# 7. Diffraction - Basics

## What you will learn about…

- Crystal Basics
  - Bravais Lattice & Basis
  - Unit Cell
  - Crystal Planes
- Diffraction Basics
  - Fourier Transforms
  - Braggs Law
  - Ewald Sphere
  - Influence of the basis
  - Basics of Diffraction Patterns

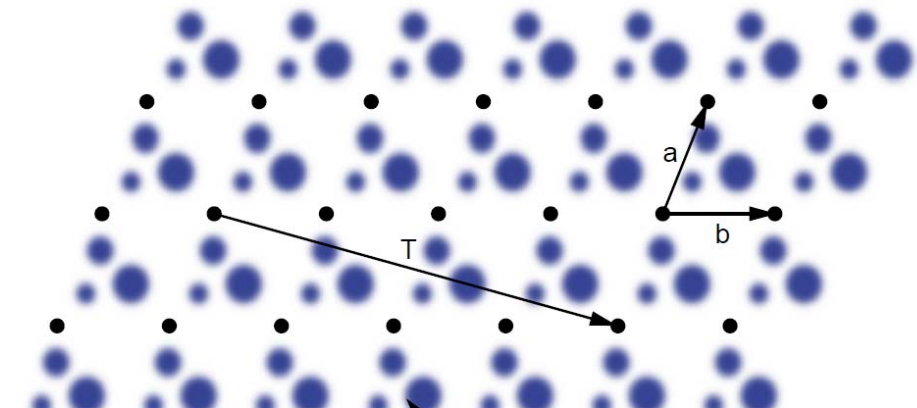
## ETH PSI — X-ray Diffraction - Introduction

Fill in the Gaps!

- ________ phenomenon
- Determine atomic structure of crystals with high precision:
  - Unit cell sizes to ___ accuracy
  - Positions of atoms in unit cell to under ______
- Requires samples to be crystalline
  - _____ of all solids are crystalline
  - Single crystals, thin films, multilayers, powders, textured material etc.
- Many important applications:
  - Structure and functionality of proteins
  - Changes in crystal structure due to external influences or defects, which can induce changes in properties e.g. electronics & sensor technologies
  - Tracking dynamics of chemical transitions
- Industrial applications: pharmaceutical products and technological materials: (Opto)electronics, Aviation, Metal industry, Mineralogy, Catalysis, Archaeological artefacts etc.

## ETH PSI — Crystals Basics

$$\boxed{\mathbf{T} = u_1\mathbf{a} + u_2\mathbf{b} + u_3\mathbf{c}}$$




Listen!

## Crystals Basics

Ideal crystal:

- No defects, infinite in extent
- Defined by:
  - **Bravais Lattice:** Infinite regular lattice of points in space → Bragg's Law
  - **Basis:** Group of atoms at each and every Bravais-lattice point → intensity of diffraction peaks
- Translational symmetry
  - Move from one Bravais-lattice point to the next by translation vector $\mathbf{T}$, where:

$$\mathbf{T} = u_1\mathbf{a} + u_2\mathbf{b} + u_3\mathbf{c}$$

  - $u_1$, $u_2$, $u_3$: integers
  - $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$: three primitive translation vectors → directions and minimum distances that translate the crystal so that it is indistinguishable from its original position

## Volume of a Unit Cell

Line-by-line...

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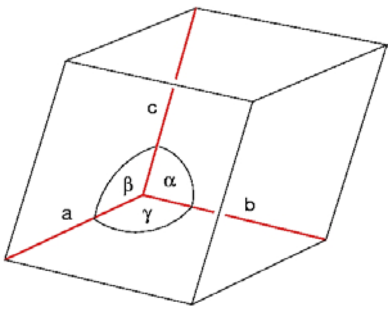


- These vectors form three edges of a parallelepiped of volume:

$$V = |\boldsymbol{a} \cdot \boldsymbol{b} \times \boldsymbol{c}|$$

  describing primitive cell with lattice points at cell corners
- Unit cell is primitive (smallest repetition unit) if lattice points only at the corners (i.e., one lattice point per cell)
- Note, however, that non-primitive cells and bases are chosen for reasons of convenience and high symmetry

Line-by-line...

## Crystal Planes

- A plane can be defined by any three (non-colinear) points
- Crystal planes specified by Miller indices ($hkl$) as follows:
  - – Determine where the plane intercepts the axes ***a***, ***b***, and ***c*** in terms of fractions of the axis lengths
  - – Determine reciprocal values
  - – If any of these reciprocal values are non-integral, multiply them all by the minimum factor to make them all integral
  - → $hkl$-values are the Miller indices of the plane

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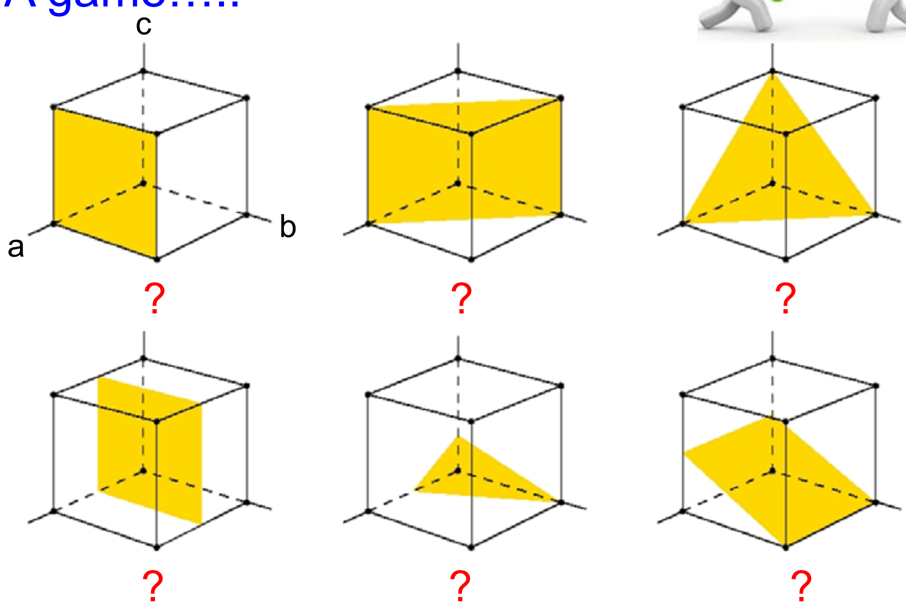
## Crystal Planes

# A game…..



## Space groups

Point groups + lattice translations → space groups

Crystal symmetry consists of
- Bravais lattices
- Choice of basis
- Translational symmetry

There are 230 space groups in three dimensions

## Diffraction Basics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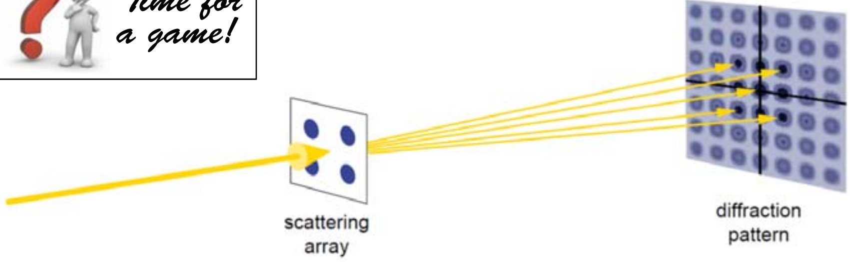
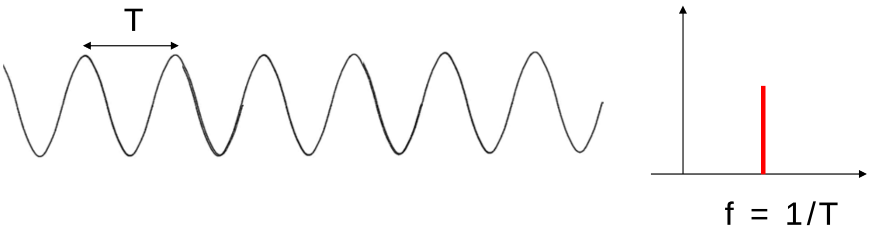



## Diffraction and FTs

- The (far-field) diffraction pattern of any object is the square of that object's Fourier transform

  Diff pattern = $|FT(object)|^2$

- A Fourier transform of an object describes that object in terms of component frequencies
- Infinitely long sine wave:




## Fourier Transforms - Animation


Animation from: http://en.wikipedia.org/wiki/Fourier_transform

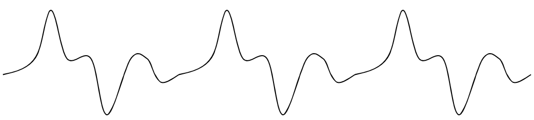
## Fourier Transforms - Animation

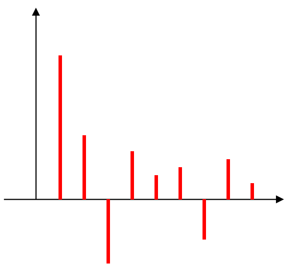

Animation from: http://en.wikipedia.org/wiki/Fourier_transform

## Fourier Series

The FTs of periodic objects have discrete components only with frequencies:

1/T, 2/T, 3/T, 4/T, …





## Fourier Series

*For periodic structures:*

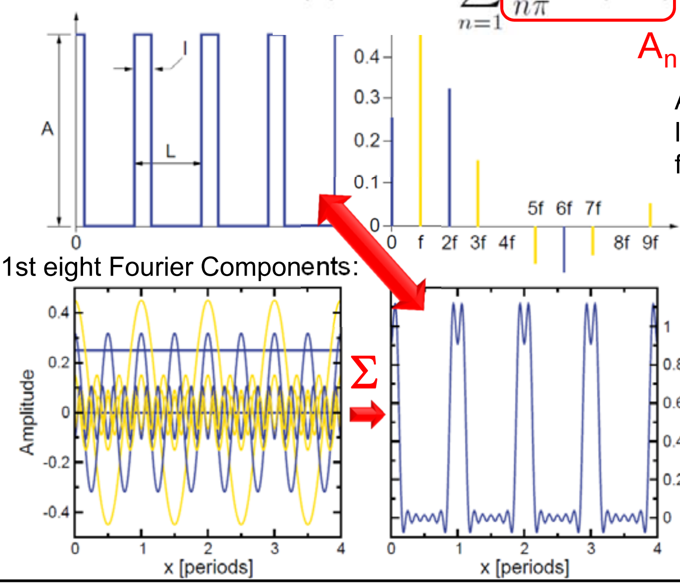
*The **Fourier Transforms** simplify to a **“Fourier Series”** consisting of discrete components with frequencies that are integer multiples of the fundamental frequency of the original function.*

*Note:*
**Fourier series** decomposes periodic functions (or periodic signals) into the **sum of** a (possibly infinite) set of **simple oscillating functions**, namely sines and cosines (or complex exponentials).

## Fourier Series of a Square Wave

d = *l*/*L* = 0.25 $F(x) = Ad + \sum_{n=1}^{\infty} \boxed{\frac{2A}{n\pi}\sin(n\pi d)} \cos(2n\pi x/L)$

$A_n$




Amplitudes ($A_n$) of lowest 10 spatial frequency components

Oscillations due to sampling to finite n

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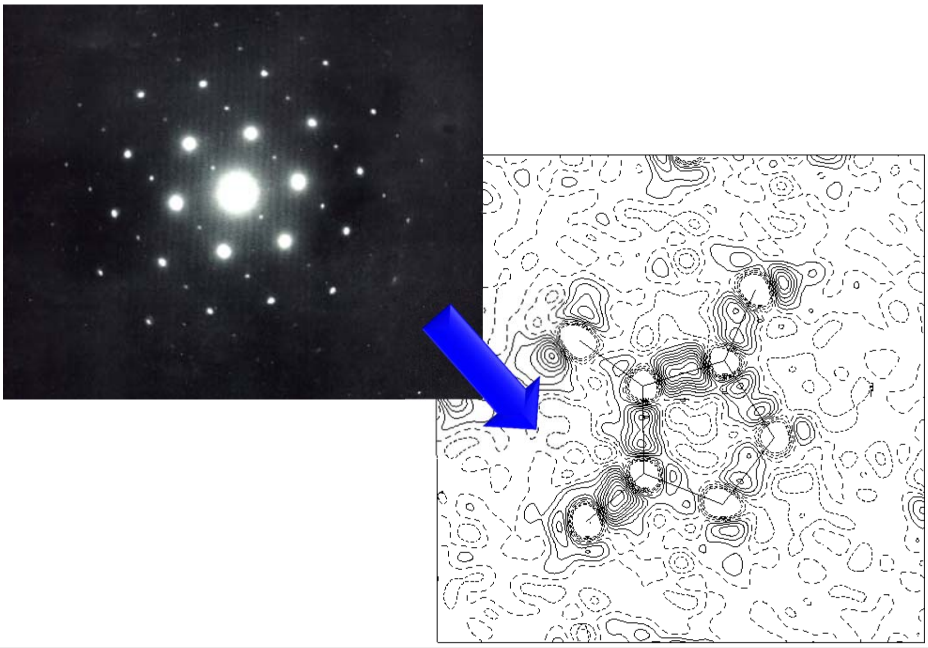
## Fourier Series of a square wave

$$F(x) = Ad + \sum_{n=1}^{\infty} \frac{2A}{n\pi} \sin(n\pi d) \cos(2n\pi x/L)$$

- Interesting limiting case: $l \to 0$
- Object is an infinite set of spikes of zero width of infinite height ($A=1/l$) and separation ($L$) i.e. a Bravais lattice
- $d = l/L$; $\sin(n\pi d) = n\pi d$; $2A/n\pi \cdot n\pi d = 2Ad = 2/L$ const.
- Therefore, Fourier transform $\to$ set of spikes of equal height ($2/L$) and separation ($1/L$)
- This implies that the Fourier Transform (or the diffraction pattern) of the Bravais lattice is also a Bravais lattice.

$\to$ …


## Understanding Diffraction Patterns



Line-by-line…

## Understanding Diffraction Patterns

- Diffraction pattern: square of the Fourier Transform of the electron density distribution within a crystal's unit cell
- Each diffraction peak (or spot) represents a sinusoidal wave of electron density with frequency and direction (given by Q) determined by peak's position [it's (*hkl*)-values] within the pattern
- Diffraction maxima also referred to as a Fourier component or structure factor, distributed in Fourier, reciprocal or Q-space
- Once phase relationship between Fourier components is known, superimposing the associated sine waves → electron density in unit cell
- While periodic spacings can be determined from the position of the diffraction peaks using Bragg's law, the peak intensities are determined by the positions and types of atoms within the unit cell of the crystal, so can be used to determine the atomic basis.

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## Understanding Diffraction Patterns

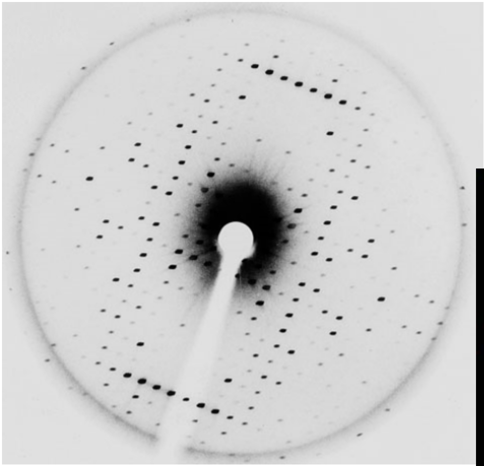
- In the case shown the diffraction pattern is not related to the electron density map
- Nevertheless, remember:

1. The peak positions are given by Braggs Law: the symmetry of the diffraction pattern reflects the __________ of the crystal
2. Intensity of the diffraction spots reflects the ______________ __________________________ in the crystal
3. Peak widths reflect the ___________ of crystal

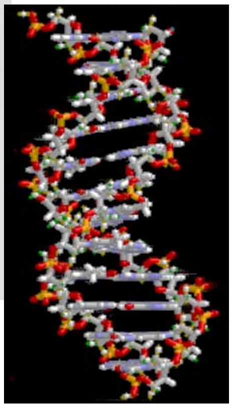
…..so the atomic arrangement within the unit cell does not necessarily reproduce the global symmetry of the crystal.

See next slide….

## ETH PSI Understanding Diffraction Patterns

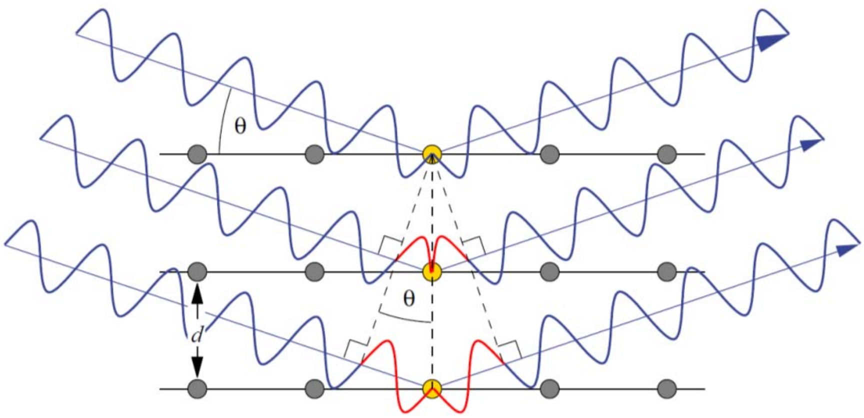


Plane through a three-dimensional diffraction pattern of a DNA crystal.



http://www.rcsb.org

## ETH PSI Bragg's Law




Constructive interference when $n\lambda = 2d\sin\theta$

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## Bragg's Law

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

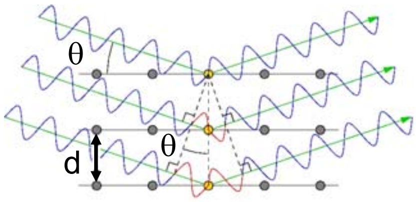
$$\lambda = hc/E \Longrightarrow \sin\theta = \frac{6.1998}{d[\text{Å}]\,E[\text{keV}]}$$

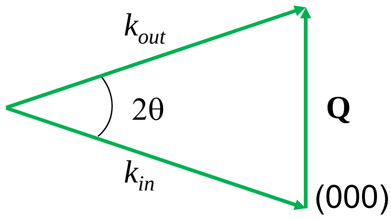
Where $d$ is spacing of $(hkl)$-scattering plane

Scattering vector $\mathbf{Q}$

- perpendicular to the scattering planes since angle subtended by $k_{in}$ and $k_{out}$ is θ
- Connects (000) spot (incident beam) to another diffraction maximum
- Note: $Q = 2|k|sin\theta = \frac{4\pi}{\lambda}\sin\theta$

$\boxed{\rightarrow |Q| = \frac{2\pi}{d_{hkl}}}$




## Bragg's Law

Therefore diffraction maxima are regularly spaced in a three-dimensional periodic array with the (000) spot in the centre.

The three periodicities describing this 'reciprocal lattice' are the 'reciprocal lattice basis vectors' and are related to the lattice vectors in real space by:

$$\mathbf{a}^* = 2\pi\frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}.(\mathbf{b}\times\mathbf{c})}$$

$$\mathbf{b}^* = 2\pi\frac{\mathbf{c}\times\mathbf{a}}{\mathbf{b}.(\mathbf{c}\times\mathbf{a})}$$

$$\mathbf{c}^* = 2\pi\frac{\mathbf{a}\times\mathbf{b}}{\mathbf{c}.(\mathbf{a}\times\mathbf{b})}$$

Denominator: unit cell volume (scalar quantity)
Numerator: vector with direction perpendicular to plane defined by the two vectors

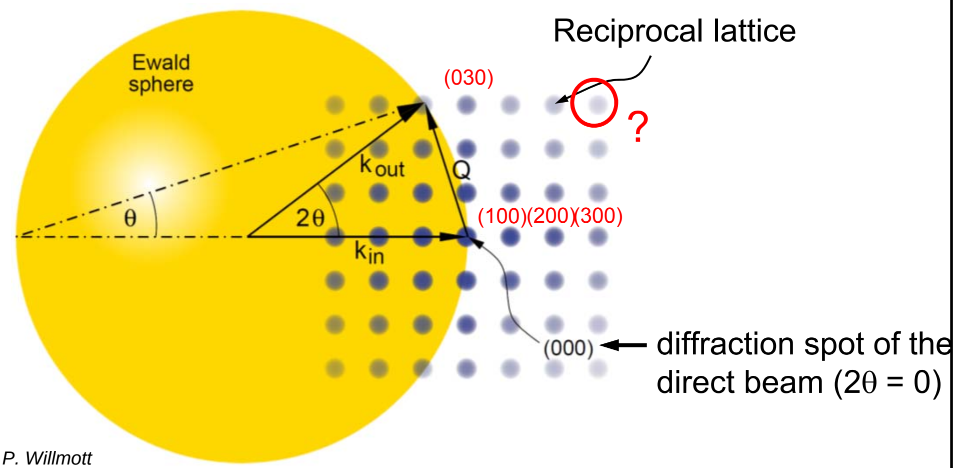
→ The reciprocal lattice vector $\boldsymbol{G_{hkl}} = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*$

## The Ewald Sphere

Write this down!

Ewald construction (in reciprocal space):
Surface of the Ewald sphere: Bragg's law is satisfied

→ Diffraction maxima (reflections, diffraction spots) only occur for reciprocal lattice points that lie on the surface of the Ewald sphere

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## The Ewald Sphere

Write this down!

- **Bragg condition**: scattering occurs when

  **the scattering vector = a reciprocal lattice vector**

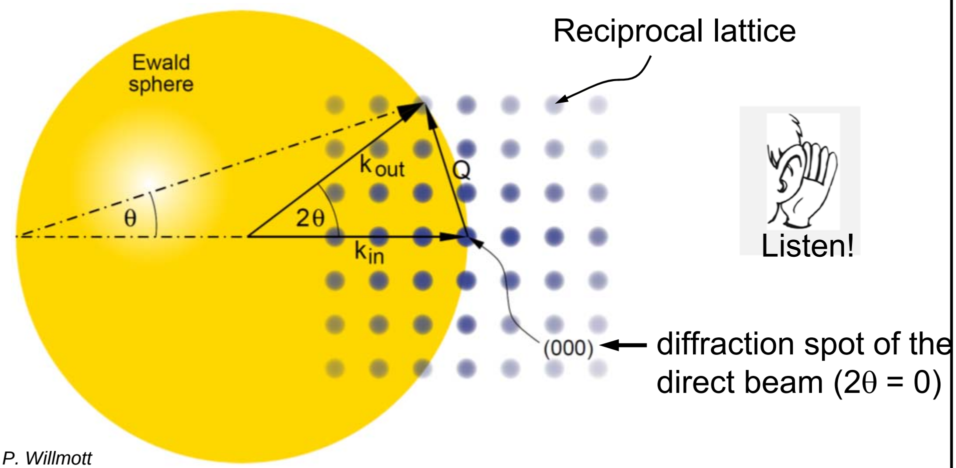
  ↙ ↘

- Ewald construction combines these two concepts in an intuitive way
- Sphere of radius $2\pi/\lambda$ is positioned so that Bragg condition is satisfied and diffraction occurs when a reciprocal lattice point coincides with the surface of the sphere.

## The Ewald Sphere

Ewald construction (in reciprocal space):
Surface of the Ewald sphere: Bragg's law is satisfied

→ Diffraction maxima (reflections, diffraction spots) only occur for reciprocal lattice points that lie on the surface of the Ewald sphere

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## An Ewald Sphere Recipe

- Elastic scattering $|k_{in}| = |k_{out}|$ and scattering vector $Q = k_{out} - k_{in}$
- The incident wavevector $k_{in}$ must end at (000)
- The scattering vector $\mathbf{Q}$ must start at (000)
- $\mathbf{Q}$ & $k_{out}$ end at another diffraction maximum: a reciprocal lattice point
- For scattering, reciprocal lattice points must lie on the surface of the Ewald sphere with radius $|\mathbf{k}| = \frac{2\pi}{\lambda}$ and centre at the start of $k_{in}$ and $k_{out}$

→ Defines the value of $\theta$ (or $2\theta$) by the magnitude of $\mathbf{k}$

→ Rotate crystal in real space → array of diffraction maxima is rotated by the same amount in reciprocal space around (000) and brings different reciprocal lattice points onto surface of Ewald sphere

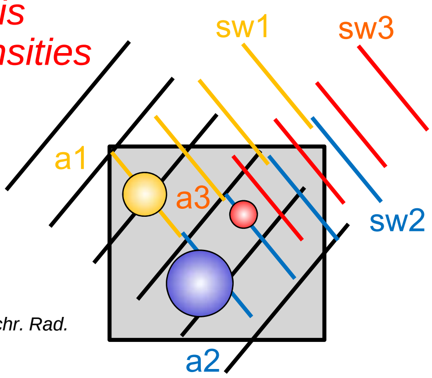
# What you will learn about…

- Influence of the basis
- Convolution
- Diffraction Sample Types



# Influence of the basis

*"The composition of the basis determines the relative intensities of the diffraction peaks."*

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- Amplitude of each scattered wave ∝ sum of scattering strengths of all electrons associated with atom → its atomic scattering factor, **f**
- Phases between scattered waves depend on relative positions of atoms
- The total scattering amplitude or structure factor, $\mathbf{F}_{hkl}$, = vector sum of individual atomic scattering factors $\mathbf{f}_1 + \mathbf{f}_2 + \mathbf{f}_3$

## Influence of the basis


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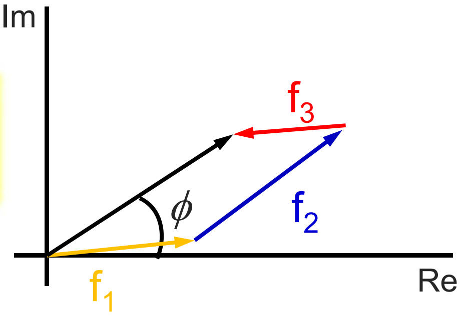
**Argand Diagram:**


## Diffraction Pattern

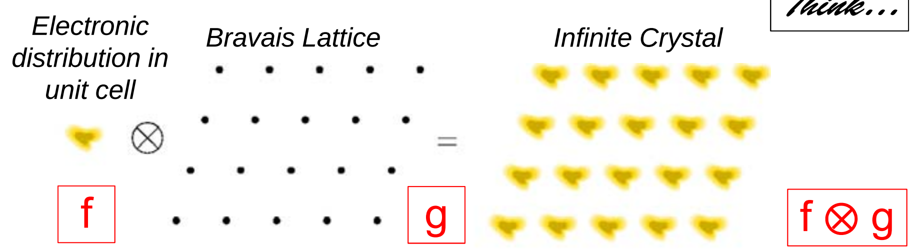

$FT(f \otimes g) = FT(f) \times FT(g)$

or

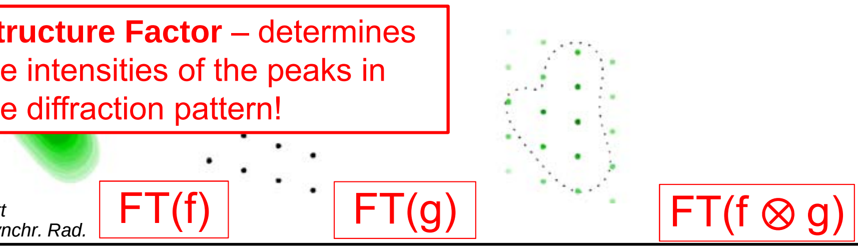
$FT(f \times g) = FT(f) \otimes FT(g)$

$\otimes$ - Convolution

x - Product


**Structure Factor** – determines the intensities of the peaks in the diffraction pattern!

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# Different Sample Types

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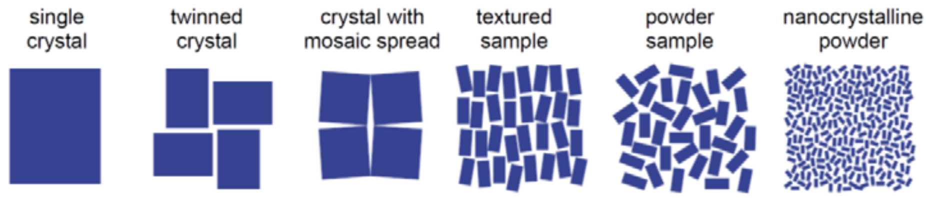


*Diffraction Pattern?*

- Note that single crystal not perfect: vacancies, interstitials, dislocations, mosaic domains
- Twinning: diffraction spots split into two or more close features
- Textured samples: preferred directions for certain crystallographic planes due to fabrication process e.g. pulling polymer fibres