Chemical Crystallography and Structural Chemistry

VO 270287

Lecture № 2 — 10th March 2022

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Course Details

3rd	March	Lecture № 1	10th	March	Lecture № 2
17th	March	**no lecture**	24th	March	Exercise № 1
31st	March	Lecture № 3			
7th	April	Lecture № 4	14th	April	**Easter break**
21st	April	**Easter break**	28th	April	Exercise № 2
5th	May	Lecture № 5	12th	May	**no lecture**
19th	May	Lecture № 6	26th	May	Exercise № 3
2nd	June	Lecture № 7	8th	June	Lecture № 8
16th	June	Exercise № 4	23th	June	Lecture № 9
30th	June	**no lecture**			

Previous Lecture

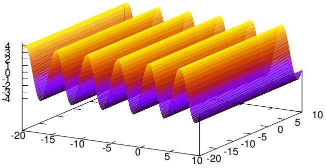
- Literature on crystallography
- online resources, journals, databases
- X-rays as electromagnetic radiation
- concept of the unit cell as repeating unit
- fractional coordinates x, y, z describe the positions inside the unit cell

Contents

1 Diffraction Theory — Atoms and X-rays

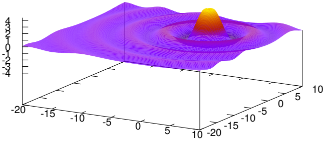
Physicists' description of light

planar wave



$$A(\vec{x},t) = A_0 \sin(\vec{k}\vec{x} - \omega t)$$

spherical wave

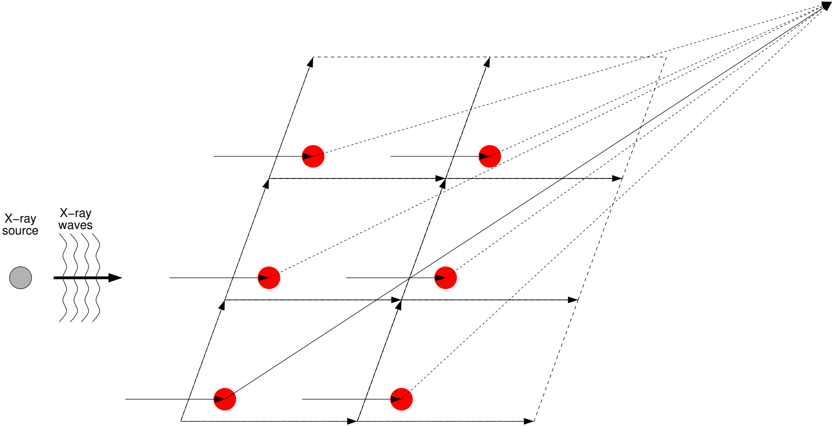


$$A(\vec{x},t) = \frac{A_0}{|\vec{x}|} \sin(|k||\vec{x}| - \omega t)$$

- Intensity $I \propto {A_0}^2$ and $I \propto (A_0/|x|)^2$, respectively
- Oscillation (ωt) is not observed on the detector, intensity I constant does not "flicker" on the detector
- Direction of propagation: $\vec{k}$; $|\vec{k}| = 2\pi/\lambda = \omega/c$

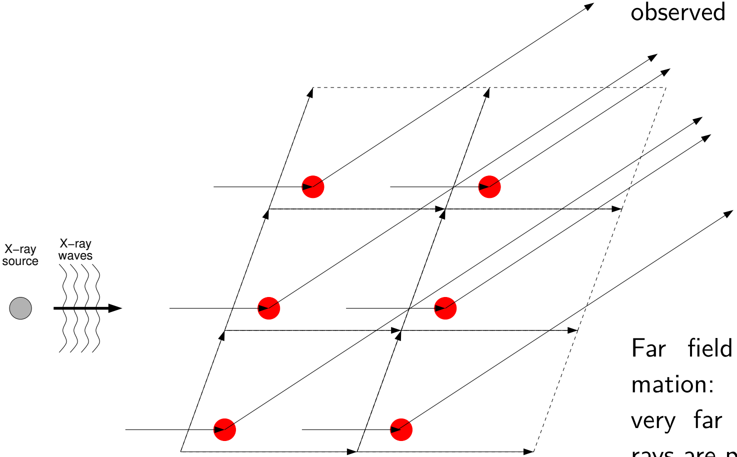
Important features of waves: the sum of two waves result in a wave

Crystal as amplifier



What intensity is observed here?

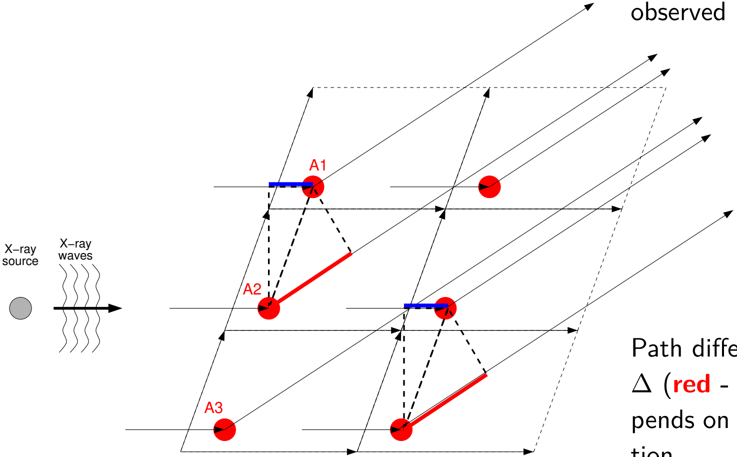
Crystal as amplifier



What intensity is observed here?

Far field approximation: Detector very far away, all rays are parallel.

Crystal as amplifier



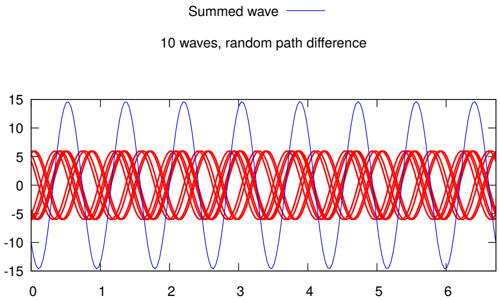
What intensity is observed here?

Path difference Δ (**red** - **blue**) depends on the direction

Path difference Δ (red - blue)

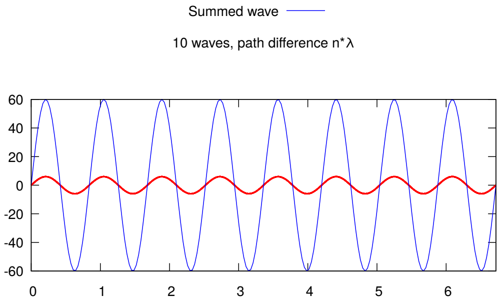
- Each point on the detector results in a specific path difference
- The signal at such point depends on the path difference
- The path difference can be
  1. an arbitrary multiple of the wavelength λ
  2. an integer multiple of the wavelength λ
  3. an integer multiple $+$ one half of the wavelength λ

Path difference Δ (red - blue) — arbitrary path difference



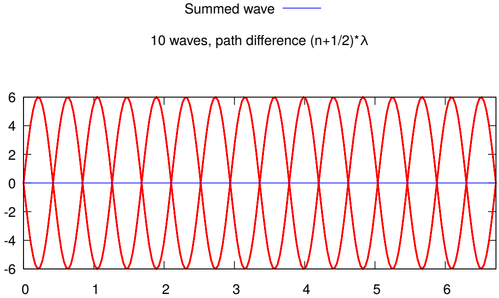
Total amplitude is a of same order as individual waves. With many atoms: signal buried in the noise

Path difference Δ (red - blue) — multiple of wavelength λ



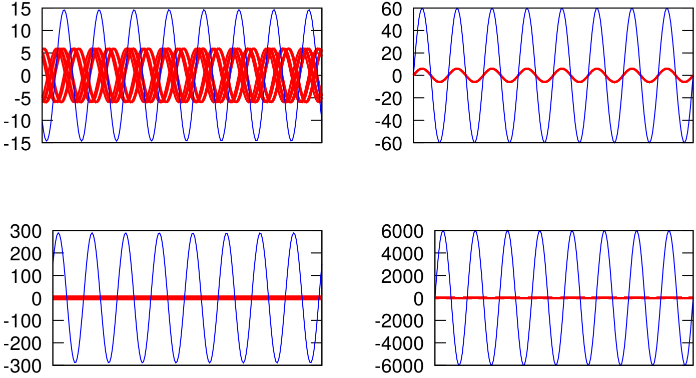
Total amplitude = 10 * individual amplitude: regular order amplifies signal

Path difference Δ (red - blue) = $(n+1/2)*\lambda$



In certain circumstances there can be complete extinction of the signal. This is important for space group determination.

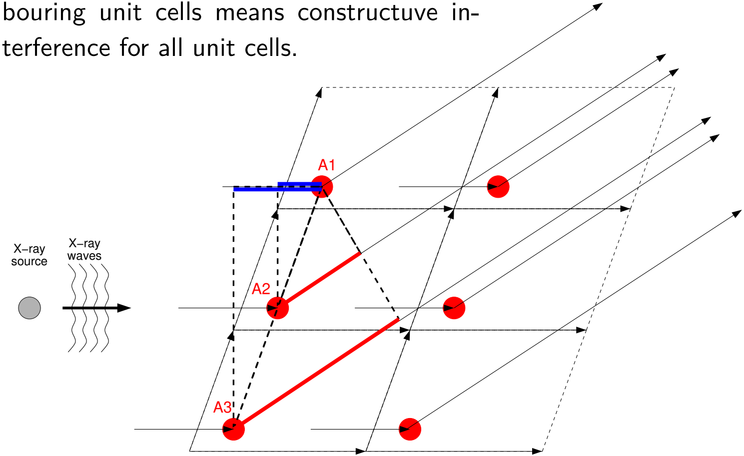
Crystal as wave amplifier



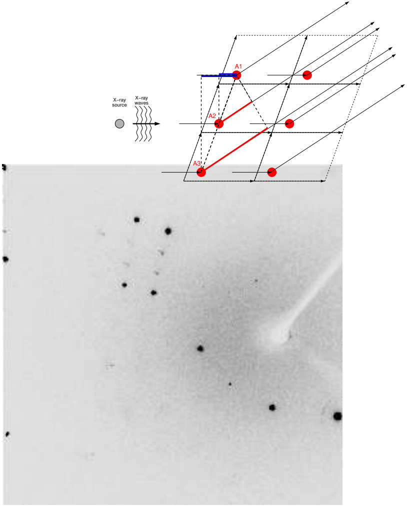
With constructive interference (right), the amplitude of the signal grows with the number of waves (unit cells), much faster than for random interference (left).

Regularity of the crystal

Constructive interference between neighbouring unit cells means constructuve interference for all unit cells.



Diffraction spots



- Spot on the detector surface = constructive interference from all unit cells of the crystal
- noise: everywhere else
- Path difference Δ (**red** - **blue**) depends on:
  1. direction of incoming ray
  2. direction of outgoing ray
  3. wavelength
  4. periodicity of the crystal = unit cell parameters

2 The Laue equations

Laue equations

- A reflection occurs at the detector, where the path difference is an integer multiple of the wave length.
- The locations lie on rays coming from the crystal
- The directions depend on unit cell parameters and crystal orientation
- The directions are described by the **Laue equations** (Max von Laue, 1879 - 1960) .

Laue equations

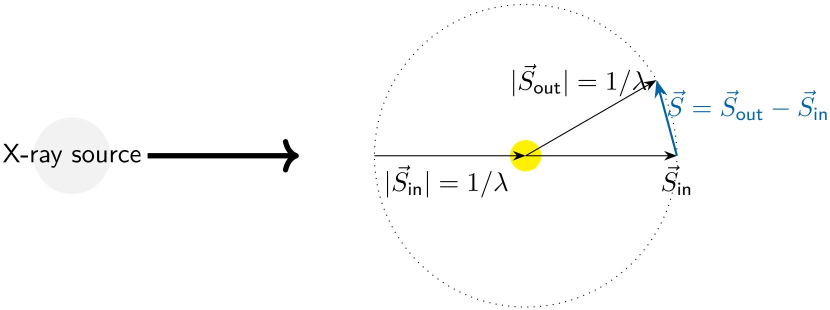
$$\vec{a}\cdot\vec{S} = |\vec{a}||\vec{S}|\cos(\vec{a},\vec{S}) = h$$
$$\vec{b}\cdot\vec{S} = |\vec{b}||\vec{S}|\cos(\vec{b},\vec{S}) = k$$
$$\vec{c}\cdot\vec{S} = |\vec{c}||\vec{S}|\cos(\vec{c},\vec{S}) = l$$

Laue equations

$$\vec{a}\cdot\vec{S} = |\vec{a}||\vec{S}|\cos(\vec{a},\vec{S}) = h$$

$$\vec{b}\cdot\vec{S} = |\vec{b}||\vec{S}|\cos(\vec{b},\vec{S}) = k$$

$$\vec{c}\cdot\vec{S} = |\vec{c}||\vec{S}|\cos(\vec{c},\vec{S}) = l$$



Laue equations

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

The Laue equations describe the geometry of the diffraction experiment:

$\vec{a}, \vec{b}, \vec{c}$**:** Orientation of the crystal

$|\vec{S}_{\textbf{in}}| = 1/\lambda$**:** wavelength of the experiment

$|\vec{S}_{\textbf{out}}|$**:** direction, *alias* position at the detector (is there a spot or not?)

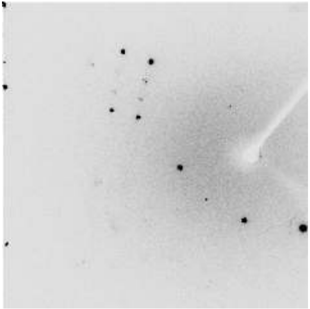
h, k, l **integer:** integer multiple of path differences $\Delta = n \cdot \lambda$

Laue equations

- Each scattering vector $\vec{S}$ describes exactly one position on the detector
- Only those positions, that fulfil all three Laue equations at once, will show a reflection
- Each reflection is uniquely described by the triplet of integers (hkl)
- The triplet (h, k, l) is called **the Miller index** of the corresponding reflection (W. H. Miller, 1801–1880)
- The *direct beam* $\vec{S}_{\text{in}}$ coincides with the reflection $(0, 0, 0)$, $\vec{S}_{\text{in}} = \vec{S}_{\text{out}}$
- The reflection $(0, 0, 0)$ cannot be measured!

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, α, β, γ **and** the crystal orientation.
- Indexing is an essential step for data processing



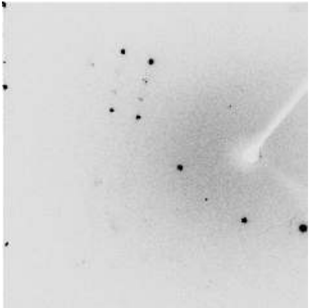
↔

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

Indexing

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 distance, wavelength, rotation axis)



↔

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

3 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 and the Miller Indices

- 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$(\vec{c},\vec{a})$

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

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

Prelude: The reciprocal lattice and the Miller Indices

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

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

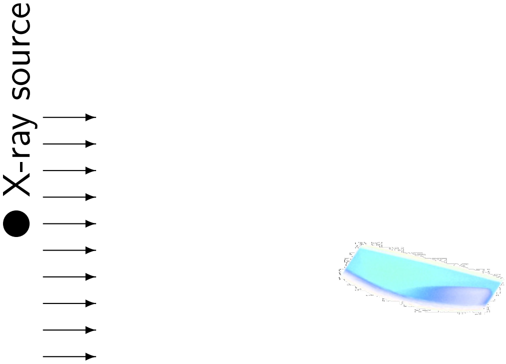
- $\vec{c}^* = \frac{\vec{a}\times\vec{b}}{V}$: $\vec{c}^* \perp$ plane$(\vec{a},\vec{b})$

The Miller indices (hkl) span the reciprocal lattice:

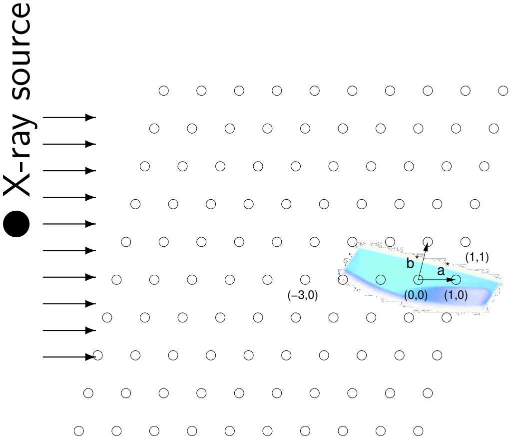
$$h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \qquad\qquad h,k,l \in \mathbb{Z}$$

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

The Ewald Sphere Construction



The Ewald Sphere Construction



Reciprocal Lattice:

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

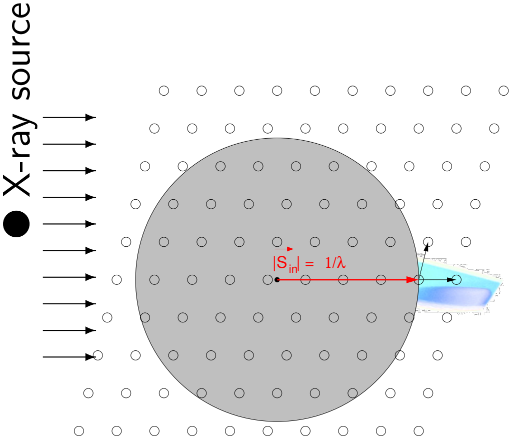
Lattice points at:

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

(hollow circles)

The crystal marks the origin (0,0,0).

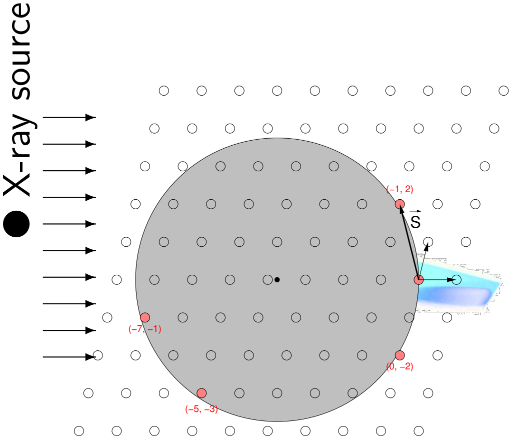
The Ewald Sphere Construction



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**.

The Ewald Sphere Construction

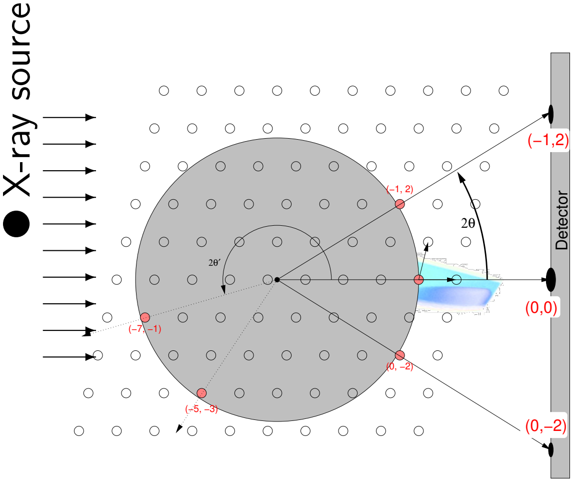


The **scattering vector** $\vec{S}$ points from the origin to the lattice point.

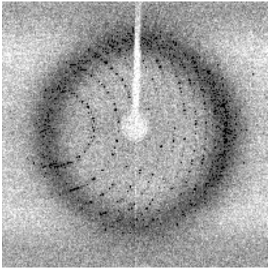
Some lattice points **touch** the surface of the Ewald sphere (red circles). These fulfil the Laue conditions.

They are the **recordable** reflections.

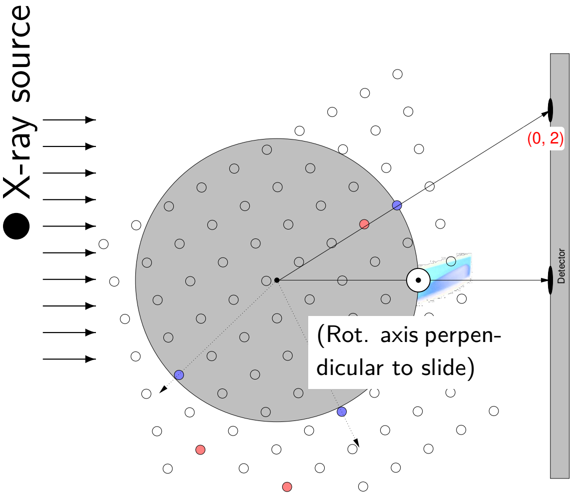
The Ewald Sphere Construction



Some of these spots hit the detector.

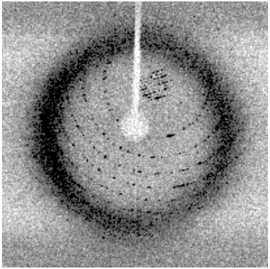


The Ewald Sphere Construction



(Rot. axis perpendicular to slide)

Crystal rotation = Lattice rotation = new spots



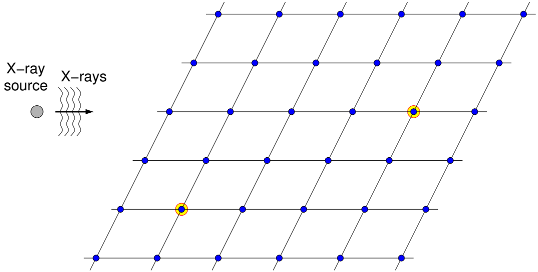
4 Bragg's Law

Bragg's Law

Idea:

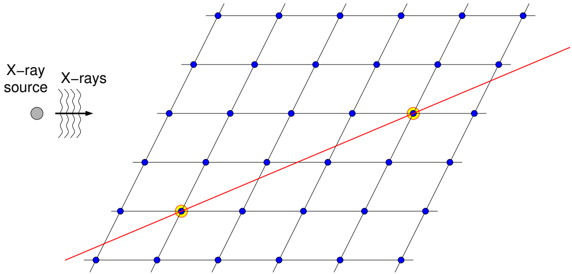
- X-rays are reflected on lattice planes (German: "Gitterebenen" or "Netzebenen")
- Reflections occur when the path difference is a multiple integer of the wave length

Bragg's Law



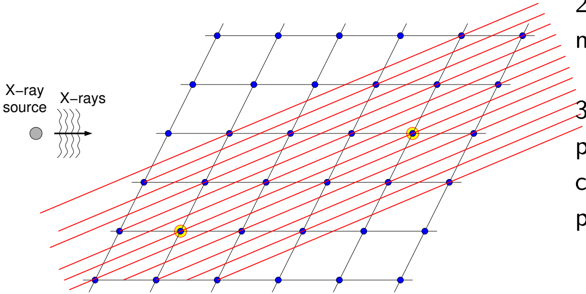
1. Lattice: Corners of the unit cells.

Bragg's Law



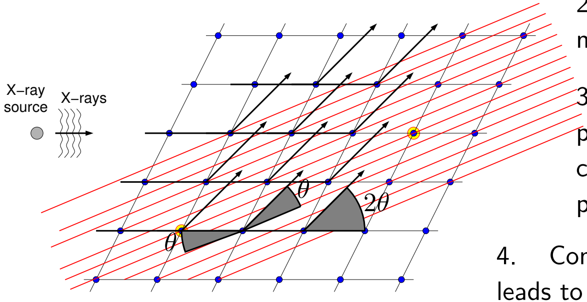
1. Lattice: Corners of the unit cells.
2. Three corner points make a plane.

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

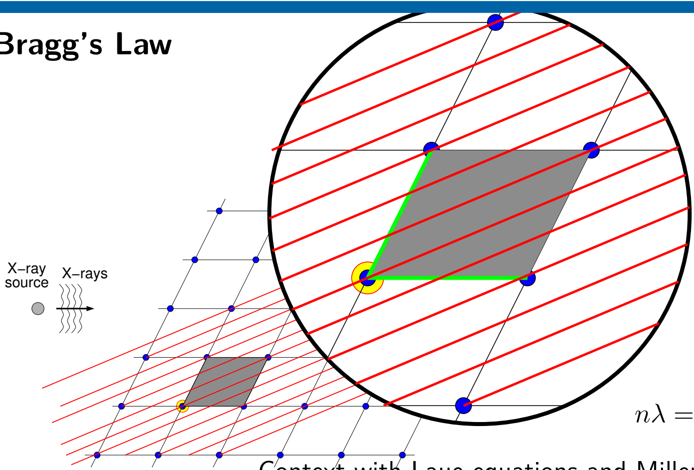


1. Lattice: Corners of the unit cells.
2. Three corner points make a plane.
3. Parallel shifting of plane through **all** lattice corners creates a set of planes.
4. Constructive interferences leads to Bragg's Law:

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

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

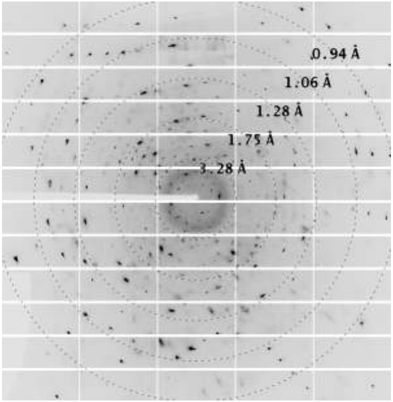
$$d^* \equiv 1/d = \frac{2\sin\theta}{\lambda}$$

  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:

$$I(hkl) \propto |\sum_{\text{atom } j} f_j \cos 2\pi(hx_j + ky_j + lz_j)|^2$$

$$\propto |\sum_{\text{atom } j} f_j e^{2\pi i(hx_j+ky_j+lz_j)}|^2$$

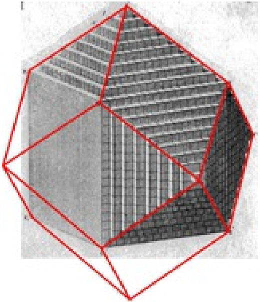
1. every atom emits a small spherical wave (cos-term)
2. the amplitude f_j is proportional to the atom number Z
3. f_j is called *atomic scattering factor*

Summary Laue equations

- Reflex positions (“patterns”) depend on the unit cell parameters $a, b, c, \alpha, \beta, \gamma$ and the orientation 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
- Ewald sphere visualises the Laue equation
- Every reflex has a resolution d, via Bragg’s law.
- High resolution $=$ small d, low resolution $=$ large d

5 Symmetry and Space Groups

Shape and Appearance of Crystals



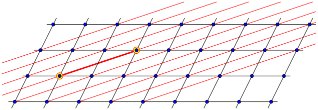
Steve Lower [1]

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



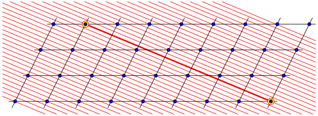
lattice plane (120)

low order Miller index

$\hat{=}$ large lattice distance d

(low resolution reflection)

high atom density along plane: stable



lattice plane $(3\bar{7}0)$

high order Miller index

$\hat{=}$ smalle lattice distance d

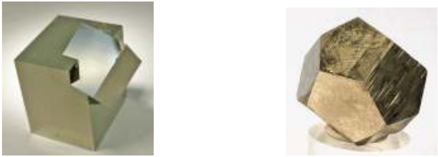
(high resolution reflection)

low atom density along plane: unstable

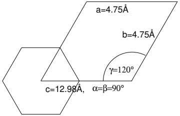
Crystal breaks between stable planes with low Miller indices

Example Crystals

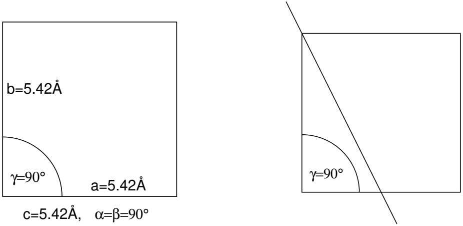
Ruby [2]
$(Al_2O_3 + Cr)$



Pyrite [3] (FeS_2)



hexagonal cell



(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 *space 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

6 Symmetry in molecules

Symmetry in molecules

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

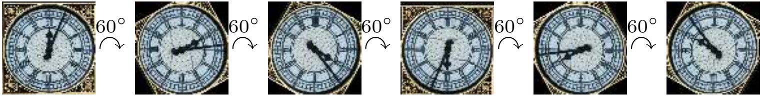
The Term "Symmetry"

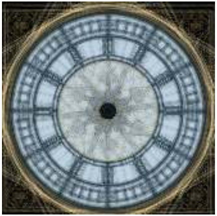
Symmetry is part of our daily lives:

Butterfly with a mirror plane

Flower with 5-fold rotational symmetry

Example: 12-fold Rotational Symmetry

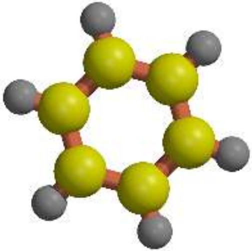




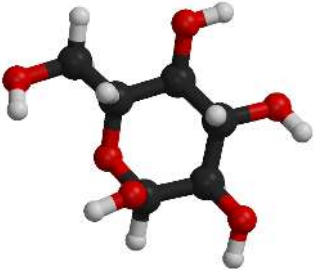
Wikipedia, [4]

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

References

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[2] M. Minge. *The natural gem shop*. URL: `http://www.diamant-edelstein.de` (visited on 23/03/2021).

[3] *Pyrit*. URL: `https://de.wikipedia.org/wiki/Pyrit` (visited on 23/03/2021).

[4] *Parliament Clock Westminster*. URL: `https://commons.wikimedia.org/wiki/File:Parliament_Clock_Westminster.jpg` (visited on 23/03/2021).

[5] Philip M. Cook et al. 'Oxidative-addition reaction of platinum acetylacetonate with iodine in solid state and solution. Crystal structure and equilibrium studies of trans-bis(acetylacetonato)di-iodoplatinum(IV)'. In: *J. Chem. Soc., Dalton Trans.* (1973), pp. 294–301. DOI: `10.1039/DT9730000294`.

[6] W. Massa. *Crystal Structure Determination*. Springer Verlag Berlin, Heidelberg, 2002.