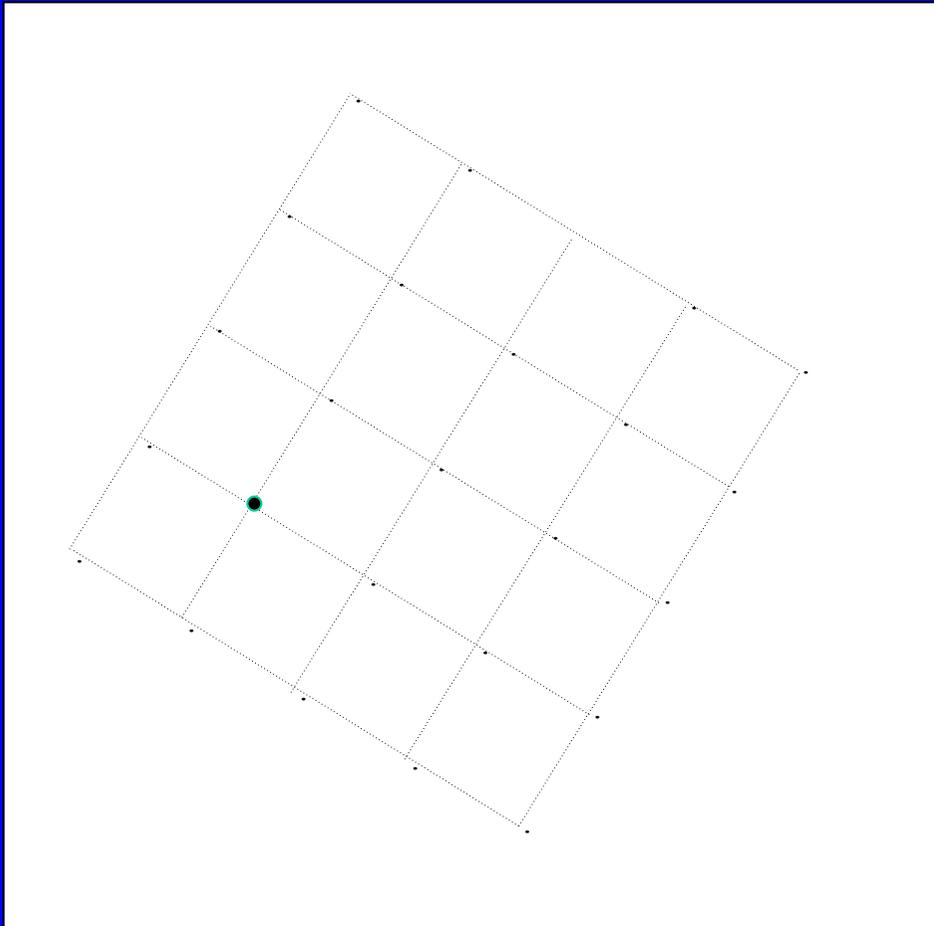
$$C_5 = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 \end{pmatrix}, m_x = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{pmatrix}$$

$$\bar{1} = \begin{pmatrix} \bar{1} & 0 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 0 & 0 & \bar{1} \end{pmatrix}$$

crystal 1

the structure is a specific 2D decoration of a Z-module of rank 4 that is best described as the projection along the main diagonal (1, 1, 1, 1, 1) of a primitif lattice in a space of dimension 5.

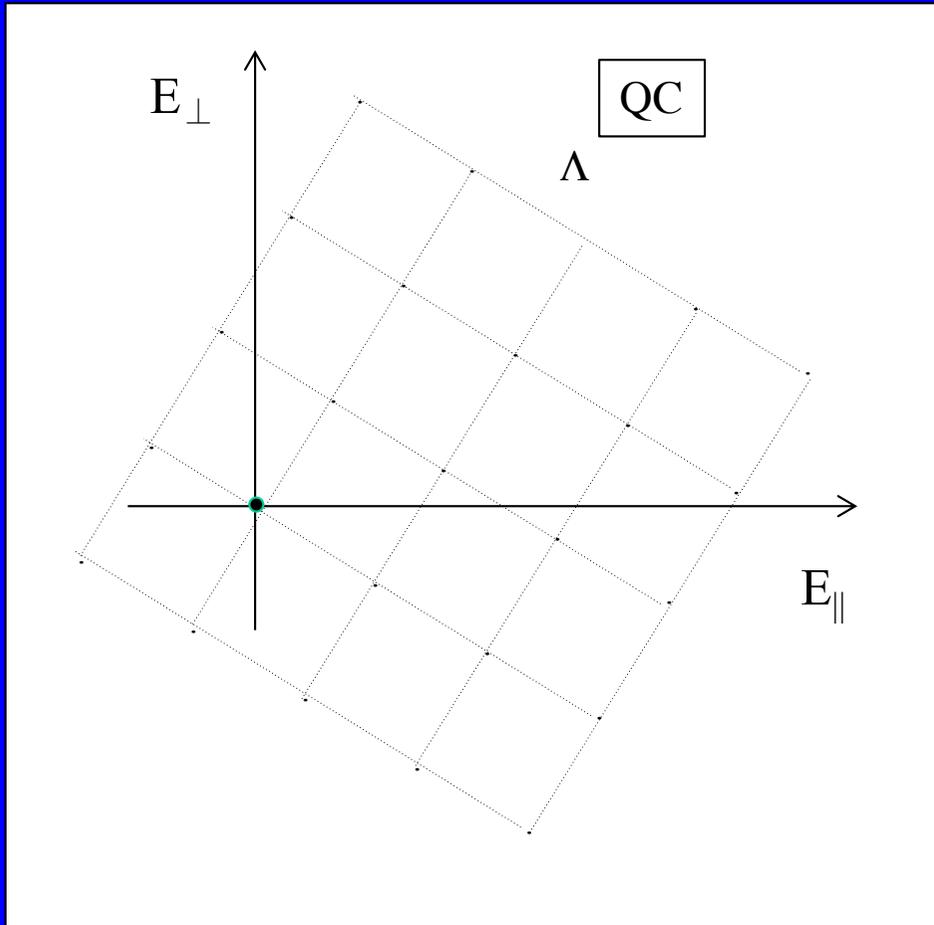




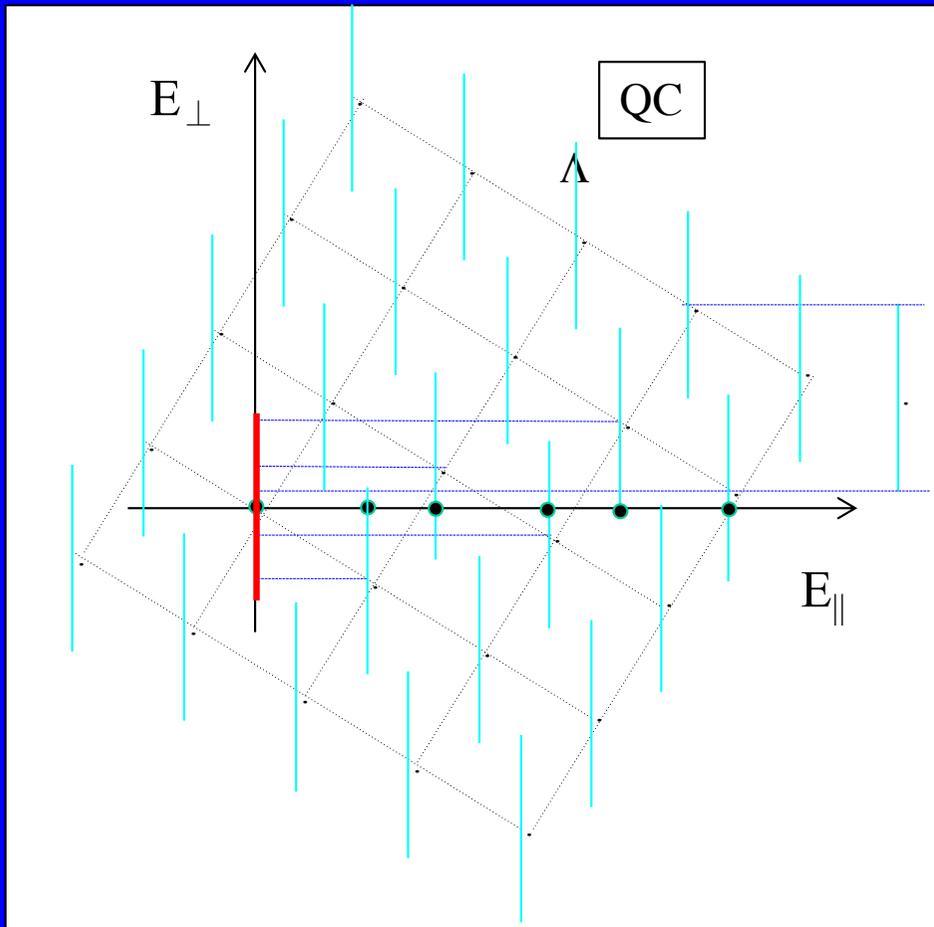
2-D space (5-D), a 2-D periodic lattice

construction of the structure using the large space in order to get it as a decoration of the Z-module

5-D \rightarrow 2-D but here 2-D \rightarrow 1-D

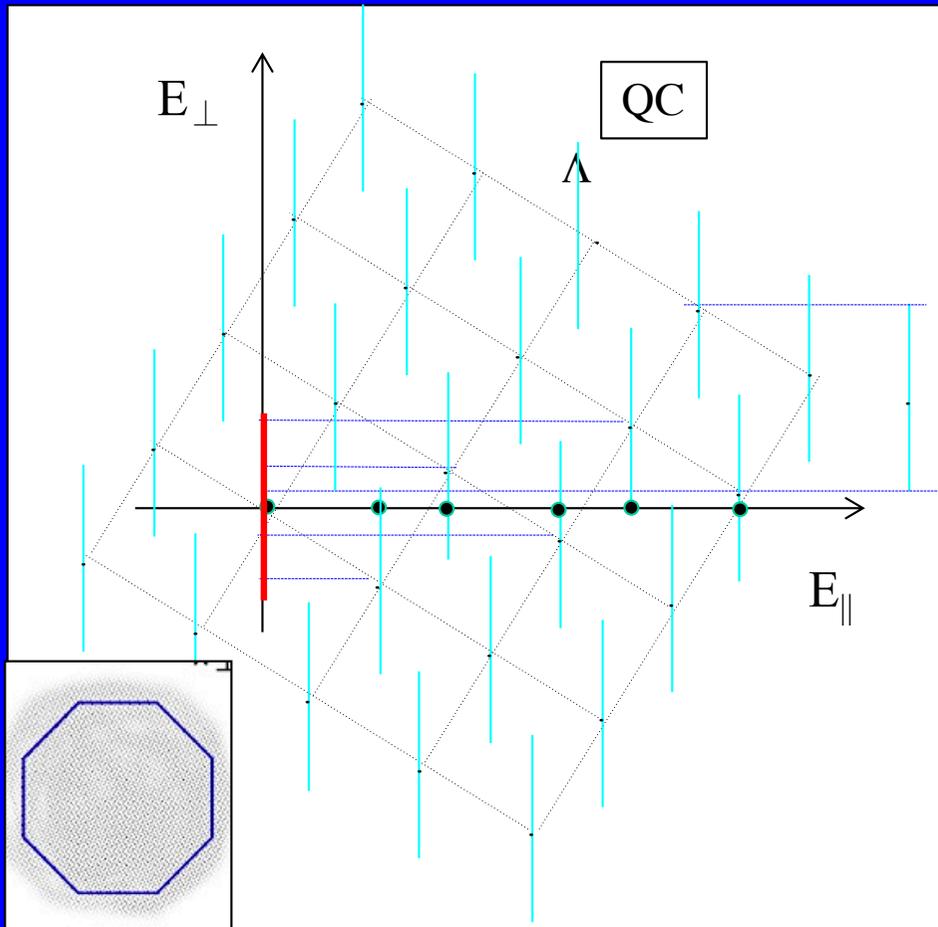


- we call $E_{//}$ the physical space 1-D (2-D) which, on the one hand will cut the large space (2-D then 5-D) and on the other hand, will receive the projection of the nodes of large space that have been selected by the section
- the orientation of $E_{//}$ (irrational) is such that it is the Penrose tiling, an aperiodic tiling, which will be generated (here, a line paved aperiodically)



- each node of the large space is decorated by an atomic surface which is the convex envelope of the hypercube projected in E_{\perp}

- the cutting method will drive the cutting space (which is also the physical space) to intercept some atomic surfaces, which will be selected to be projected on the physical space



great space 2-D : square

5-D : hypercubic

\downarrow
 E_{\parallel} 1-D

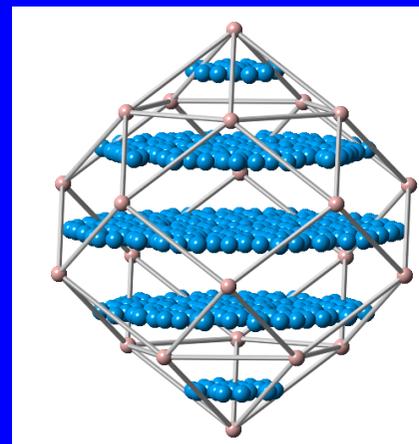
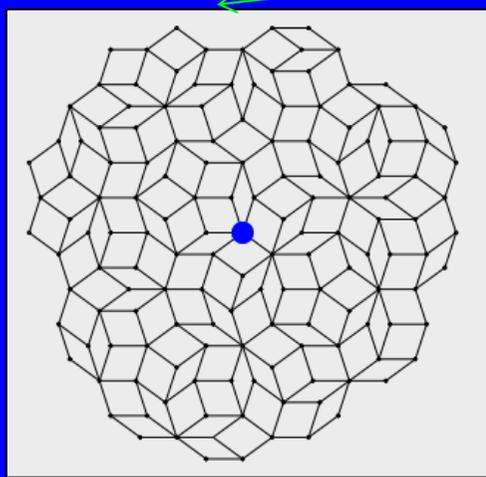
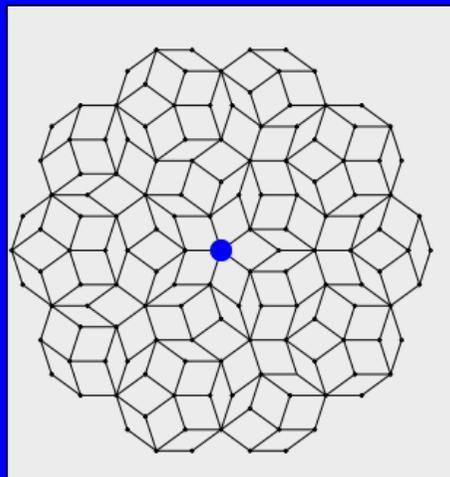
\downarrow
 E_{\parallel} 2-D

aperiodic tiling of a straight line

penrose

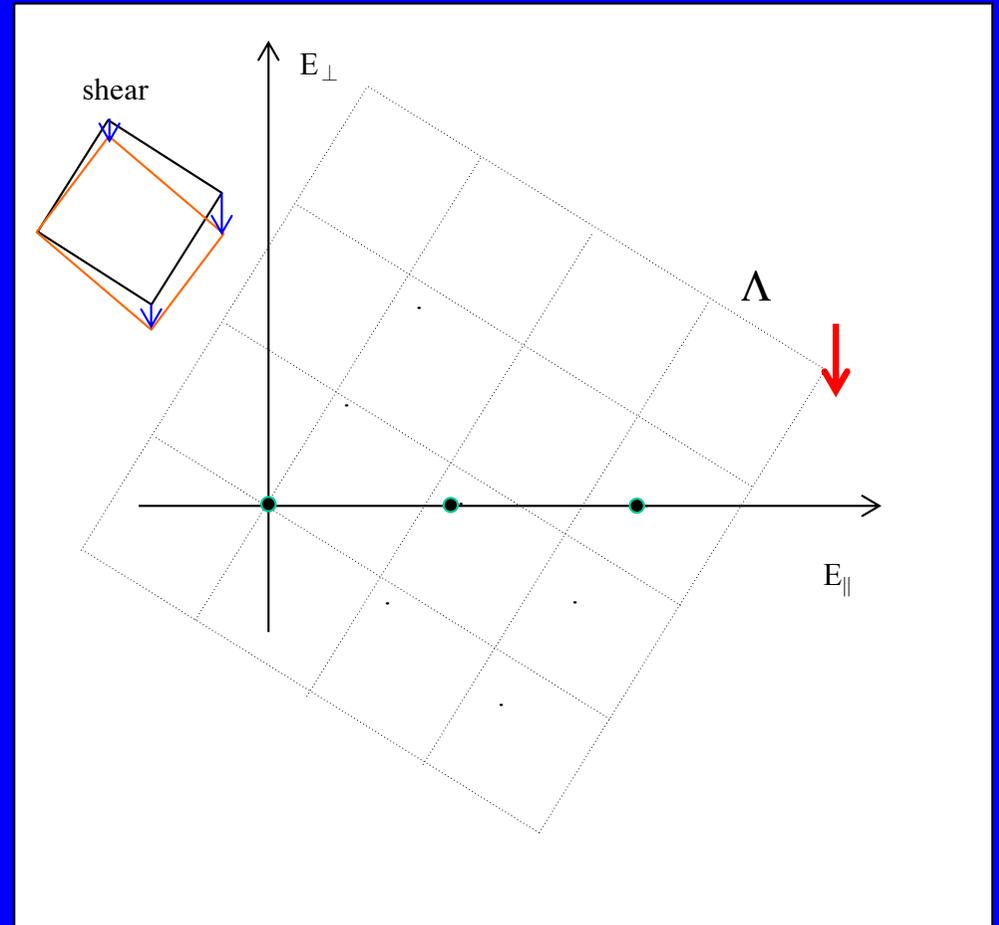
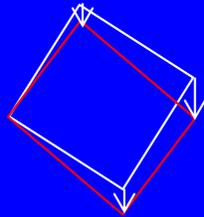
E_{\perp} 1-D

E_{\perp} 3-D



- For a periodic structure

shear parallel to E_{\perp} method



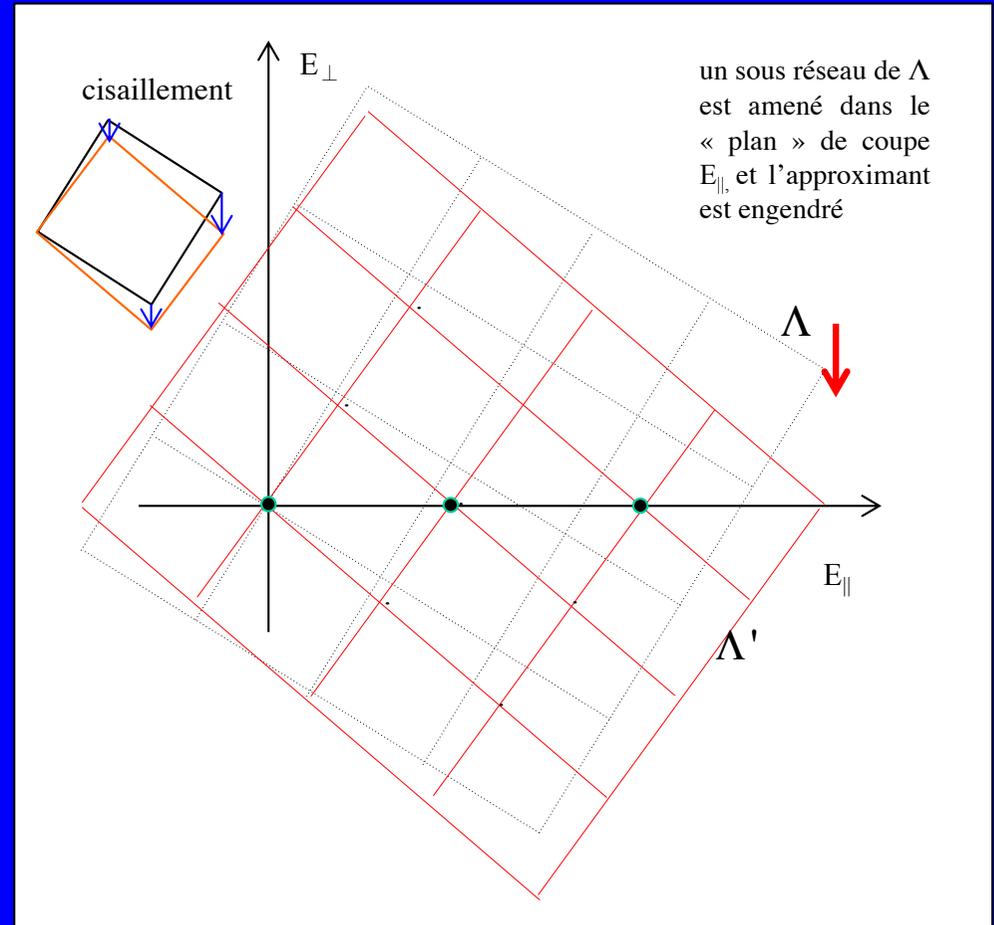
shear parallel to E_{\perp} method

- for that, we will put the vector (2) of the periodic structure in $E_{//}$

: this is the **shear**

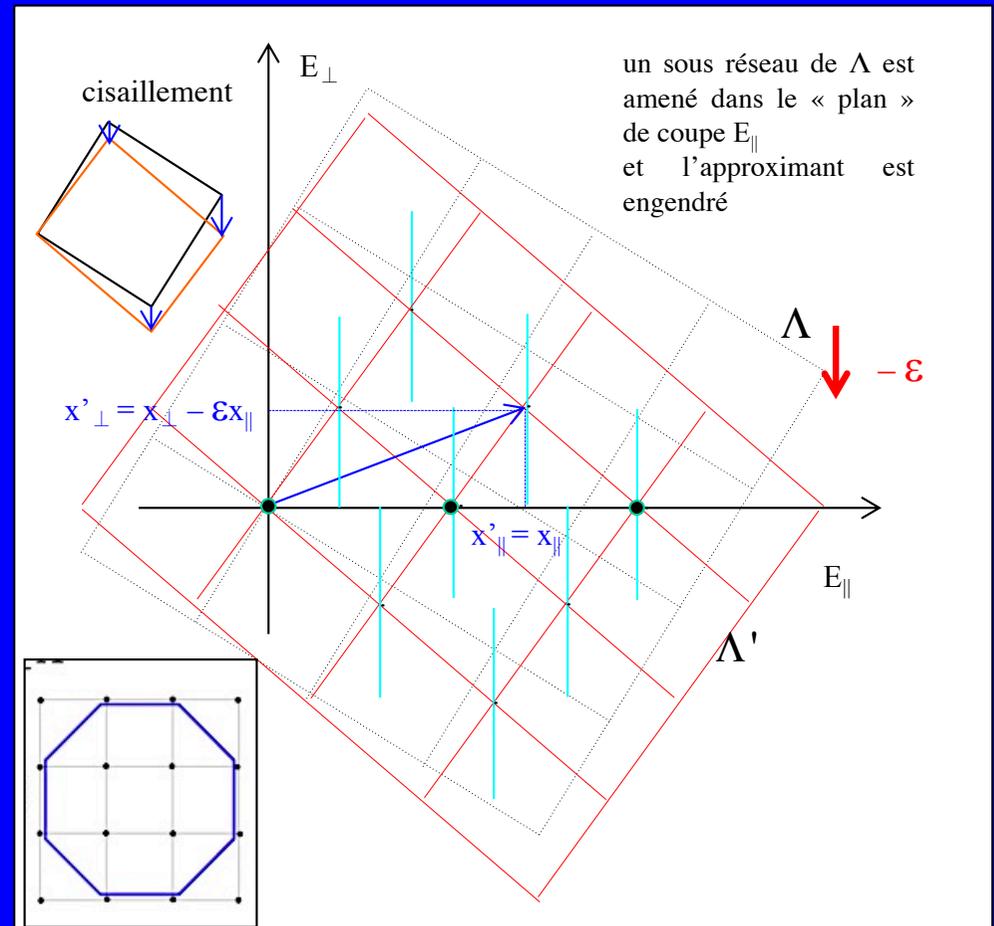
and it will be sufficient to examine the projection obtained to recognize (or not) the phase, the nodes corresponding to the 2 basic vectors and their combinations, and other nodes for the atoms inside the unit cell

- it is not obvious that all the phases can be described like that



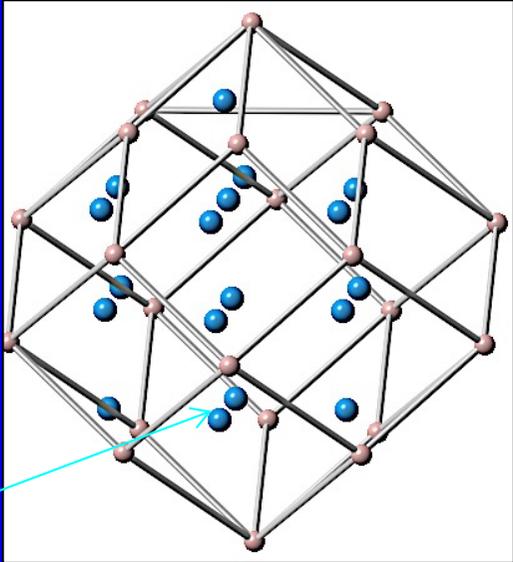
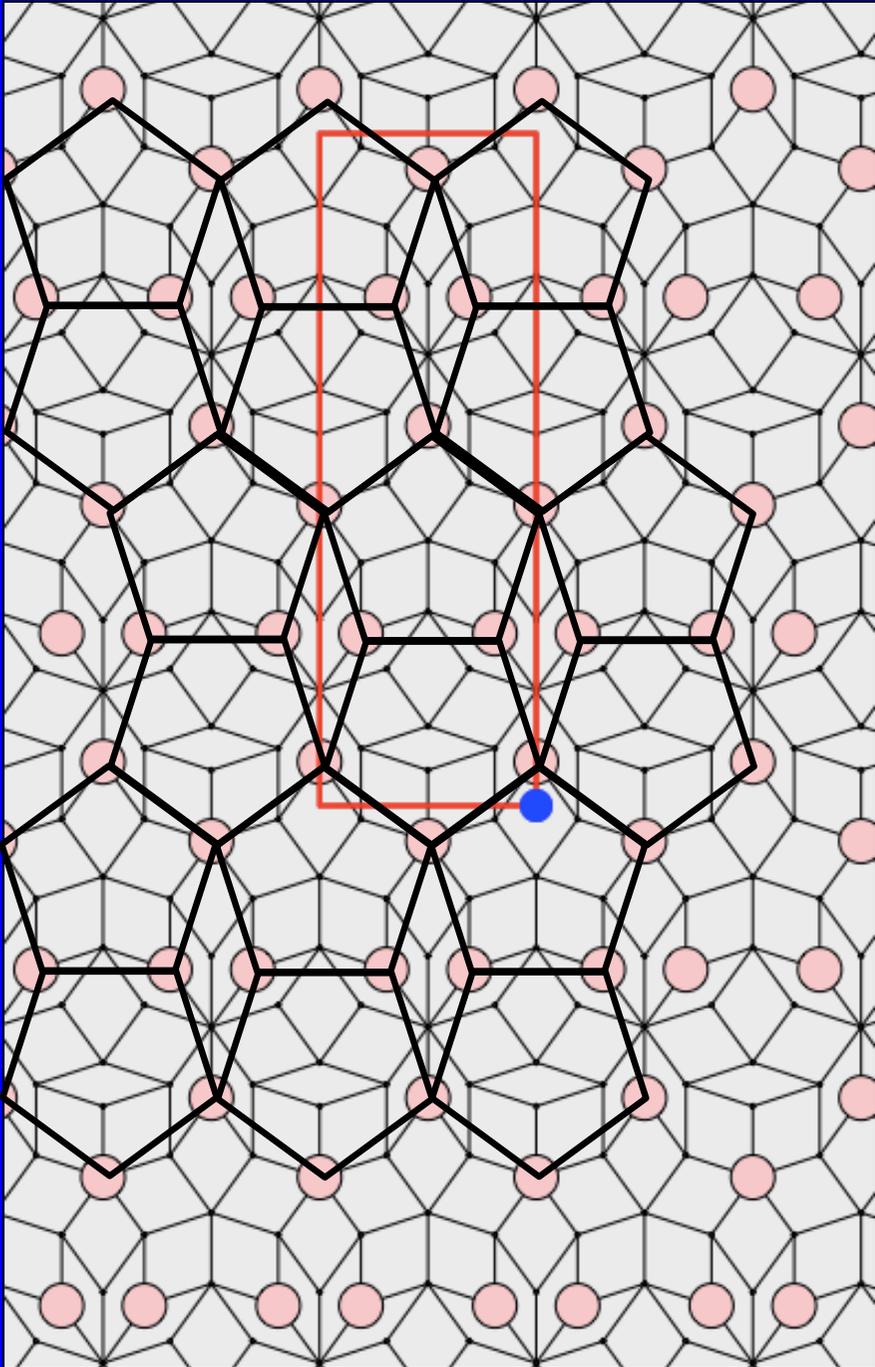
the resulting structure will be a periodic decoration of a Penrose type tiling (with the two rhombus)

- this will respect the projection in E_{\parallel} and so we will keep the same Z -module
- so the tessellation will sit on a periodic assembly of the two Penrose's rhombuses



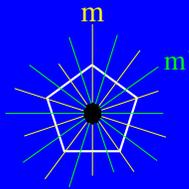
the resulting structure will be a periodic decoration of a Penrose type tiling

$$A=(0 \ -1 \ -1 \ 1 \ 1), B=(4 \ 1 \ -3 \ -3 \ 1)$$



Dürer tiling: twin description

the twin is characterized here by the invariance of the regular pentagon (and its inverse) : the two individuals share the same kind of pentagons.



$$N_{Z_5} = 10\text{mm} (20)$$

$$G_{\text{Dürer}} = 2\text{mm} (4)$$

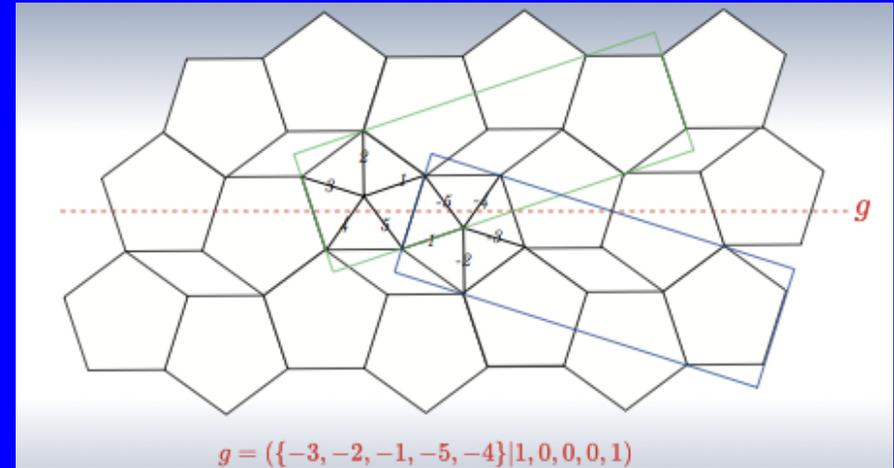


$$20/4=5$$

$$I = 2\text{mm} (4)$$

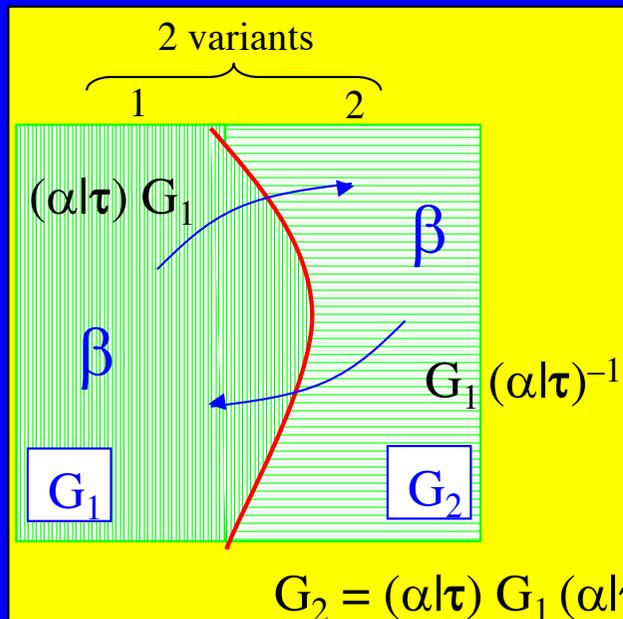
twin classification (Georges Friedel, 1904)

- (i) merohedral twins where the crystals share the same **lattice**
- (ii) twins by reticular merohedry where the crystals share only a fraction (sublattice) of the crystal lattice
- (iii) pseudo-merohedral twins or twins by reticular pseudomerohedry where the previous definitions are satisfied only approximately.



$$\mathbf{h} = \begin{pmatrix} 0 & 0 & \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 & 0 & 0 \\ \bar{1} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \bar{1} \\ 0 & 0 & 0 & \bar{1} & 0 \end{pmatrix}, \hat{\mathbf{h}} = (\mathbf{h} | 1, 0, 0, 0, 1)$$

glide mirror



- *H invariant group* $H = G_1 \cap G_2 = G_1 \cap (\alpha\tau) G_1 (\alpha\tau)^{-1}$

- *exchange operation set* $\mathcal{E} = (\alpha\tau) G_1 \cap G_1 (\alpha\tau)^{-1}$

- *bicrystal group (2 colors)* $\mathcal{S} = H \cup \mathcal{E} = H + \varepsilon_1 H$

$$(\alpha\tau) G_1$$

$2\pi/10$ rotation

Dürer-like structures can easily be found using identical regular polygons of order n connected by edges

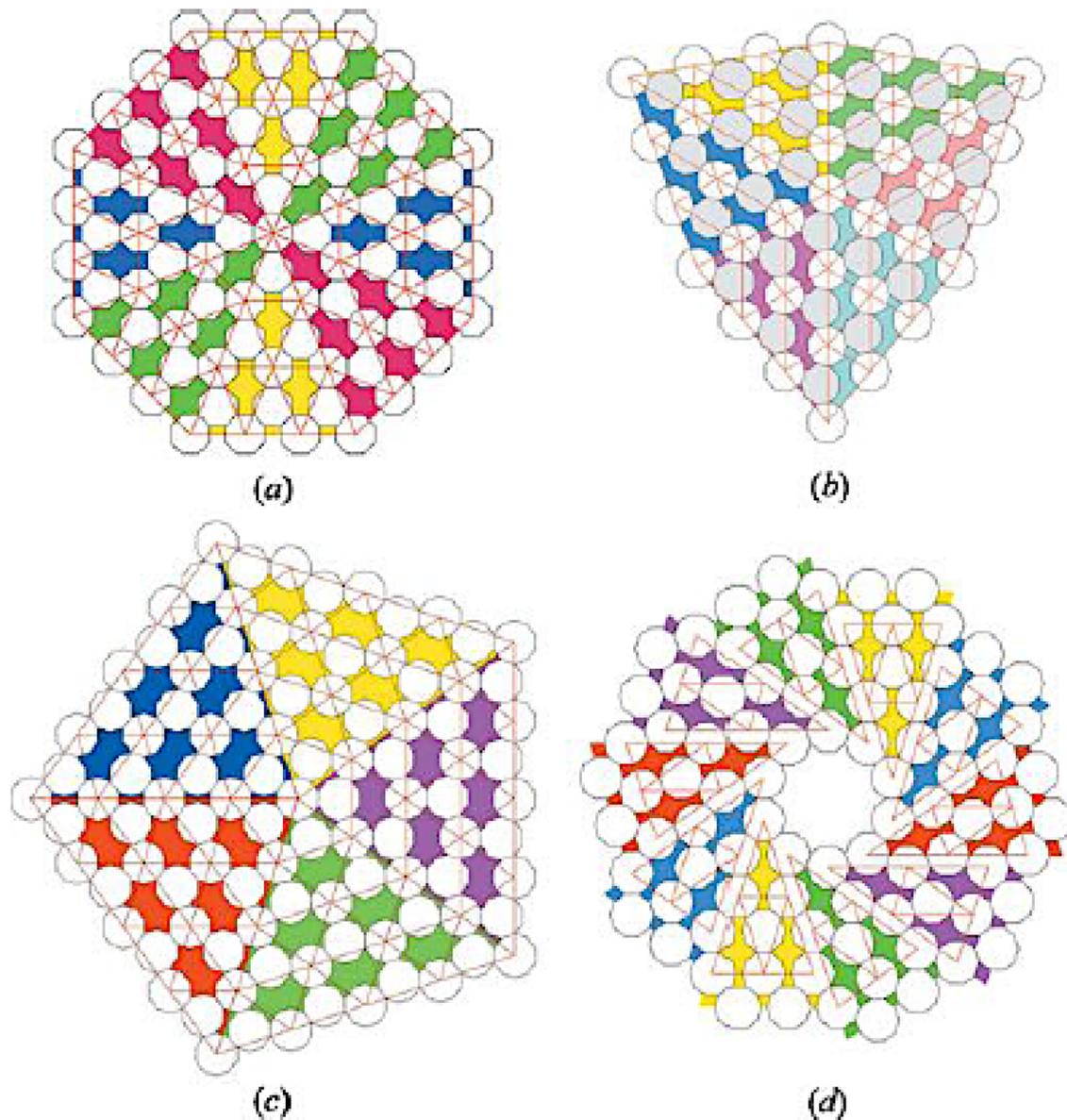


Figure 9

Examples of Dürer-like multiple twins for the (a) 8-gon (1, 2, 2), (b) 9-gon (1, 2, 3), (c) 10-gon (2, 2, 3) and (d) 10-gon (1, 3, 3) structures. In each drawing, the twinned crystals are built with the same n -gon.

Alloys (quasicrystals, approximant structures, ...)

considérations sur les structures

→ polyedron description

→ high compacity

structure metallique

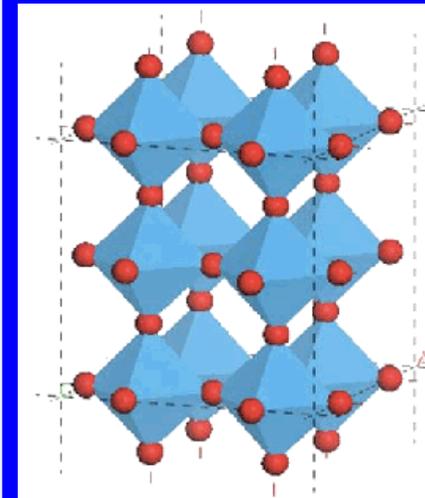
- space group
- elementary cell
- nature and coordinates (Wyckoff positions) of atomes

oxydes structures

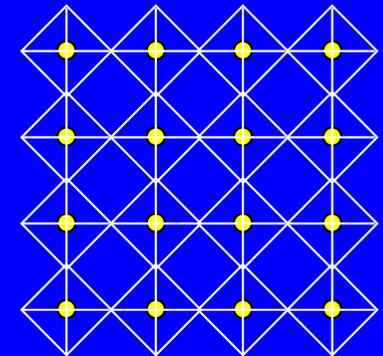
- elementary polyedron MO_x
- polyedron linkage

complex metallic structures

- many complex intermetallic phases (periodic or quasi-periodic) have structures whose atoms are located on a fraction of the nodes of a Z-module
- they will be referred as alloys based on Z-module
- they will be generated by the standard cutting method.



WO₃



metallic structures

spheres stacking

metallic cations
+
nearly free electrons

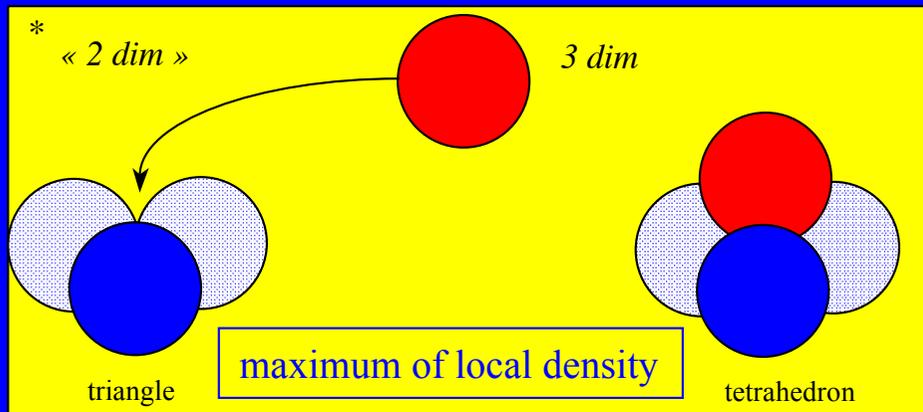
structure

metallic bond = non directional

Laves rules

- highest local density
- space filling
- highest coordination
- highest symmetry

same diametes



tetrahedron {3, 3}

$\rho = 0,78$

impossibility to fill up
the space
=
geometrical frustration



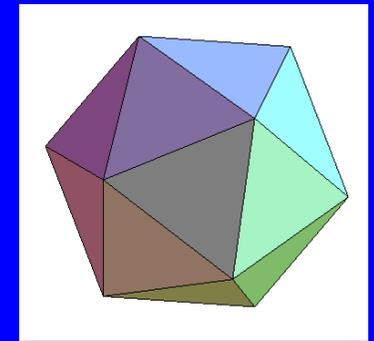
alloys → spheres diameter slighty different

CFC
HC $\rho = 0,74$

- cuboctaedron (CFC, $R = 1$) $\approx R = 1$

- icosaedron ($R = 1$ et) $\approx R = 0,902$

→ highest compacity →

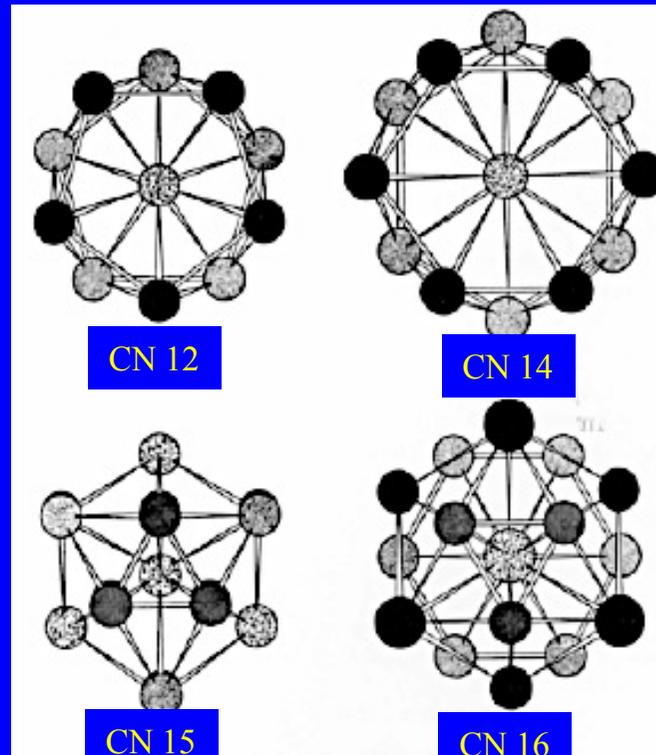


triangular faces

tetraedra interstices
slightly deformed

other possible coordinations

it becomes possible to fill
space with only these slightly
'distorted tetrahedra



4 Frank Kasper
polyhedra

→ complexe intermetallic phases

icosaedric quasicrystal

icosaedric clusters in metallic glasses (SRO)
and melt alloys

*icosaedron = important
cluster for metallic
structures*

experimental results

Denis Carron PhD 1995

nuclear reactor
(water under pressure)
316 L stainless steel

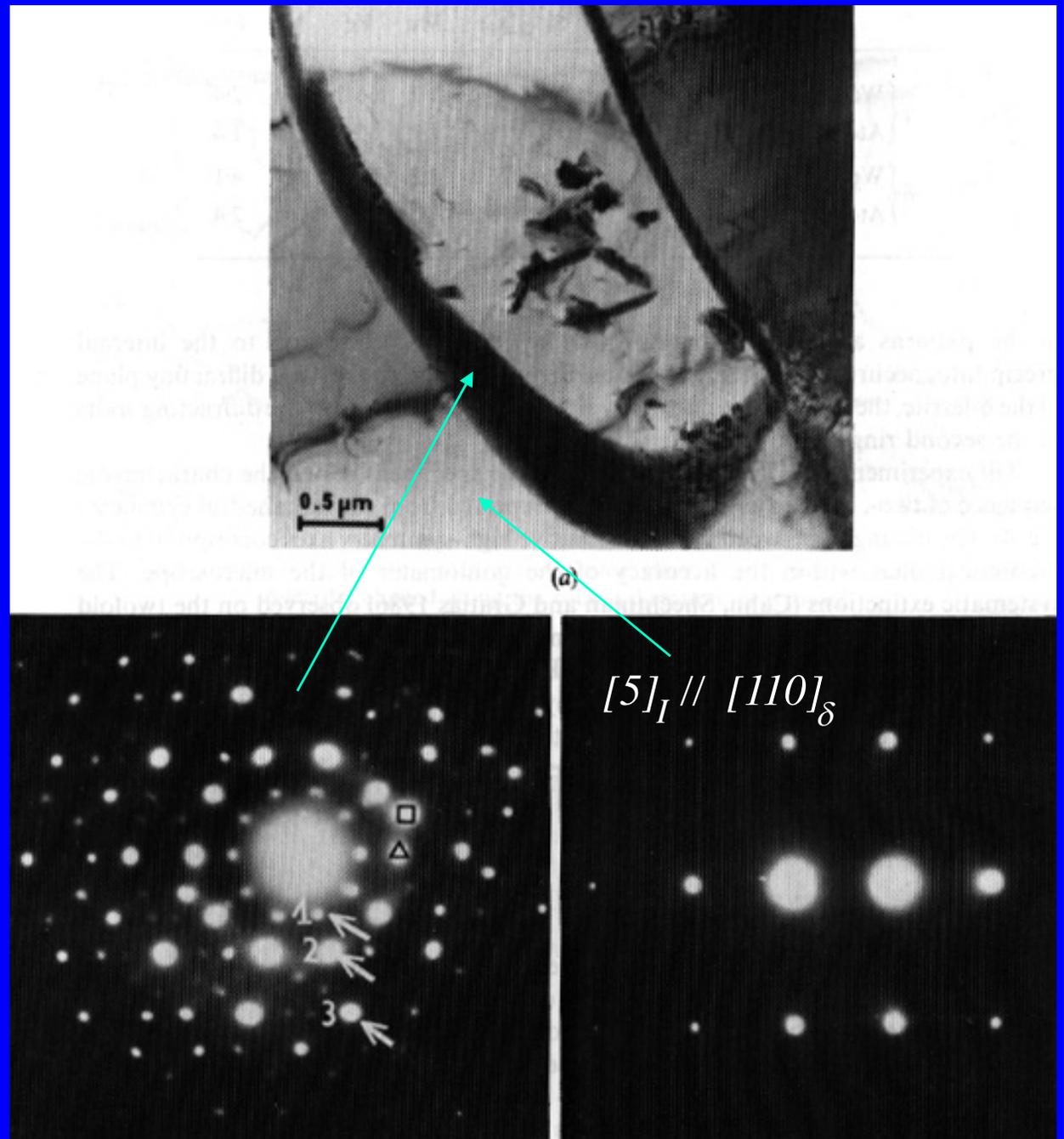
ferritic (29Cr-4Mo-Ti)

+ 550 ° C 100 H
 γ/δ interface

chemical analysis

Fe-29%Mo-12%Cr-8.5%Ti

FAST SOLIDIFICATION



ico-phase ?



HREM

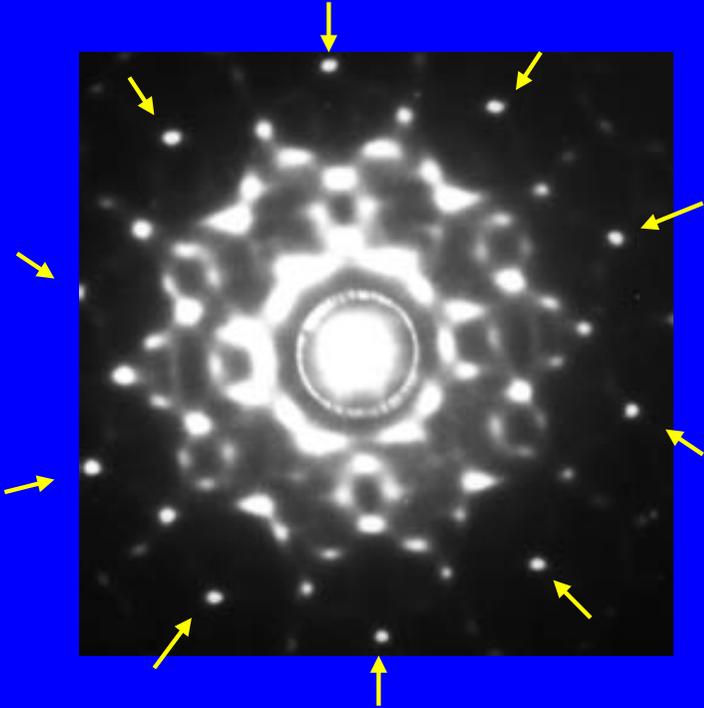
nanodomains of periodic crystals
high density of faults

→ Bragg peaks

= [5], [10]
order at short distance

diffuse diffusion

= disorder at long distance



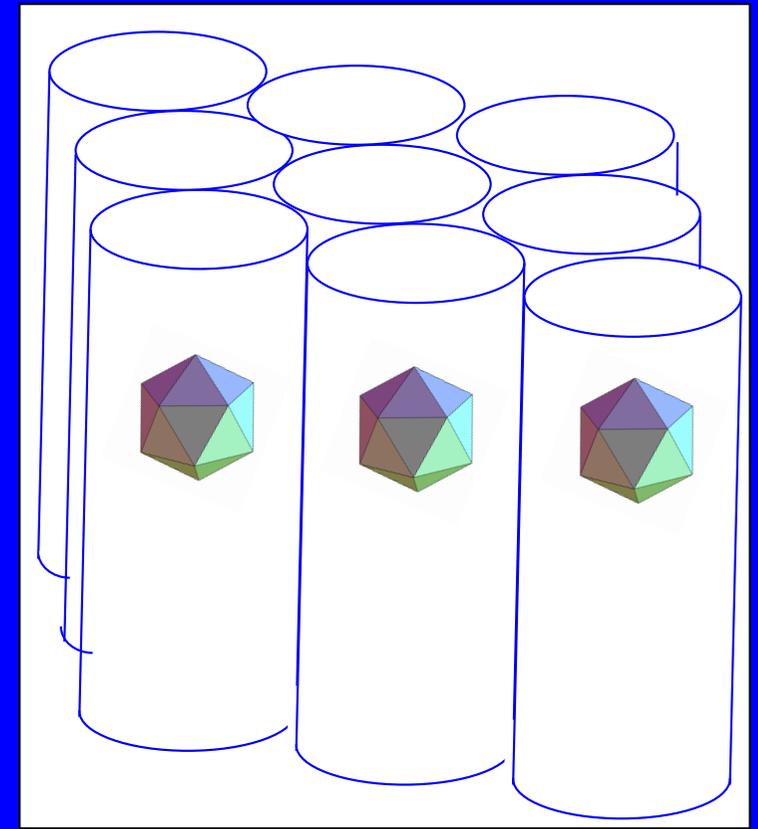
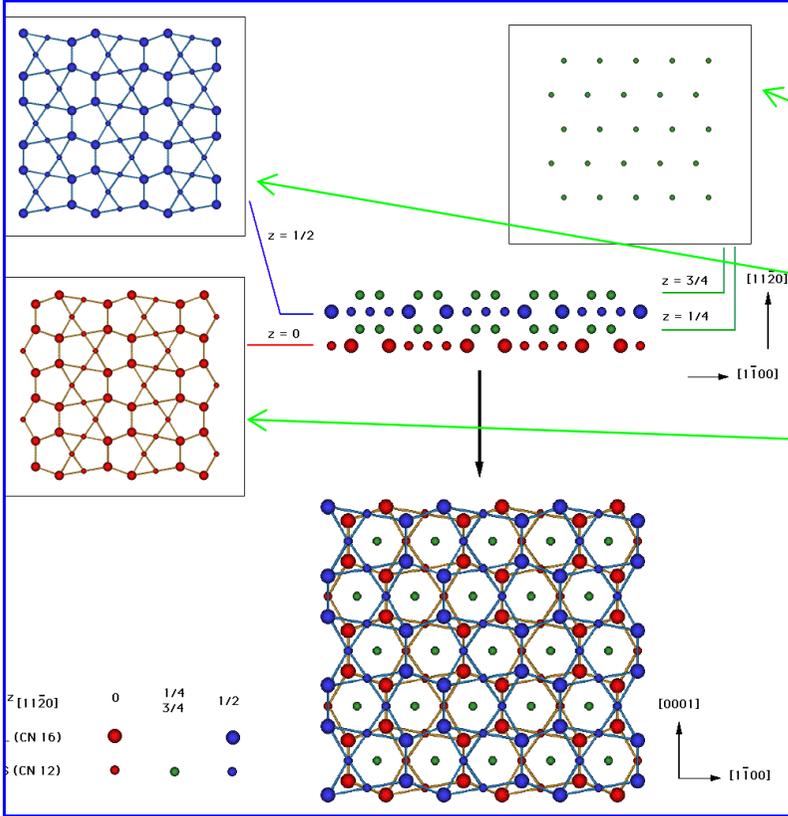
SA diffraction (diameter 1 μm)

tetrahedrally close-packed metallic phases

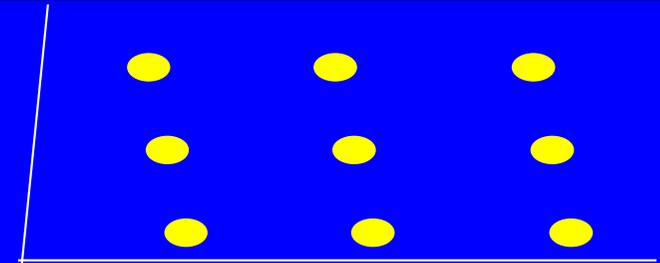
Laves phase
C14

best compacity

local [5] symmetry



2-D tessellation
of the icosahedral
columns



pertinent description
of the structure

C 14 structure
+ fautes

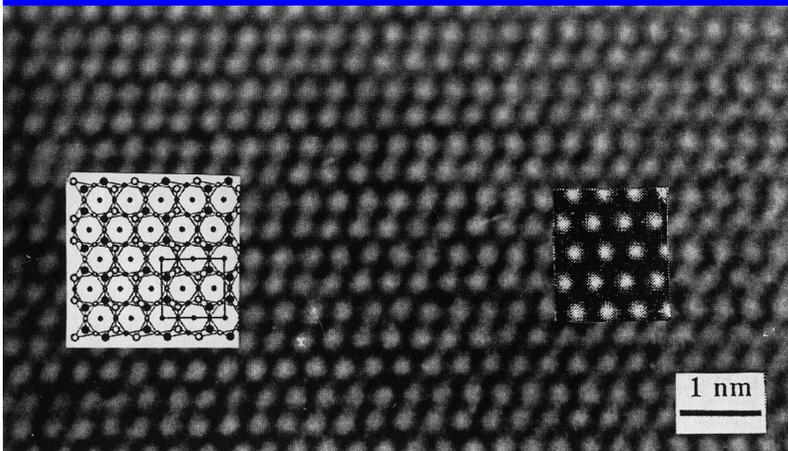
simulation (JEMS)

1/1 correspondance

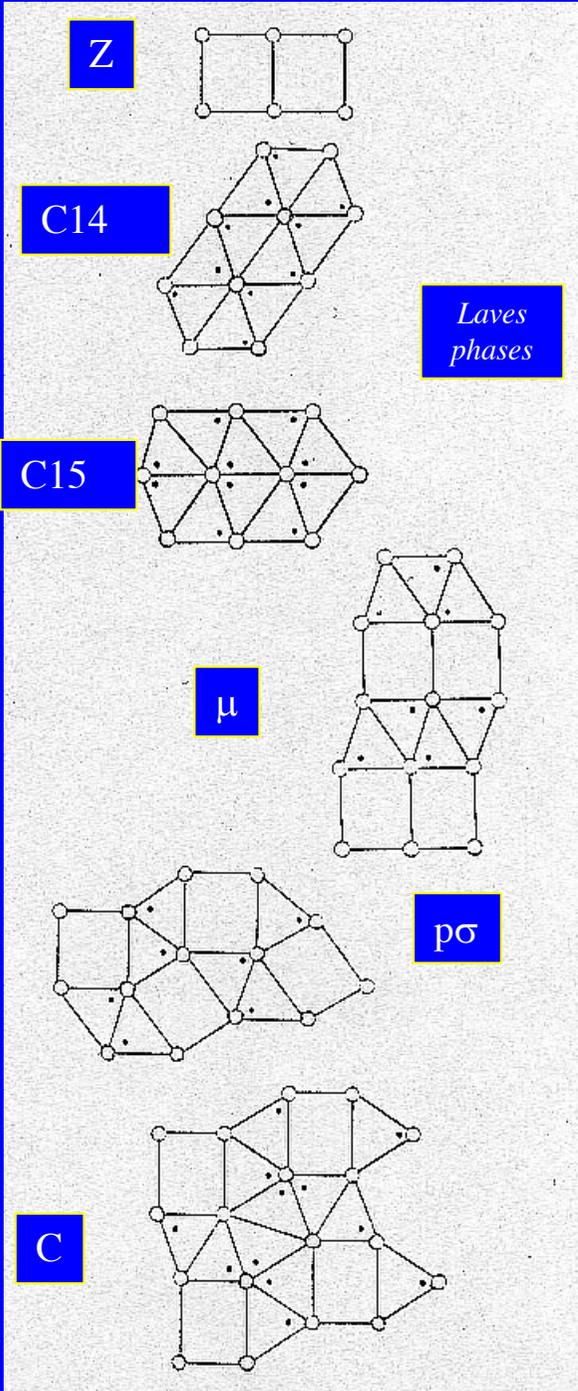
white spot



icosahedra columns



Frank-Kasper phases



2-D tessellation
of the icosahedral
columns

only permitted
connections by

edges

longer
length

triangular faces

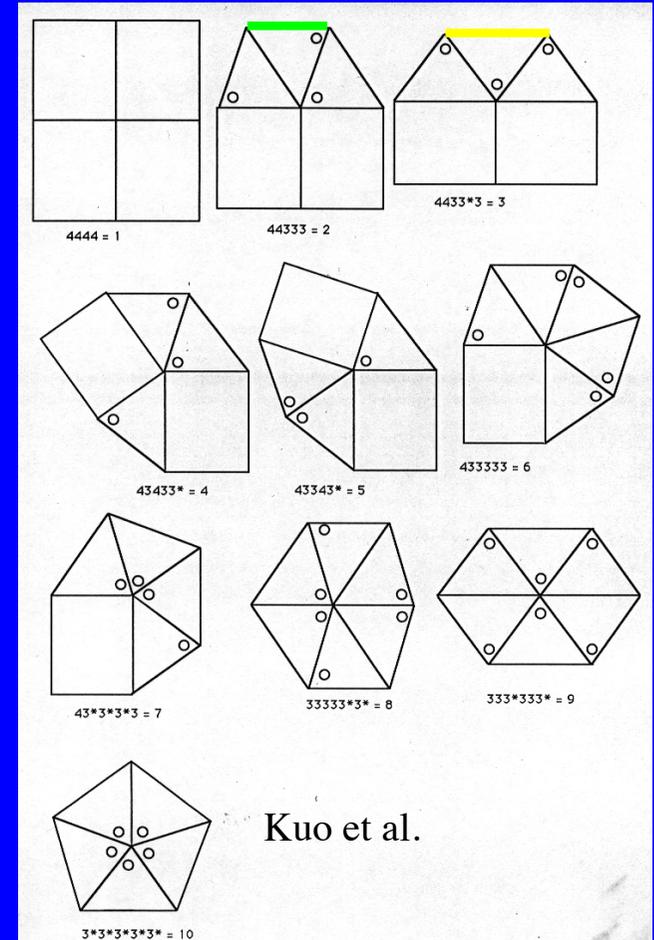
smaller
length

tessellation =

{triangles + rectangles}

symétrie quinaire contrôle la tessellation

possible incidences



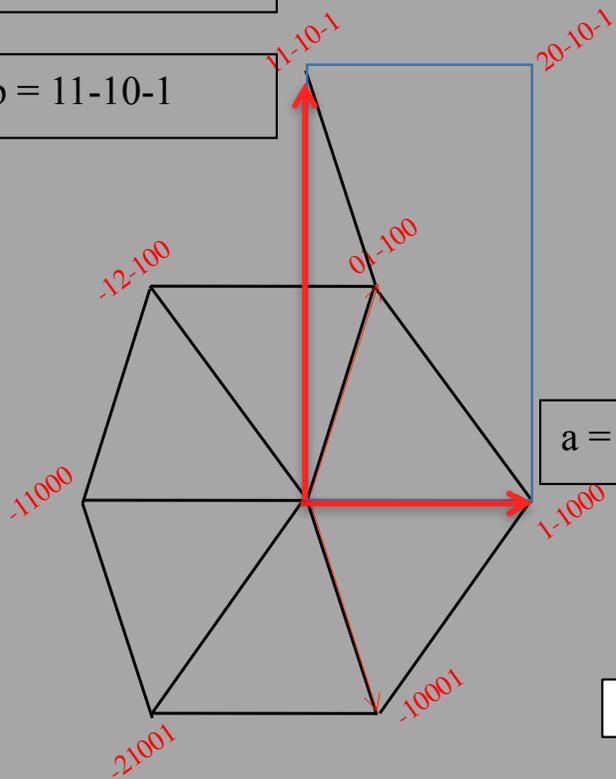
Kuo
(IMR) Shenyang

phase C14

$b = 11-10-1$

maille $a = 1-1000$
 $b = 11-10-1$

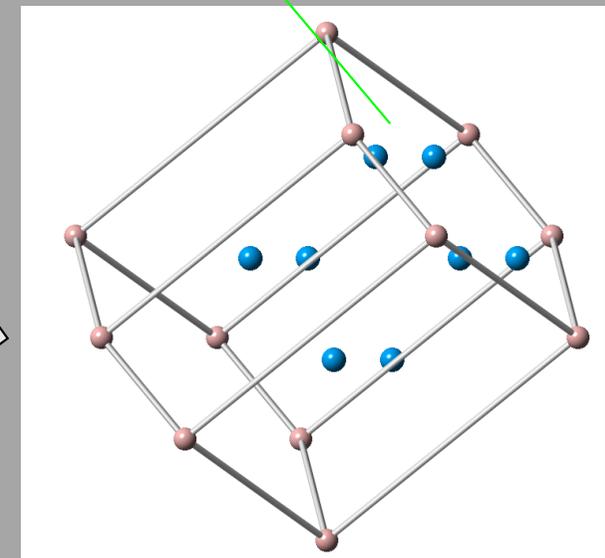
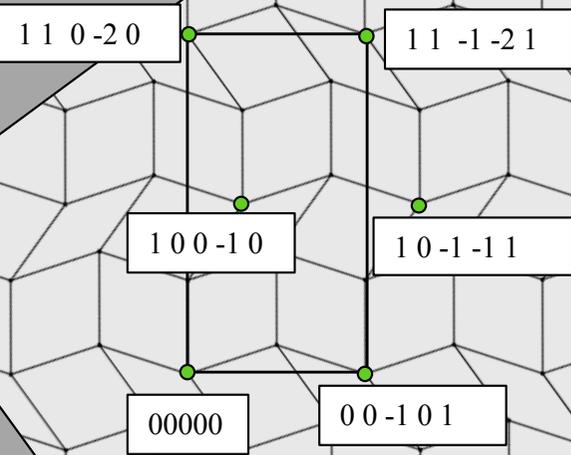
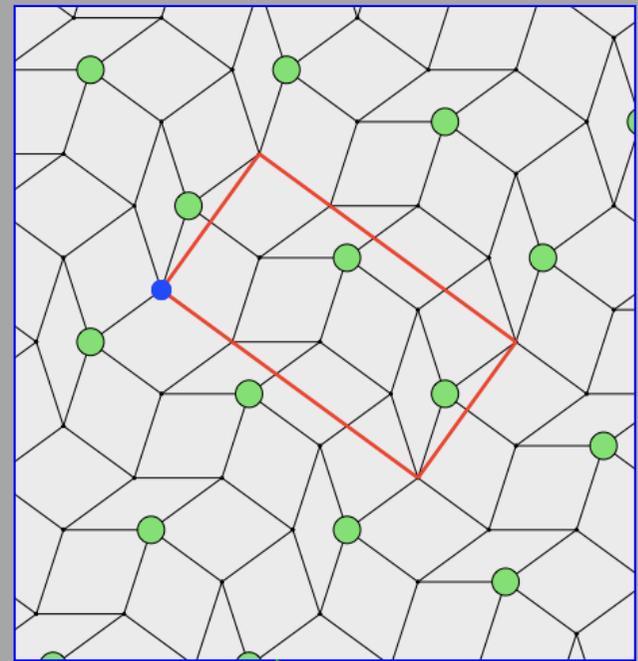
motif à 2 « atomes » en
00000
01-100



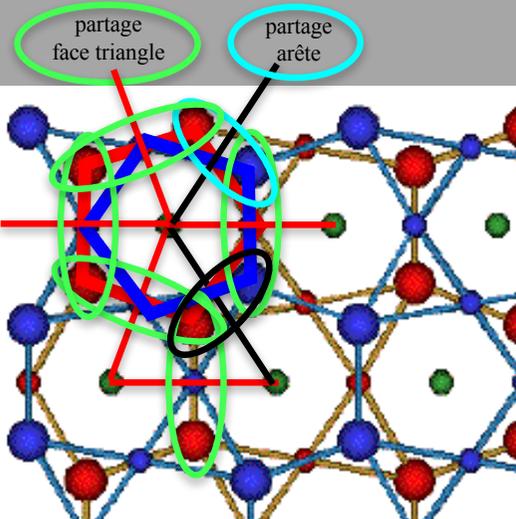
$a = 1-1000$

$\times \tau$

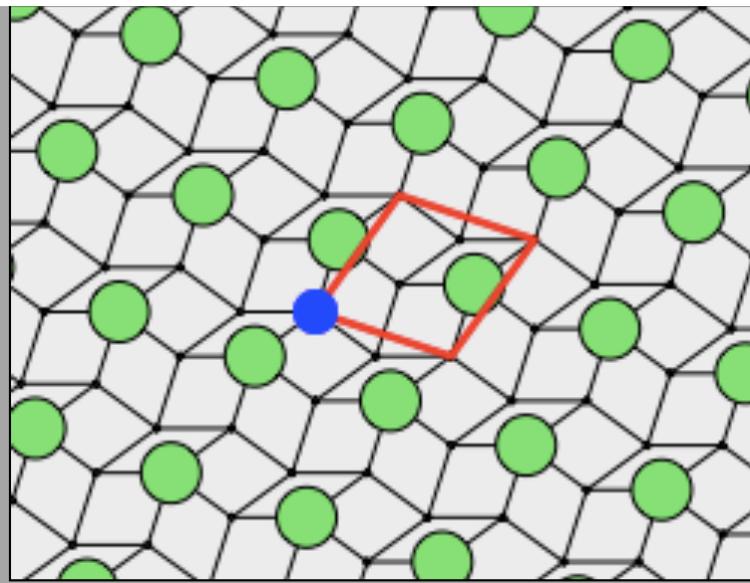
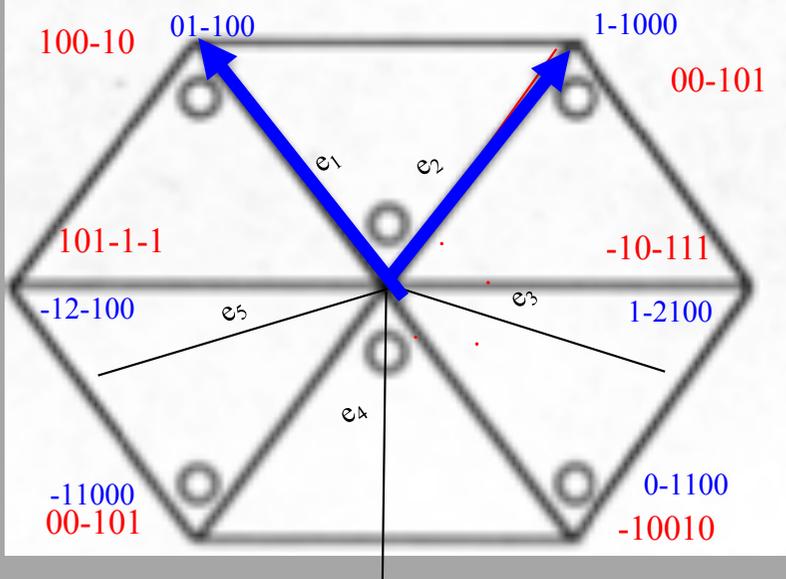
$E_{//}$



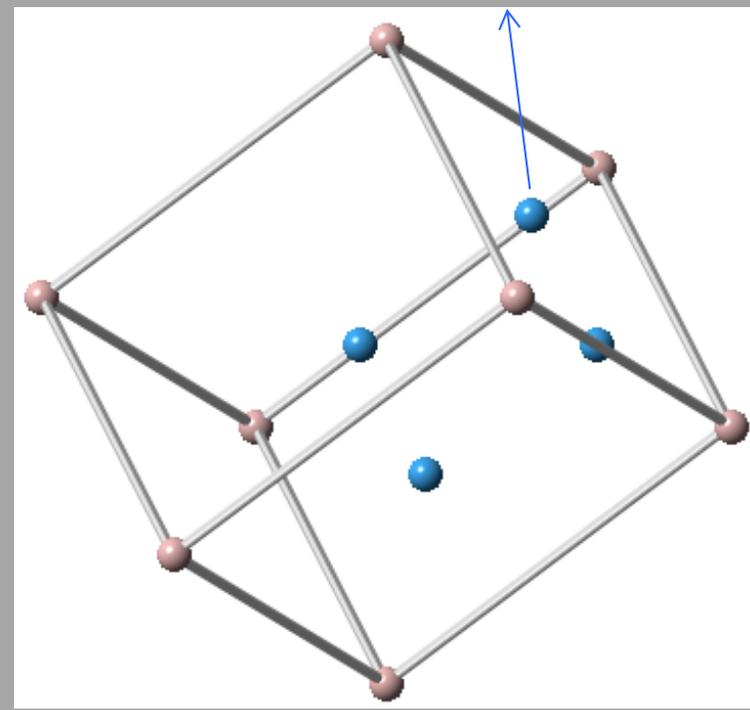
E_{\perp}



phase C15

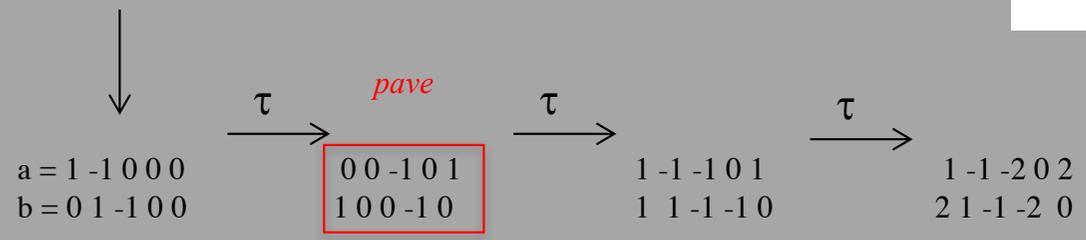


$E_{||}$



E_{\perp}

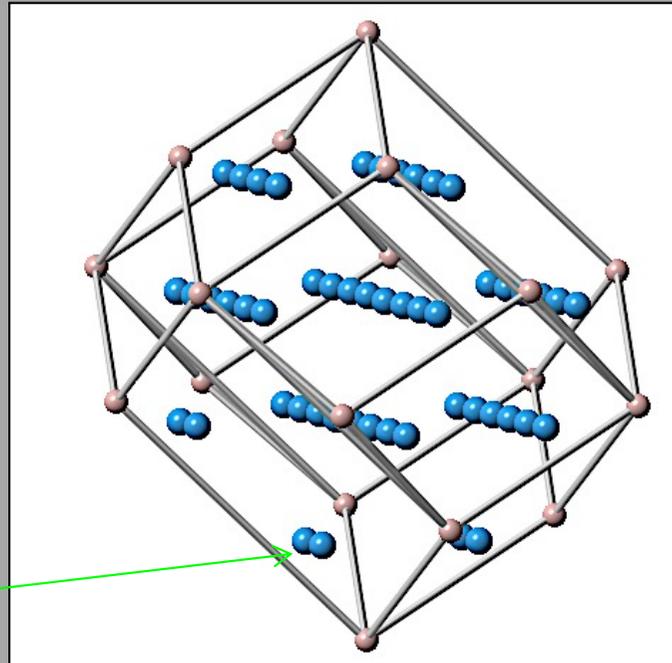
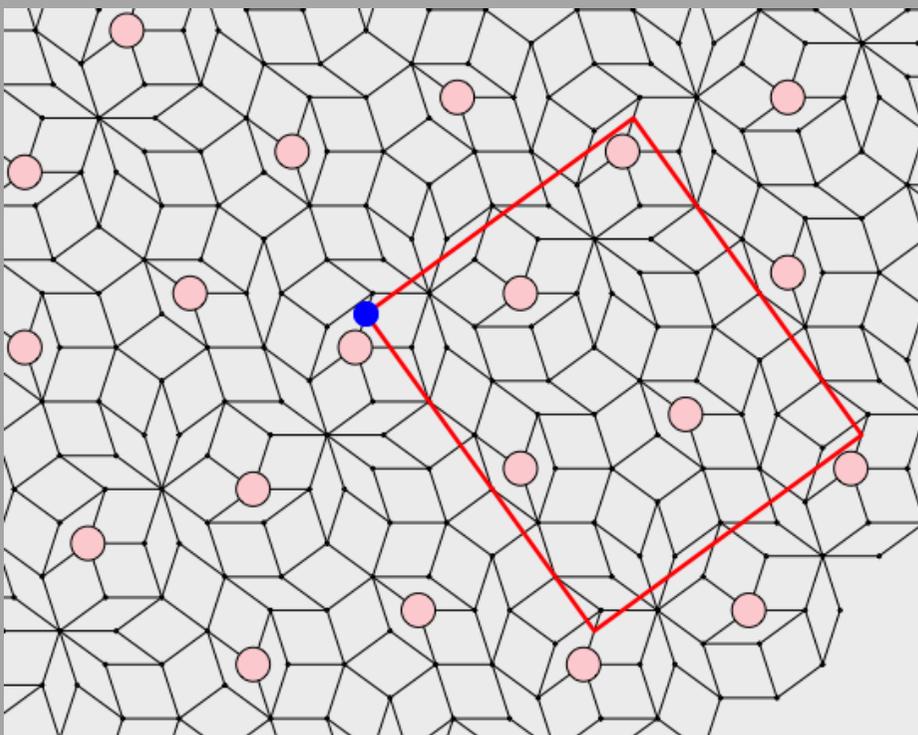
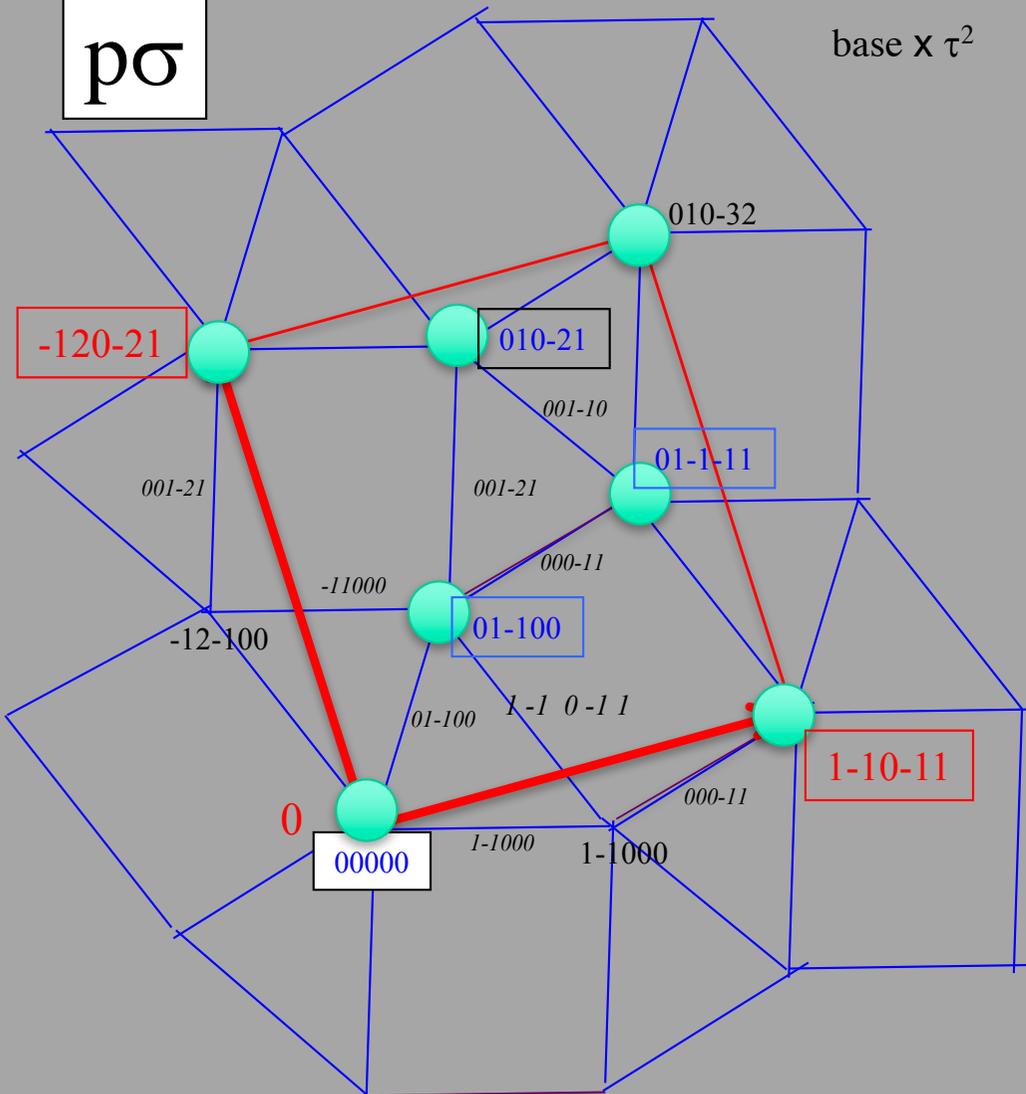
ne pave pas



- $n_1 + n_2 + n_5$
- $n_1 + n_2 + n_3$
- $n_2 + n_3 + n_4$
- $n_3 + n_4 + n_5$
- $n_1 + n_4 + n_5$

$\rho\sigma$

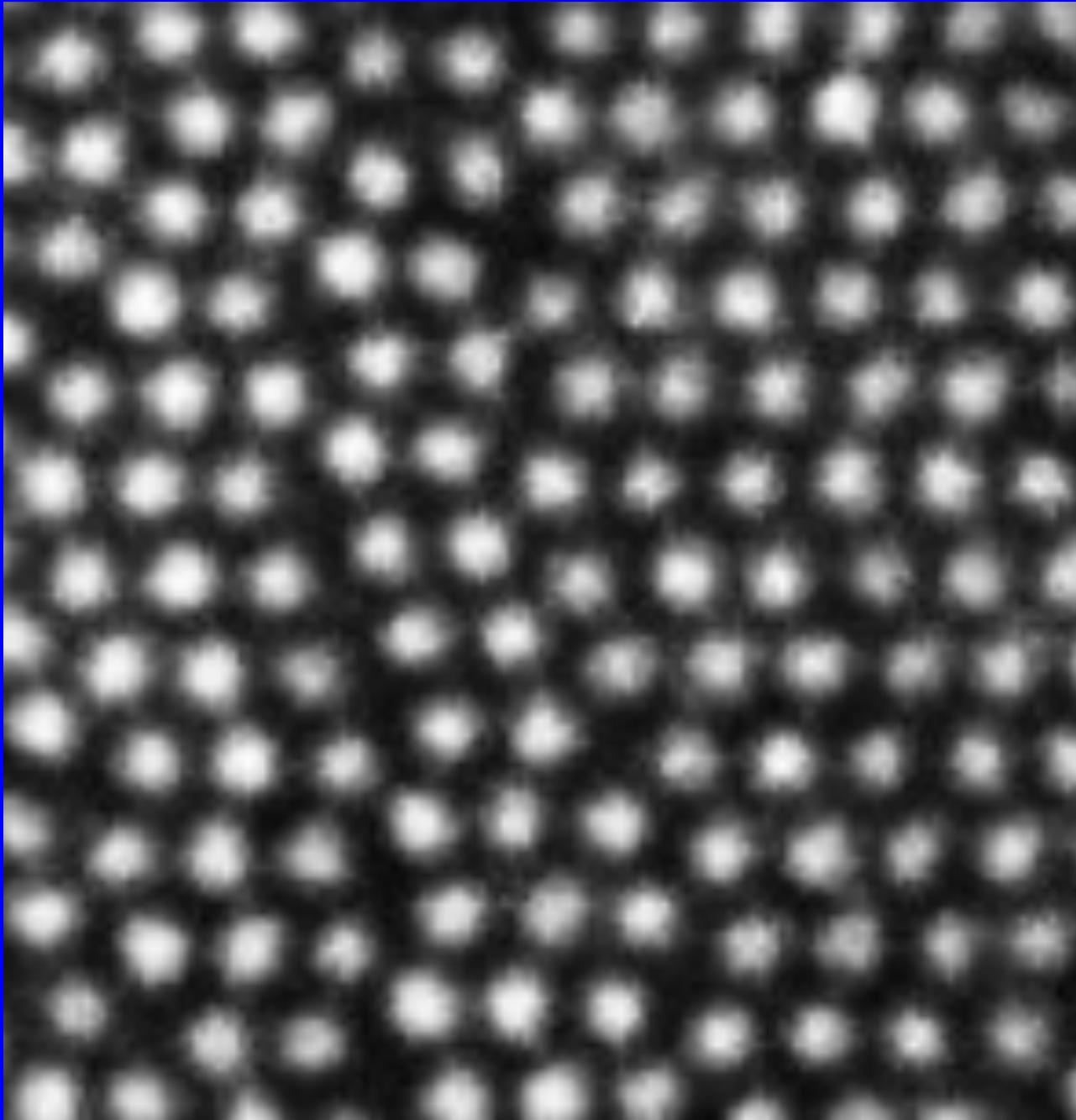
base $\times \tau^2$



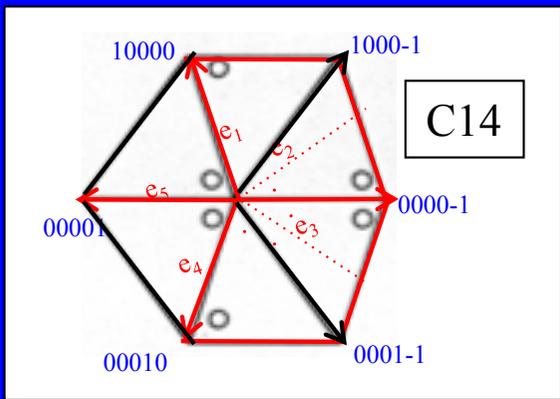
ne pave pas

	τ	τ	τ	
a = 1 -1 0 -1 1	→	1 0 -2 0 1	→	2 -1 -2 -1 2
b = -1 2 0 -2 1	→	2 1 0 -1 -2	→	1 3 0 -3 -1

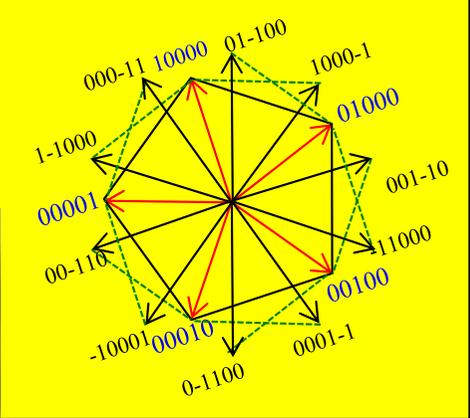
pave



1 nm



C14



C14

C14

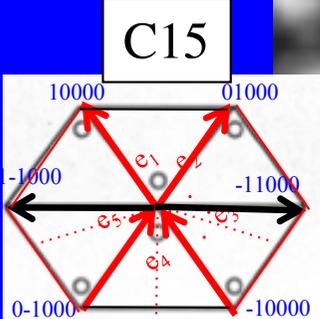
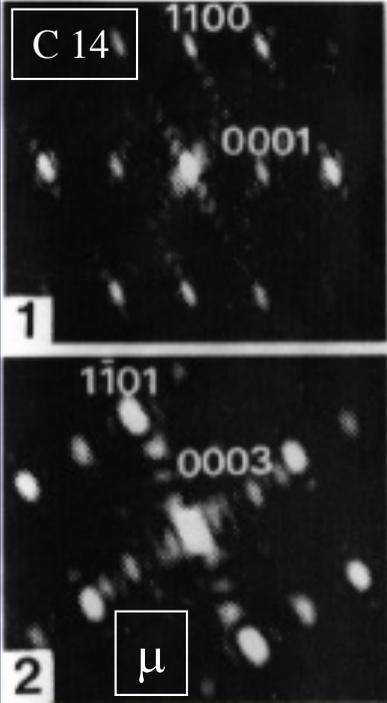
C15

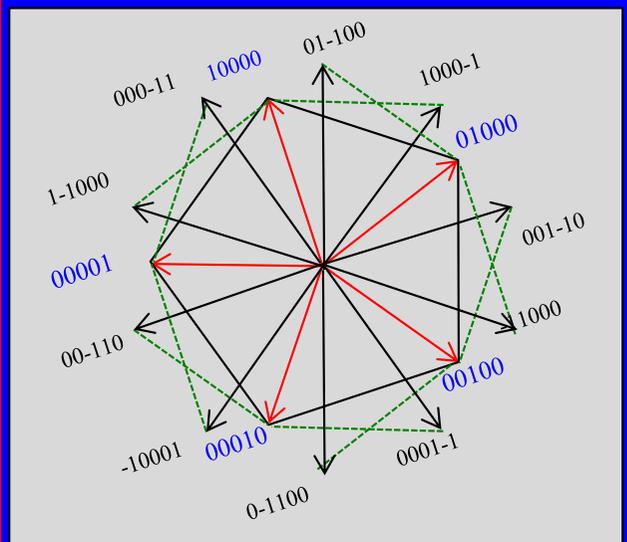
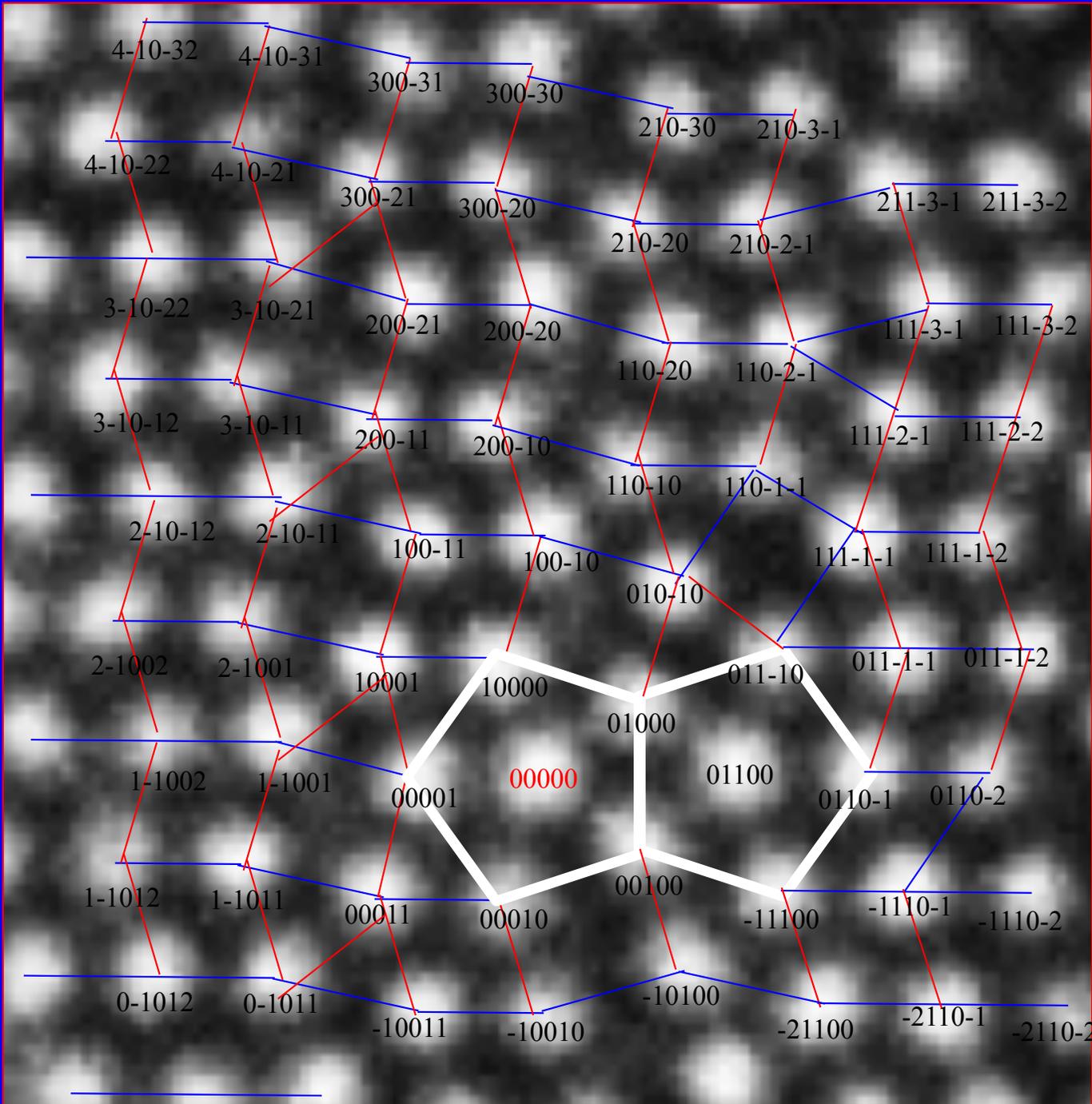
C15

C14

Z

μ





2 pentagons

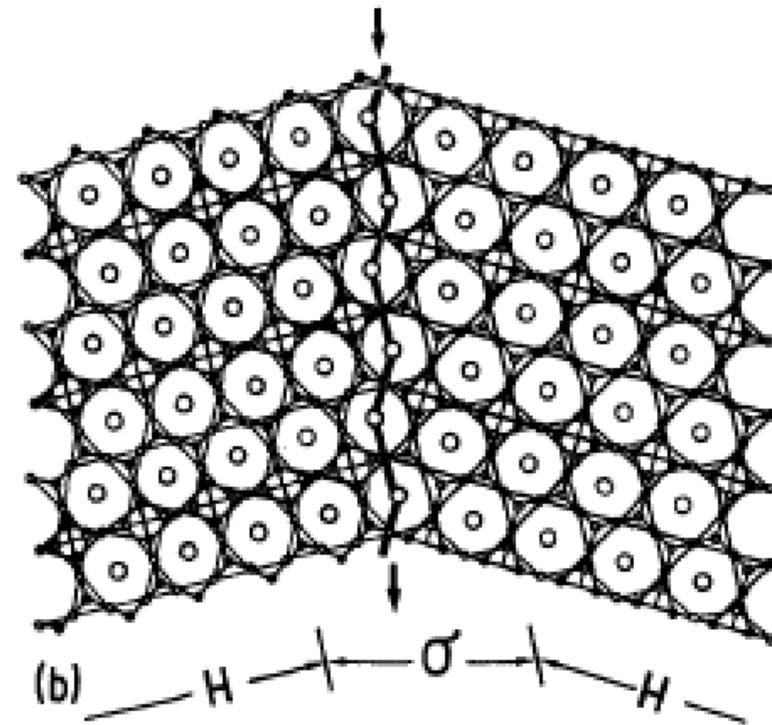
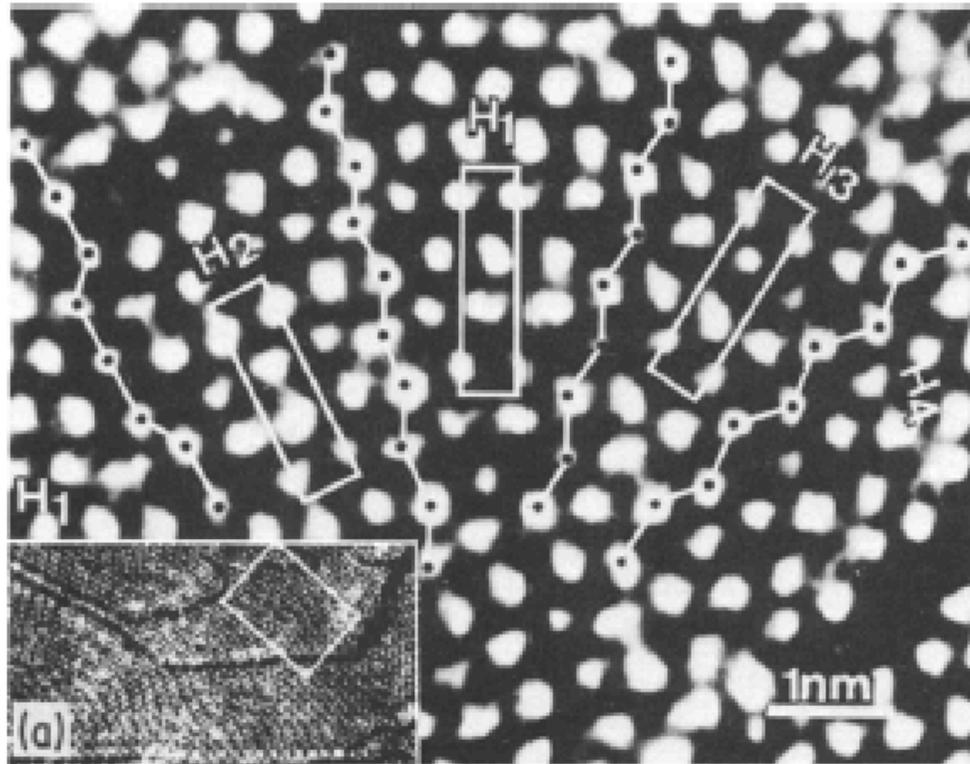
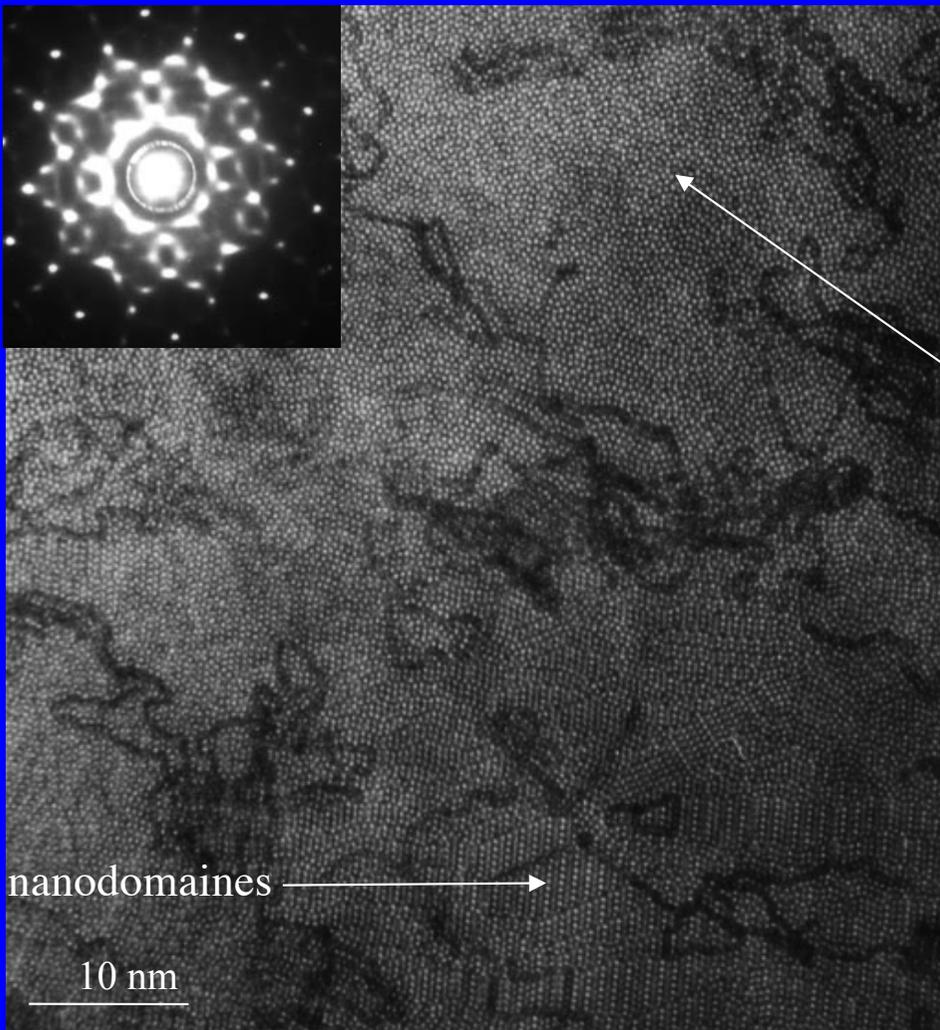


Figure 42 (a) Structural image of fan-like successive rotation domains of H, and (b) its structure model. σ appears also at the rotation domain boundary.

Tetrahedrally close-packed phases in superalloys: new phases and domain structures observed by high-resolution electron microscopy

K. H. KUO, H. Q. YE, D. X. LI

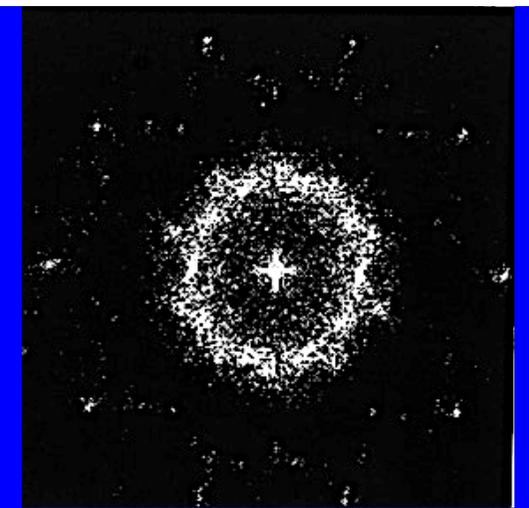
JOURNAL OF MATERIALS SCIENCE 21 (1986) 2597-2622



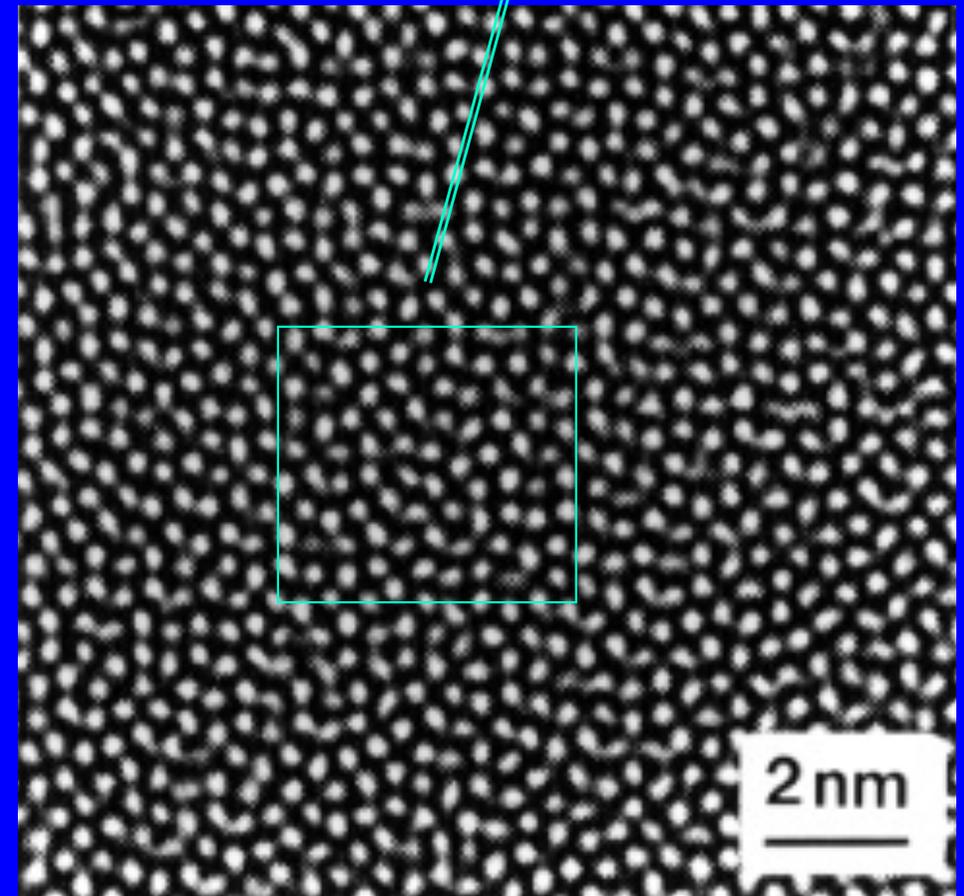
disordered
region

nanodomains

10 nm



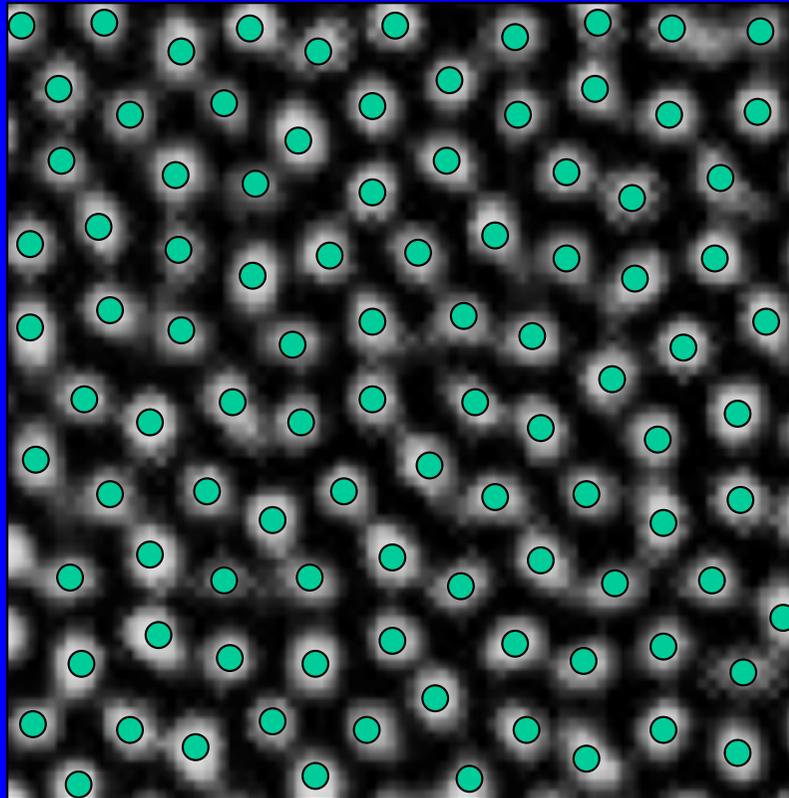
power spectrum
pseudo [5]



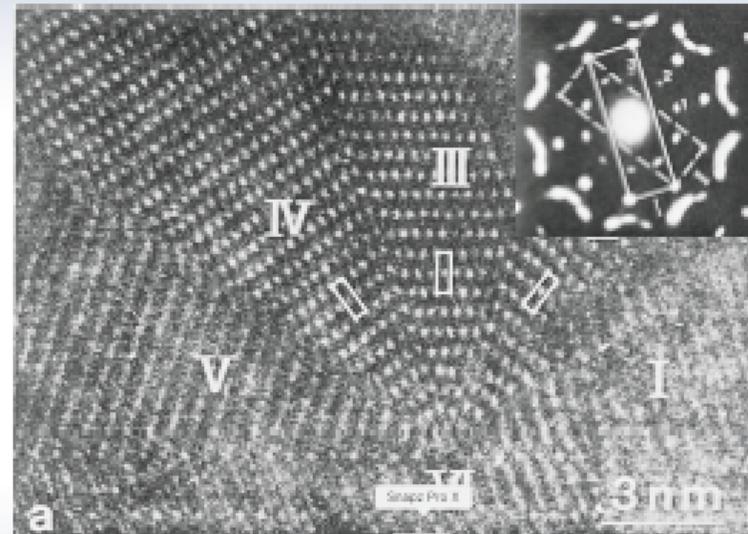
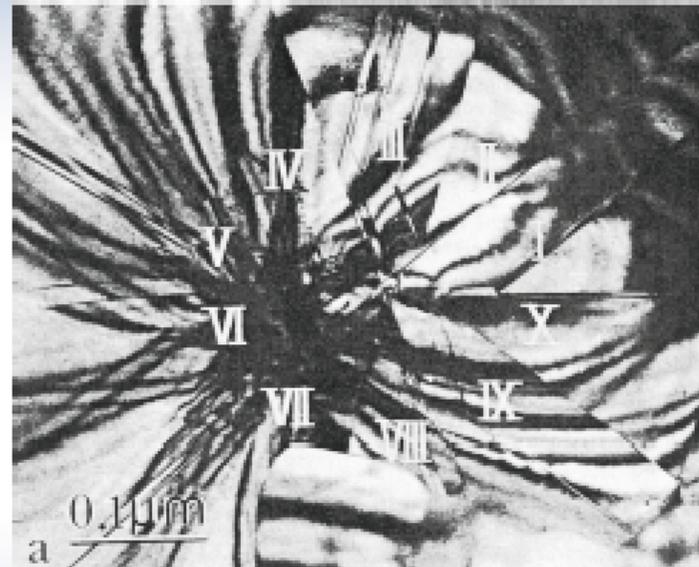
hidden order:

- no translation invariance
- hidden orientational order (controlled by CN 12)

disordered distribution, no 2-D base leads to the indexing
of all these nodes with a doublet of integer numbers !



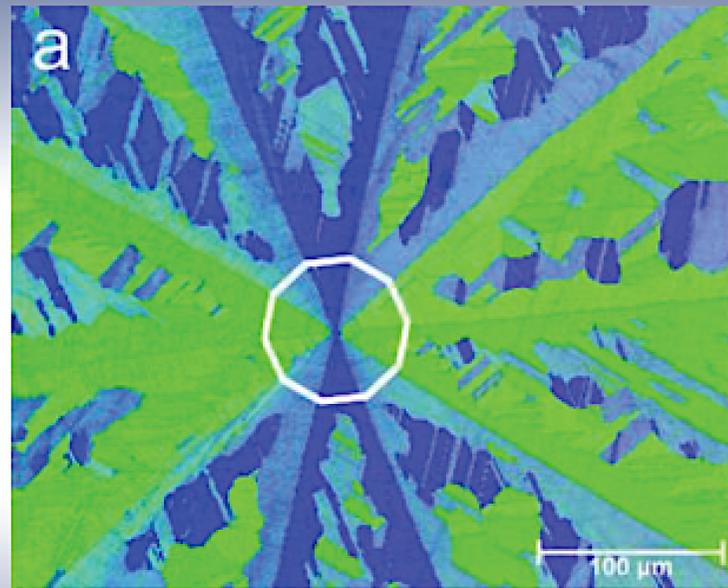
NiZr alloy



Jiang, W. J., Hei, K., Guo, Y. X. and Kuo, K. H. (1985), *Phil. Mag. A* 52:6, L53–L58.
Bouzy, E., Le Caer, G. and Bauer-Grosse, E. (1991) *Phil. Mag Lett.* 64 n1, 1–6.

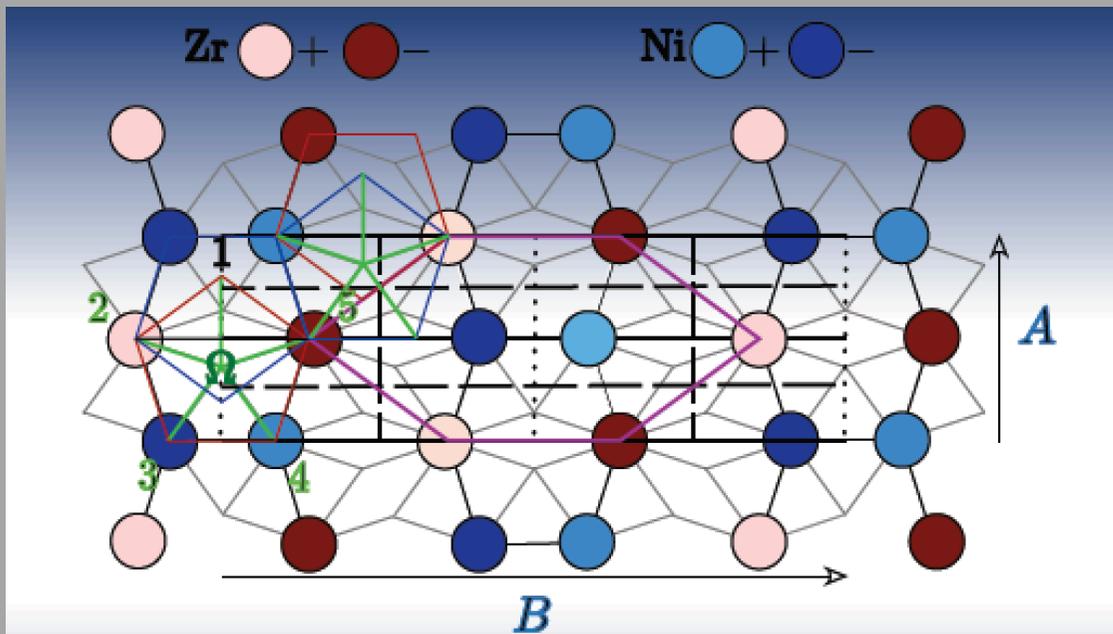
very complex twinning with a strong relationship with the five fold symmetry

A. Sirindil PhD thesis
B. 2018

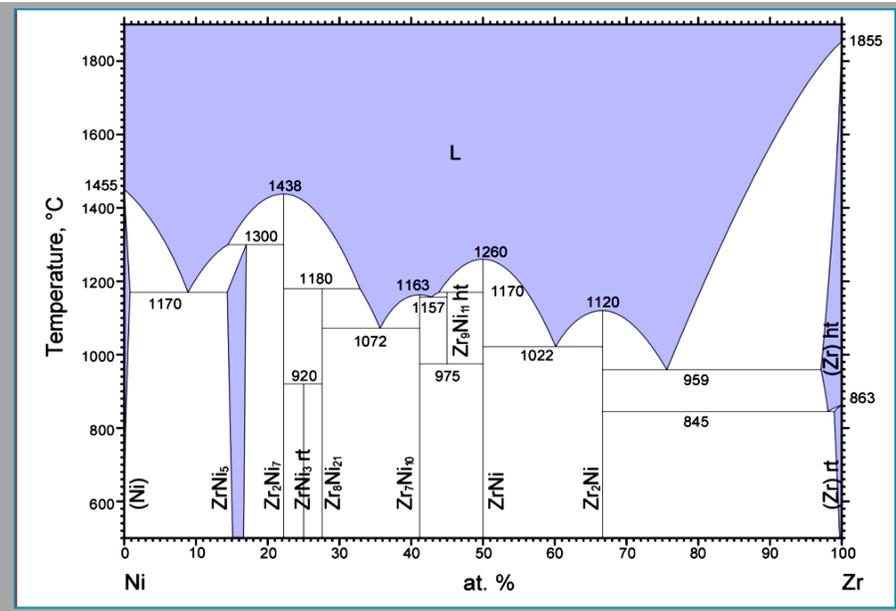


Hornfeck, W., Kobold, R., Kolbe, M. and Herlach, D. (2014). Quasicrystal nucleation in an intermetallic glass-former, arXiv:1410.2952 [cond-mat.mtrl-sci].

NiZr



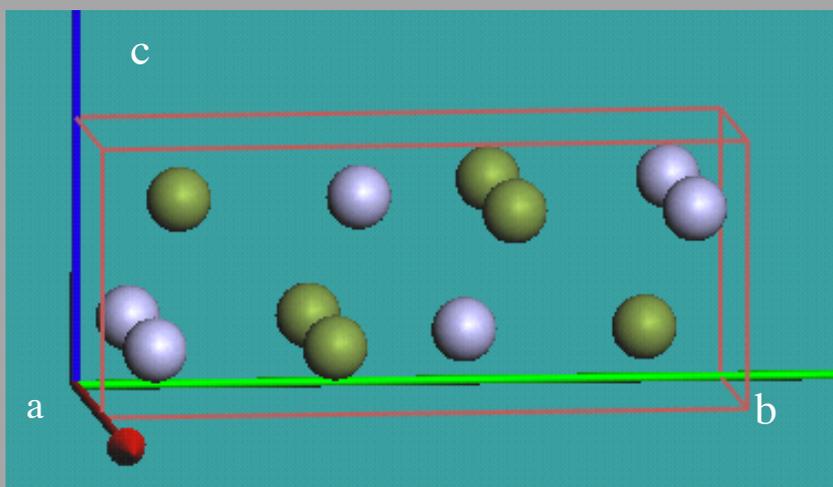
The NiZr structure (Kirkpatrick *et al.*, 1962) is a CrB type structure $Cmcm$ with lattice parameters $A = 0.3268$ nm, $B = 0.9973$ nm and $C = 0.4101$ nm, defined by two Wyckoff positions : Ni at $(0, 0.0817, 1/4)$ and Zr at $(0, 0.3609, 1/4)$. Ni and Zr atoms projected in the $[001]$ plane form hexagons that are the superimposition of two opposite regular pentagons sharing a same diagonal with an accuracy better than 1% .
 Kirkpatrick, M., Bayley, D. and Smith, J. (1962), *Acta Cryst.* 15, 252–261.



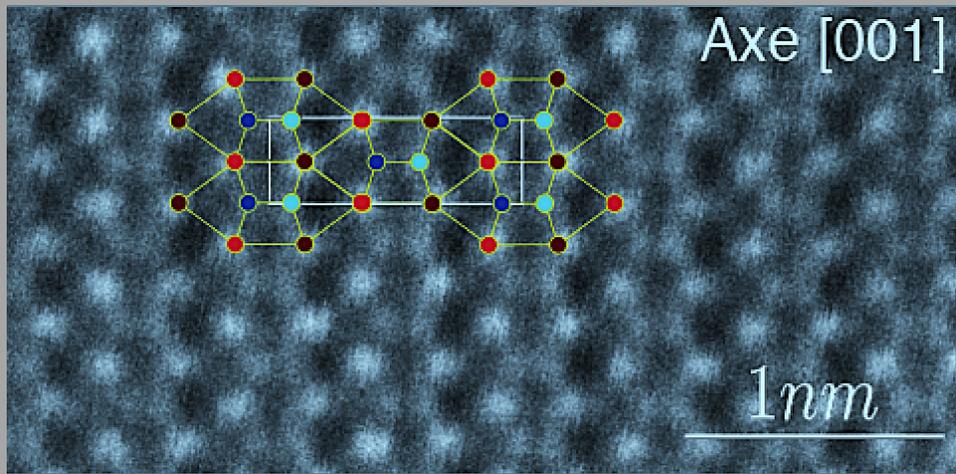
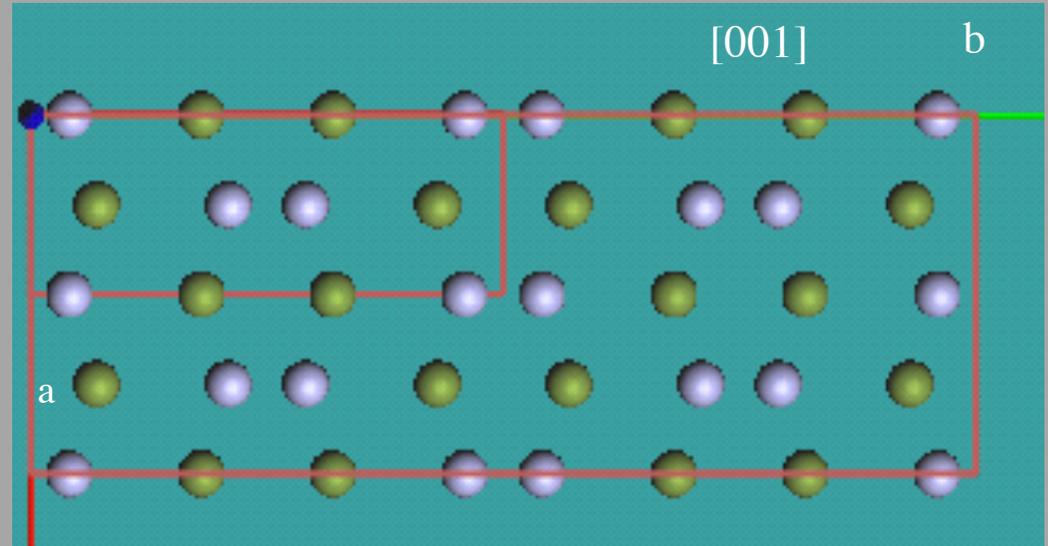
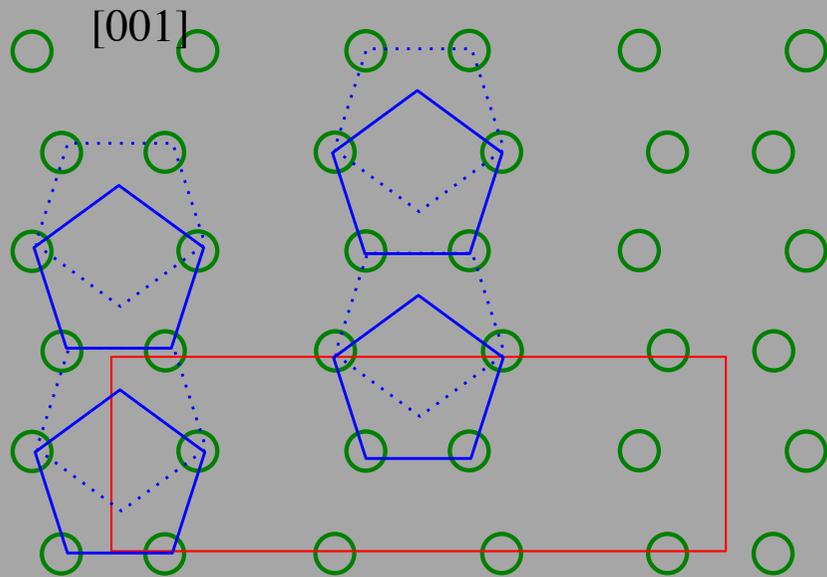
Cmcm

$a = 0.3268$ nm
 $b = 0.9937$ nm
 $c = 0.4101$ nm

Ni	0	0.0817	0.25
Zr	0	0.3609	0.25



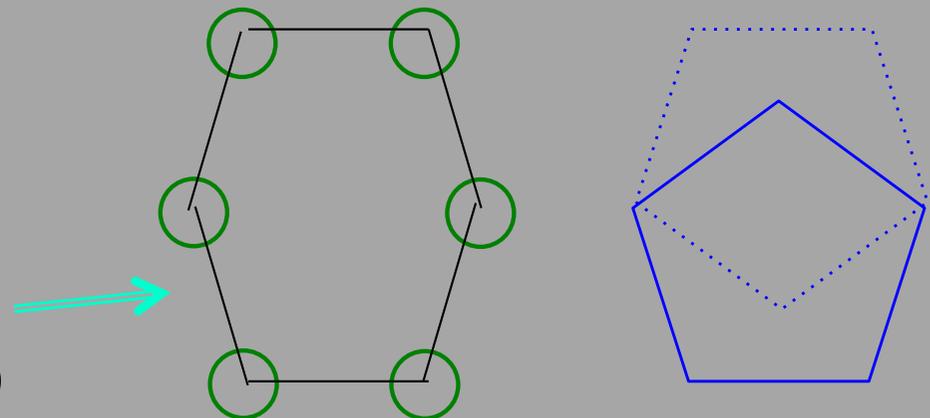
projection de la structure selon [001] on reconnaît ces alignement d'hexagones formés de deux pentagones opposés avec un sommet manquant et un décalage de $(a + b)/2$ entre deux alignements



the structure is advantageously described as a tiling of a unique equilateral hexagonal prototile

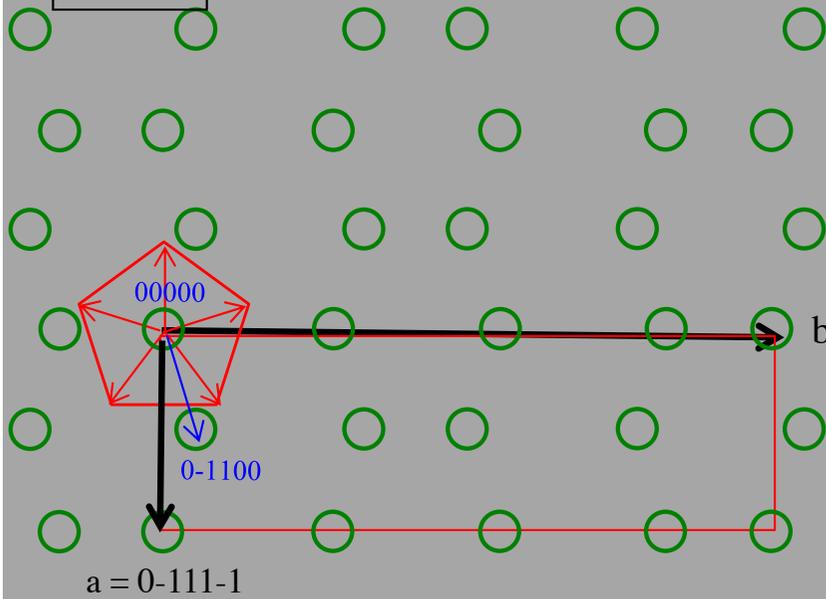
STEN-HAADF

« discovery » of the pentagon hidden 5-fold symmetry (local)



[001]

5 indices



b = 0-3-113

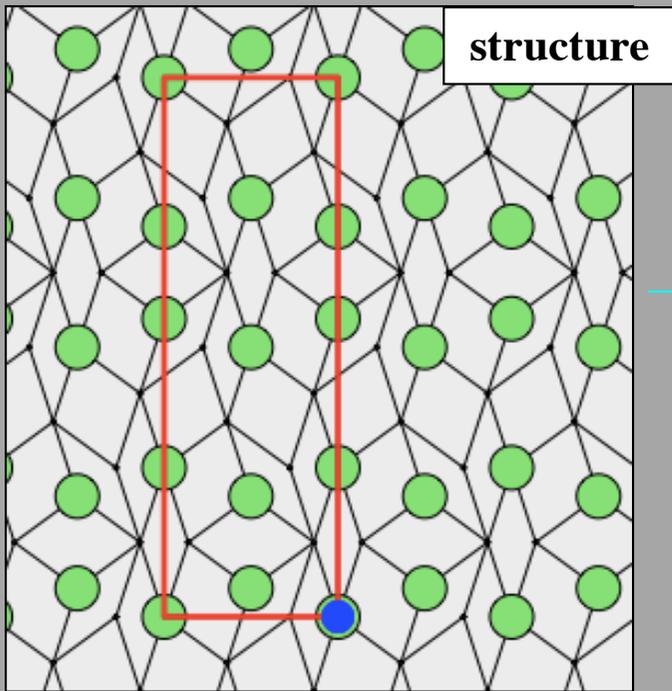
a = 0-111-1

b = 0-3-113

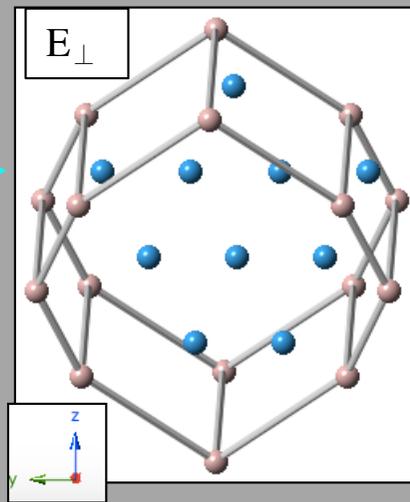
1 → 00-110

3 → 0-1001

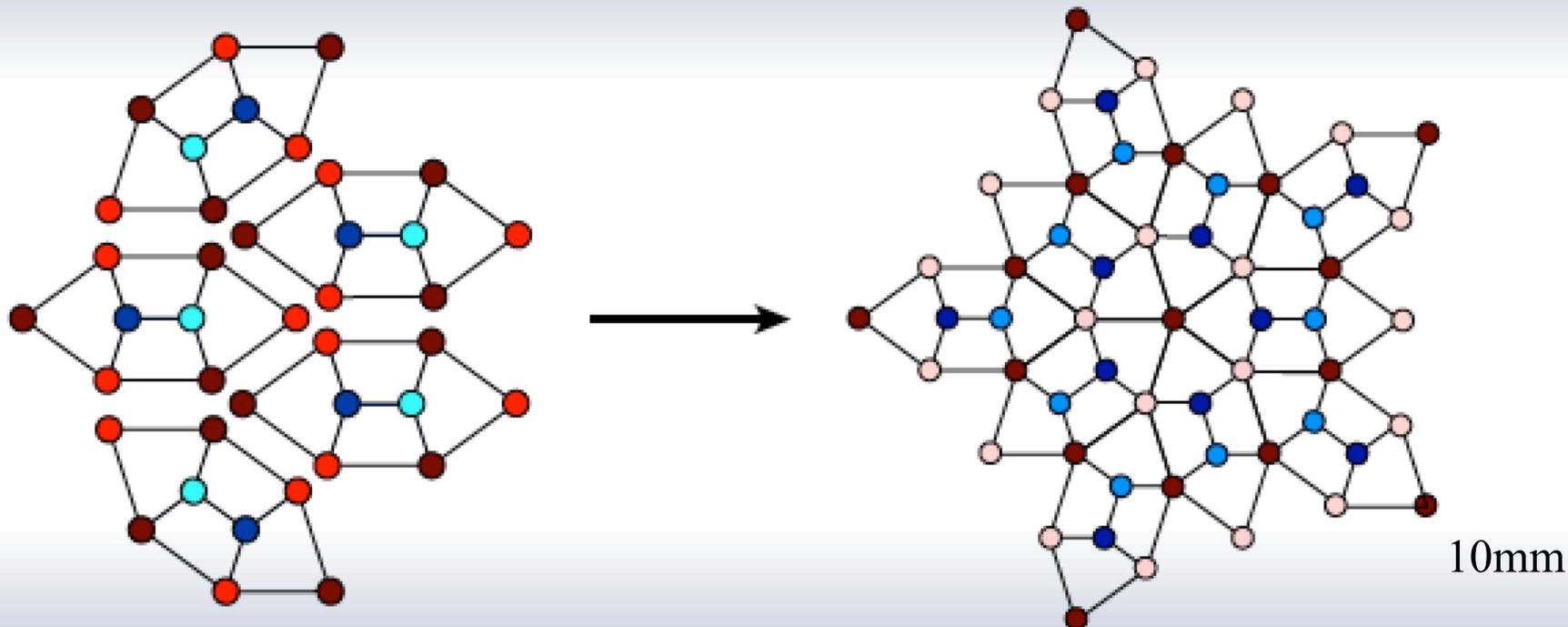
5-index determination of the basic vectors of the projected cell according to [001]



Penrose type Z-module decoration of NiZr



The equilateral hexagonal prototile that generates the orthorhombic NiZr structure opens a wide variety of possible tilings among which the high symmetry pentagonal snowflake. Whatever the tiling, all atoms, but the unique central one, share the same kind of environment to first neighbours as the one of the Cr-B reference NiZr structure.

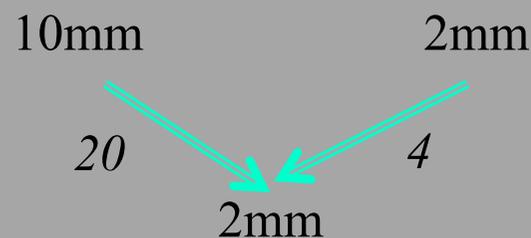


The set describes the whole possible twins in the decomposition from $10mm'$ to $2mm'$: each variant can have two adjacent variants, obtained by a rotation $\pm\pi/5$ (or equivalently by a c mirror in the planes $(\pm 1, 1, 0)$).

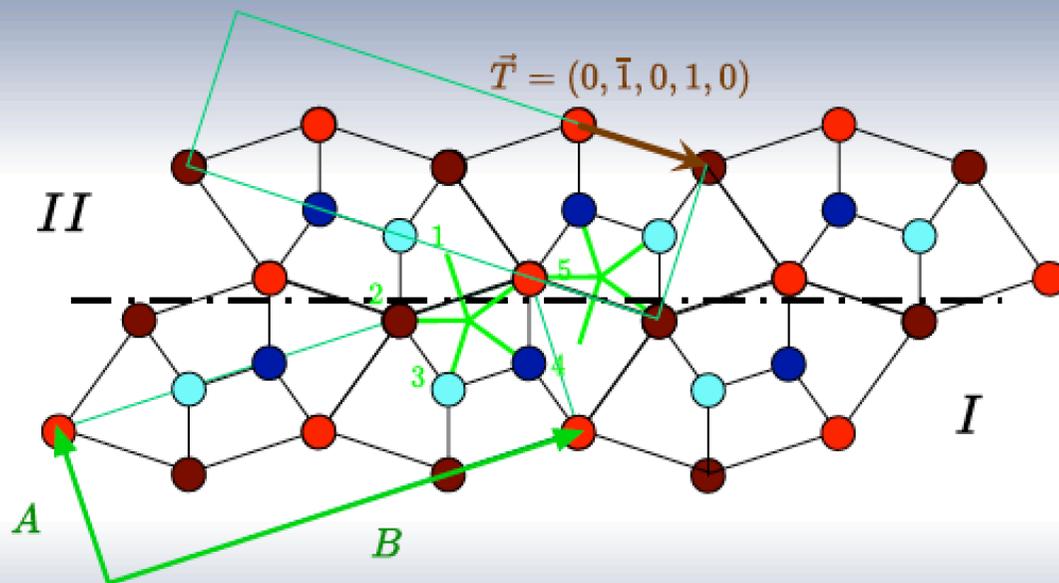
NiCr $2mm$

$20/4 = 5$ twins

rot $\pi/5$, mirror, ...



Quinary twins $(\hat{m}_{(110)}|0, \bar{1}, 0, 1, 0)$

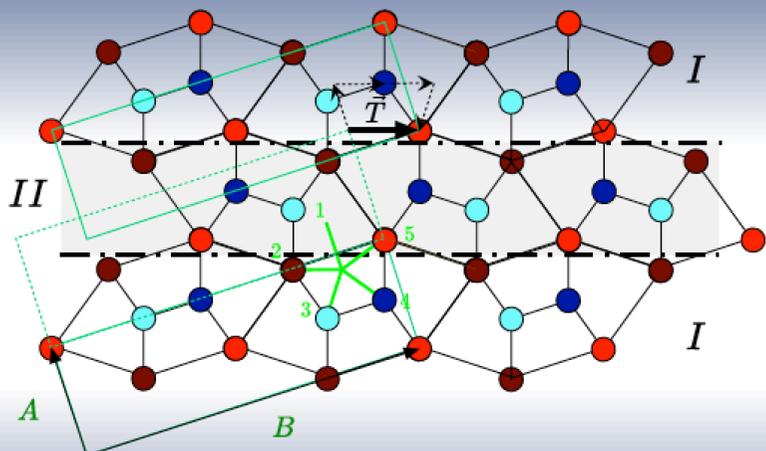


The simplest model of the structure of the quinary twin issued from the analysis in term of \mathbb{Z} -module invariance as illustrated by the two pentagons in green. The twin operation $(\hat{m}_{(110)}|0, \bar{1}, 0, 1, 0)$ expressed in the $Cmcm$ unit cell coordinates of crystal II has the translation $\vec{T} = (0, 1/(2 + \tau), 1/2)$.

associated translation / $Cmcm$

$$0, 1/(2 + \tau), 1/2$$

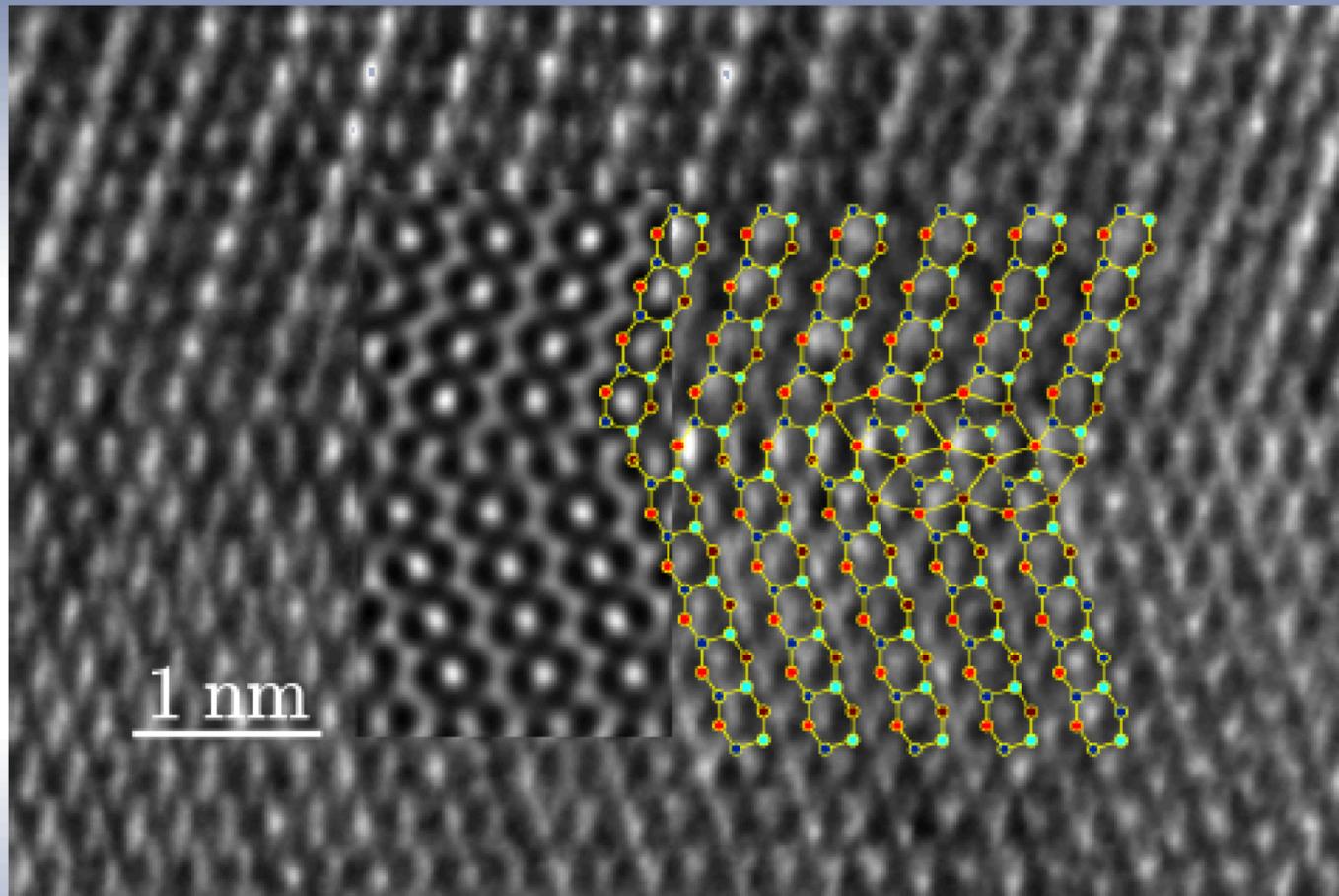
Translation defects



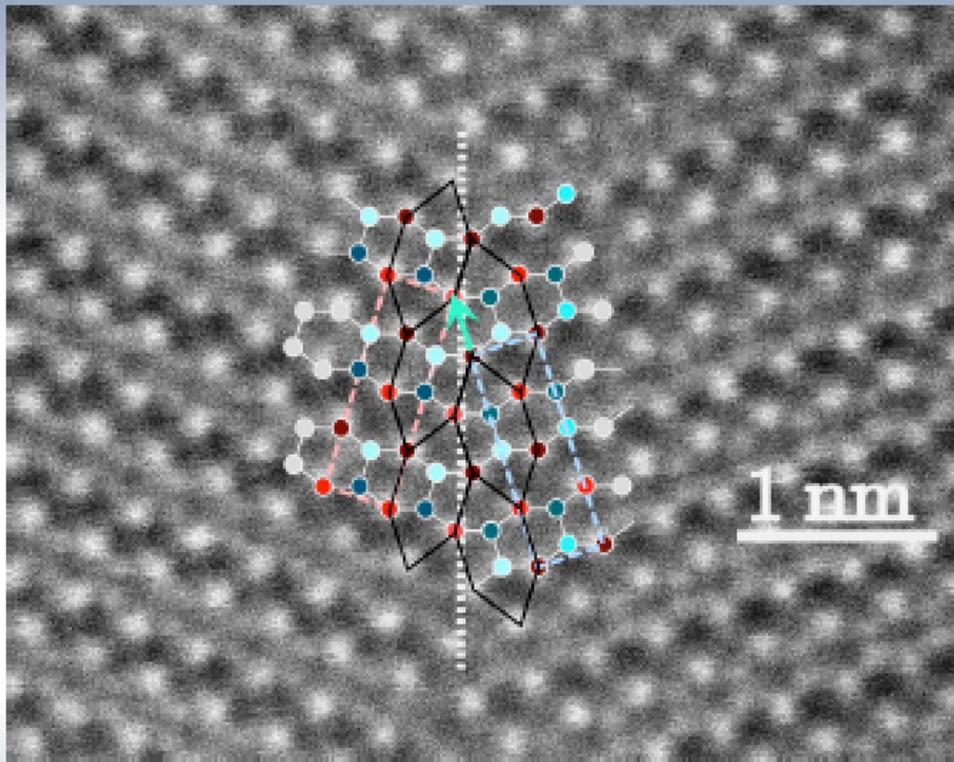
The simplest \mathbb{Z} -module translation defect model consists in introducing a thin slab of twinned hexagons (noted II) along a $(\bar{1}, 1, 0)$ plane. This generates an elementary translation between the upper and lower parts of crystal I of $\vec{T} = (1, \bar{2}, 1, 0, 0)$ corresponding to $\vec{t} = (2 - \tau)/2[\bar{1}, 1, 0]$ in the $Cmcm$ unit cell.

translation defect with
An irrational translation

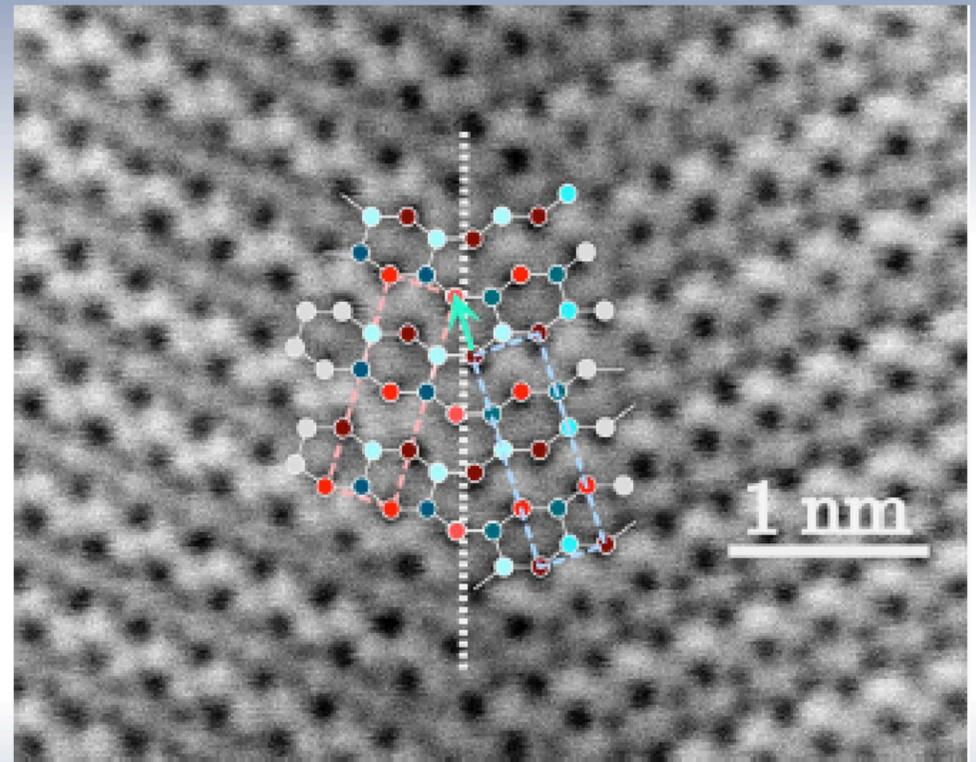
possible CSL !



HREM image of a quinary twin observed along the [001] direction showing the translation associated to the mirror twin with the expected model and an insert of image simulation made with the theoretical translation $\vec{T} = (0, \bar{1}, 0, 1, 0)$ of our model.



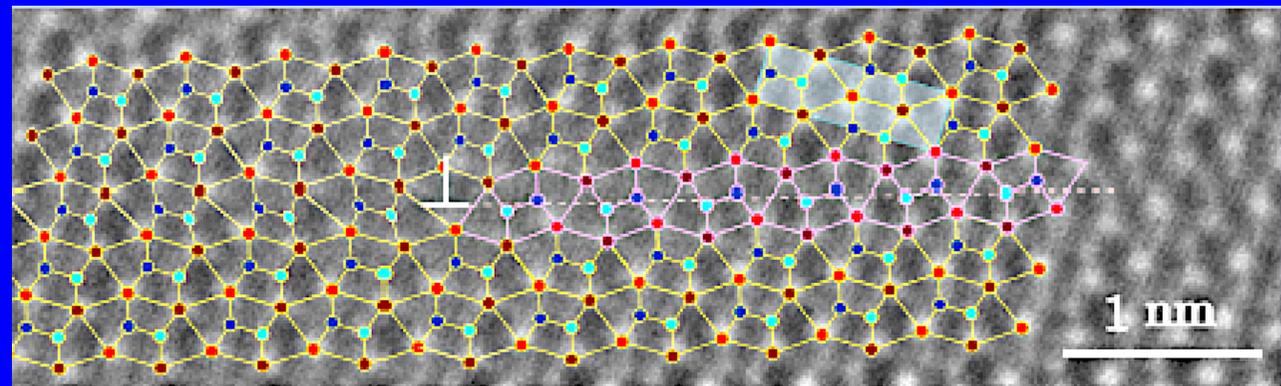
(a)



(b)

(a) STEM-HAADF atomic resolution of the quinary twin; (b) STEM-BF showing the remarkable invariance of the contrast on both sides of the boundary due to the very small local elastic field at the level of the boundary

dislocations,



This work demonstrates that using Z -modules in direct space is an interesting and fruitful unifying concept as both an elegant formulation and an efficient tool to predict new possible defects, including interface dislocations, in structures with hidden non crystallographic symmetries

the Frank-Kasper structures are described with the same Z -module

NiZr described in a 5D space with an internal pentagonal hidden symmetry

this generates possible defects at the symmetry breaking induced by the perpendicular shear when projecting back in the physical 3D space

Merohedral twins revisited: quinary twins and beyond

Marianne Quiquandon, Denis Gratias,* Abdullah Sirindil and Richard Portier

Acta Cryst. (2016). A72, 55–61

Z-module defects in crystals

Abdullah Sirindil, Marianne Quiquandon and Denis Gratias

Acta Cryst. (2017). A73, 427–437

Atomic scale analyses of Z-module defects in an NiZr alloy

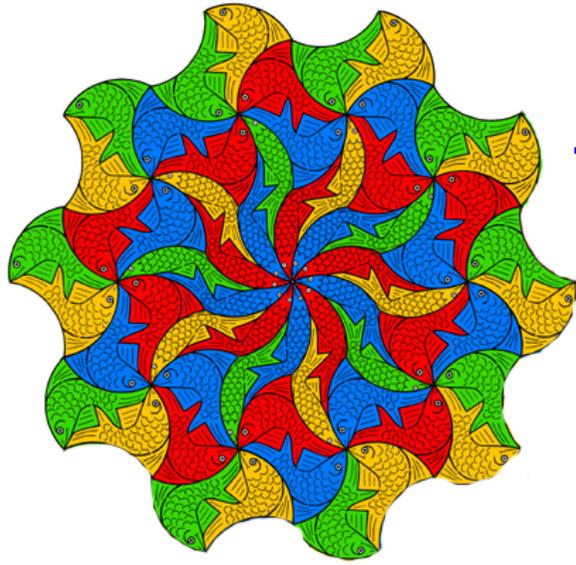
Abdullah Sirindil, Raphael Kobold, Frederic Momprou, Sylvie Lartigue-Korinek,

Loic Perriere, Gilles Patriarche, Marianne Quiquandon and Denis Gratias

Acta Cryst. (2018). A74

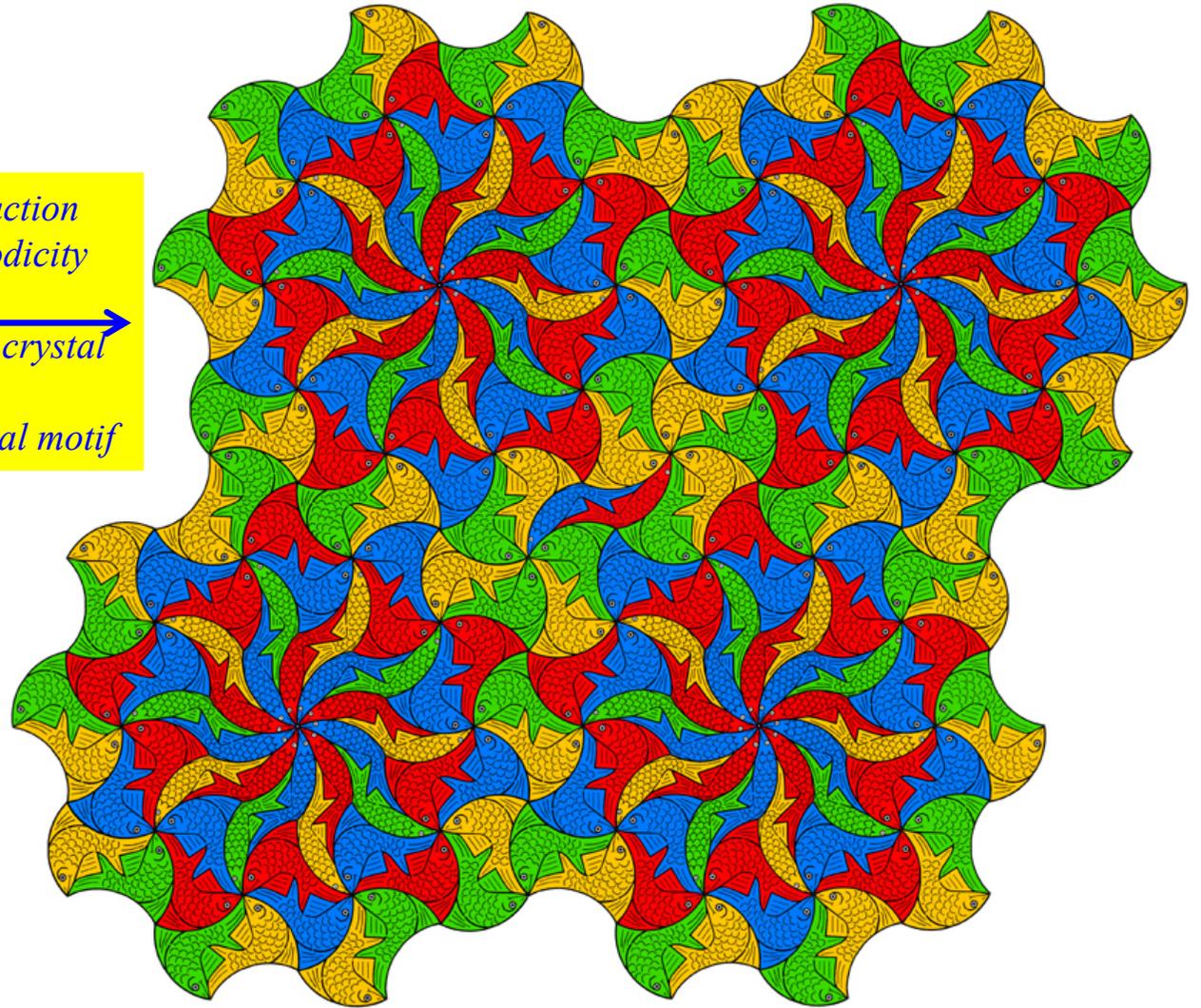
The Azerbaidjan tessellations

Imam Amiraslan (Bakou)

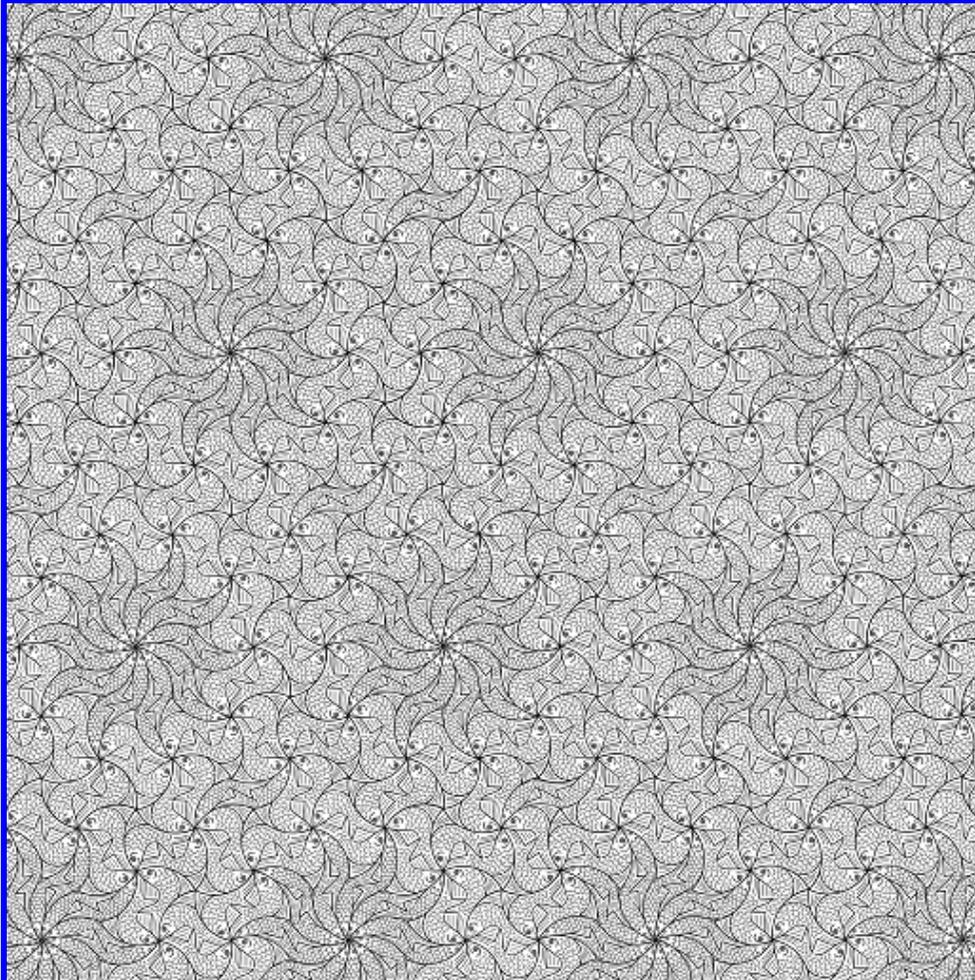


*introduction
of periodicity*

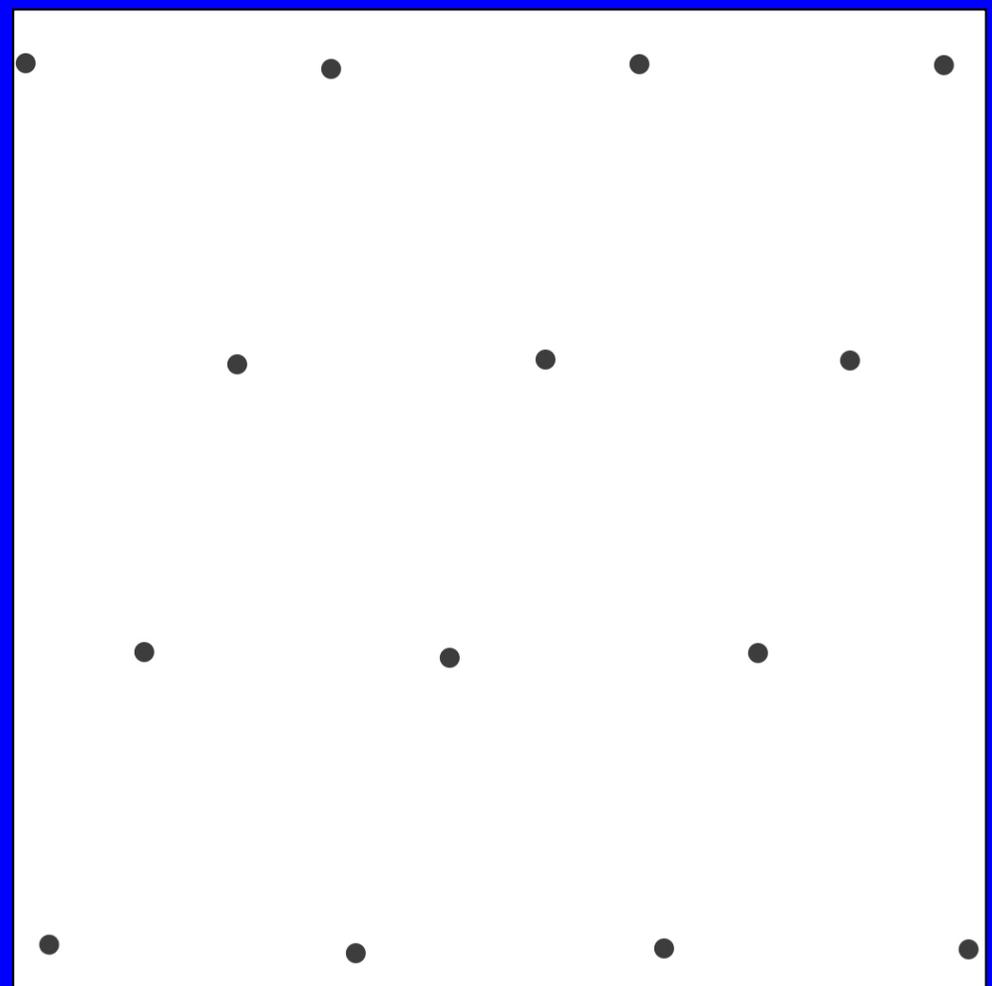
*periodic crystal
+
pentagonal motif*



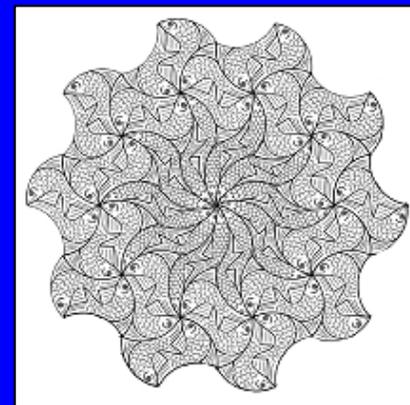
colours \rightarrow grey level

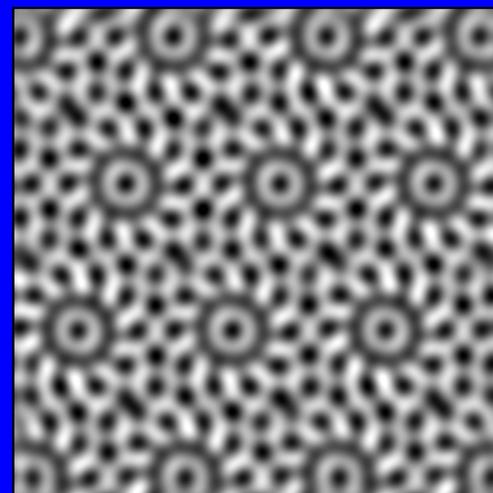
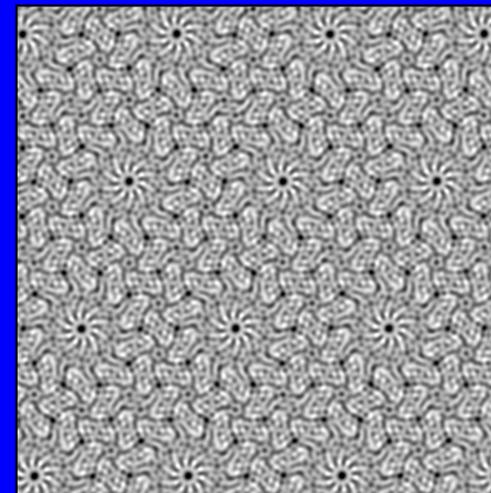
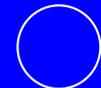
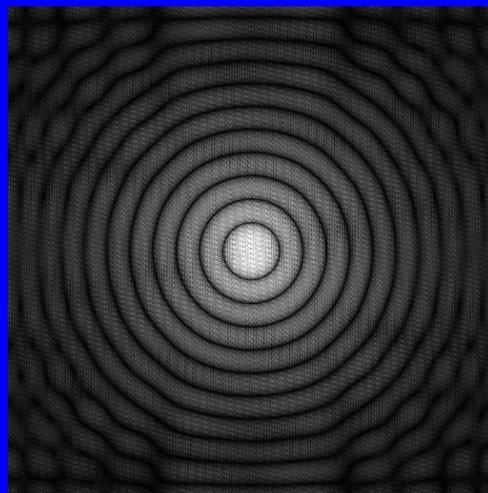
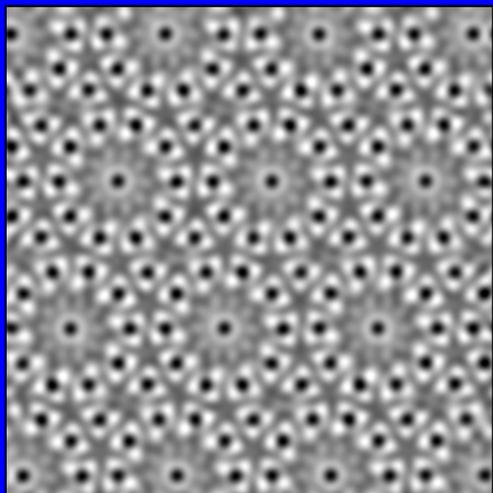


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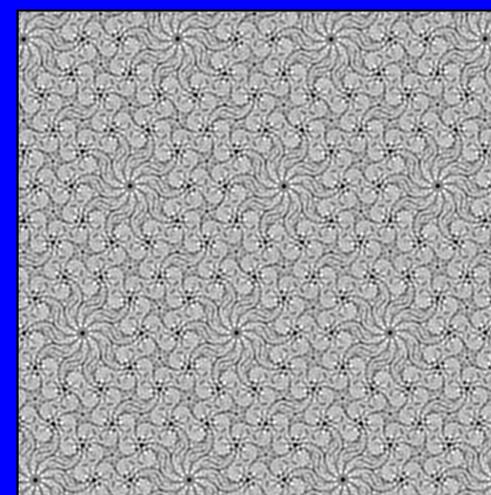
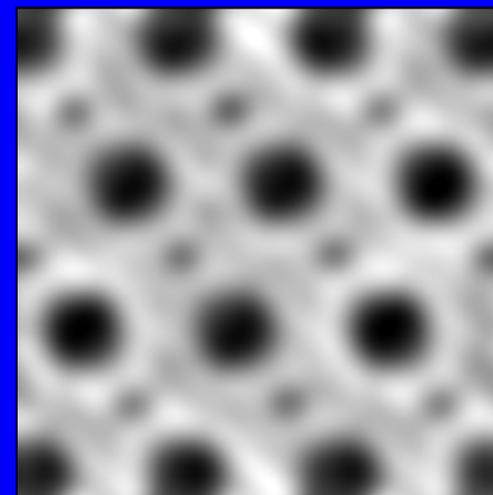
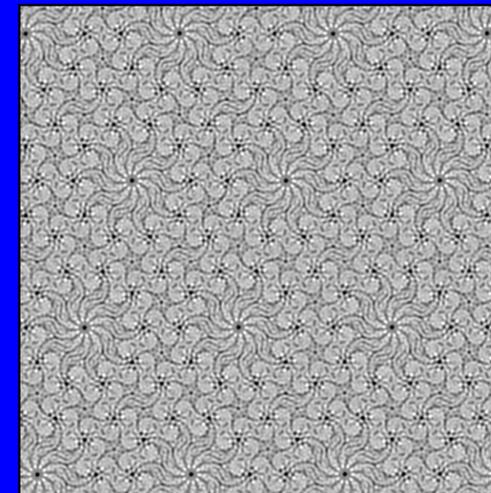
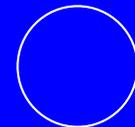




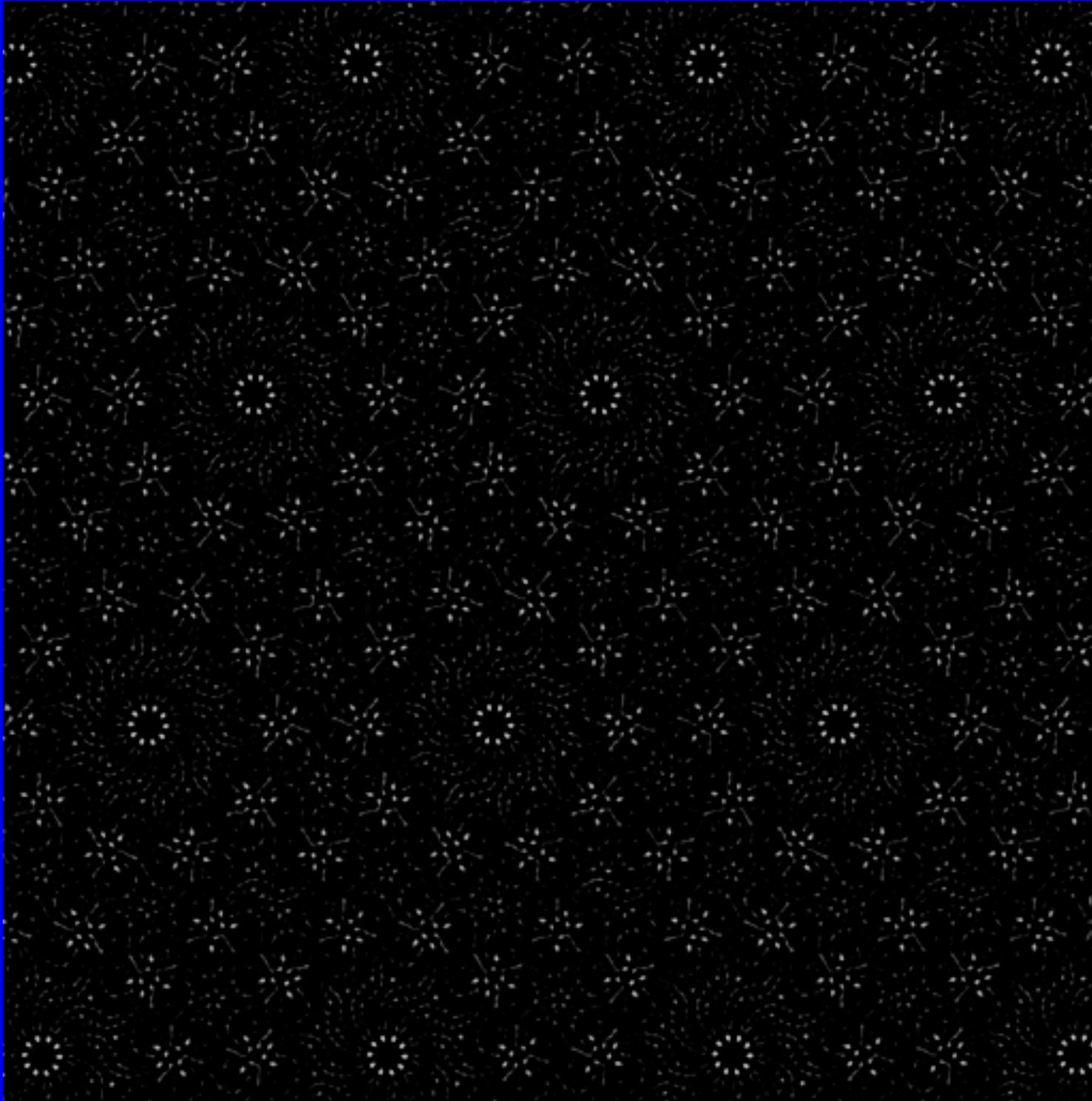
the power spectrum

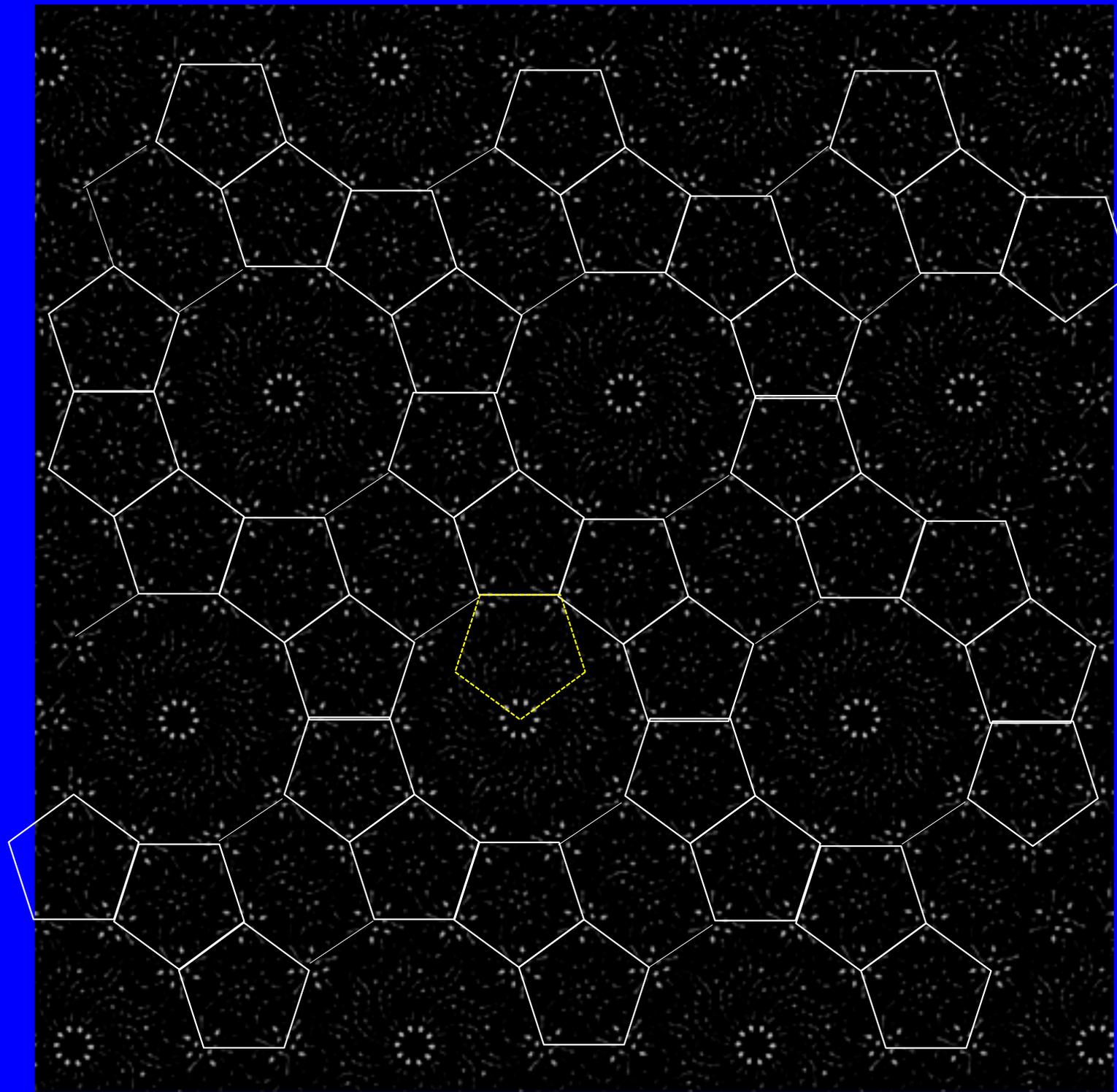


image reconstruction with different filters



*A vision in the reciprocal space
Digital Micrograph (Gatan)*





indexation

