Chemical Crystallography and Structural Chemistry

(VO 270287)

Lecture 3

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Previous Lecture

1. Conducting a diffraction experiment - cont’d
2. Objectives of a Crystal Structure
3. Diffraction theory
4. Unit Cell and Reflections
5. Laue Equations

Today's Lecture

1. Laue Equations
2. Ewald Sphere Constructions
3. Bragg's Law and Resolution
4. Symmetry, Point Groups and Space Groups

Laue equations

$$
\begin{aligned}
\vec{a}\cdot\vec{S} &= |\vec{a}||\vec{S}|\cos(\vec{a},\vec{S}) = h\\
\vec{b}\cdot\vec{S} &= |\vec{b}||\vec{S}|\cos(\vec{b},\vec{S}) = k\\
\vec{c}\cdot\vec{S} &= |\vec{c}||\vec{S}|\cos(\vec{c},\vec{S}) = l
\end{aligned}
$$

The Laue equations describe the diffraction experiment:

- The triplet (h,k,l) is called **the Miller index**. Each tripled (h,k,l) describes exactly one reflection. (W. H. Miller, 1801–1880)
- The crystal orientation $\vec{a},\vec{b},\vec{b}$ and the scattering vector $\vec{S}$ describe the position where to record the reflection (h,k,l).
- The Laue equations say **where** each reflection can be recorded, but **nothing** about the intensity
- The Laue equations depend on the unit cell parameters $a,b,c,\alpha,\beta,\gamma$. They are **independent** from the chemical composition inside the unit cell.

Indexing

- the term **indexing** describes the assignment of the Miller indices to and the reflections recorded on the detector.
- Indexing is equivalent to determining the unit cell parameters $a, b, c, \alpha, \beta, \gamma$ **and** the crystal orientation.
- Indexing is an essential step for data processing
- In most cases, indexing algorithms work very easily and fast
- Reasons for difficulties with indexing:
  - More than one crystal lattice (twinning)
  - Very large unit cell leads to overlapping reflections
  - Wrong values for the experimental parameters (detector dstance, wavelength, rotation axis)

The Ewald Sphere Construction

The Ewald Sphere

Laue equations: mathematically handy, but difficult to imagine

Ewald sphere: Construction to help understand the diffraction pattern

Prelude: The reciprocal lattice

- The corners of the unit cell span the crystal lattice
- The unit cell vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ build the basis for the crystal lattice
- Many aspects of diffraction can be described more easily with the help of the **reciprocal lattice**.

- $\vec{a}^* = \frac{\vec{b}\times\vec{c}}{V}$: $\vec{a}^* \perp$ plane$(\vec{b},\vec{c})$
- $\vec{b}^* = \frac{\vec{c}\times\vec{a}}{V}$: $\vec{b}^* \perp$ plane$(\vec{c},\vec{a})$
- $\vec{c}^* = \frac{\vec{a}\times\vec{b}}{V}$: $\vec{c}^* \perp$ plane$(\vec{a},\vec{b})$

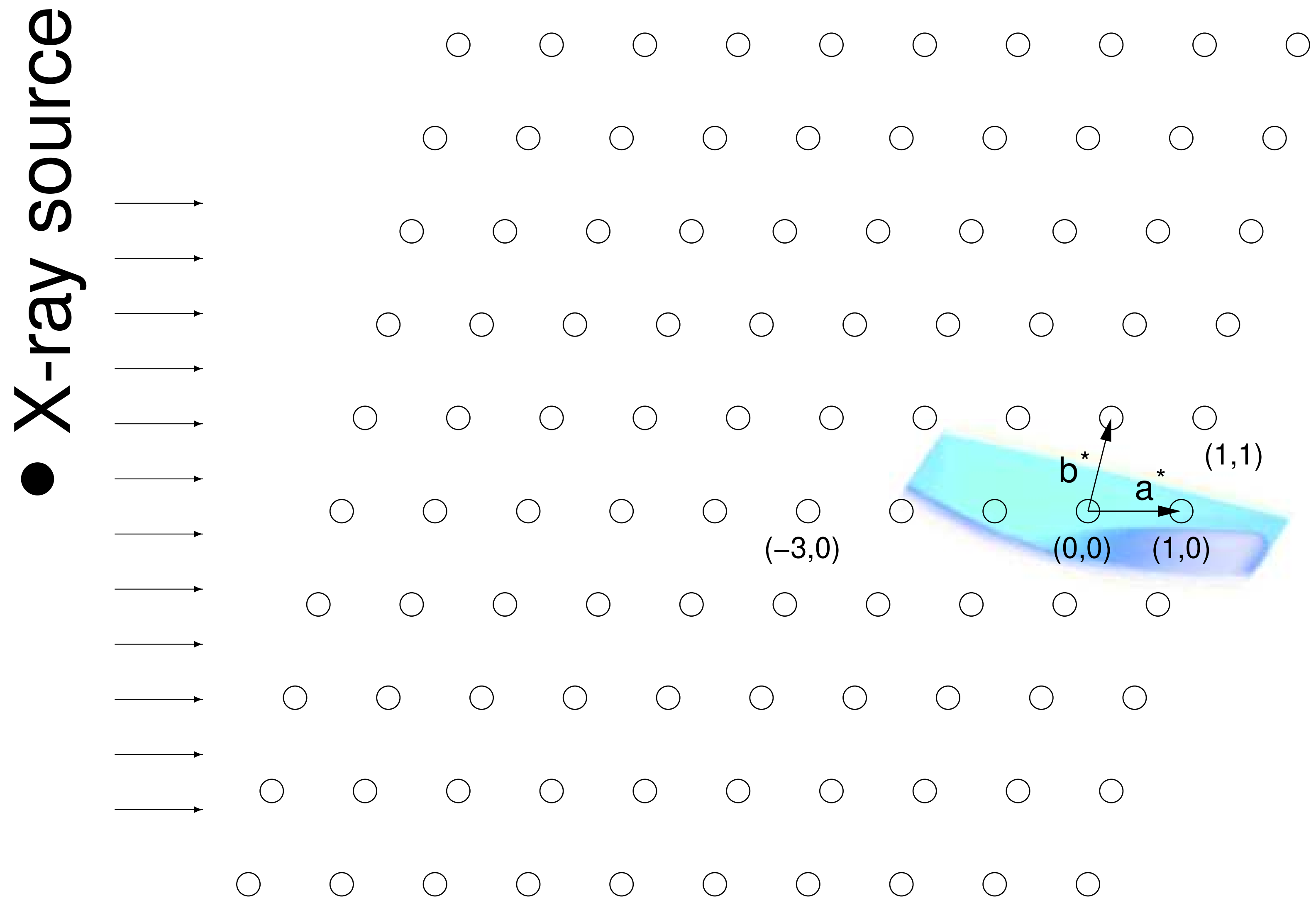
V: unit cell volume (Å^3), $V = (\vec{a}\times\vec{b})\cdot c$

The Miller indices (hkl) span the reciprocal lattice:

$$h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \qquad h,k,l \in \mathbb{Z}$$

- Each reflection corresponds to one point of the reciprocal lattice.
- When $\alpha = \beta = \gamma = 90^\circ$ (orthorhombic unit cell): $|\vec{a}^*| = 1/a$, $|\vec{b}^*| = 1/b$, $|\vec{c}^*| = 1/c$

Laue Equations: The Ewald Sphere Construction



Reciprocal Lattice:

$$\vec{a}^* = \frac{\vec{b}\times\vec{c}}{(\vec{a}\times\vec{b})\cdot\vec{c}}$$
$$\vec{b}^* = \frac{\vec{c}\times\vec{a}}{(\vec{a}\times\vec{b})\cdot\vec{c}}$$
$$\vec{c}^* = \frac{\vec{a}\times\vec{b}}{(\vec{a}\times\vec{b})\cdot\vec{c}}$$

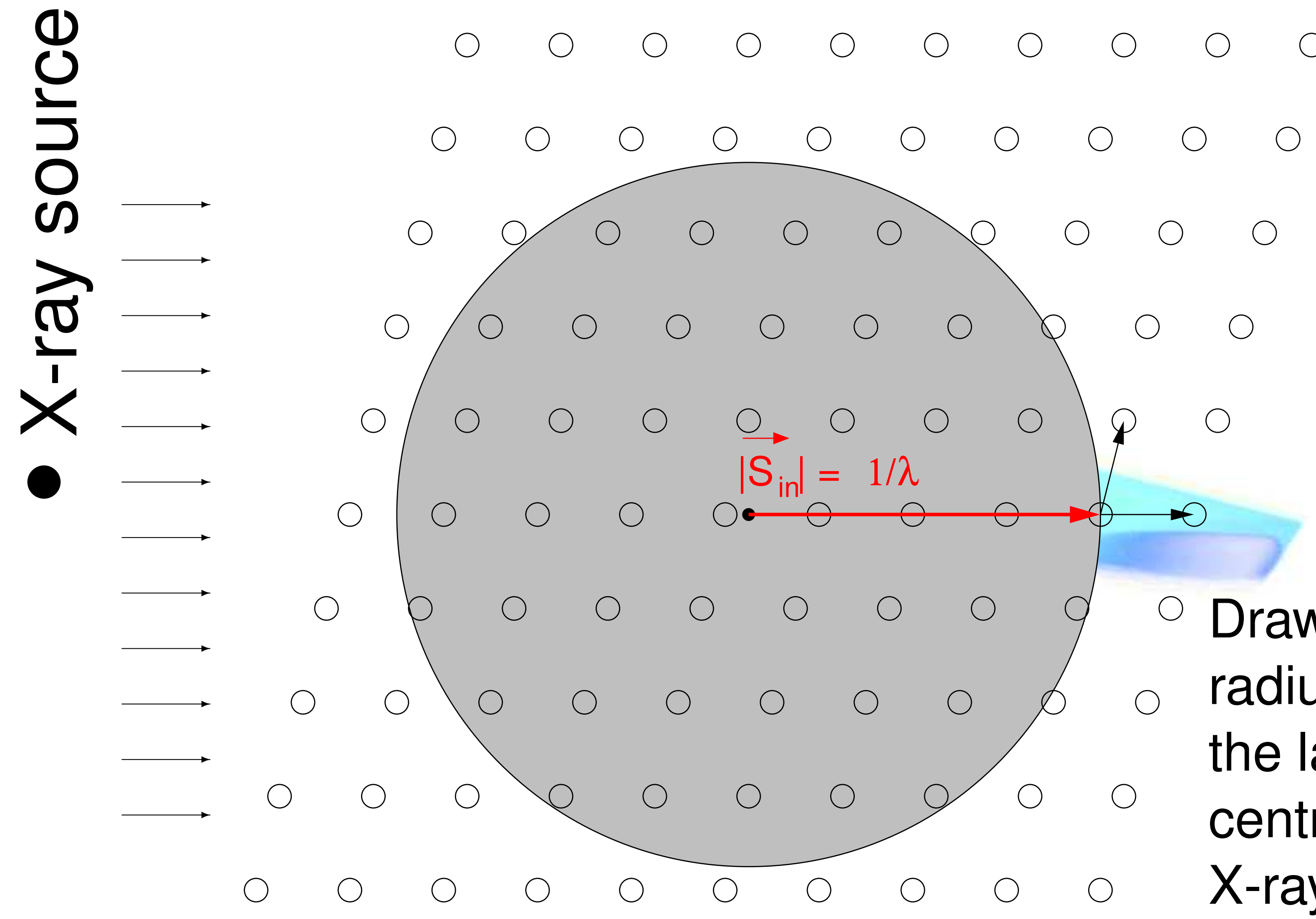
Lattice points at:

$h\vec{a}^* + k\vec{b}^*(+l\vec{c}^*)$

(hollow circles)

The crystal rotates about the origin of the reciprocal lattice.

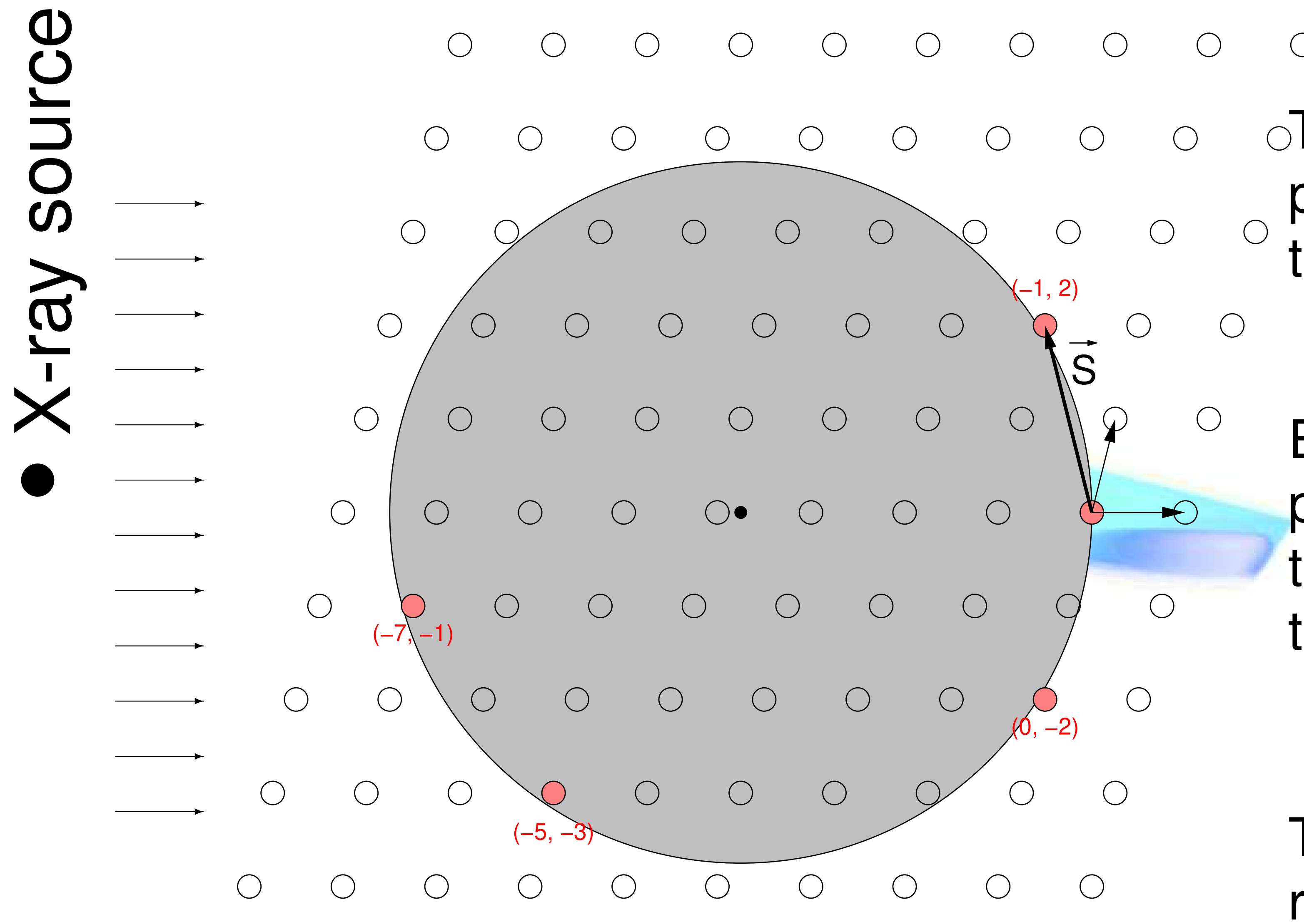
Laue Equations: The Ewald Sphere Construction



Draw a sphere with radius $1/\lambda$ that **touches** the lattice origin. The sphere centre lies aligned with the X-ray source.

This sphere is the **Ewald Sphere**.

Laue Equations: The Ewald Sphere Construction

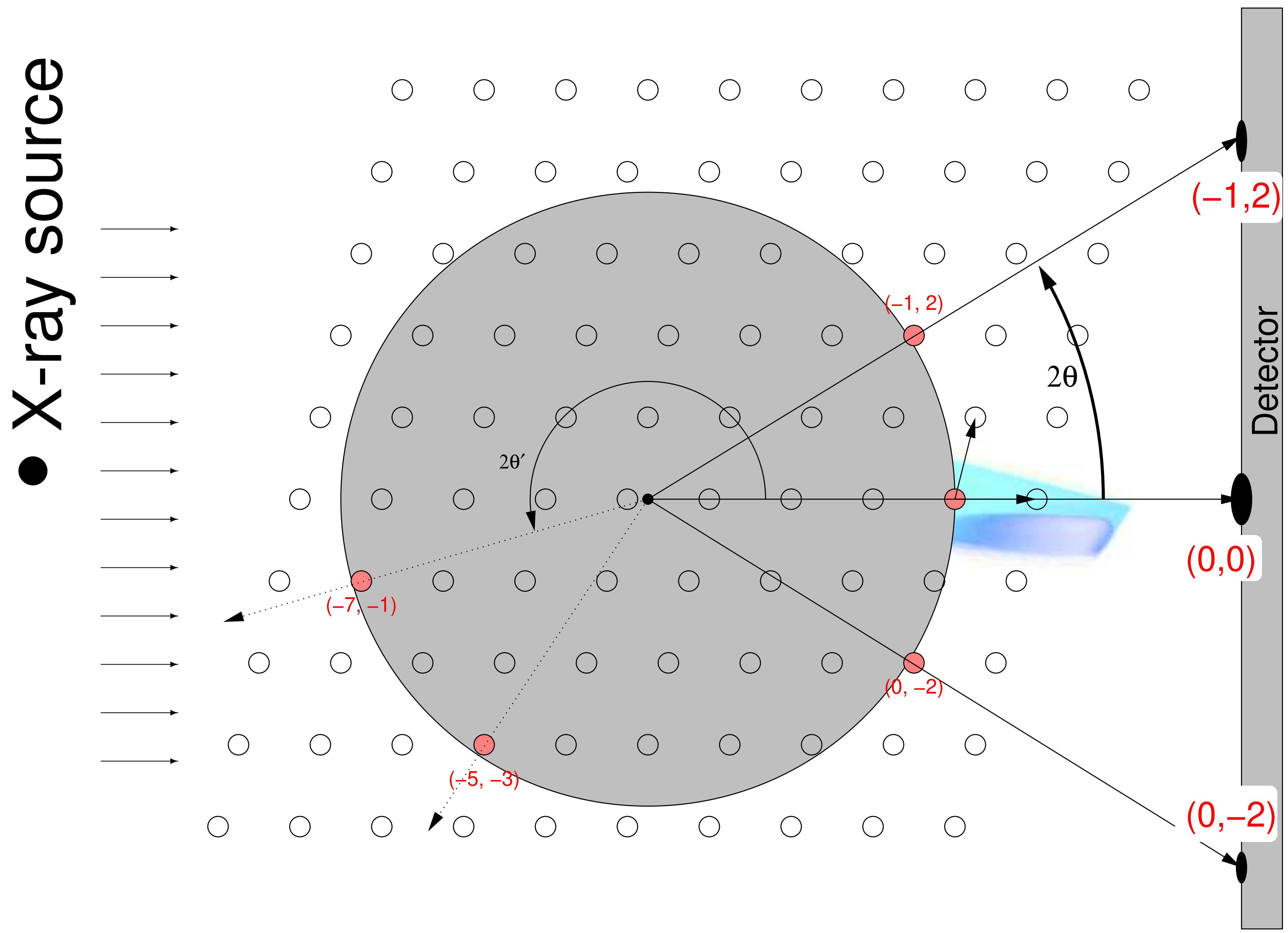


The **scattering vector** $\vec{S}$ points from the origin to the lattice point.

Exactly those lattice points on the surface of the Ewald sphere fulfil the Laue conditions.

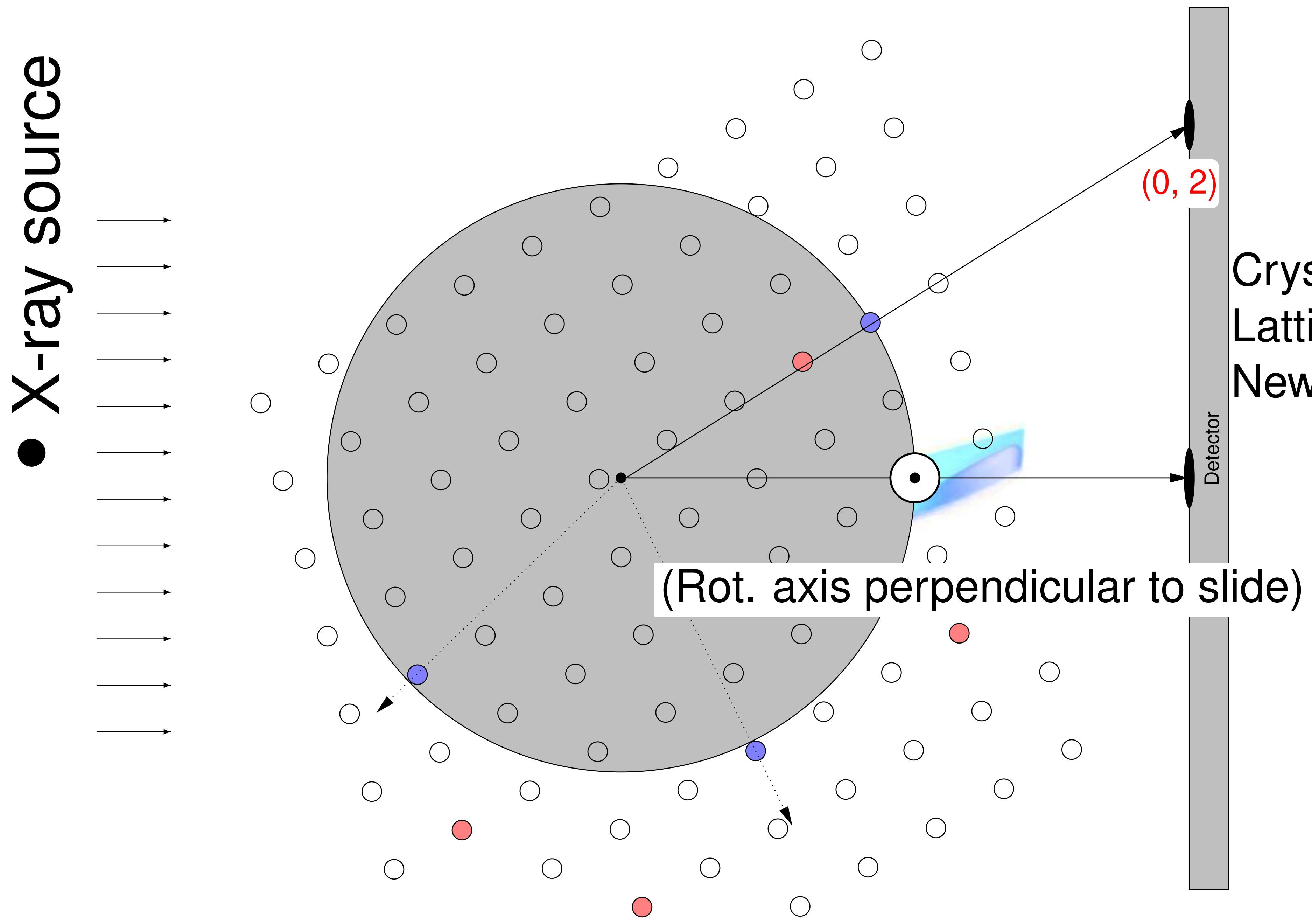
They are the **recordable** reflections.

Laue Equations: The Ewald Sphere Construction



Some of these spots hit the detector.

Laue Equations: The Ewald Sphere Construction



(Rot. axis perpendicular to slide)

Crystal rotation =
Lattice rotation =
New spots

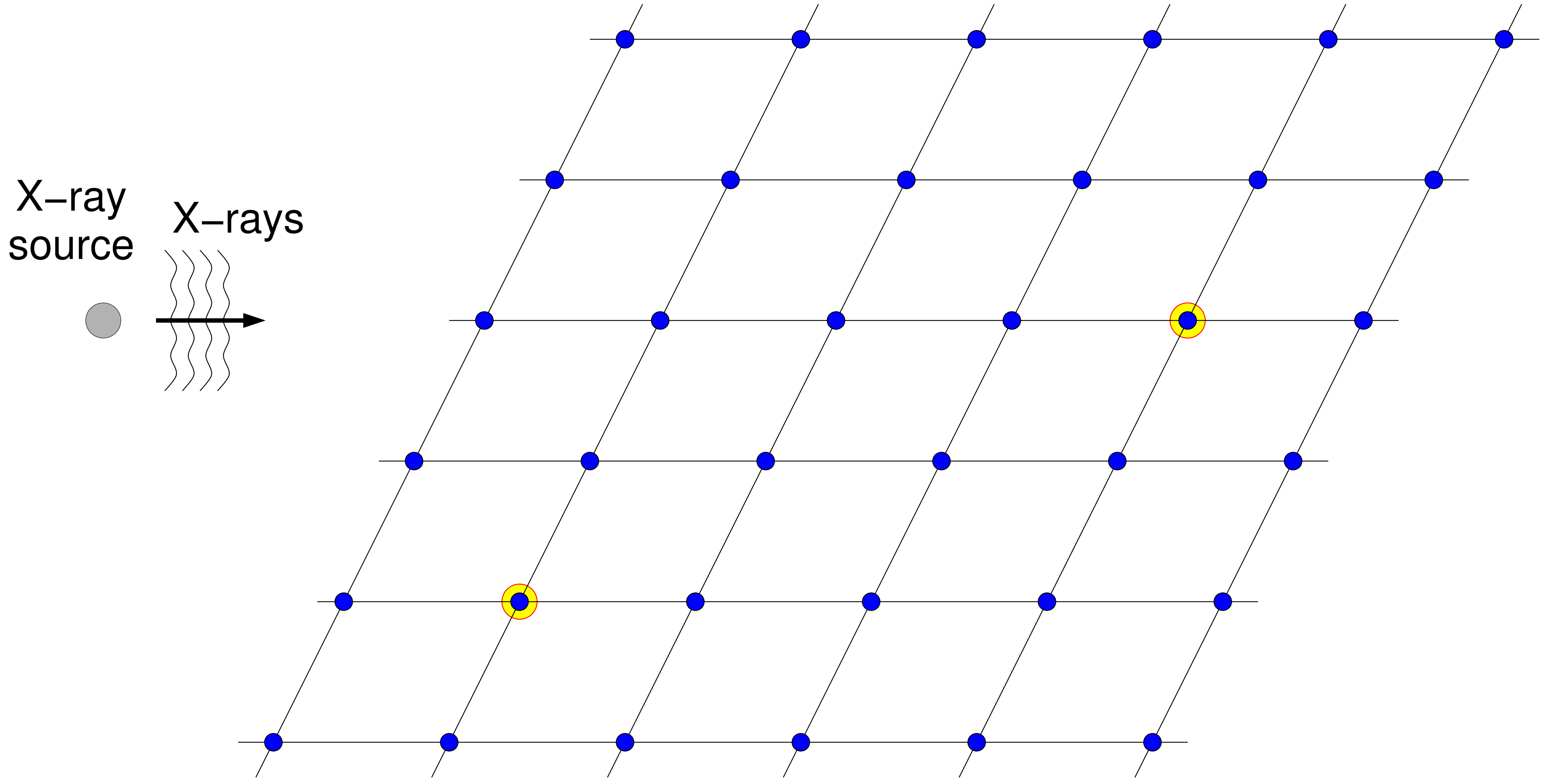
Bragg’s Law

Bragg’s Law

Idea:

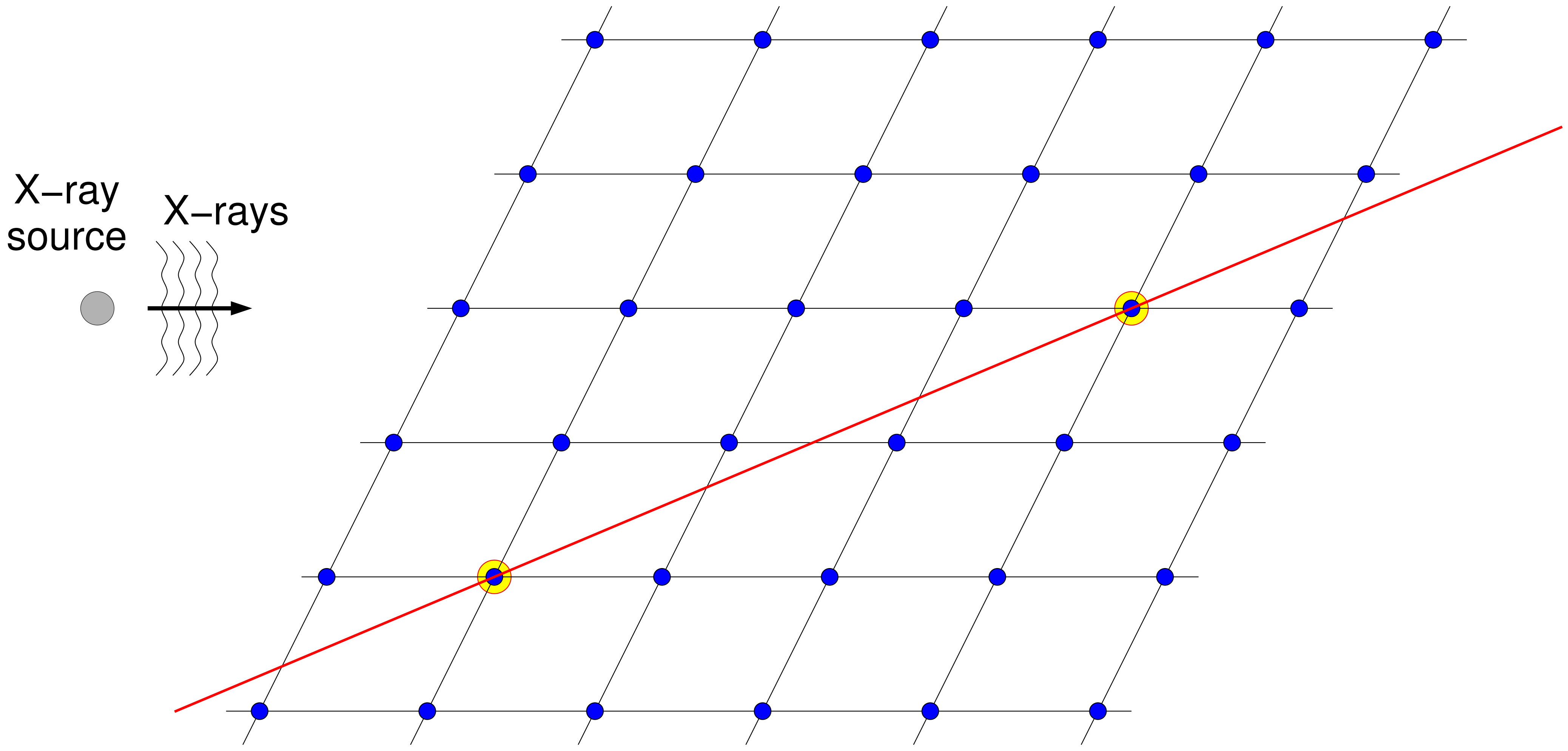
- X-rays are reflected on lattice planes (German: “Gitterebenen” or “Netzebenen”)
- Reflections occur when the path difference is a multiple integer of the wave length

Bragg's Law



1. Lattice: Corners of the unit cells.

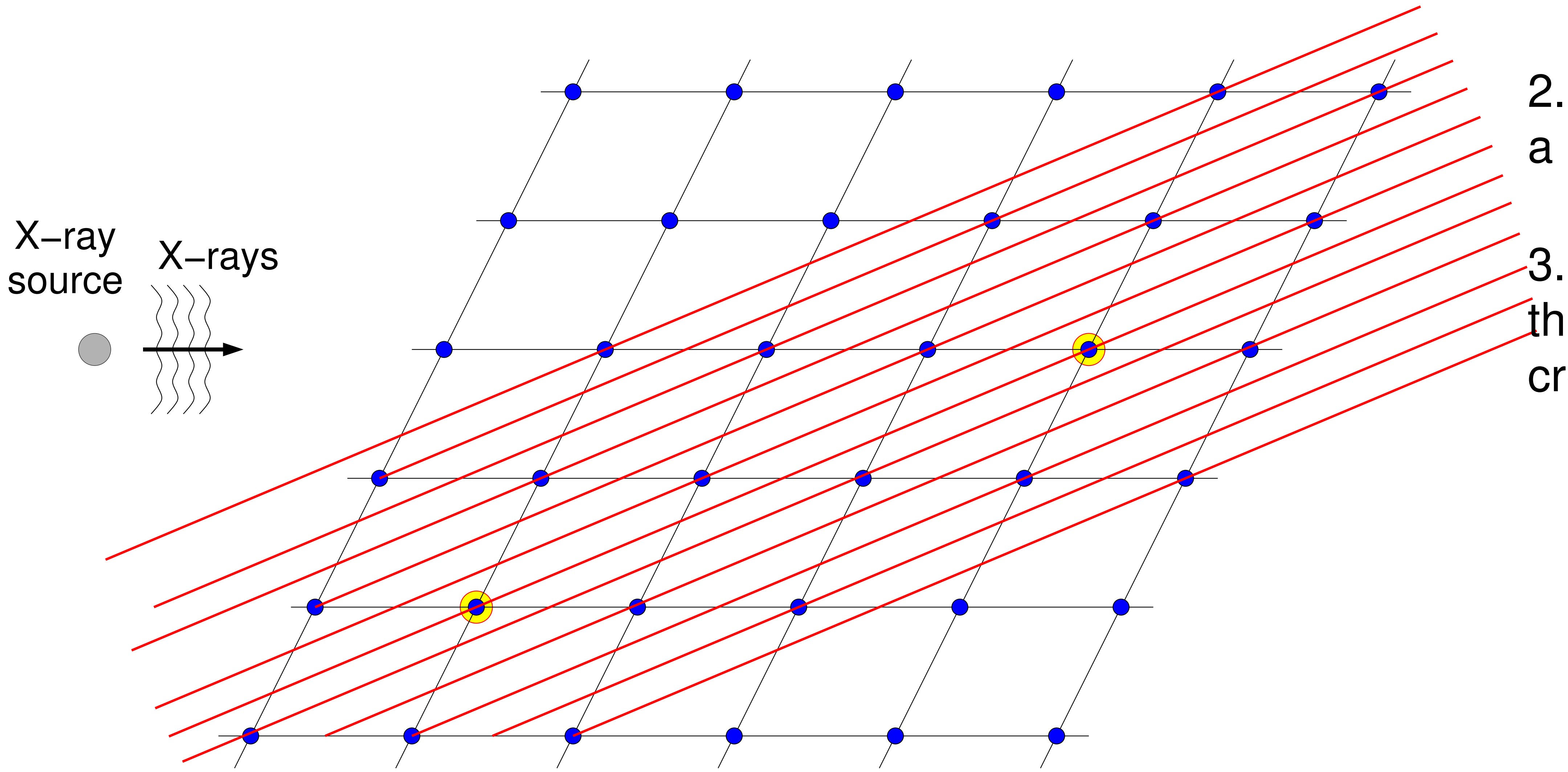
Bragg's Law



1. Lattice: Corners of the unit cells.

2. Three corner points make a plane.

Bragg's Law

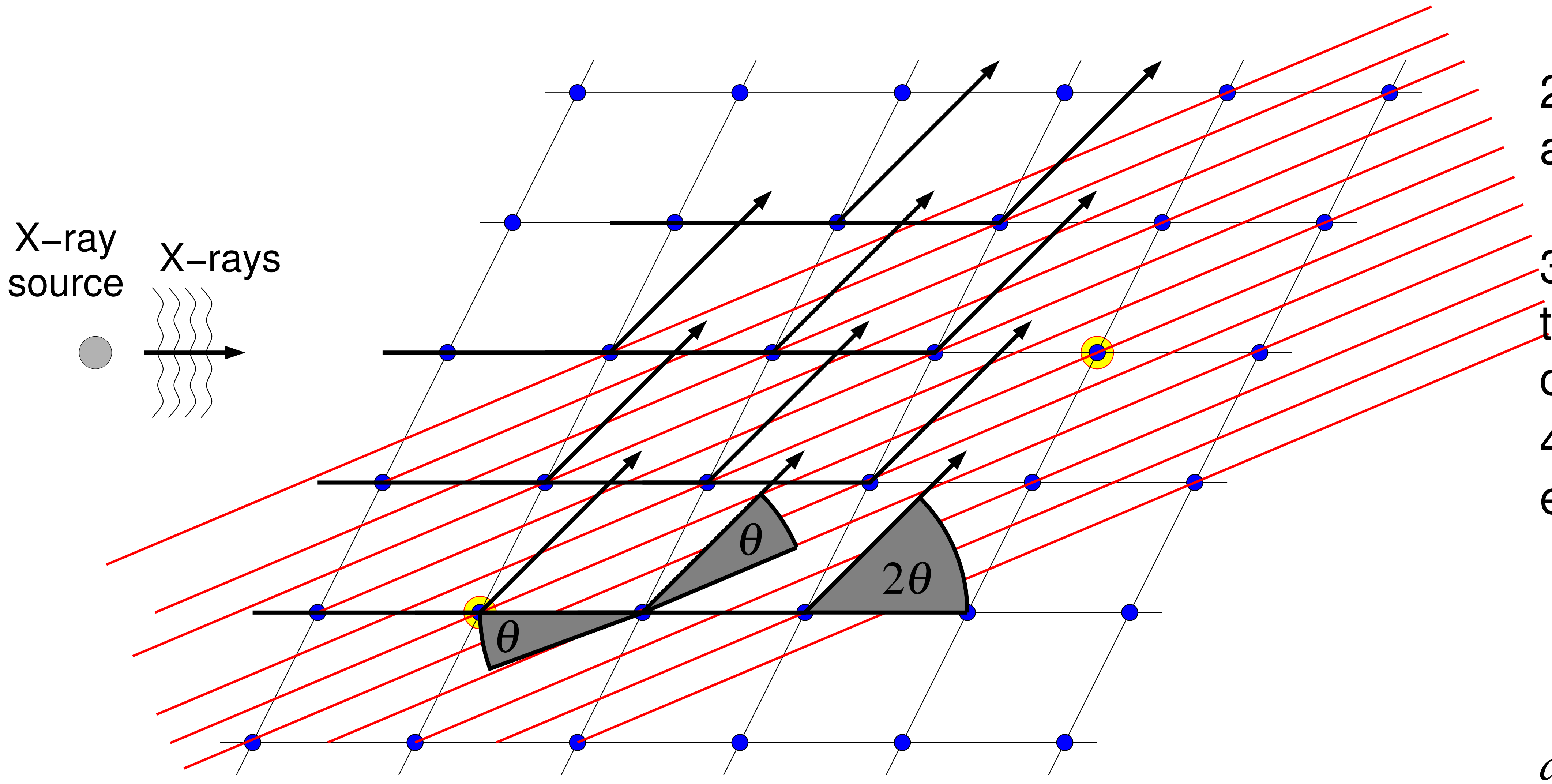


1. Lattice: Corners of the unit cells.

2. Three corner points make a plane.

3. Parallel shifting of plane through **all** lattice corners creates a set of planes.

Bragg’s Law



1. Lattice: Corners of the unit cells.

2. Three corner points make a plane.

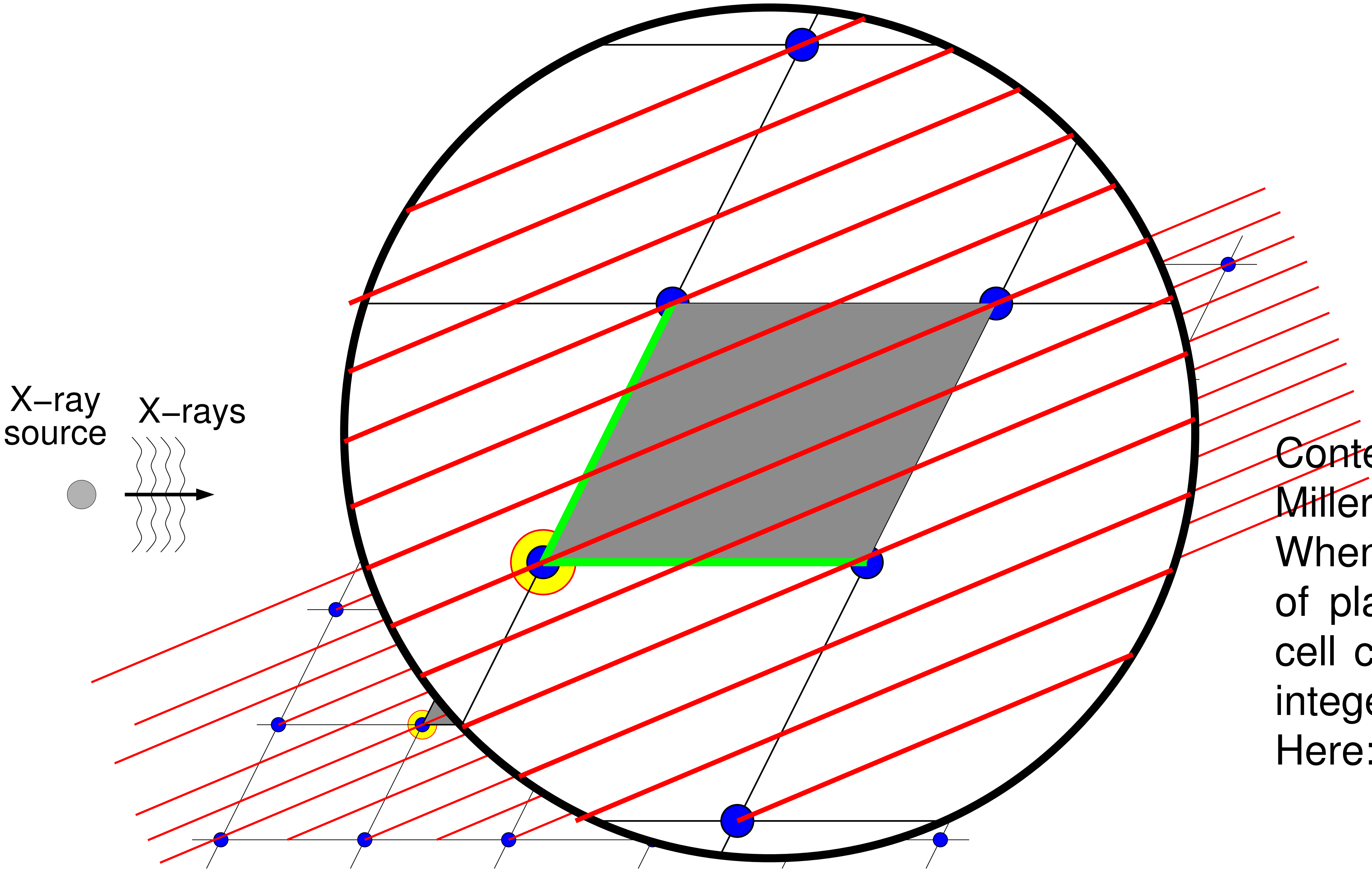
3. Parallel shifting of plane through **all** lattice corners creates a set of planes.

4. Constructive interferences leads to Bragg’s Law:

$$n\lambda = 2d\sin\theta$$

d : distance between planes.

Bragg’s Law



$$n\lambda = 2d\sin\theta$$

Context with Laue equations and Miller indices:
When Bragg’s law holds, the set of planes divides the three unit cell constants a, b, and c into a integer number of segments.
Here: $(2,3,0)$

Bragg's Law and Resolution of a Reflection

$$n\lambda = 2d\sin\theta$$

- The value d is called **the resolution** of the reflection (hkl)
- d is measured in Å.
- **N.B.:** High resolution corresponds to a small value of d
- $n \geq 2$ higher order reflections, which usually do not occur. We only need to consider the case $n = 1$, *i.e.*

$$\lambda = 2d\sin\theta$$

Bragg’s Law and Resolution of a Reflection

$$\lambda = 2d \sin\theta$$

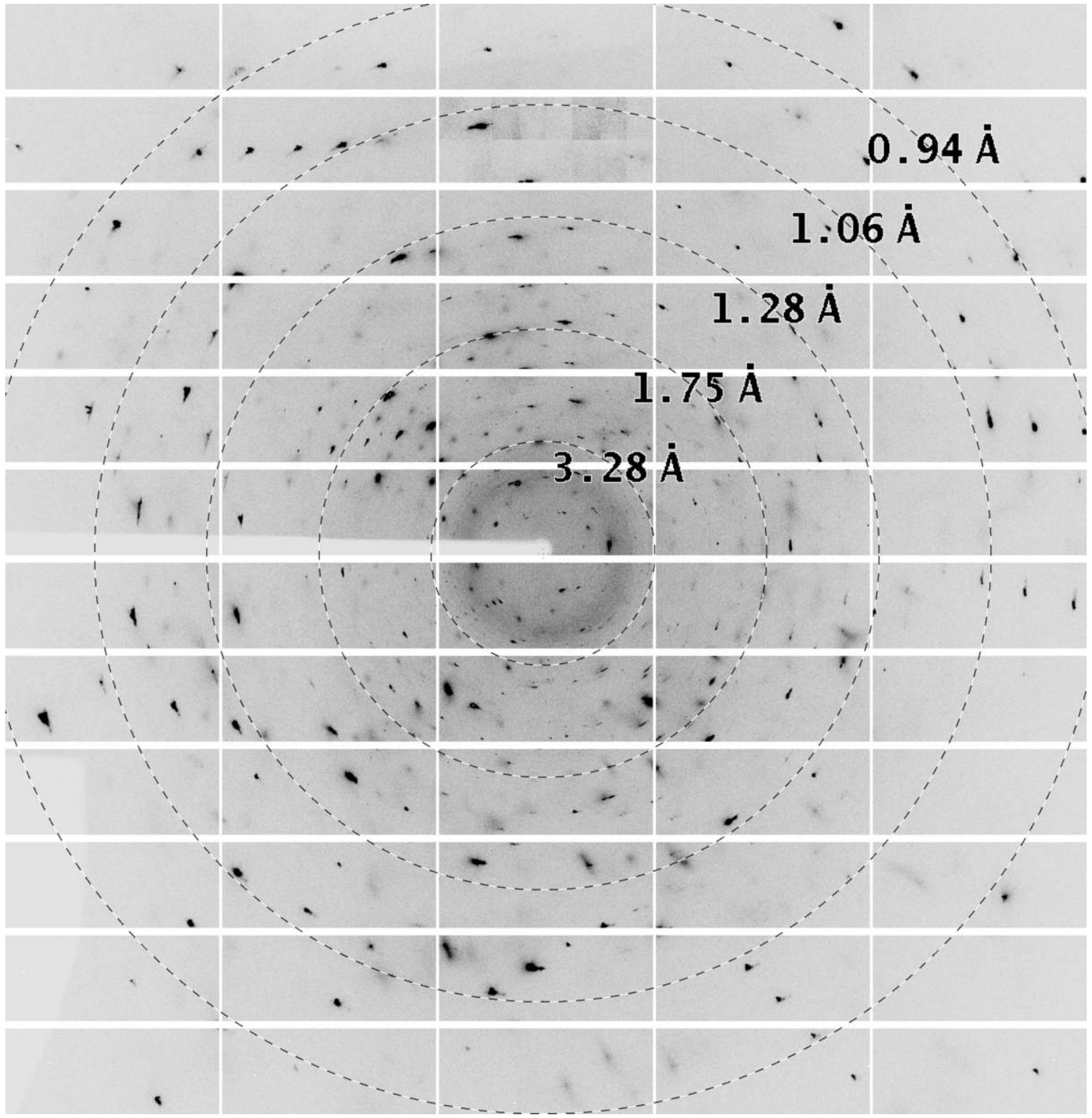
- Sometimes, the inverted value

$$d^* \equiv 1/d = \frac{2\sin\theta}{\lambda}$$

  is called resolution, measured in 1/Å
- High values of d^* correspond to high resolution and *vice versa*
- d^* has the length of the reciprocal lattice vector

$$d^* = 1/d = \|h\vec{a}^* + k\vec{b}^* + l\vec{c}^*\|$$

Example image with resolution rings



- All reflections on a circle about the direct beam have the same resolution
- When the detector if offset ($2\theta \neq 0^\circ$), the circles become ellipses (intersection of a cone and a plane)

Reflection Intensity

- The Laue equations, the Bragg equation, and the Ewald sphere construction all refer to the spot positions.
- They contain no information about spot intensity
- The molecule inside the unit cell determines the intensity of every reflections:

$$\begin{aligned} I(hkl) &\propto \Big|\sum_{\text{atom } j} f_j \cos(hx_j + ky_j + lz_j)\Big|^2 \\ &\propto \Big|\sum_{\text{atom } j} f_j e^{2\pi i(hx_j+ky_j+lz_j)}\Big|^2 \end{aligned}$$

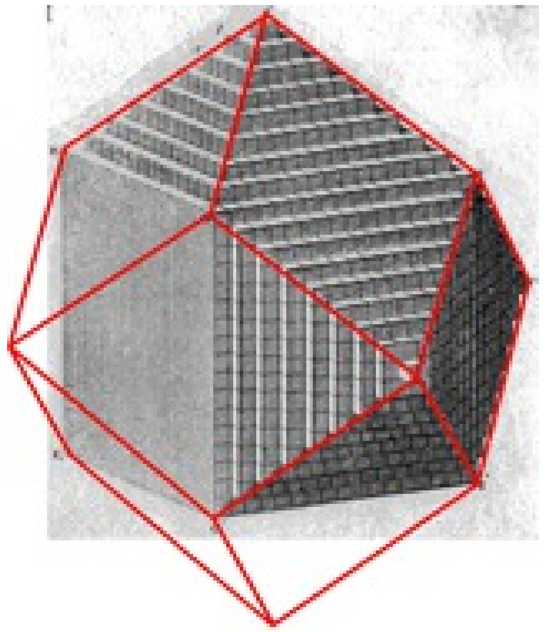
1. every atom emits a small spherical wave ($\cos$-term)
2. the amplitude f_j is proportional to the atom number Z
3. f_j is called *atomic scattering factor*

Summary Laue equations

- Reflex positions (“patterns”) depend on the unit cell parameters $a, b, c, \alpha, \beta, \gamma$ and the orientiation of the crystal.
- Reflex positions *do not* depend on the chemical content of the unit cell.
- Reflex intensities depend on the chemical content of the unit cell
- “chemical content”: atom type and atom positions
- Ewald sphere visualises the Laue equation
- Every reflex has a resolution d, via Bragg’s law.
- High resolution = small d, low resolution = large d

Symmetry and Space Groups

Shape and Appearance of Crystals

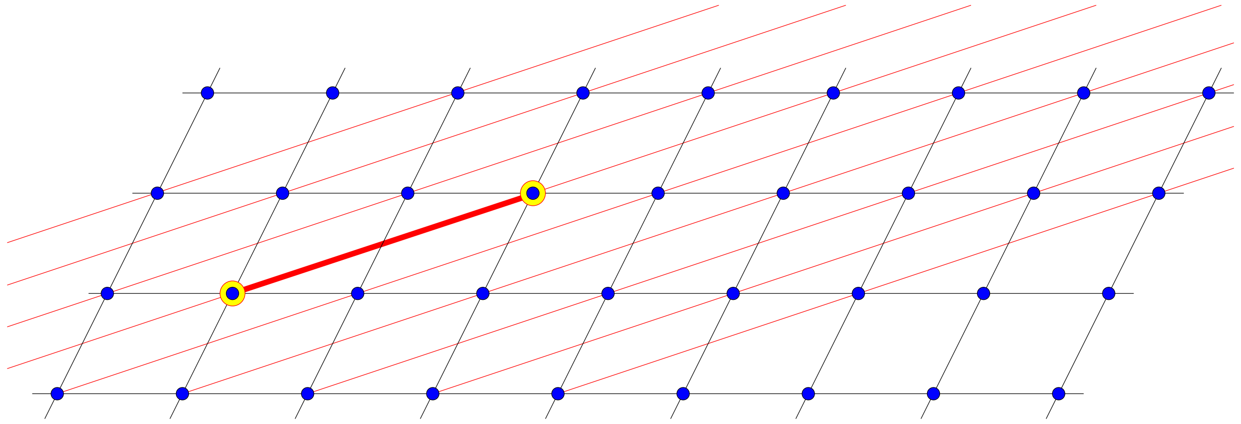


Steve Lower, http://www.chem1.com/acad/webtext/virtualtextbook.html

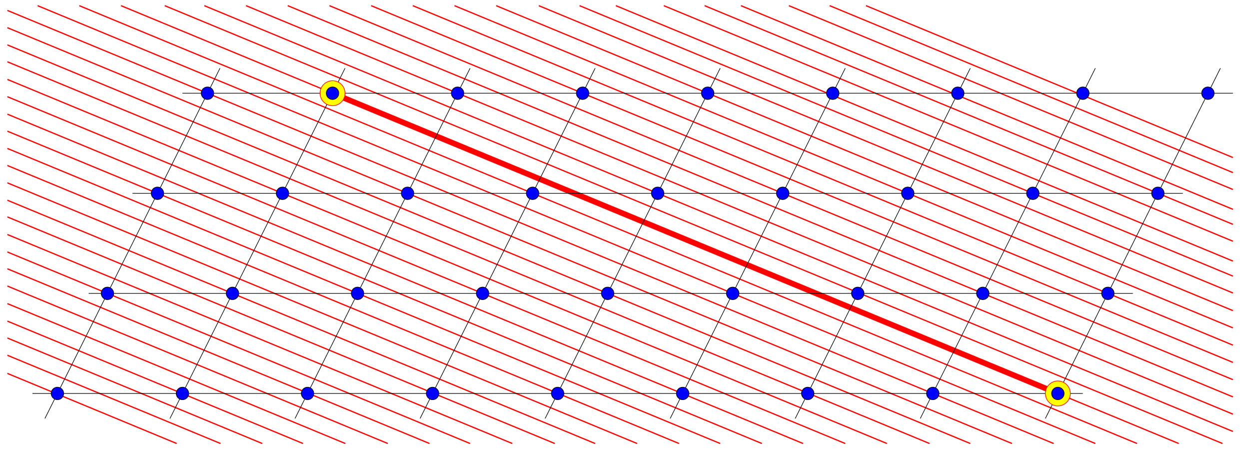
Historically, the science of crystallography describes the appearance and (visual) regularity of crystals.
Nicolaus Steno (1638–1686) states the “law of constant angles” or the “first law of crystallography” (1669)

> Angles between corresponding faces on crystals are the same for all specimens of the same mineral

Steno: Law of Constant Angles



lattice plane (120): small Miller index
$\hat{=}$ large lattice distance d
(low resolution reflection)
high atom density along plane: stable



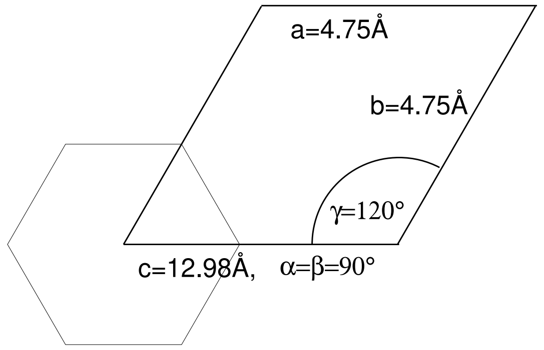
lattice plane $(3\bar{7}0)$: large Miller index
$\hat{=}$ smalle lattice distance d
(high resolution reflection)
low atom density along plane: unstable

Crystal breaks between stable planes

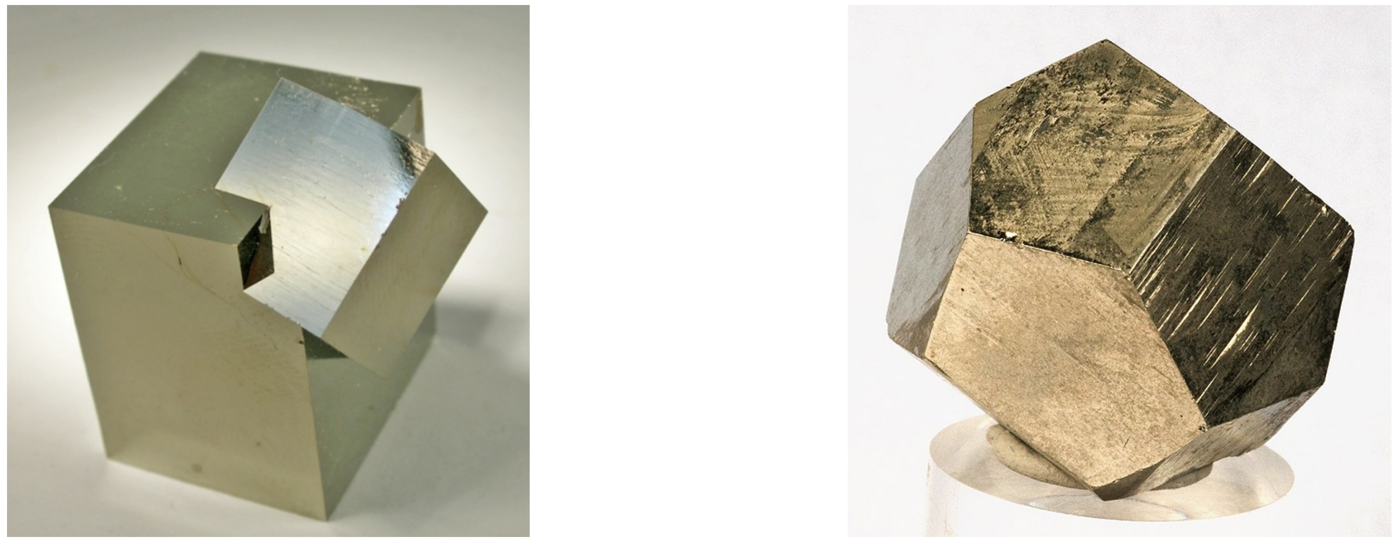
Example Crystals

Image courtesy Mark Minge, http://www.diamant-edelstein.de

Ruby ($Al_2O_3 + Cr$)



hexagonal cell



Pyrite (FeS_2)

(100)-direction

(210)-direction

cubic cell

History of Symmetry of Crystals

1801	René-Just Haüy describes crystal symmetries using group theory.
1850	Auguste Bravais describes the 14 Bravais lattices.
1890/1891	Arthur Moritz Schönflies und Jewgraf Stepanowitsch Fjodorow derive all 230 emphspace groups.
1912	Max von Laue, Walter Friedrich und Paul Knipping carry out the first X-ray diffraction experiment. They prove: • X-rays are waves • crystals consists of a lattice

Meaning of Symmetry for Structure Determination

The symmetry of a crystal is important because it affects

- data acquisition and scaling
- structure solution
- refinement

Symmetry in molecules

1. What is symmetry?
2. elementary symmetry operations: rotation, mirror plan, inversion centre
3. Combination of symmetry operations: point groups

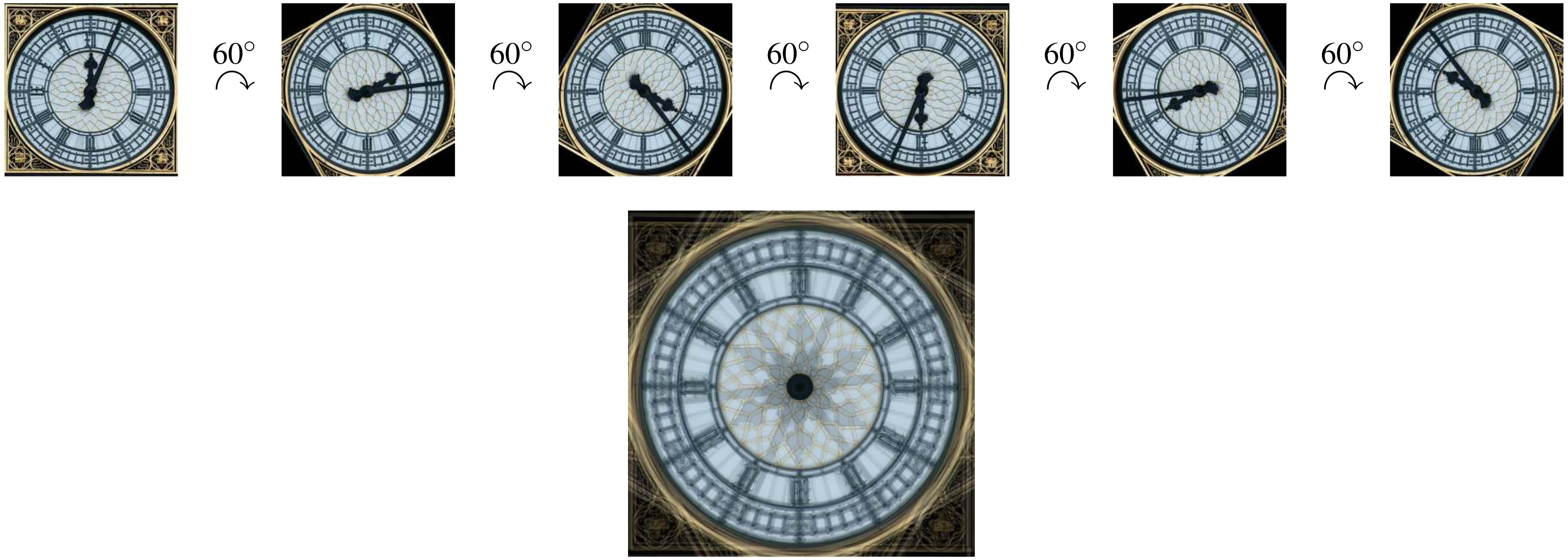
The Term “Symmetry”

Symmetry is part of our daily lives:

Butterfly with a mirror plane

Flower with 5-fold rotational symmetry

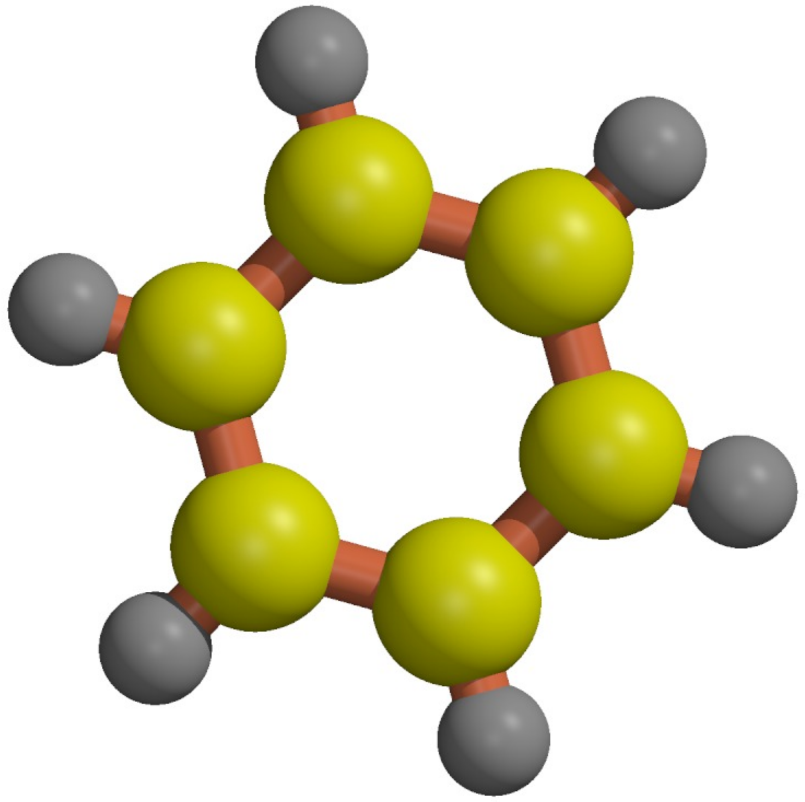
Example: 12-fold Rotational Symmetry



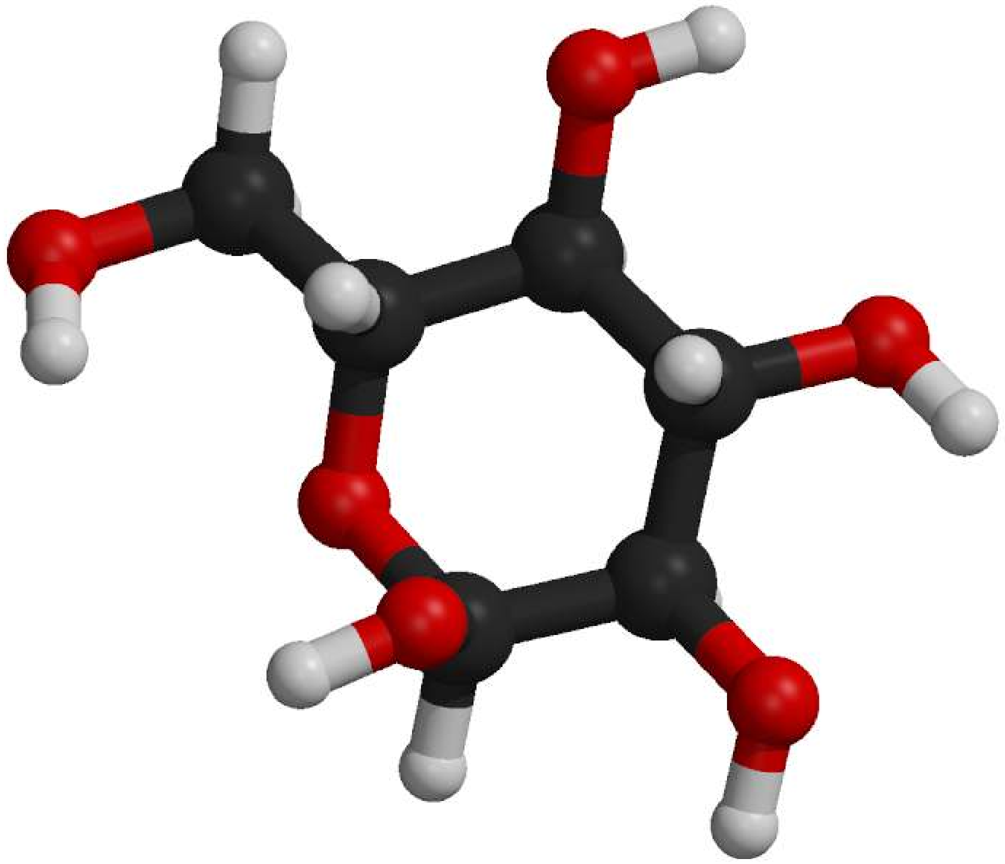
(`http://commons.wikimedia.org/wiki/File:Parliament_Clock_Westminster.jpg`)

Symmetry (in real life) is never ideal.
Ideally, all six images would be identical.
The symmetry of crystals and of individual molecules is much closer to the mathematical meaning of symmetry than macroscopic symmetry.

Symmetric molecules



Benzene: 6-fold rotational symmetry
+ mirror planes

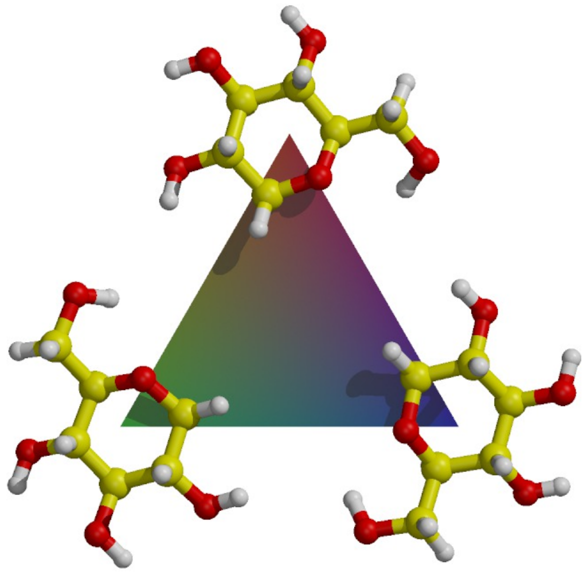


α-D-Glucose: no proper symmetry

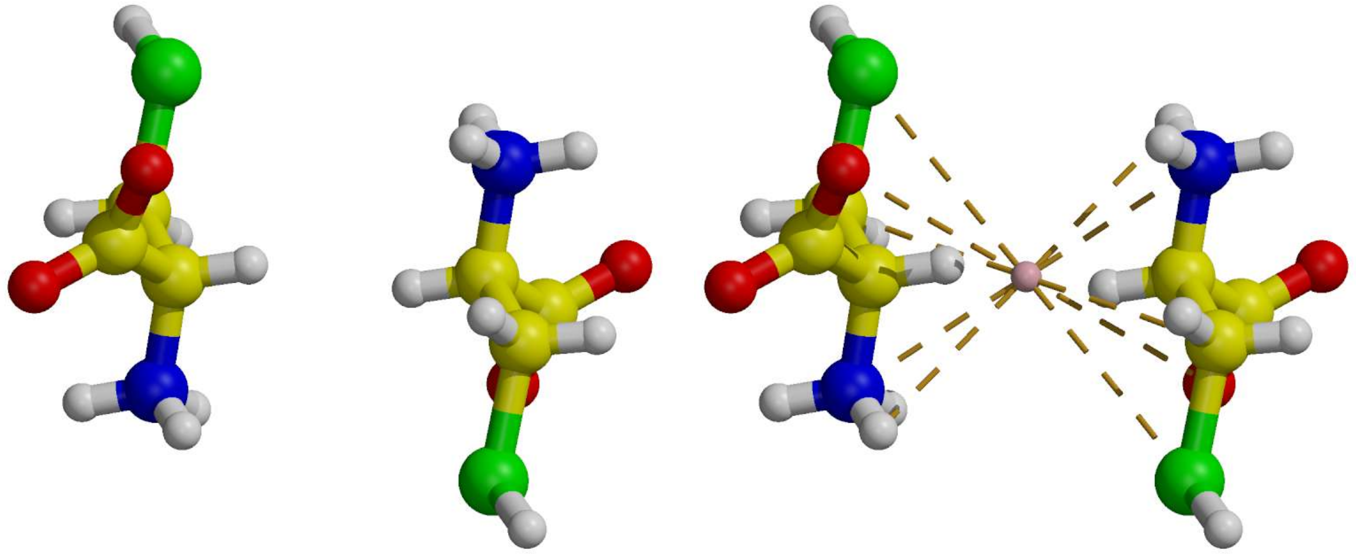
non-symmetric molecules can still crystallise

Symmetry by arrangement: towards a crystal

Crystals without proper symmetry can still be arranged symmetrically.



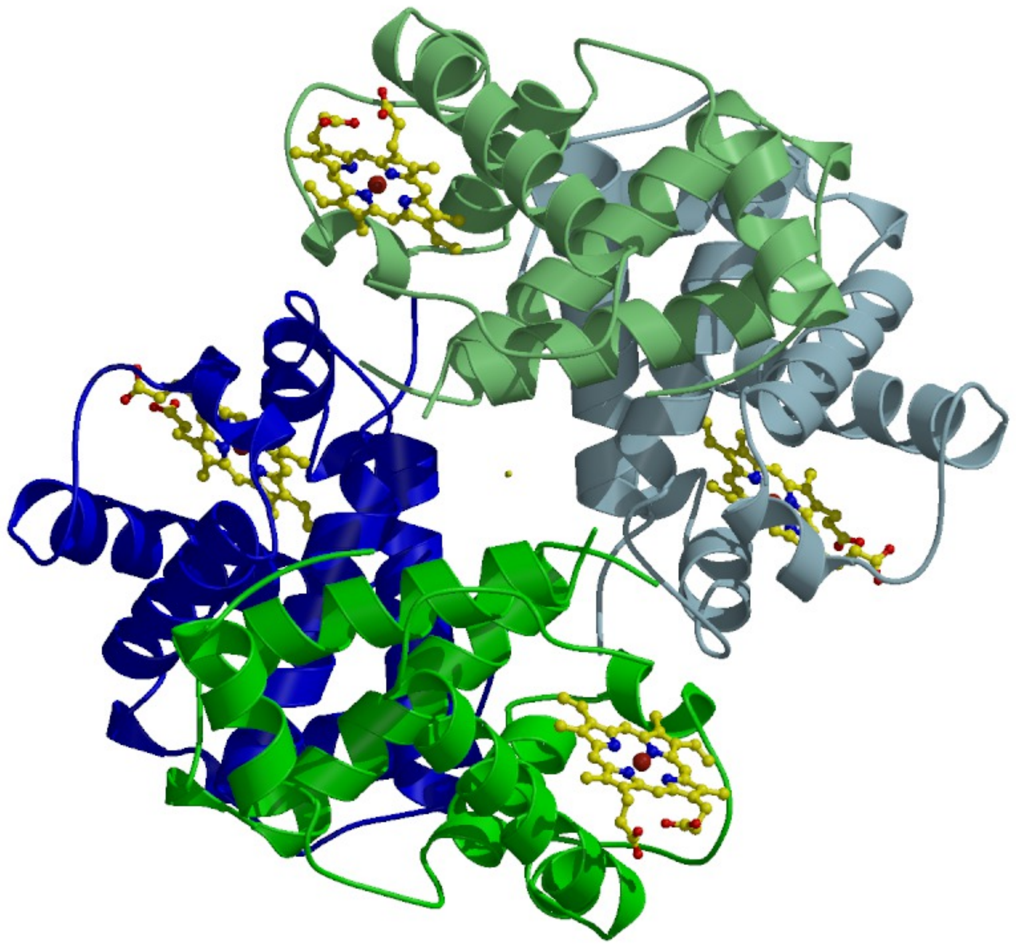
α-D-Glucose about 3-fold rotation axis



L-Cys und D-Cys with centre of inversion

Symmetric arrangement

Sometimes, the arrangement in a crystal may have a chemical meaning.



Hemoglobin in blood cells forms a dimer (dark/light) of two hetero dimers (α/β-globin green and blue) with a 2-fold rotation axis.
Hemoglobin crystallises with the same arrangement

Elementary Symmetry Operations

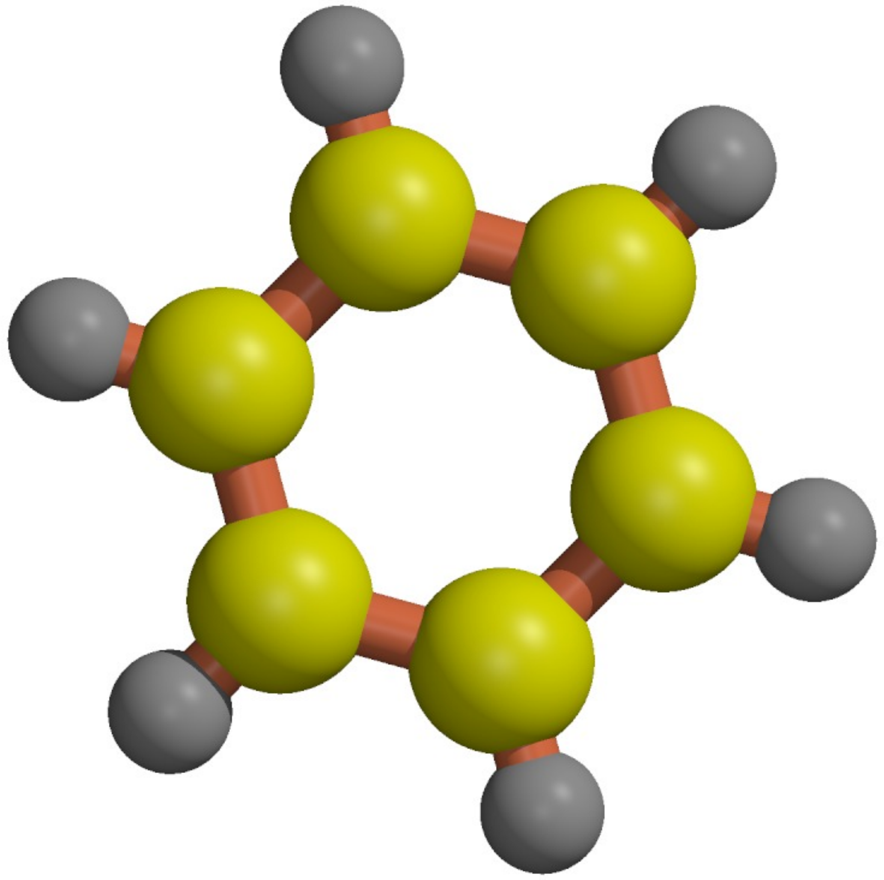
Symmetry Operations

“Definition”: A Symmetry operation is a “movement” that does not change what an image looks like.
Any (finite) object as three elementary symmetry operations:

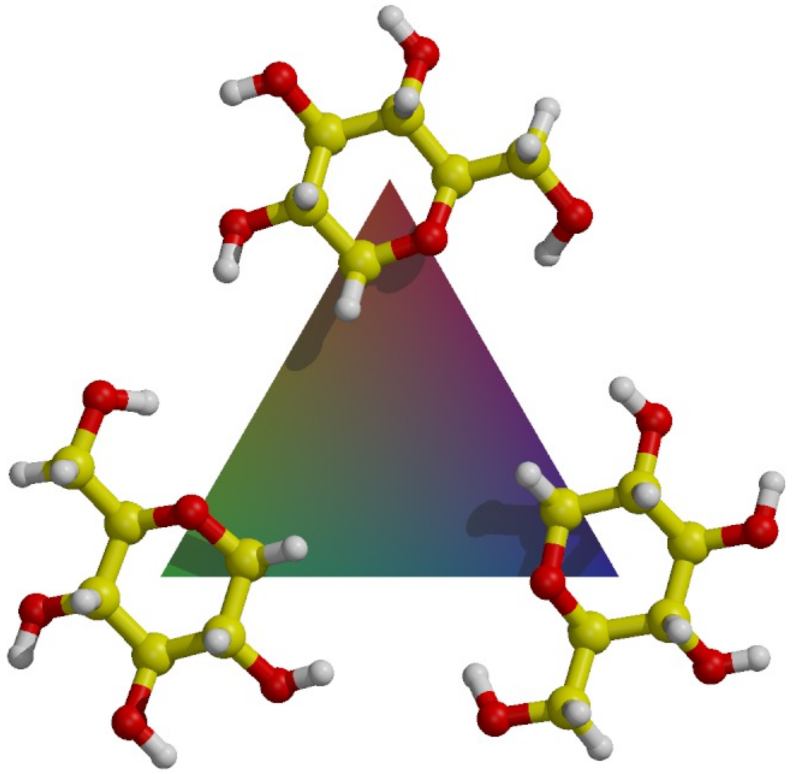
1. (n-fold) **rotation**
2. **mirror plane**
3. **inversion** (=point point reflection)

Symmetry operations: Rotation

An object with an n-fold axis of rotation can be rotated about this axis by $\frac{360^\circ}{n}$ without changing its apparition.
With n such rotations, the object is back to where it was at the beginning.



Benzene: 6-fold axis of rotation *perpendicularly* to plane of this slide

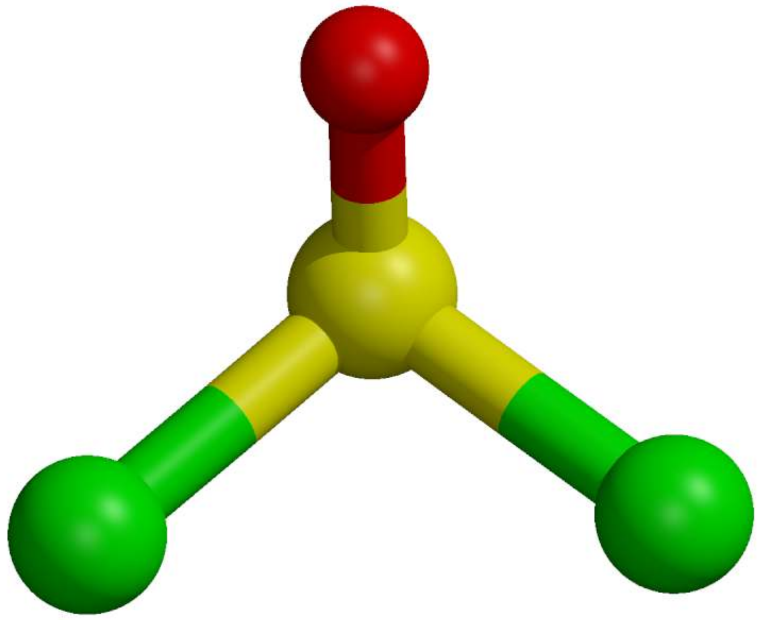


Three glucose molecules with a 3-fold axis of rotation.

Clock face with 12-fold axis of rotation

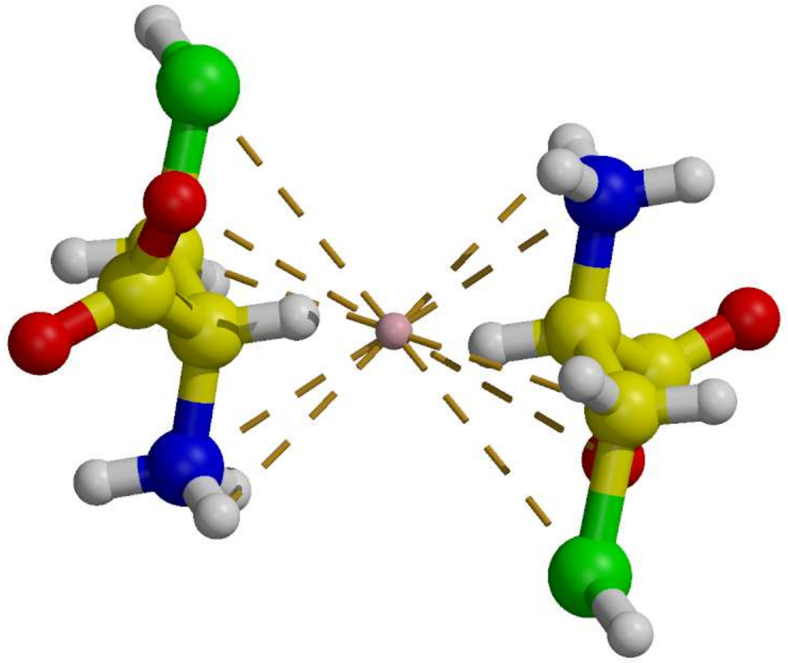
Symmetry operations: Mirror plane

Butterfly with mirror plane

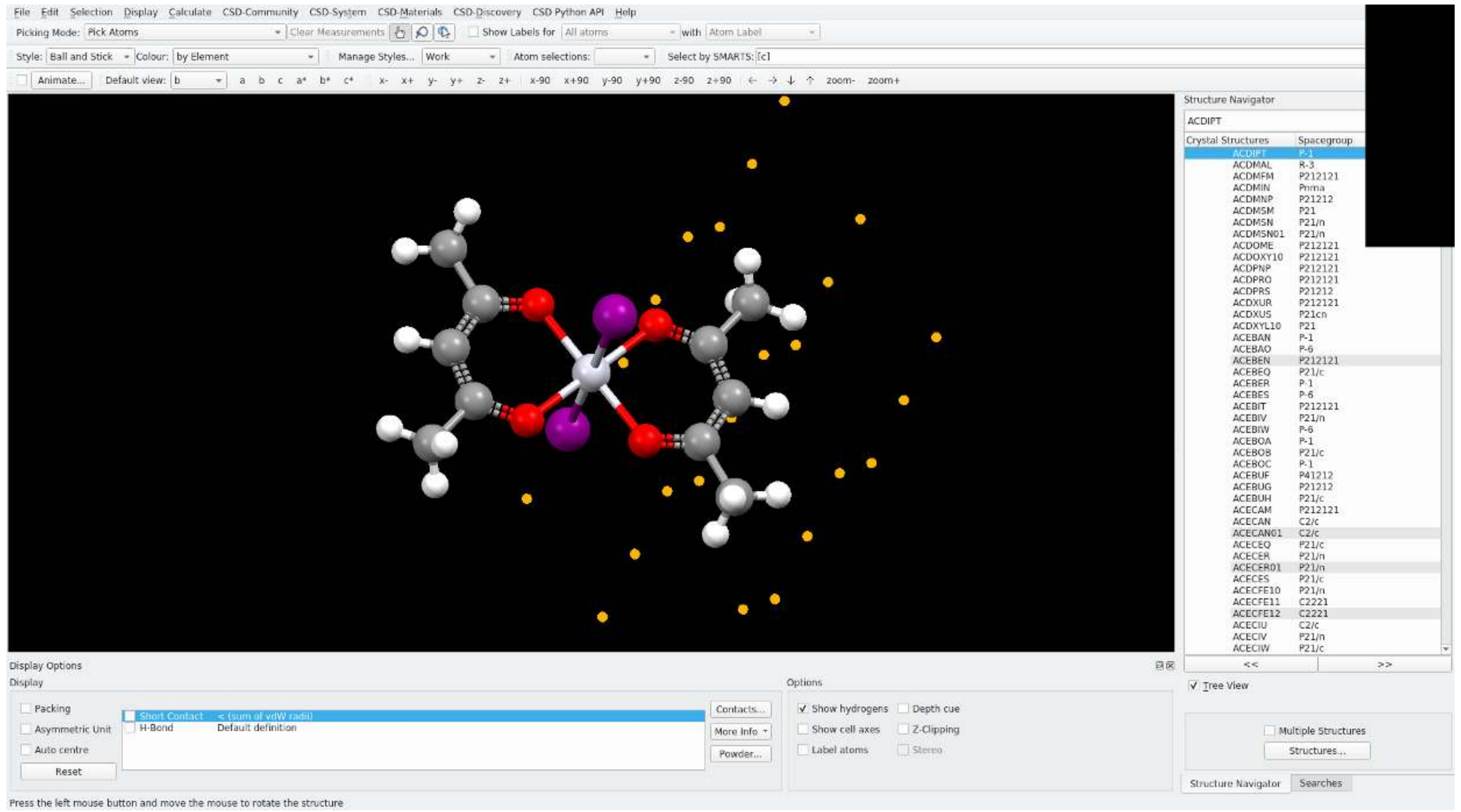


Thionyl chloride ($SOCl_2$) with mirror plane.

Symmetry operations: Inversion



L- and D-Cysteine



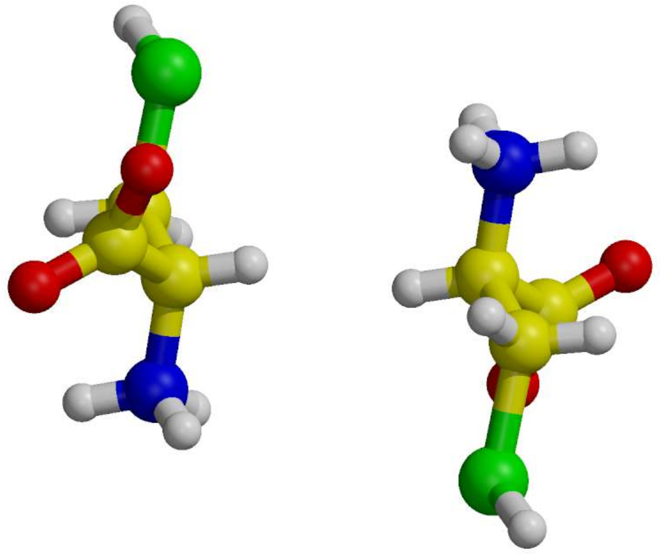
Press the left mouse button and move the mouse to rotate the structure

$C_{10}H_{14}I_2O_4Pt$, CSD entry Nº `ACDIPT`
displayed with MERCURY

All connections of corresponding atoms run through one single point, the *inversion centre* of the object.

Chiral Molecule

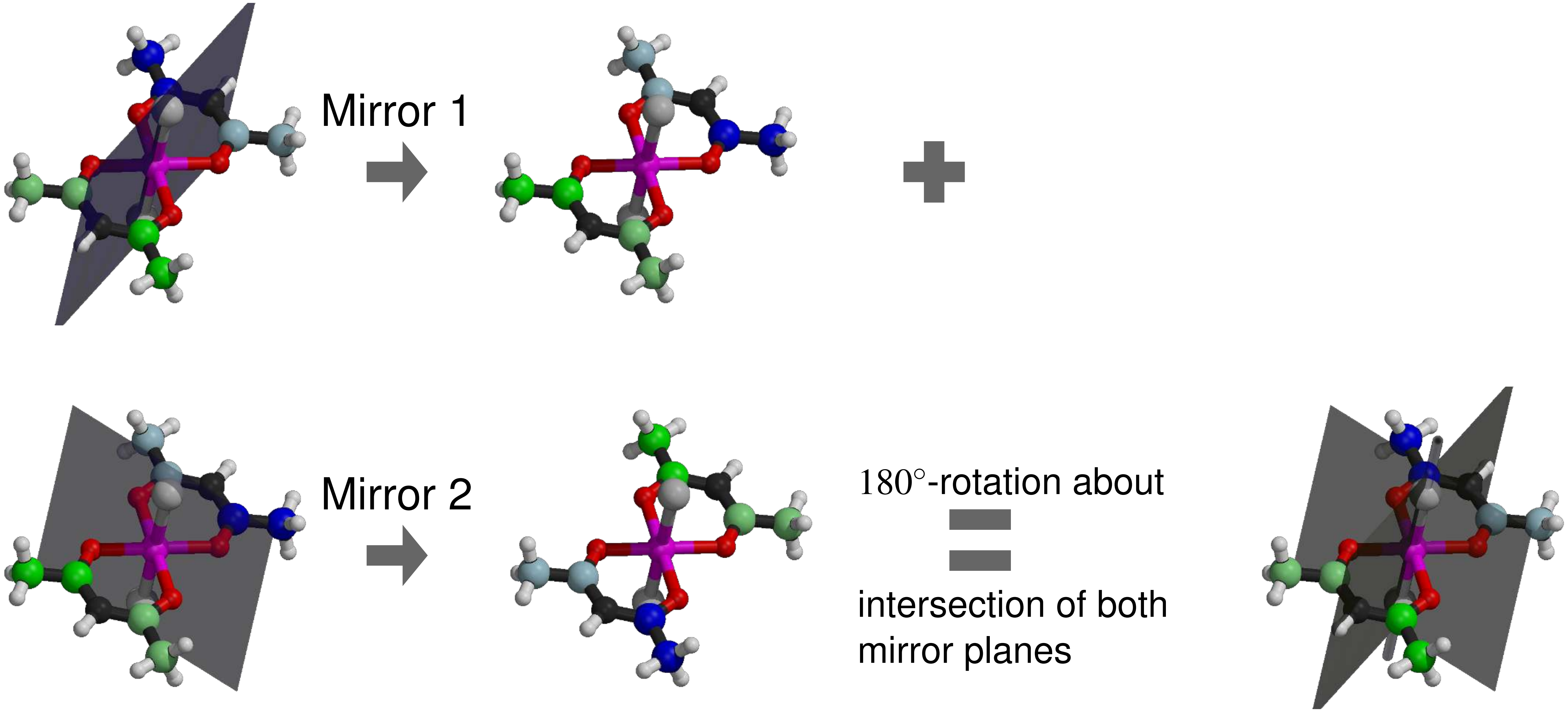
A molecule without *centre of inversion* and without *mirror plane* is called *chiral*.
Inversions or mirroring the molecule creates a *different* molecule.
The two forms are called right handed (R(ectus)) and left handed (S(inister)).



Important example: amino acids (and therefore all proteins), and nucleic acds (and therefore DNA and RNA)

Combination of symmetry operations

Symmetry operations can be combined arbitrarily: any object with two different symmetry operators is also symmetry with respect to the third symmetry operators, the combination of the two.



Mirror 1

+

Mirror 2

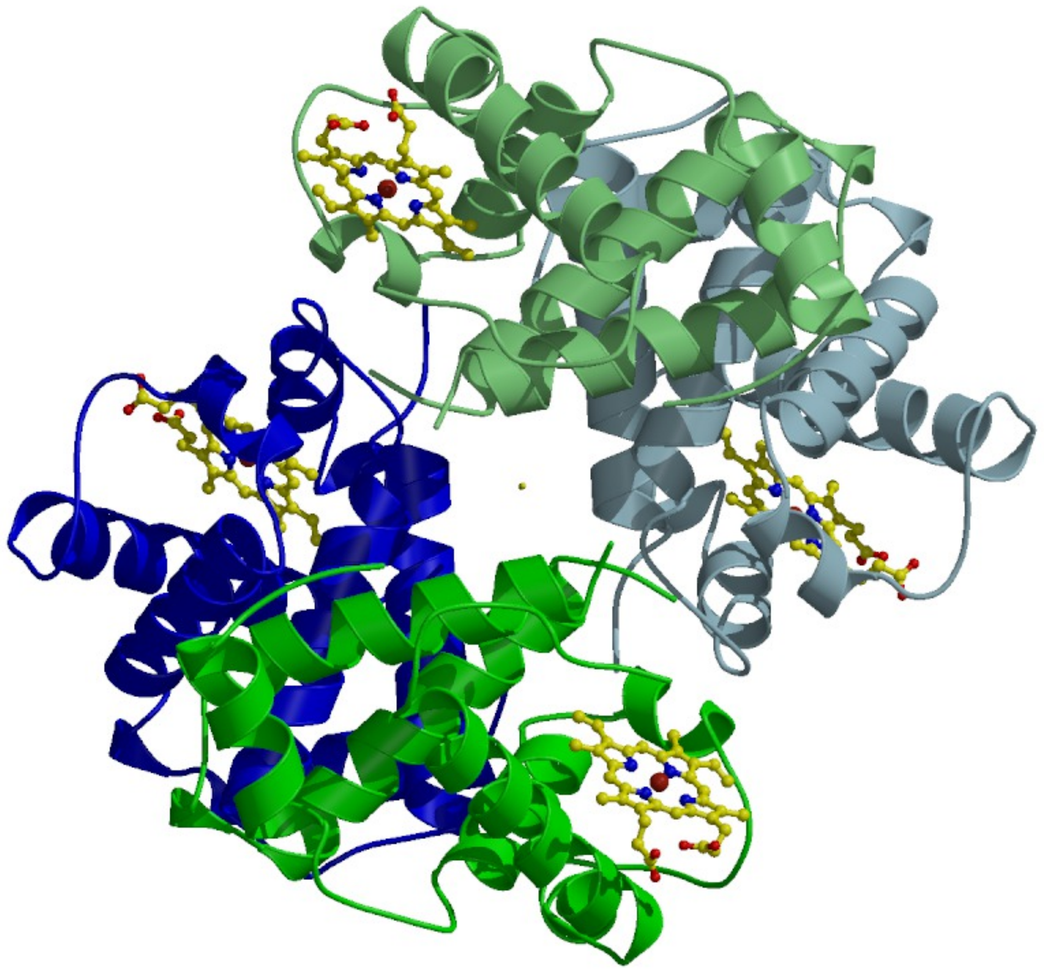
180°-rotation about

=

intersection of both mirror planes

“De-”combination of Symmetry operations

N. B.: The inverse statement is not necessarily correct: not every molecule with a 2-fold rotation axis contains two mirror planes:



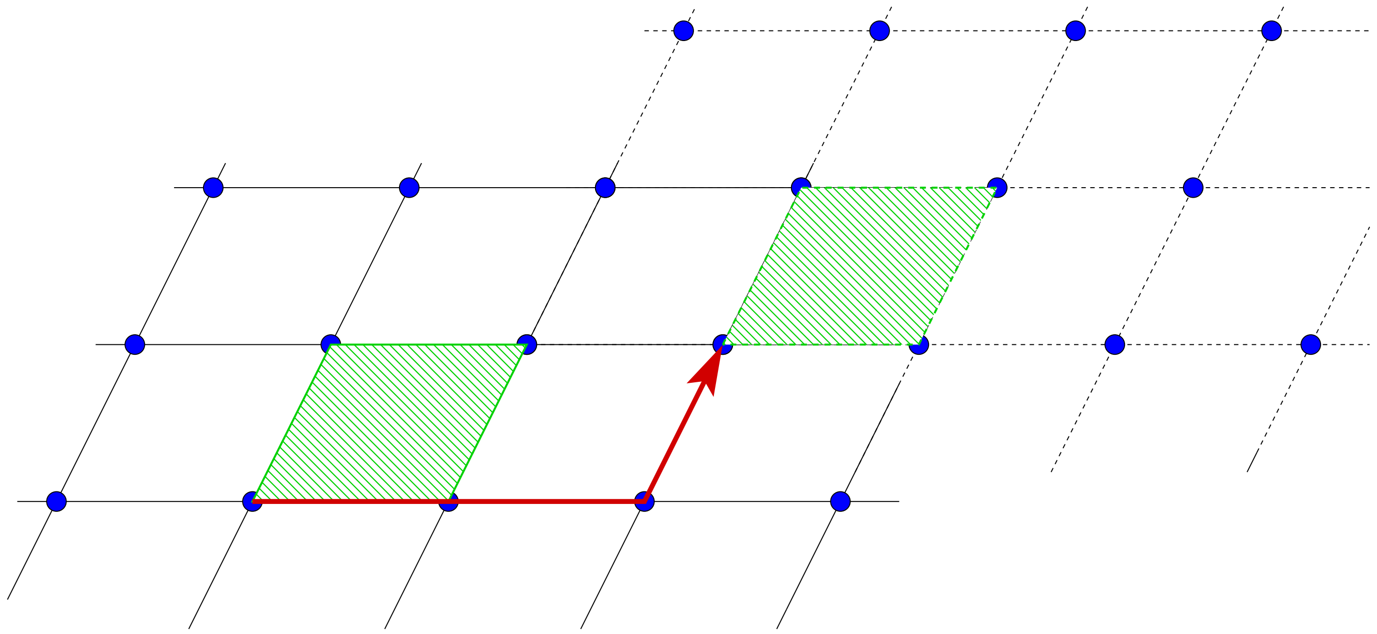
natural proteins are composed of S-amino acids and are always chiral. They never contain a centre of inversion, or a mirror plane.

Symmetry of crystals

1. Additional symmetry operations due to translational symmetry
2. Restrictions for the total number of symmetry

Symmetry of crystals: Translation

ideal crystal: infinitely large
Therefore: Additional symmetry due to translation by integer shifts of the unit cell.

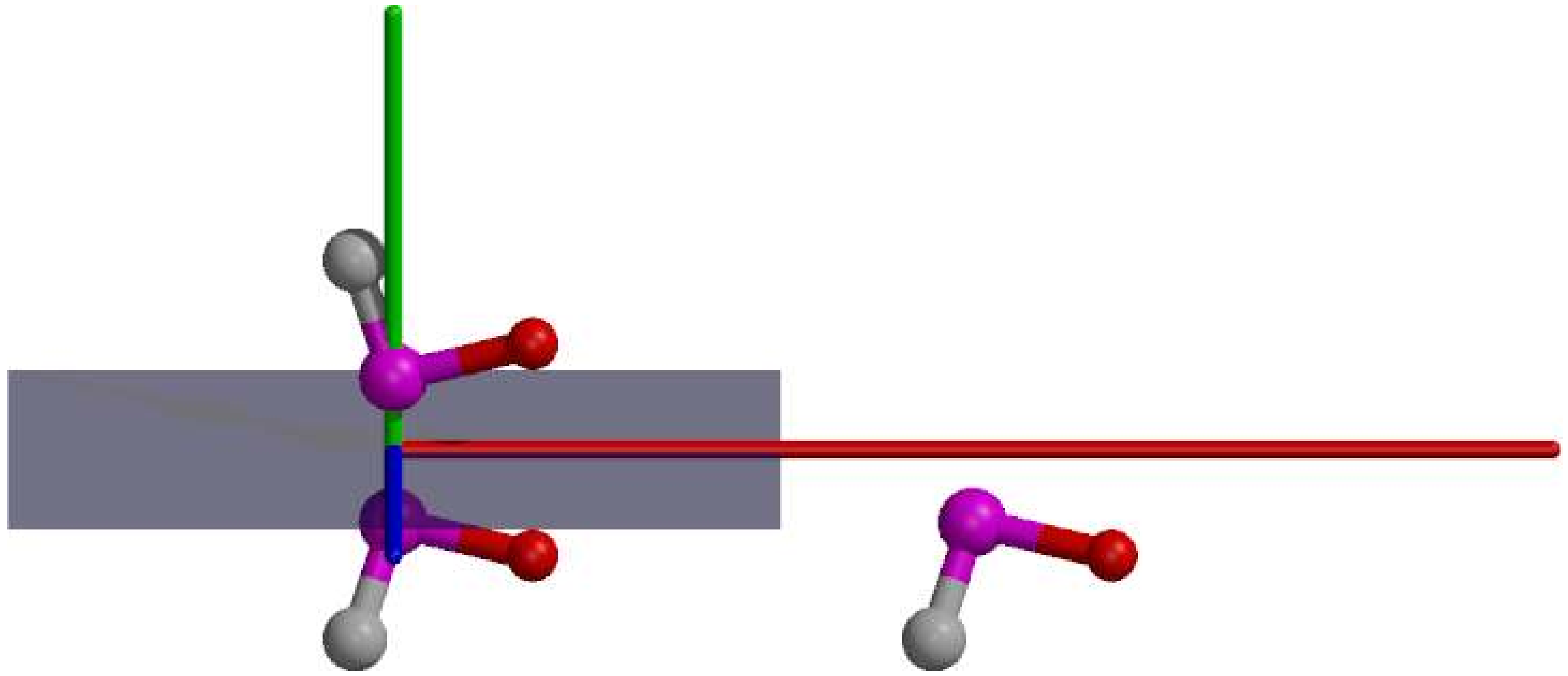


Additional symmetry operations:

1. **glide plane**
2. **screw axis**

Glide Plane

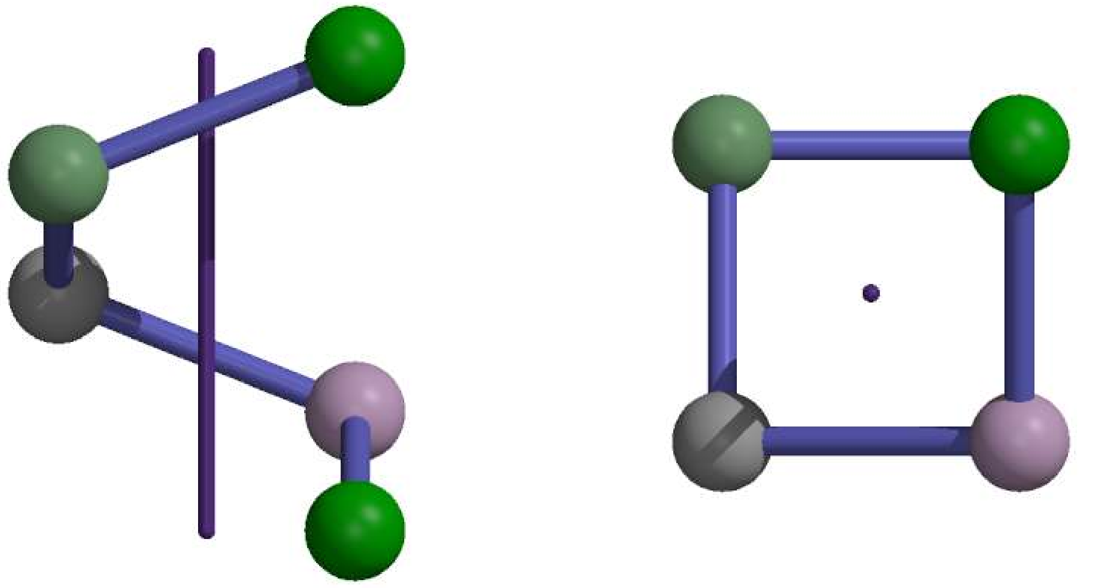
1. mirror plane
2. translation along one unit cell axis by 1/2 of its length L"ange



racemates (*i.e.* equimolar mixtures of R- and S-form) often crystallise with glide mirror planes: efficient packing.

Screw Axis

A combination of an n-fold rotation axis by $\frac{360^\circ}{n}$ with a shift along one of the unit cell axes by $1/n$ of its length is called a *scree axis*. Screw axis always run parallel to one it the unit cell axes.



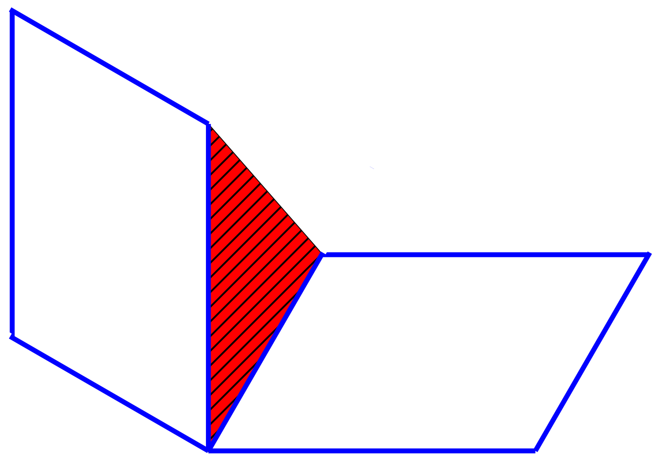
Side view

top view

Example for a 4_1 screw axis:
Rotation about $1/4 \cdot 360^\circ = 90^\circ$ plus shift by $1/4$ along the rotation axis

Symmetry of crystals: Limitations

The lattice of crystals creates additional symmetry operations in comparison with single molecules (glide mirror plancs and scew axes). However, since every symmetry operation must map the lattice into itself, the number of combinations is finite.

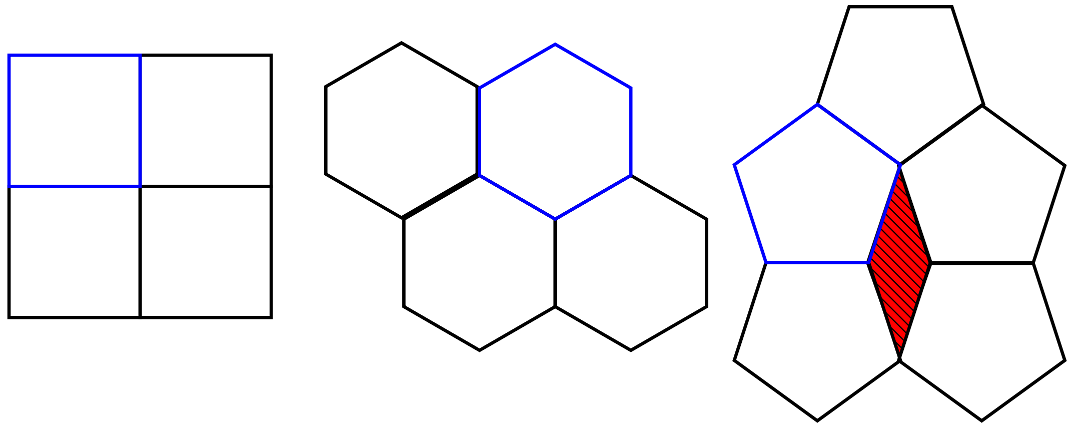


This cell as angles $\neq 90^\circ$. This prohibits a 4-fold rotation: a rotation by 90° creates gaps in the crystal lattice.

We cannot combine any symmetry operation with any cell.

Symmetry of crystals: Limitations

- A mirror plane, or a centre of inversions, or a rotation axis imposes restrictions onto the crystal lattice.
- Therefore, not every combination of lattice and symmetry operation is possible.
- Only 2-fold, 3-fold, 4-fold, or 6-fold rotations are possible



(gap-free tiling of the plane with regular squares or hexagons. Impossible with regular pentagons.)

Point groups and Space groups

Point Groups and Space Groups

1. Classification and nomenclature
2. Symbols for symmetry elements

Point Groups

For **finite** objects, *e.g.* molecules, the various symmetry operations create

32 point groups

Every molecule or chemical compound belongs to one out of 32 different point groups.

Space Groups

The combination of 32 point groups with translation of the (infininte) crystal lattice create

230 space groups

Every crystal belongs to one out of 230 different space groups.
Chiral compounds belong to a subset, 65 different Sohncke groups [1]. The Sohncke groups do not violate the chirality of the compound. erhalten
All point groups and space groups are listed in the in *"International Tables of Crystallography"*, Volume A (International Union of Crystallography, IUCr)

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[1] Leonhard Sohncke, 1842–1897, German mathematician andphysicist

Nomenclature

There are mainly two different types of nomenclatures for point groups and for space groups:

- Hermann-Mauguin System (primarily used in crystallography)
- Schönflies System (primarily used for symmetry of molecules, spectroscopy)

Next Lecture: April2nd, 2020

(no excercise)