Introduction to Single Crystal X-ray Diffraction

Practical Aspects of Single Crystal X-ray Crystallography

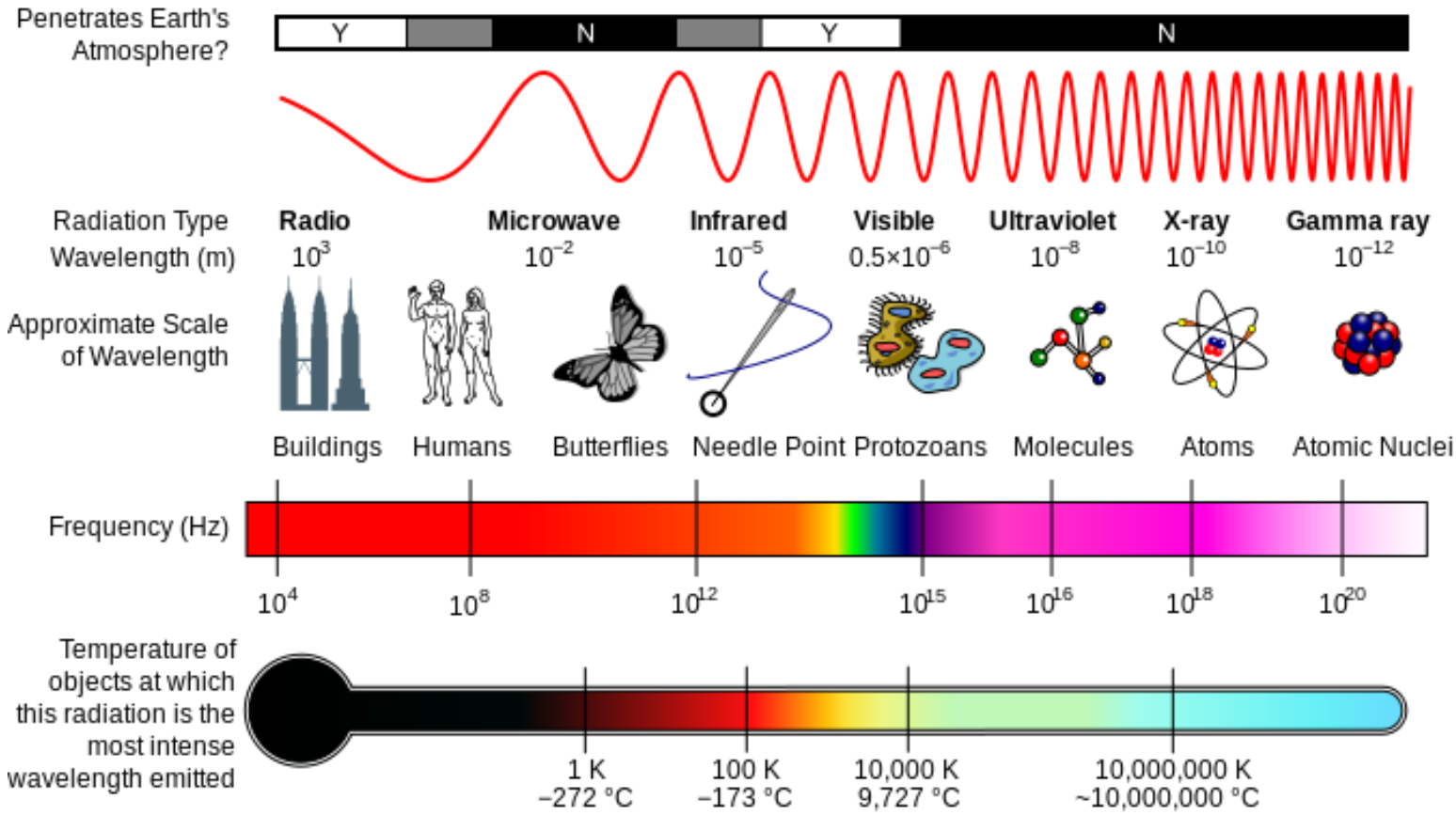
X-ray Diffraction

X-ray crystallography is a method of determining the arrangement of atoms within a crystal.

- Structure of a compound on a molecular level
  - Connectivity
  - Chirality
  - Framework and Pore size
- Bond length and angle parameters
- Interatomic forces that aid in crystallization
  - Solvent inclusion
  - Hydrogen bonding networks
  - π-interactions
  - Agostic interactions

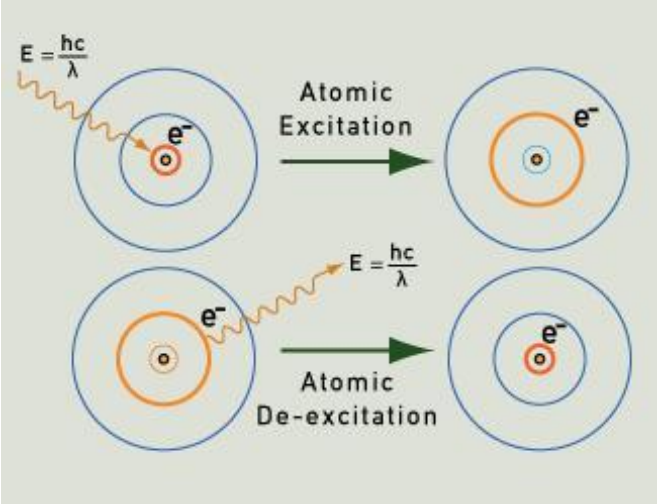
X-ray Diffraction

X-ray is a form of electromagnetic radiation



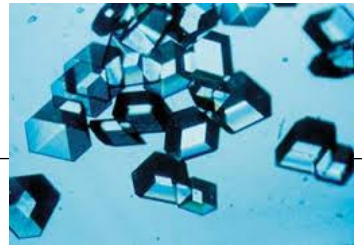
X-ray Diffraction

X-ray Diffraction is the observation of X-ray wave interference by crystalline materials.

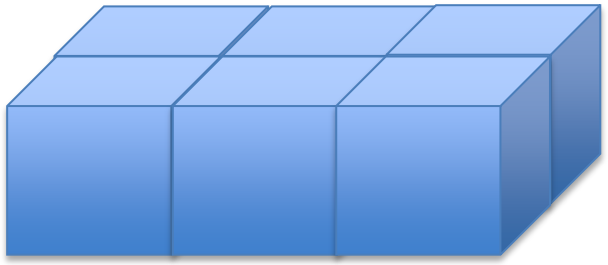


The probability of this happening is very low; atoms are mostly empty space!!!

The Crystal

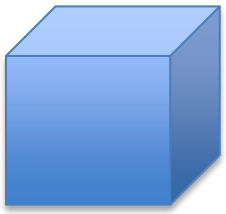


A **crystal** is a solid material whose atoms are arranged in an orderly repeating pattern extending in all three spatial dimensions



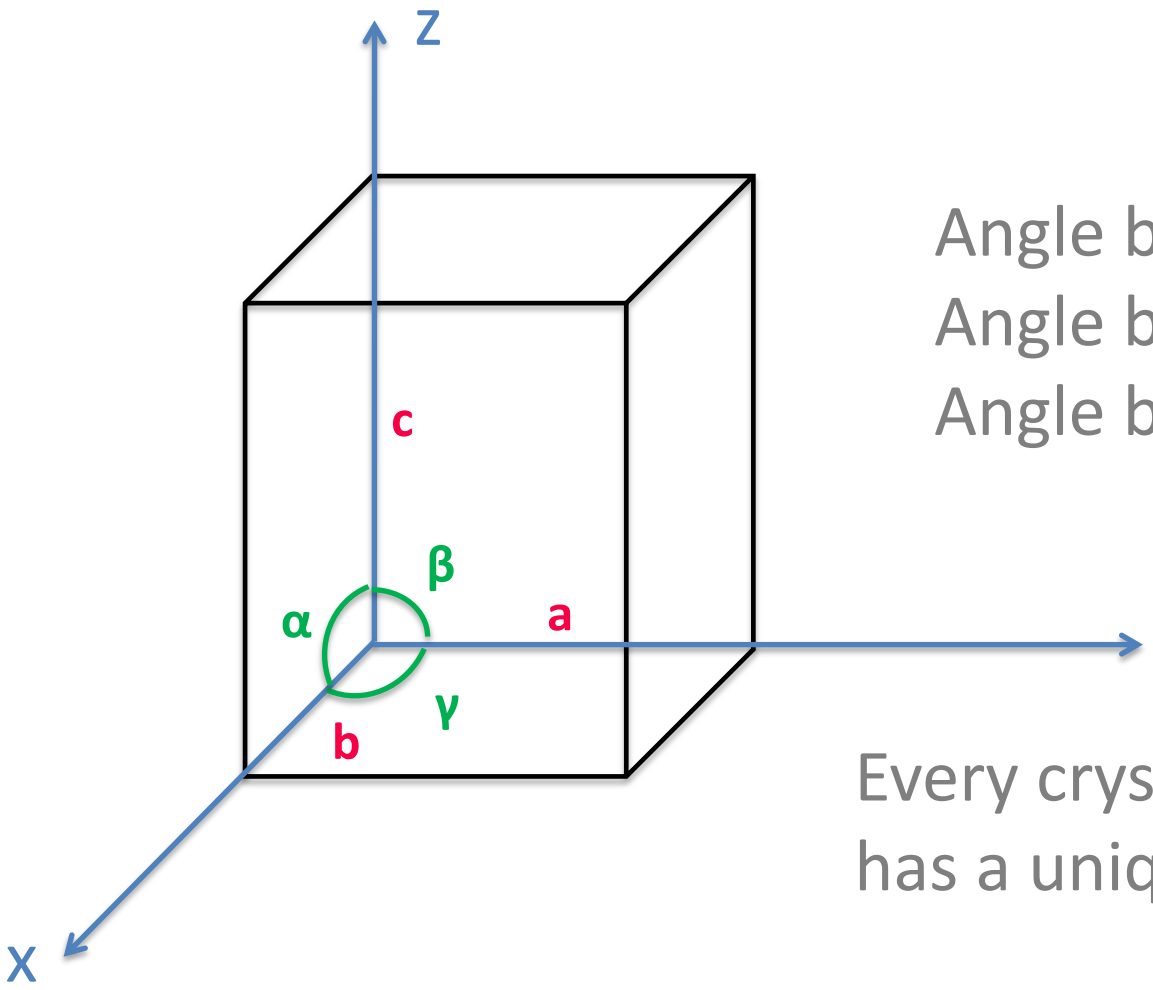
Smallest component of a crystal is the **unit cell**

- Smallest possible **volume** that when repeated, is representative of the entire crystal.
- The unit cell contains the maximum **symmetry** that uniquely defines the crystal structure.



More than one molecule can be found inside the unit cell!!!

Unit Cell

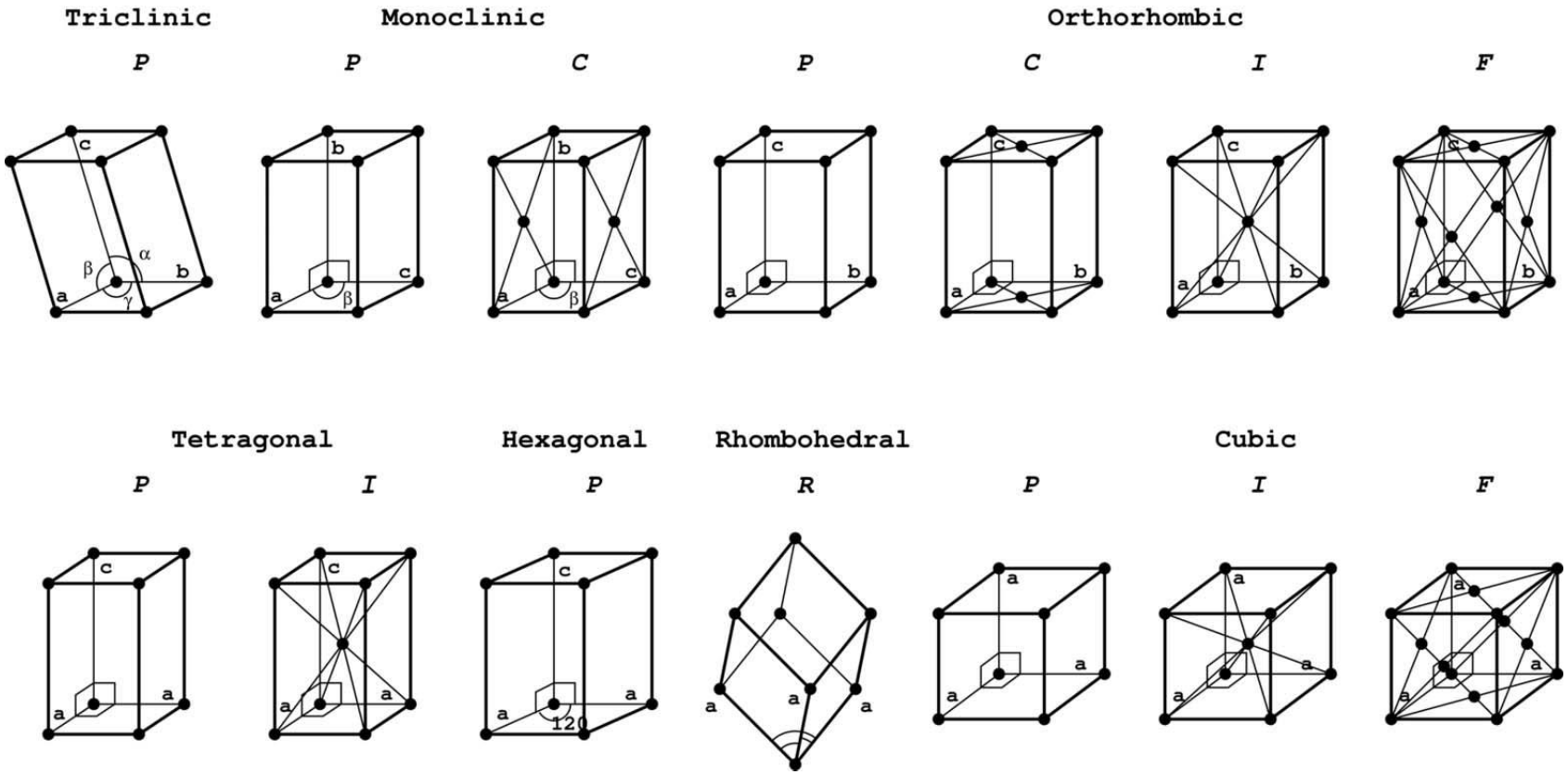


Angle between b & c is α
Angle between a & c is β
Angle between a & b is γ

Every crystal structure has a unique unit cell!!

Describing order in Space

7 crystal systems and 14 Bravais lattices (centering lattice points)



Symmetry Elements

- Identity, 1
- Inversion center, $\bar{1}$
- Rotation axis, 2,3,4,5,6
- Mirror plane, m
- Screw axis, 2_1, 3_1, 3_2, 4_1 (rotation with a translation)
- Improper rotation, $\bar{3}$,$\bar{4}$,$\bar{5}$
- Glide planes, a, b, c, n, d (mirror reflection with a translation)

Zbigniew Dauter and Mariusz Jaskolski. *J. Appl. Cryst.* **2010**, *43*, 1150–1171

Describing order in Space

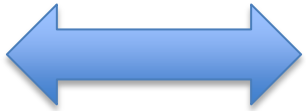
System	Unit cell dimension	Unit cell angles (°)	Characteristic symmetry	International notation	Bravais Lattice (14)	Space Groups (230)
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90$	Only inversion center	**1**, $\bar{1}$	*P* (Primitive)	P1, P$\bar{1}$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90$, $\beta \neq 90$	Twofold axis or/and mirror plane	**2**, *m*, ***2/m***	*P*, *C* (centered, A, B, C)	$P2_1$, $P2_1/c$, C2, C2/c
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90$	Three perpendicular twofold axesor/and mirrors	**222**, *mm*2, ***mmm***	*P*, *C*, *I* (Body Centered), *F* (Face centered)	$P222_1$, Pmma
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90$	Fourfold axis	**4**, $\bar{4}$, ***4/m,*** **422**	*P*, *I*	$P4_3$, I4
Trigonal	$a = b \neq c$	$\alpha = \beta = 90$, $\gamma = 120$	Threefold axis	**3,** $\bar{3}$**, 32**, 3m, **3m**		$P3_212$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90$	Threefold axis		*R* (Rhombohedral)	R3, R$\bar{3}$2
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90$, $\gamma = 120$	Sixfold axis	**6**, $\bar{6}$, **6/m**	*P*	$P6_2$, P6/mcc
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90$	Four threefold axes	**23**, **m$\bar{3}$**	*P*, *I*, *F*	F432

Only 230 possible ways of arranging identical objects in an infinite three dimensional lattice!!!

Real Space vs. Reciprocal space

We do not have a microscope that can directly see atoms!!!

Real Space
Crystal Structure
Unit cell
Electron density
Coordinates (x, y, z)

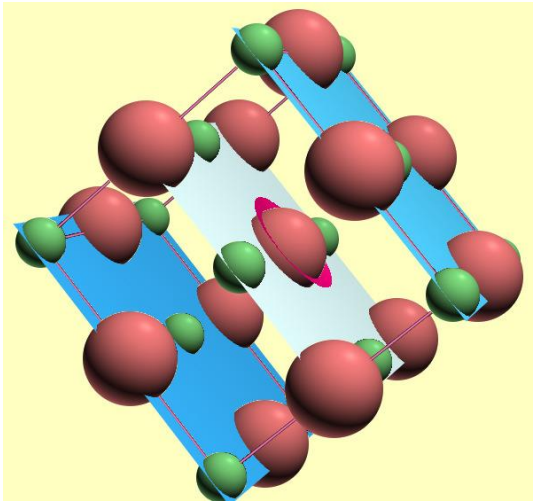


Fourier Transforms

Reciprocal Space
Diffraction pattern
Reciprocal lattice
Amplitudes and phase
Coordinates (h, k, l)

Describing order in space

Parallel planes of atoms intersecting the unit cell define directions and distances in the crystal.



The (200) planes of atoms in NaCl

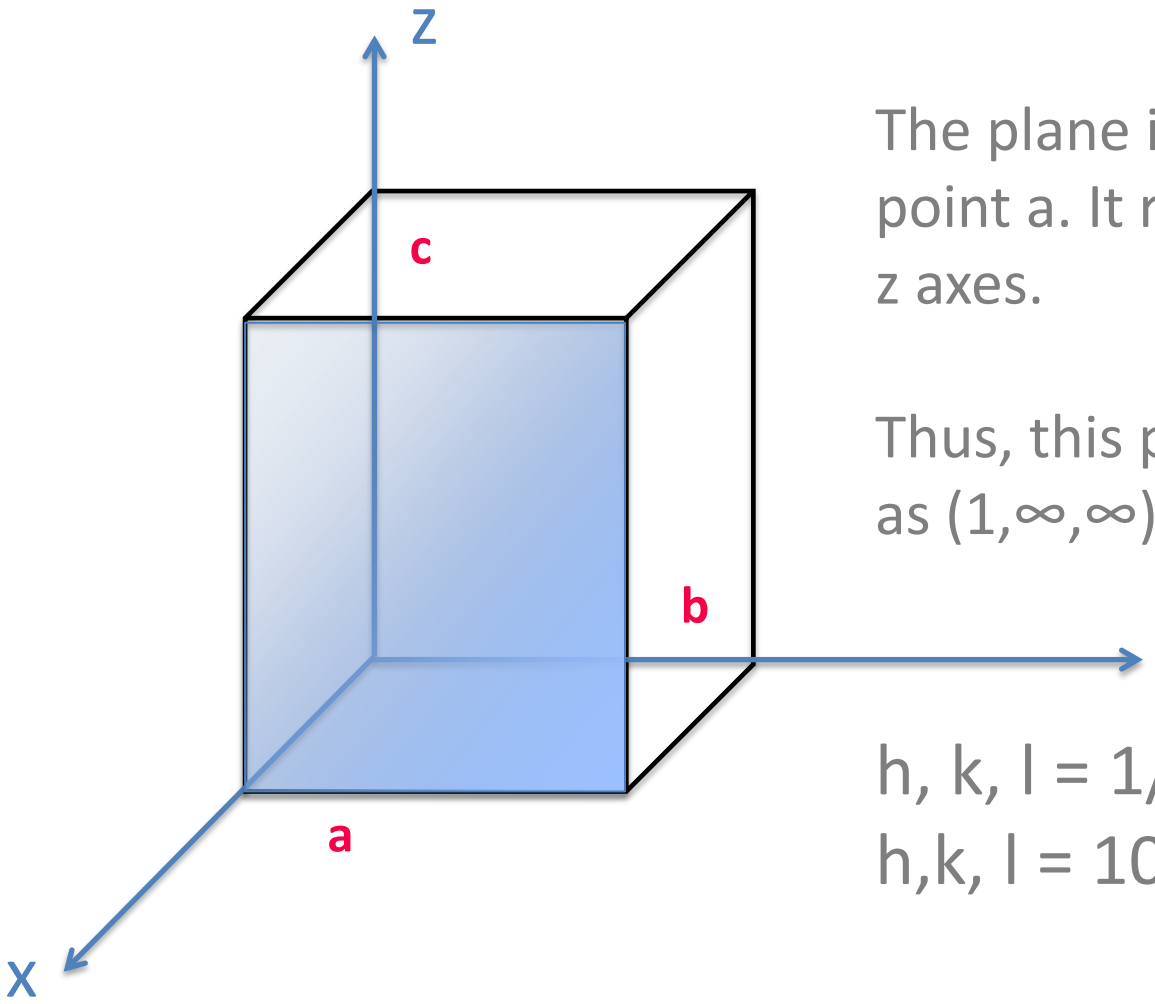
Planes are separated by a distance, d_{hkl}.

This distance is crucial to determine where diffraction peaks will be observed!!!!!

The planes and the distance between them is what we measure!!

Miller Indices

Miller indices (hkl) are used to identify different planes of atoms. These are the **reciprocal** of the intercepts of the planes that dissect the unit cell with the crystallographic axis



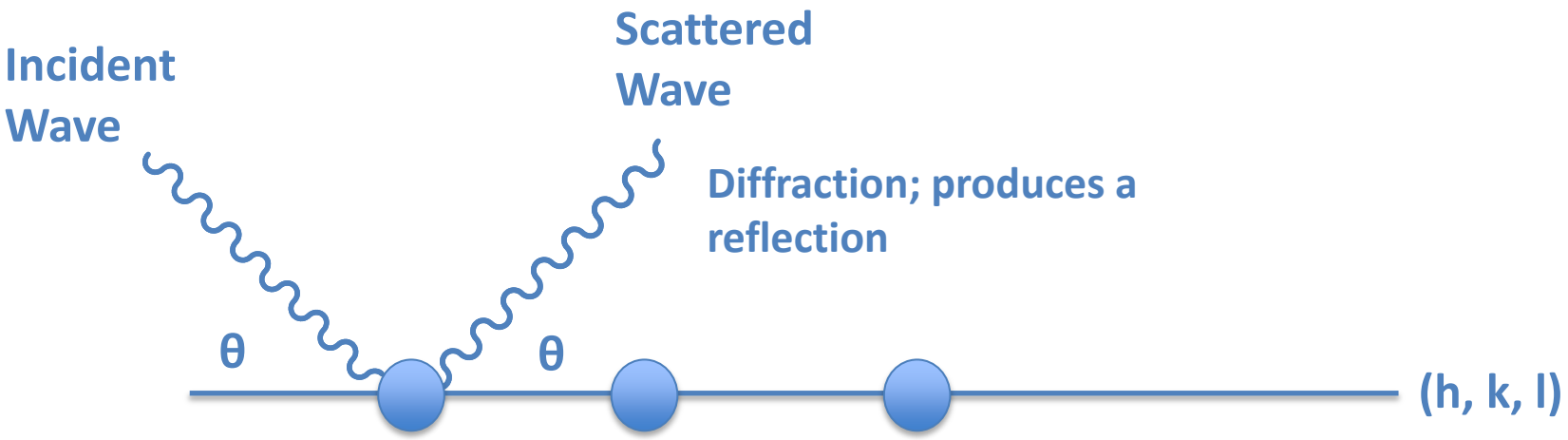
The plane intersects the x-axis at point a. It runs parallel along y and z axes.

Thus, this plane can be designated as (1,∞,∞)

h, k, l = 1/1, 1/∞, 1/∞

h,k, l = 100

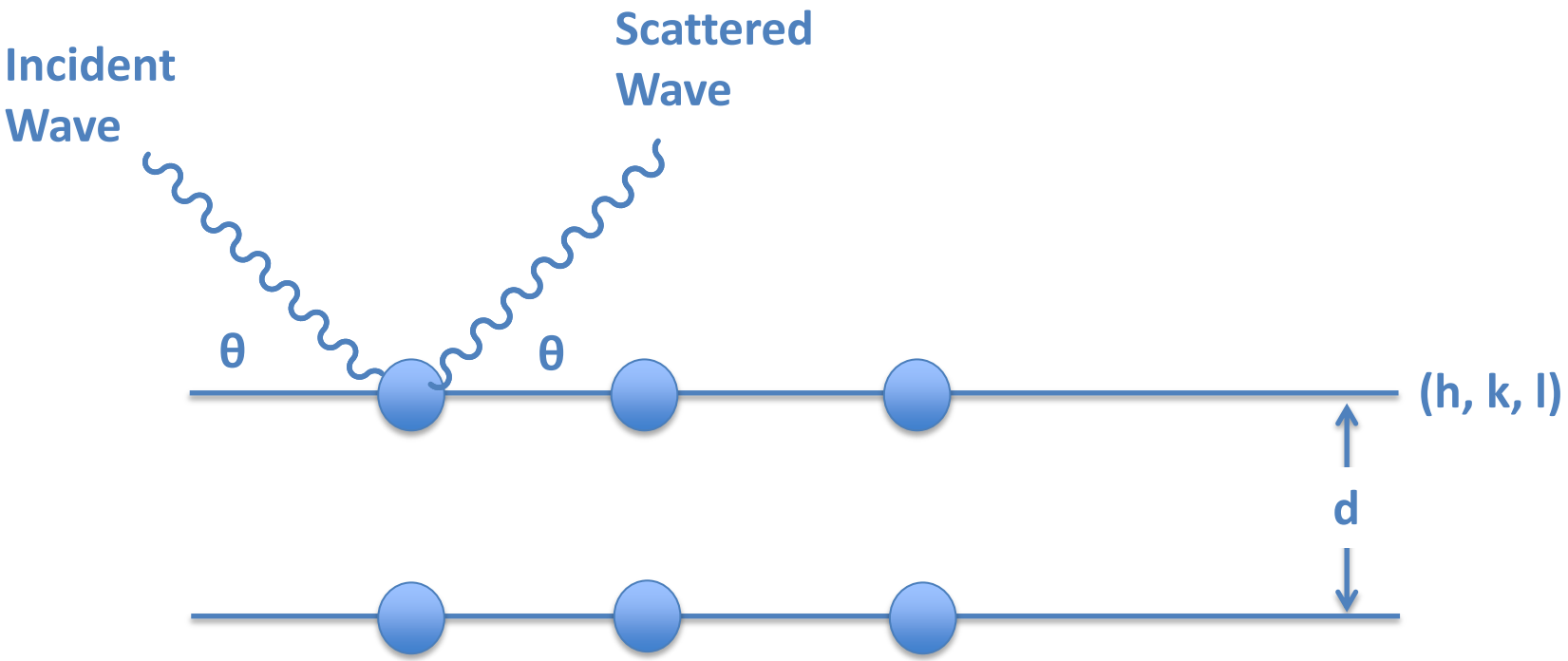
Bragg's Law



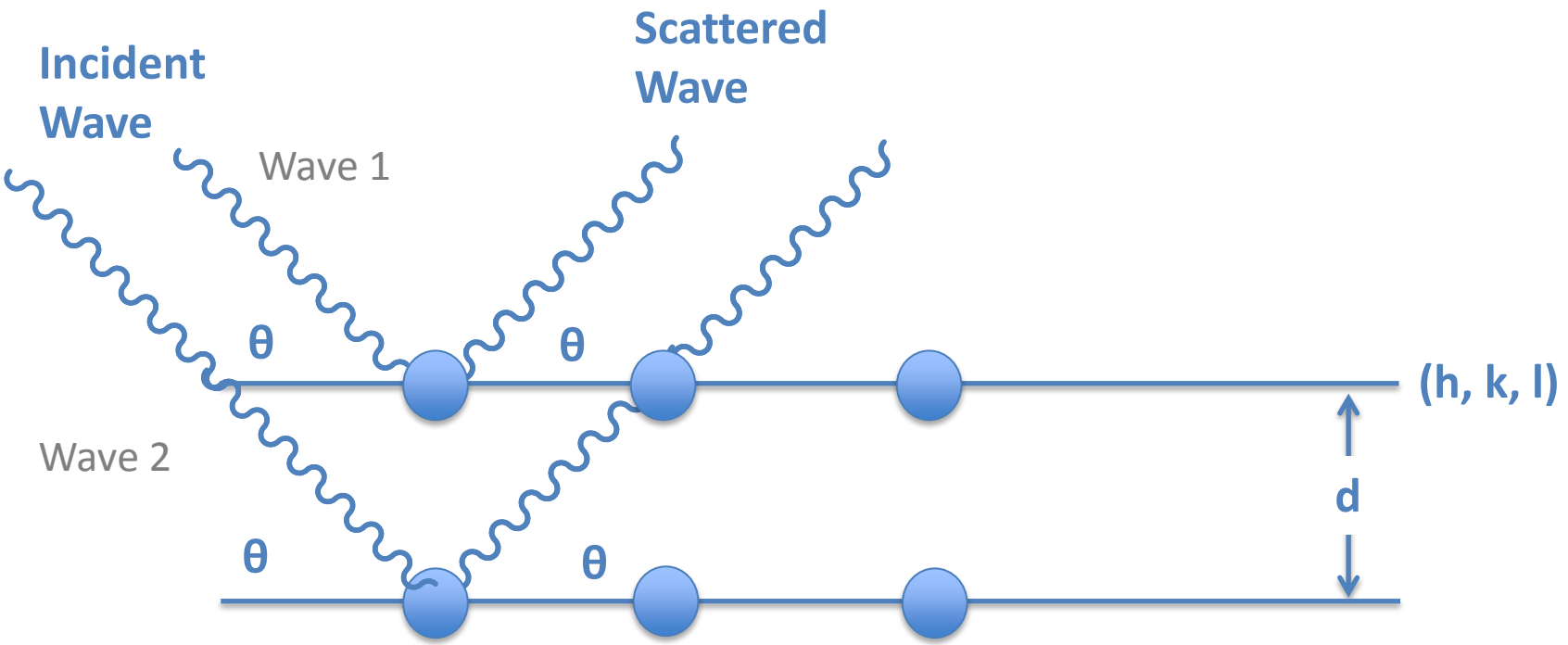
Only when the incident angle (θ) and the scattered angle (θ) are the same will constructive interference will occur

The scattering of an atom is the value for a free electron multiplied by the atomic number – Scattering factor

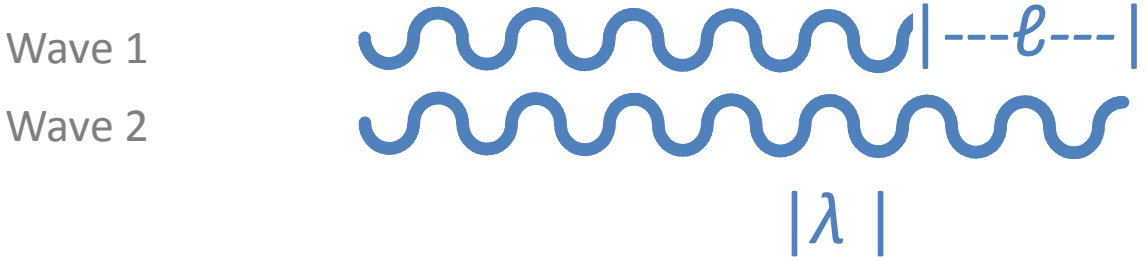
Bragg's Law



Bragg's Law

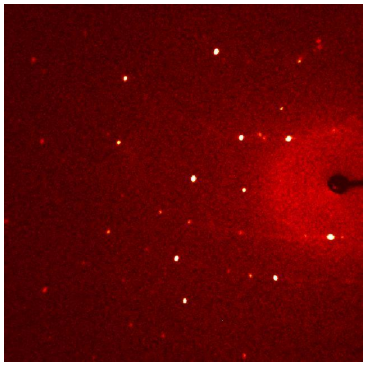


For constructive interference to occur the waves must be in phase



$$\ell = n\,\lambda$$

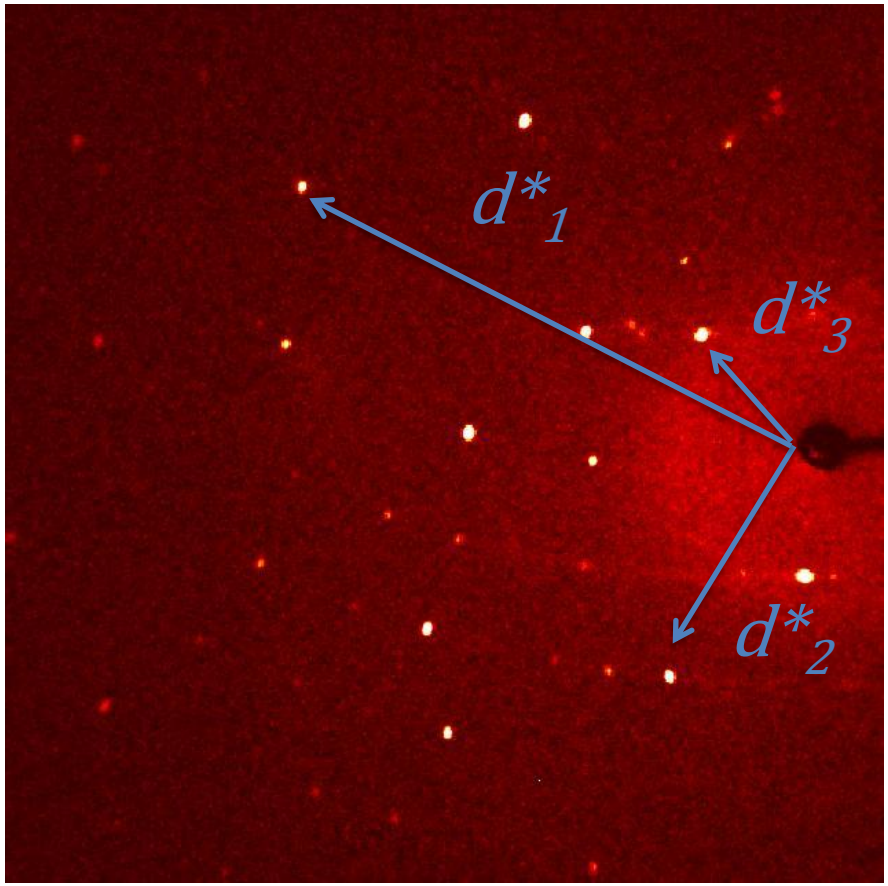
Bragg's Law



According to Bragg, *when* $\ell + \ell = \lambda$, the waves are in phase, resulting in constructive interference or Diffraction!!!

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

Applying Bragg's Law – Reciprocal Space



"Real Space"

$$2\,d_{hkl}\sin\theta_{hkl} = n\lambda$$

Reciprocal Space

$$d^*_{hkl} = \frac{2\sin\theta_{hkl}}{\lambda}$$

Diffraction Pattern – Unit Cell (real space)

Reciprocal Space

$$d^*_{hkl} = \frac{2 \sin\theta_{hkl}}{\lambda}$$

Real Space

$$d^*_{100} = a^* = \frac{bc\sin\alpha}{V}$$

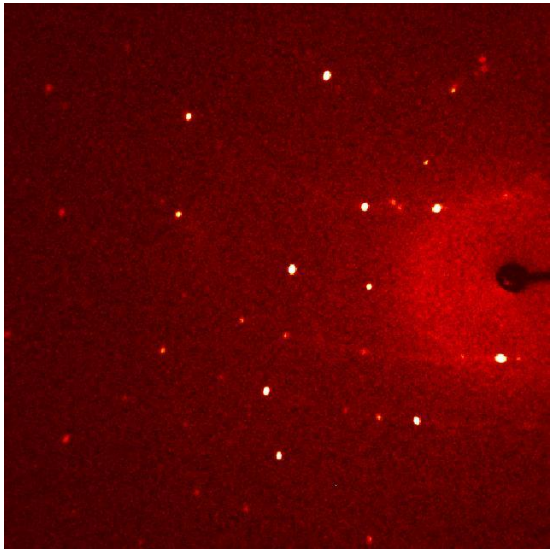
$$d^*_{010} = b^* = \frac{ac\sin\beta}{V}$$

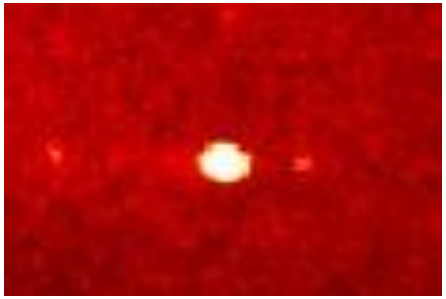
$$d^*_{001} = c^* = \frac{ab\sin\gamma}{V}$$

We can define our unit cell parameters

Diffraction Pattern

Each frame has several reflections



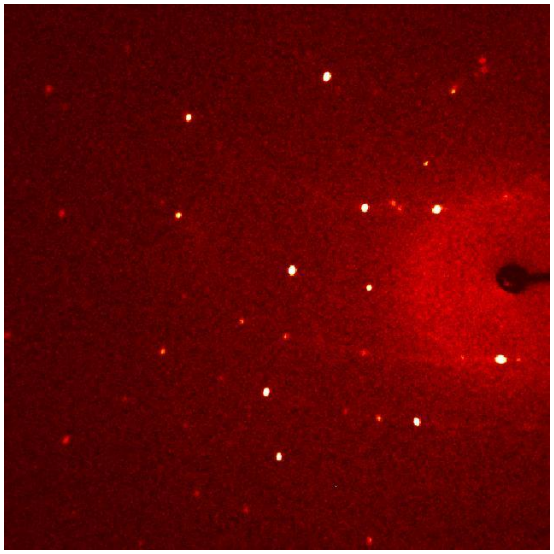


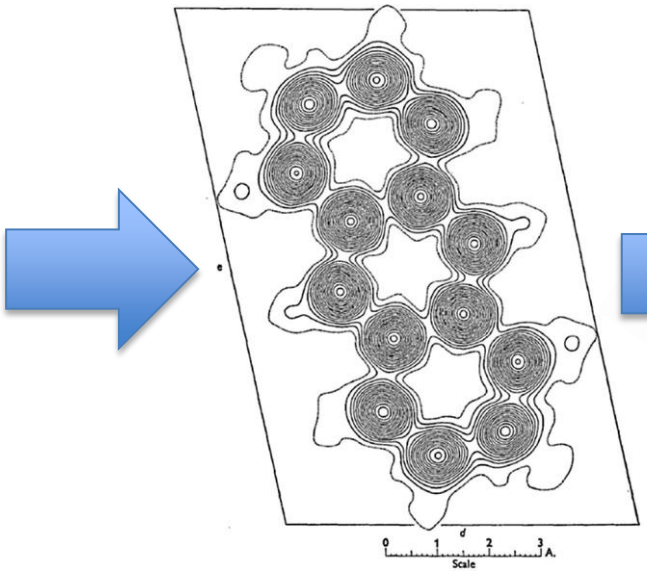
Each spot is called a reflection

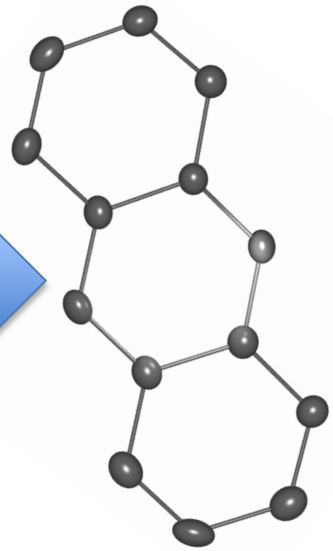
What does each spot tell us?

- *hkl* position of atoms (x, y, z) ← Reciprocal Space!!!
  - Where the atoms are
    - Miller Indices and d_{hkl}
- Intensity ~ number of scattering electrons in the atom
  - What the atom is
    - Scattering Factor

Electron Density







Intensities – Structure factor

Phasing ?

$$\rho_{xyz} = (1/V) \sum_{hkl} | F_{hkl} |_{observed} \cos 2\pi (hx+ky+lz-\alpha_{hkl})]$$

Phasing Problem

$$\rho_{xyz} = (1/V) \sum_{hkl} | F_{hkl} |_{observed} \cos 2\pi (hx+ky+lz-\alpha_{hkl}^{?})]$$

Phase information is more important than the intensity
We cannot focus an X-ray like a microscope!!

Direct Methods

- Test random phases for a solution (1000-3000 cycles)

Patterson Methods

- Heavy atom method

Refinement - Does the model fit the data?

Data Collection

Close to 100% completeness

- Most of the reflections in the asymmetric unit

Refinement Residuals

R1 values (below 10 %)

- Measure of how well the refined structure predicts the observed data.

wR_2 values (below 20 %)

- Least-squares residual; measure of how intensities calculated for the X-ray reflections match those measured experimentally.

Crystallographic Programs

Apex 2

- Collecting data
- Solving and Refining the structure
- Preparing structure for publication
  - Picture (black and white)
  - Crystallographic tables
  - CIF (crystallographic information file)
    - CIF must be checked online and issues fixed
      - **PLATON**

Endnote or PublCIF

- Preparing CIF file for publication

Crystallographic Programs

Mercury

- Reads CIF files for visualization of crystal structures
  - Measure bond lengths and angles
  - Measure inter- and intramolecular interactions

Diamond

- Pictures of crystal structures
  - Interactions
  - Frameworks
  - Colorful!

Further Information

Reference Materials

- "Crystal Structure Determination"
  - Werner Mass
- "Crystal Structure Analysis: Principles and Practice"
  - William Clegg
- "Crystal Structure Refinement: a crystallographer's guide to SHELXL
  - Peter Müller
- "How to read (and understand) Volume A of International Tables for Crystallography: an introduction for nonspecialists"
  - Zbigniew Dauter and Mariusz Jaskolski. *J. Appl. Cryst.* **2010**, *43*, 1150–1171

Next Week

Mounting Samples

- Individual basis

Refining

- File types (res, ins, cif)
- Issues with completeness
- Issues with refinement

SADABS

- Absorption methods