Quasicrystals: Structure and Growth

Thomas Fernique

Moscow, Spring 2011

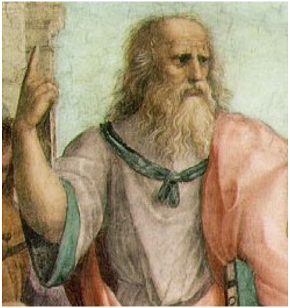
1. Crystals and tilings

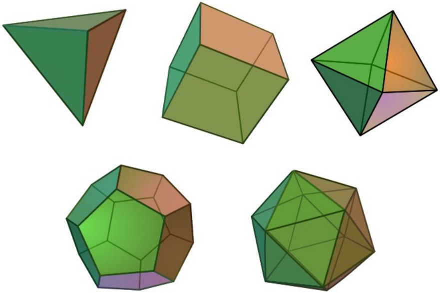
2. X-ray diffraction

3. Quasicrystals

4. Outline of lectures

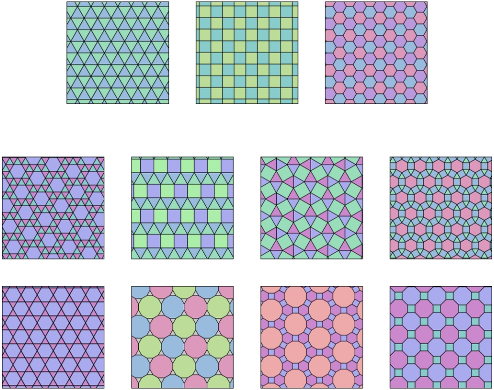
Platonic solids (Platon, *Timaeus*, ca. 360 B.C.)





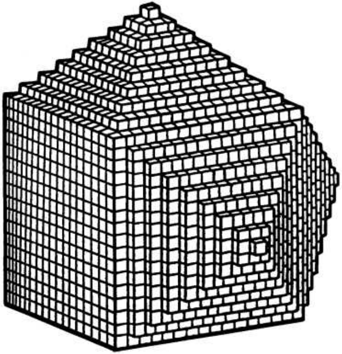
Platonic solids: regular convex polyhedra “representing” elements.

Archimedean tilings (Kepler, *Harmonices Mundi*, 1619)



Archimedean tiling: regular polygons, uniform vertex arrangement.

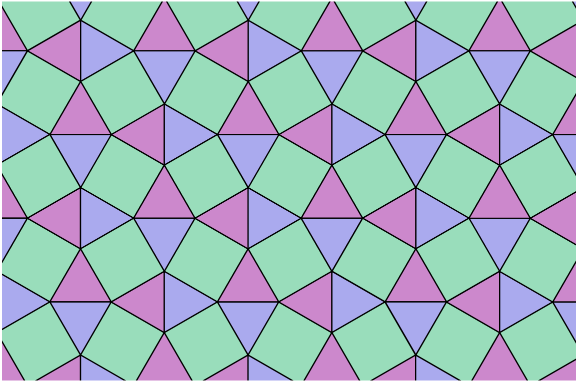
The birth of modern crystallography (18-th)



Law of constancy of interfacial angles (Romé de l'Isle, 1772)

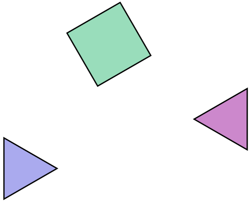
From *building blocks* to crystal shapes (Haüy, 1784)

Structure: matching rules *vs.* lattices and basis



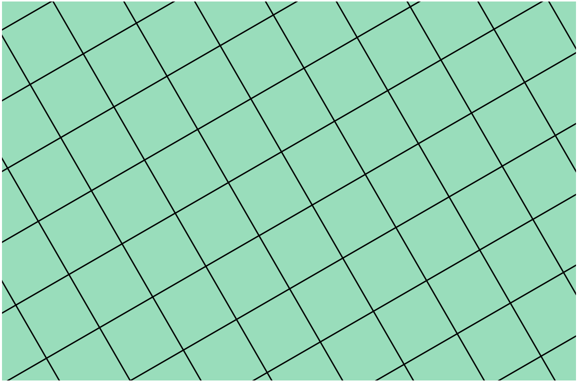
Consider, *e.g.*, the *snub-square* Archimedean tiling.

Structure: matching rules *vs.* lattices and basis



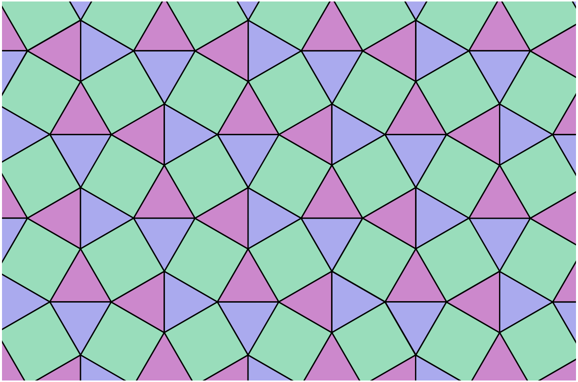
It is made of three different tiles (up to rotation/translation).

Structure: matching rules *vs.* lattices and basis



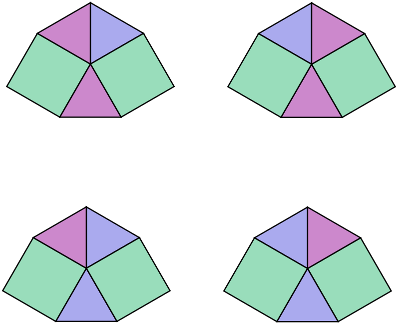
These tiles do not characterize the tiling.

Structure: matching rules *vs.* lattices and basis



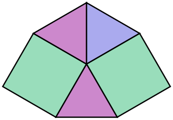
But recall uniform vertex arrangement: $3 \cdot 4 \cdot 3^2 \cdot 4$.

Structure: matching rules *vs.* lattices and basis



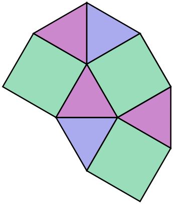
With the colors, this yields an *atlas* of four vertices.

Structure: matching rules *vs.* lattices and basis



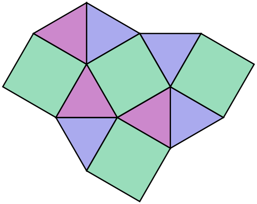
This vertex atlas turns out to characterize the snub-square tiling.

Structure: matching rules *vs.* lattices and basis



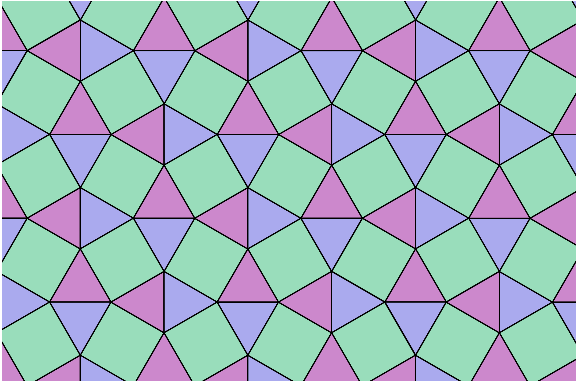
This vertex atlas turns out to characterize the snub-square tiling.

Structure: matching rules *vs.* lattices and basis



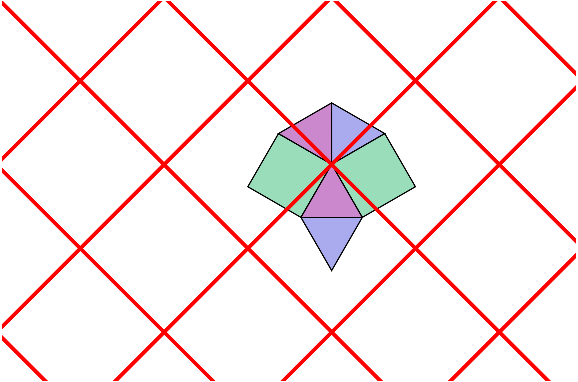
This vertex atlas turns out to characterize the snub-square tiling.

Structure: matching rules *vs.* lattices and basis



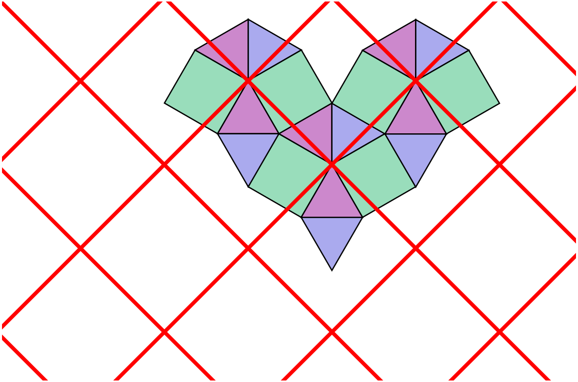
This vertex atlas turns out to characterize the snub-square tiling.

Structure: matching rules *vs.* lattices and basis



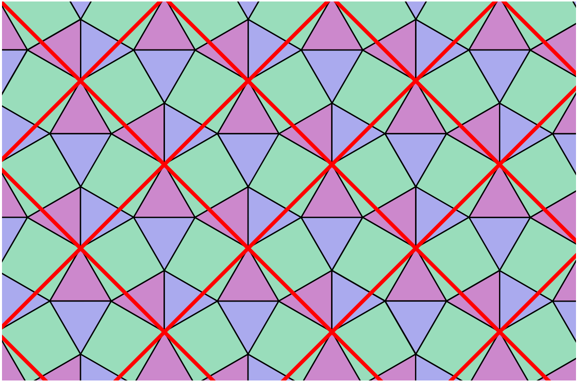
But this tiling can also be described by a *lattice* and a *basis*.

Structure: matching rules *vs.* lattices and basis



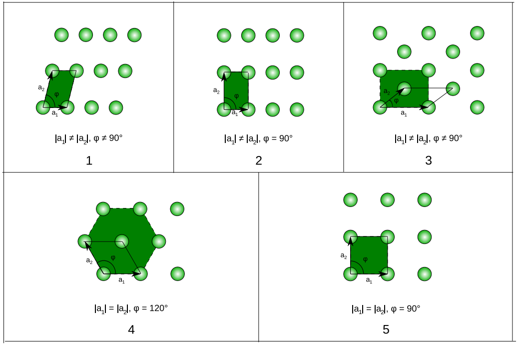
The basis is copied at each lattice point.

Structure: matching rules *vs.* lattices and basis



The basis is copied at each lattice point.

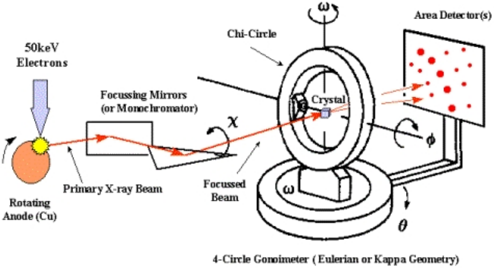
Lattice classification (Bravais 1850, Fedorov 1891,. . .)



Lattices are classified according to their symmetries (group theory).

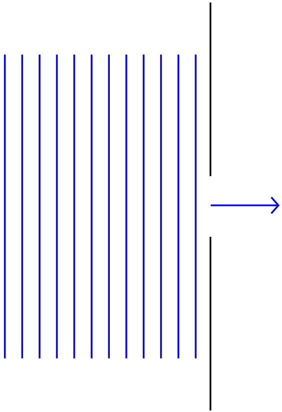
Convenient model for periodic atom packing.

X-ray diffraction (von Laue, 1912)



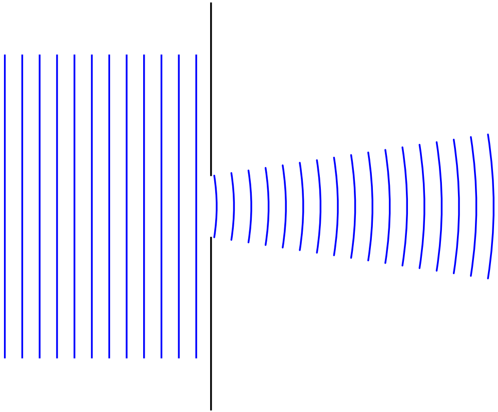
Led to consider crystals as periodic atom packings.

One-point diffraction (experiment $\rightsquigarrow$ Huygens principle)



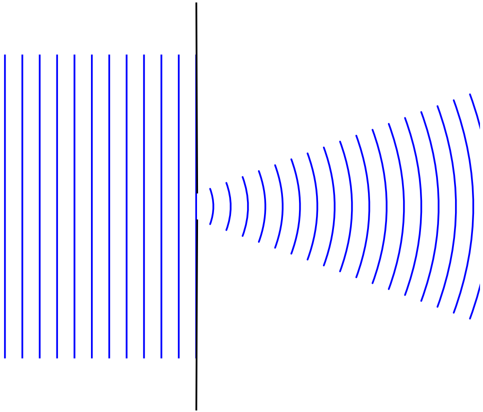
A plane wave of length λ (blue crests) enters a hole of size a.

One-point diffraction (experiment ⇝ Huygens principle)



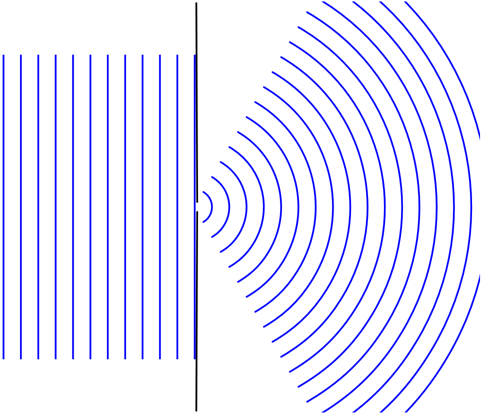
The output wave turns out to fill a cone of angle $\theta = \frac{\lambda}{a}$.

One-point diffraction (experiment $\rightsquigarrow$ Huygens principle)



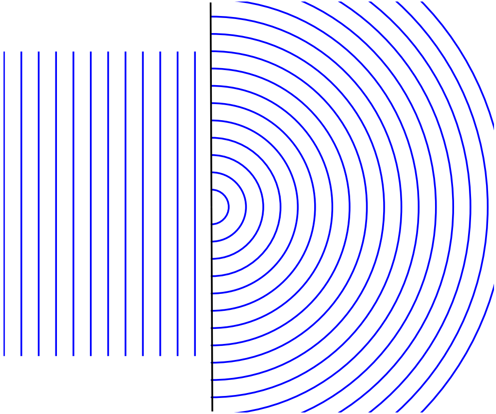
The smaller is the hole, the more spherical is the output wave.

One-point diffraction (experiment $\rightsquigarrow$ Huygens principle)



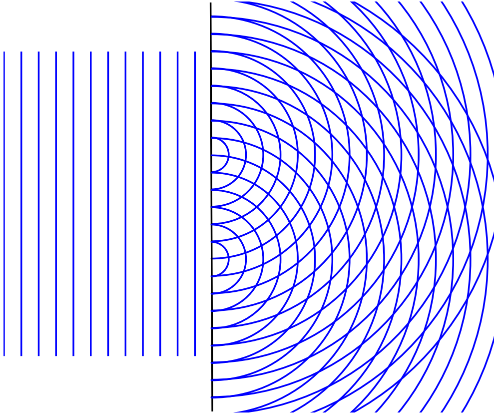
The smaller is the hole, the more spherical is the output wave.

One-point diffraction (experiment $\rightsquigarrow$ Huygens principle)



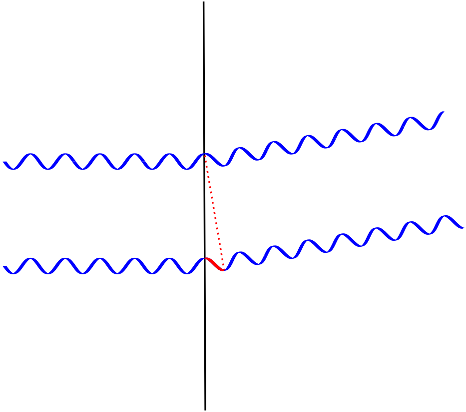
At the limit (point-hole), we get a spherical output wave: $|A(\vec{s})| \equiv 1$.

Two-point diffraction



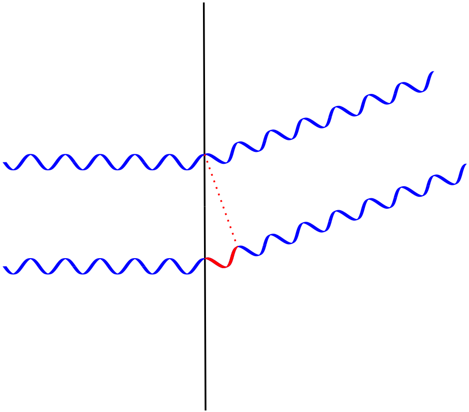
Two point-holes $\rightsquigarrow$ *interferences* between spherical output waves.

Two-point diffraction



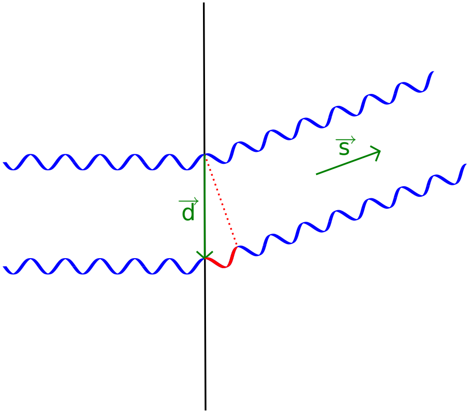
A crest and a trough cancel out $\rightsquigarrow$ zero intensity in this direction.

Two-point diffraction



Two crests (or troughs) sum up ⇝ high intensity in this direction.

Two-point diffraction



More precisely: $J(\vec{s}) := |A(\vec{s})|^2 = |A_1(\vec{s}) + A_2(\vec{s})|^2 = |1 + \mathrm{e}^{2i\pi \vec{d}.\vec{s}}|^2.$

N-point diffraction

For N point-holes in position $\vec{d}_1, \ldots, \vec{d}_N$:

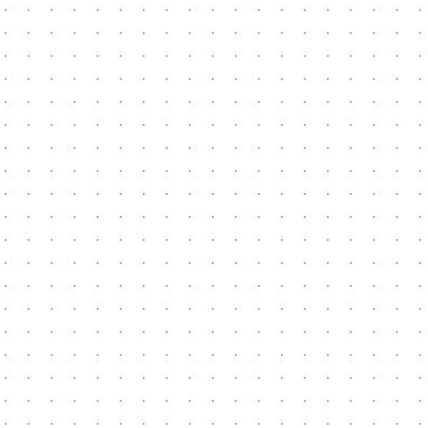
$$A(\vec{s}) = A_1(\vec{s}) + \ldots + A_N(\vec{s}) = A_1(\vec{s}) \left(1 + \sum_{j=1}^{N} \mathrm{e}^{2\mathrm{i}\pi \vec{d}_j . \vec{s}} \right).$$

Amplitude: *Fourier transform* of *Dirac comb* (Dirac $\simeq$ point-hole).

$$J(\vec{s}) = |A(\vec{s})|^2 = \sum_{j=1}^{N} \sum_{k=1}^{N} \mathrm{e}^{2\mathrm{i}\pi (\vec{d}_j - \vec{d}_k) . \vec{s}}.$$

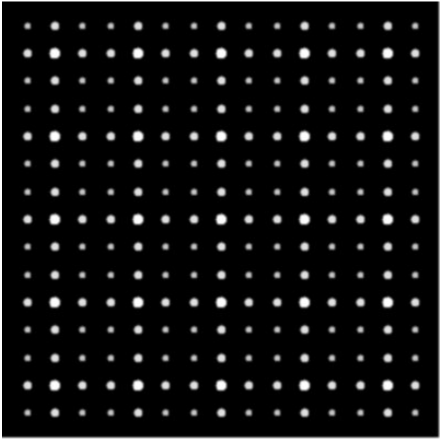
Intensity: observable on a screen "at infinity" (parallel rays meet).

Examples



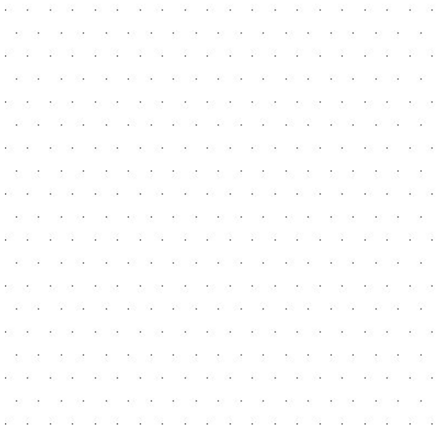
Point-holes: square lattice.

Examples



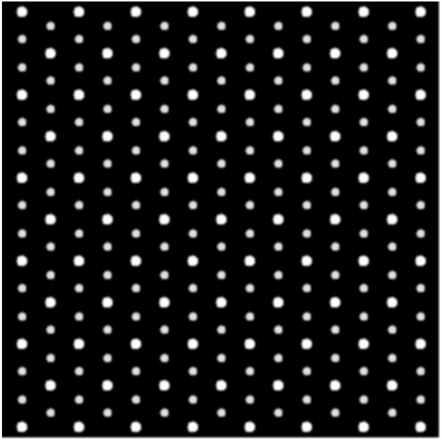
Point-holes: square lattice.

Examples



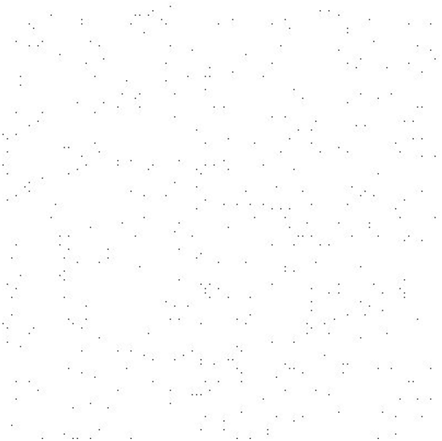
Point-holes: triangular lattice.

Examples



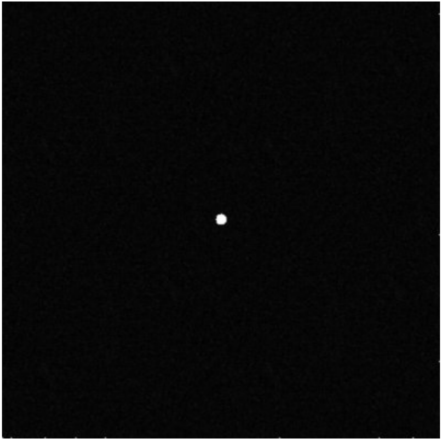
Point-holes: triangular lattice.

Examples



Point-holes: random.

Examples



Point-holes: random.

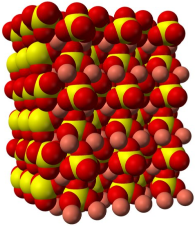
Crystal diffraction

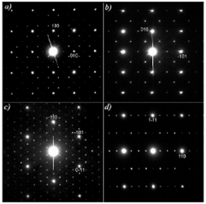
Assuming that crystal are periodic atom packing:

1. atoms $\rightsquigarrow$ scatter waves as point-holes (spherical output);
2. wavelength $\simeq$ inter-atomic dist. $\rightsquigarrow$ observable interferences;
3. periodic packing $\rightsquigarrow$ sharp bright spots (Bragg peaks).

von Laue, 1912: Bragg peaks with X-ray on copper sulfate.

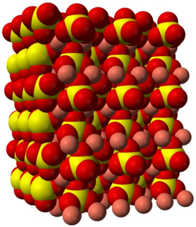
Crystal structure





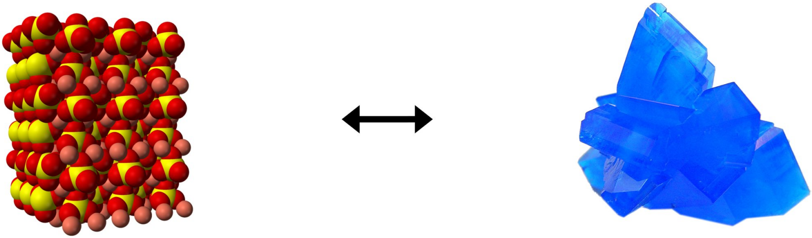
Periodic atom packings and (known) crystals: same diffractograms.

Crystal structure



Periodic atom packings and (known) crystals: same diffractograms.
They should therefore be equal (Shadok: no solution ⇒ no problem).

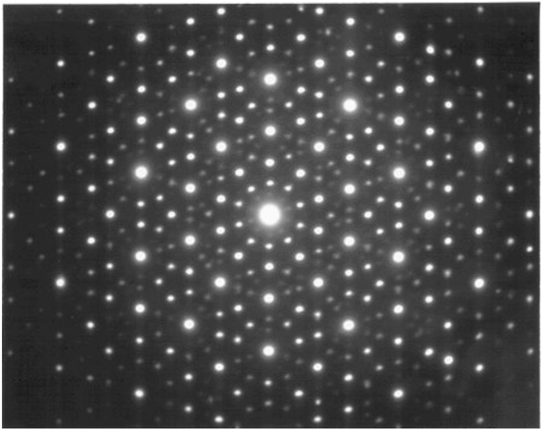
Crystal structure



Periodic atom packings and (known) crystals: same diffractograms. They should therefore be equal (Shadok: no solution ⇒ no problem).

- Direct methods (Patterson 1934, Karle & Hauptman 1953–85);
- Mathematical diffraction (Baake & al. 1998–. . .);
- Electron microscopy (Ruska 1931–86, TEAM 2004–. . .).

A Strange crystal (Shechtman & al., 1984)



Rapidly cooled alloy of Al with a 10-fold symmetric diffractogram.

Forbidden symmetries

The lattice $\Lambda \subset \mathbb{R}^2$ has *n-fold symmetry* if $R_{\frac{2\pi}{n}}(\Lambda) = \Lambda$.

Crystallographic restriction

A lattice can be n-fold only for $n \in \{1, 2, 3, 4, 6\}$.

Proof:

- preserving rotation in a base of Λ: integer matrix;
- trace of R_θ in any base: $2\cos(\theta)$;
- $2\cos(\theta) \in \mathbb{Z} \Rightarrow \theta \in \{\frac{2\pi}{1}, \frac{2\pi}{2}, \frac{2\pi}{3}, \frac{2\pi}{4}, \frac{2\pi}{6}\}$.

Forbidden symmetries

The lattice $\Lambda \subset \mathbb{R}^2$ has *n-fold symmetry* if $R_{\frac{2\pi}{n}}(\Lambda) = \Lambda$.

Crystallographic restriction

A lattice can be n-fold only for $n \in \{1, 2, 3, 4, 6\}$.

Proof:

- preserving rotation in a base of Λ: integer matrix;
- trace of R_θ in any base: $2\cos(\theta)$;
- $2\cos(\theta) \in \mathbb{Z} \Rightarrow \theta \in \{\frac{2\pi}{1}, \frac{2\pi}{2}, \frac{2\pi}{3}, \frac{2\pi}{4}, \frac{2\pi}{6}\}$.

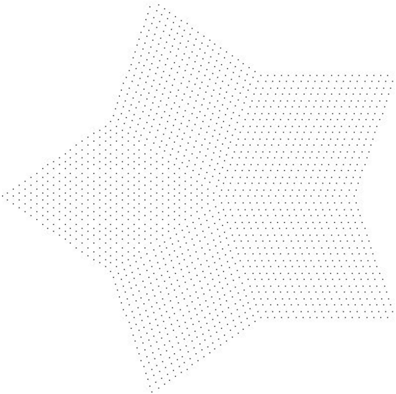
Here:

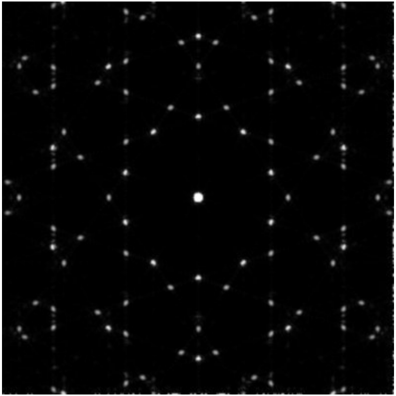
- 10-fold diffraction $\Rightarrow$ not a lattice $\overset{\text{Curie}}{\to}$ non-periodic material.
- Bragg peaks $\overset{\text{Def.}}{\leftrightarrow}$ long-range order $\overset{\text{Axiom}}{\leftrightarrow}$ crystalline structure.

Birth of a controverse (Twinning)

Non-periodic crystal (Shechtman) or *twinned* crystal (Pauling)?

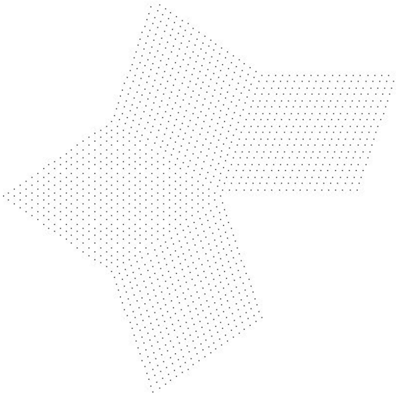
Birth of a controverse (Twinning)

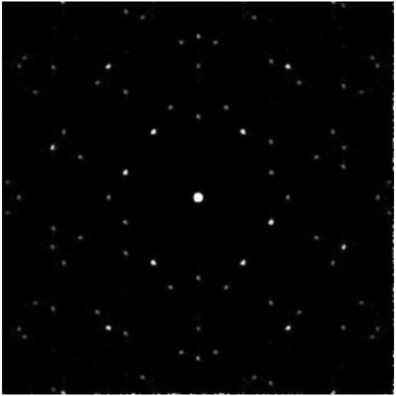




Twinned crystal: macro-combination of periodic crystals.

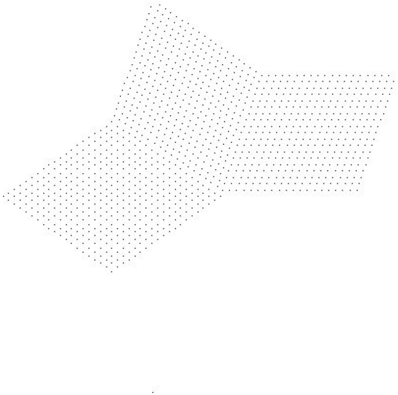
Birth of a controverse (Twinning)





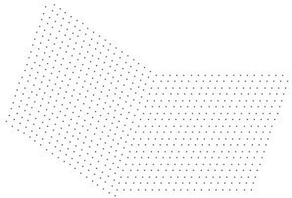
Diffractogram: sum of periodic diffractograms.

Birth of a controverse (Twinning)



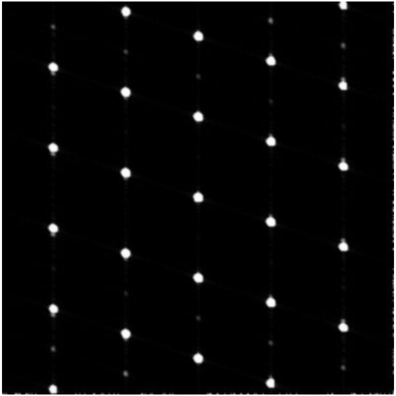
Diffractogram: sum of periodic diffractograms.

Birth of a controverse (Twinning)



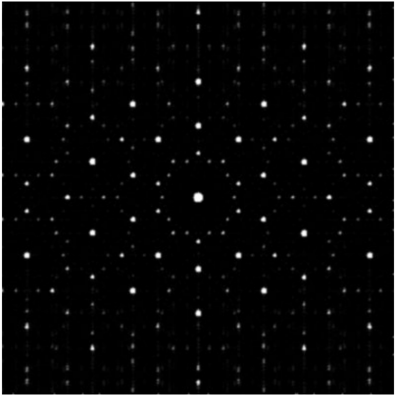
Diffractogram: sum of periodic diffractograms.

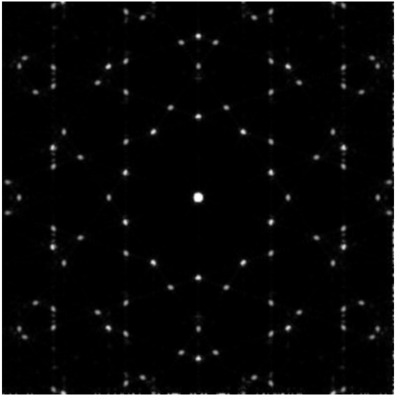
Birth of a controverse (Twinning)



Diffractogram: sum of periodic diffractograms.

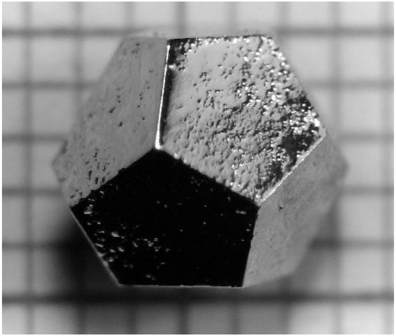
Birth of a controverse (Twinning)





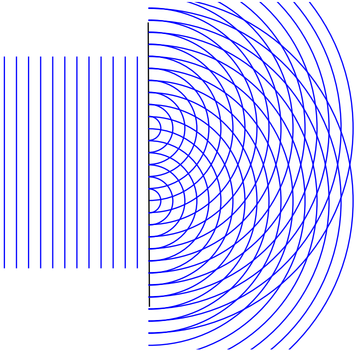
Symmetry: 10-fold (right), as the “shechtmanite” (left).

The strange crystal explosion (1984–1985)



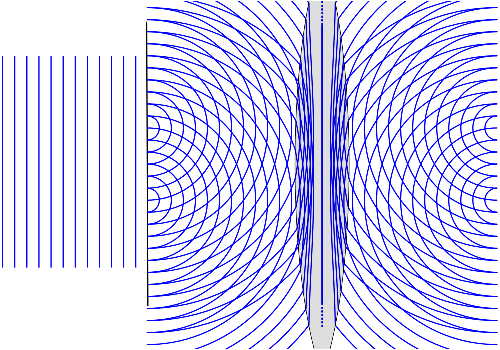
Many other such materials, synthetic or even natural (in Koryakia).

End of a controverse (Electron Microscopy)



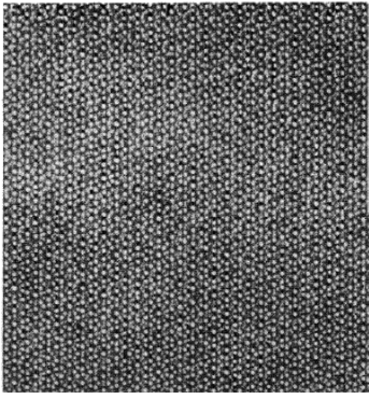
Several arguments against twinning. Maybe the best one: HRTEM.

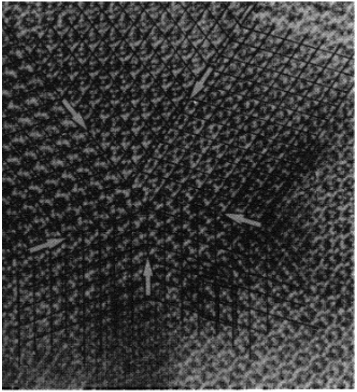
End of a controverse (Electron Microscopy)



Several arguments against twinning. Maybe the best one: HRTEM.

End of a controverse (Electron Microscopy)





Several arguments against twinning. Maybe the best one: HRTEM.

A Paradigm shift

Definition (Folk, 18th-20th century)

Crystal: periodic atom packing.

Definition (International Union of Cristallography, 1992)

Crystal: material whose diffractogram has Bragg peaks.

Since periodicity implies Bragg peaks, the new definition is broader.

Non-periodic crystals: *quasicrystals* (Levine & Steinhardt, 1984).

General overview

Content:

- almost no physics of quasicrystals;
- lot of combinatorics and geometry;
- calculability (first lecture);
- Markov chain and mixing times (two last lectures).

Form:

- lectures mainly rely on a few papers that should be accessible;
- slides (lot of pictures) will be accessible;
- as a primer, no guarantee on the outline.

Two parts: Structure and Growth.

Outline

Structure:

1. Robinson tilings 03/03
2. Penrose tilings 10/03
3. Rhombus tilings 17/03
4. Hierarchical tilings 24/03

Growth:

1. Self-assembled tilings 14/04
2. Random tilings 21/04
3. Cooled tilings 28/04

Inbetween: visa renewal in France.

Some references for this lecture:

- Marjorie Senechal, *Quasicrystals and Geometry*, Cambridge University Press, 1995. Chap. 1–3.
- Dan Shechtman, Ilan Blech, Denis Gratias, John Cahn, *Metallic phase with long-range orientational order and no translational symmetry*, Phys. Rev. Lett. **53** (1984).
- Michael Baake, Uwe Grimm, *Surprises in aperiodic diffraction*, J. Phys.: Conf. Ser. **226** (2010).

These slides and the above references can be found there:

`http://www.lif.univ-mrs.fr/~fernique/qc/`