Bragg's Law and Miller Indices

Understanding Crystallography and Diffraction

CCCW23

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Learning Objectives

By the end of this lecture, learners will be able to…

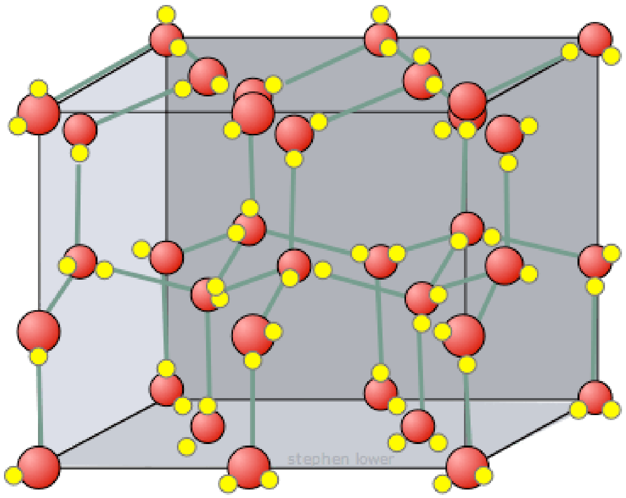
- Explain the principle of X-ray diffraction and its role in studying crystal structures.
- Describe and derive Bragg's Law.
- Introduce Miller Indices as a notation system for describing crystal planes and directions.
- Understand the process of determining Miller Indices for crystal planes.
- Encourage further exploration and study of crystallography and diffraction.

Introduction

Understanding the Structure of Materials

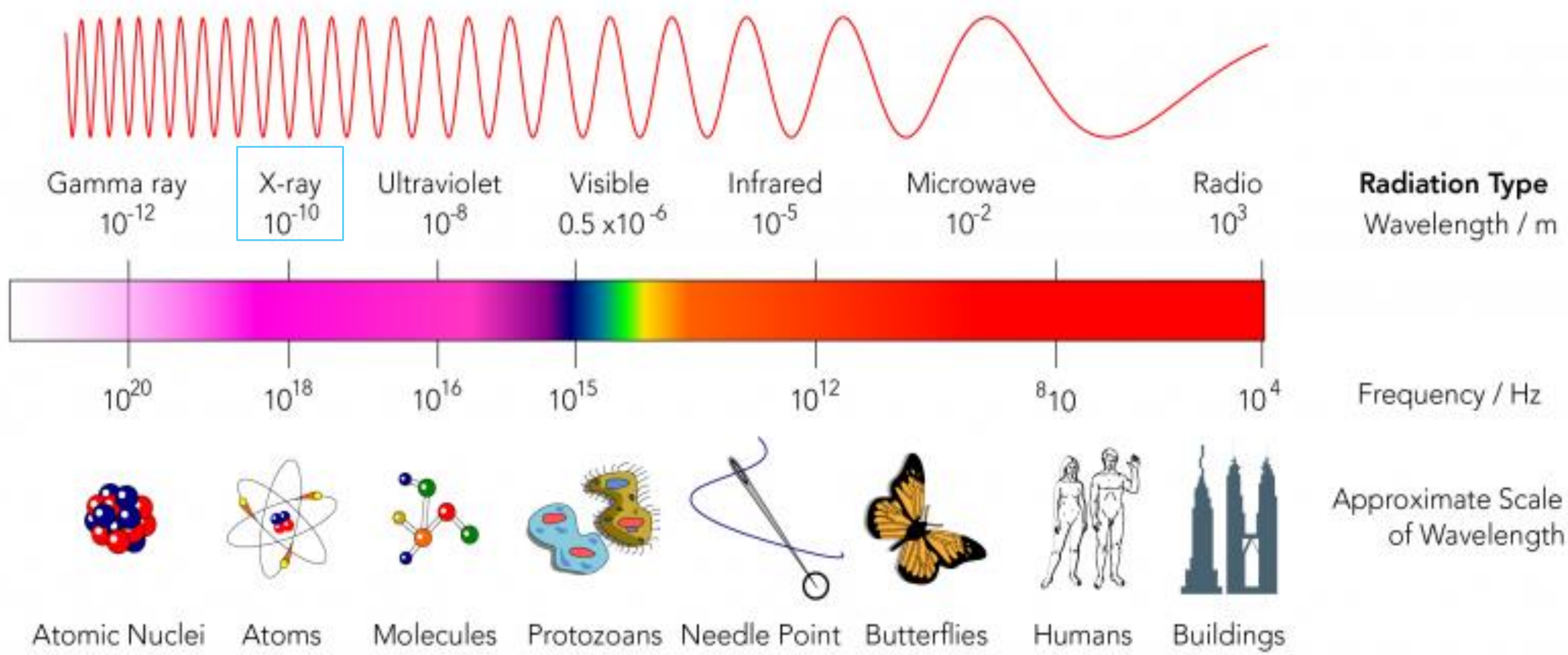
- We use **crystallography** to understand the structure of **crystalline** solids.
    - Crystallography: The study of *crystal structures*.
    - Crystal structure: A description of the ordered arrangement of atoms, ions, or molecules in a crystalline solid.

- Why do we care about the structure of crystalline solids?
    - The arrangement of these building blocks within a crystal determines its unique properties and behavior.



Hexagonal Ice, I_h

Electromagnetic Radiation



- Smaller wavelengths with higher energy than visible light.
- X-rays can penetrate matter more easily than visible light.

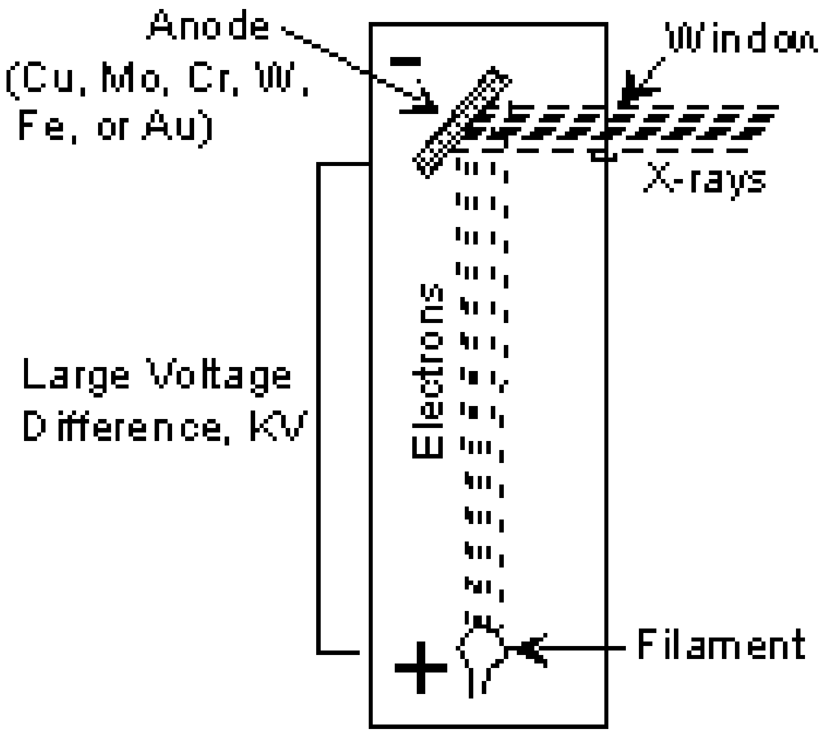
X-Ray Tube

- Tungsten filament at one end (cathode) and metal target at the other (anode).

- Electrons are generated at the cathode, and directed to the anode by placing a large difference in voltage between the two sites.

- When electrons strike the target, electronic transitions occur and X-rays are generated.

- Target materials produce X-rays of specific wavelength.



Characteristic Wavelength

The X-rays we use for diffraction have a wavelength of 0.7-1.5 Å.

- Cu radiation (1.54 Å)
  - Great for organic compounds and chiral molecules.
  - Diffracted spots are more widely spread; great for large unit cells.

- Mo radiation (0.71 Å)
  - Great for inorganics. Better resolution.
- Ag radiation (0.56 Å)
  - Hard radiation; often used to analyze samples at a deeper level.

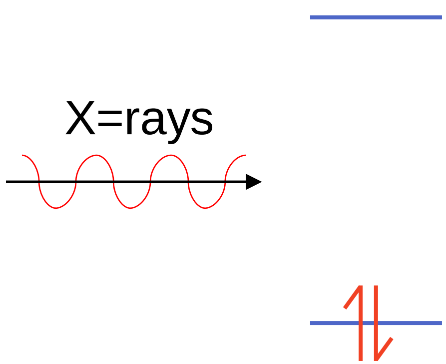
Element	Wavelength (λ) Å ($K\alpha_1$)
Ag	**0.5594**
Mo	**0.7097**
Cu	**1.5405**
Co	1.7889
Fe	1.9360
Cr	2.2896

PXRD Analysis

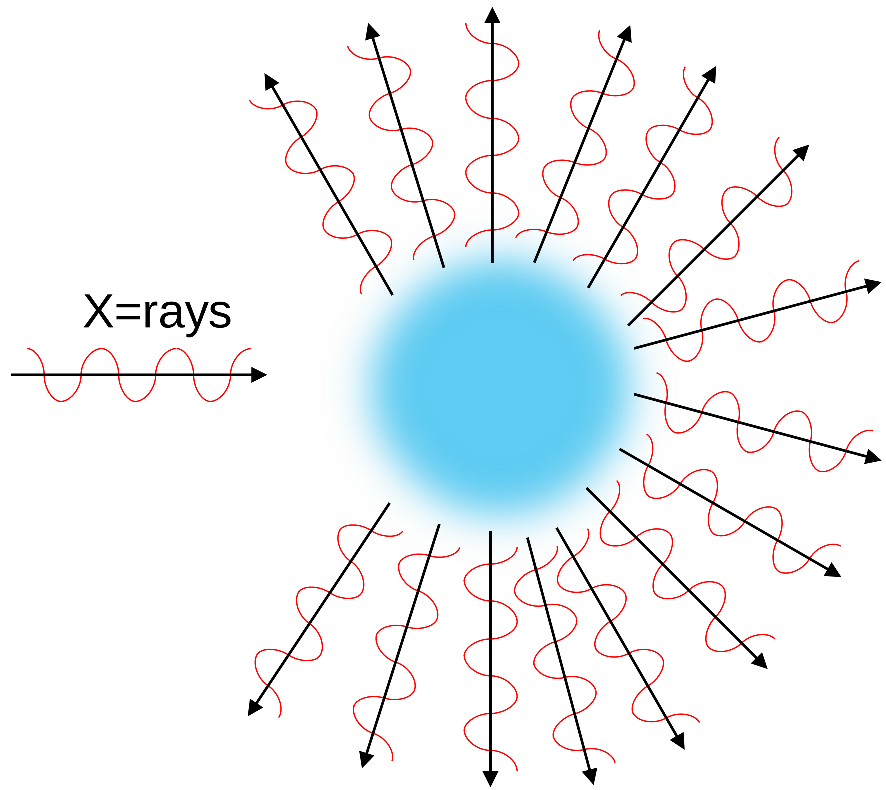
Electromagnetic Radiation

How does electromagnetic radiation interaction with matter?

Absorption

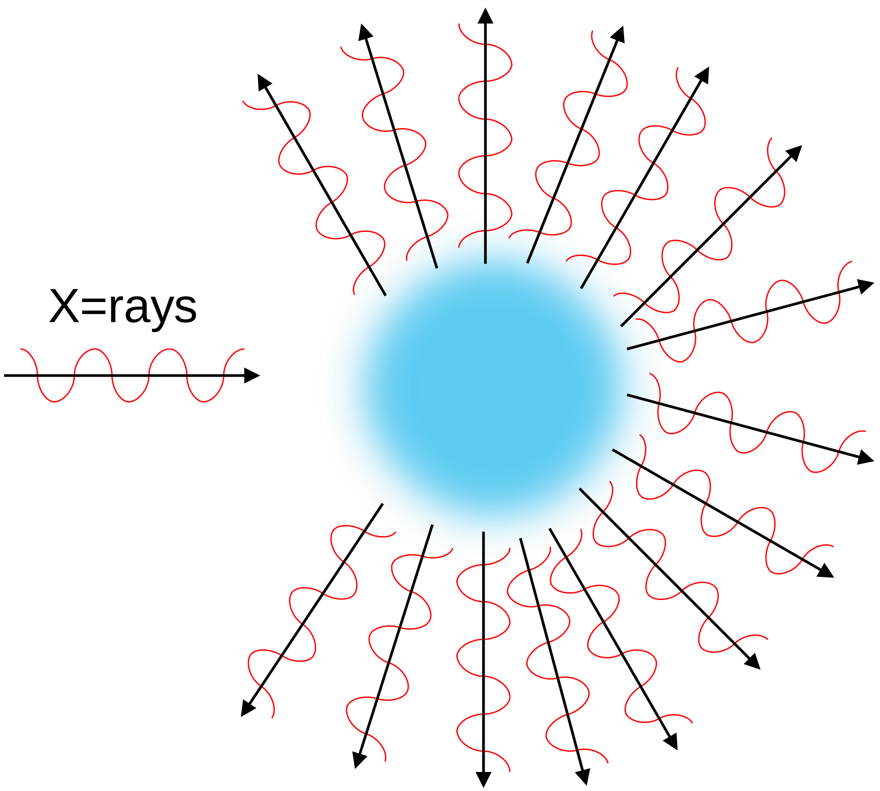


Scattering



X-Ray Scattering

X-ray scattering is what we care about!

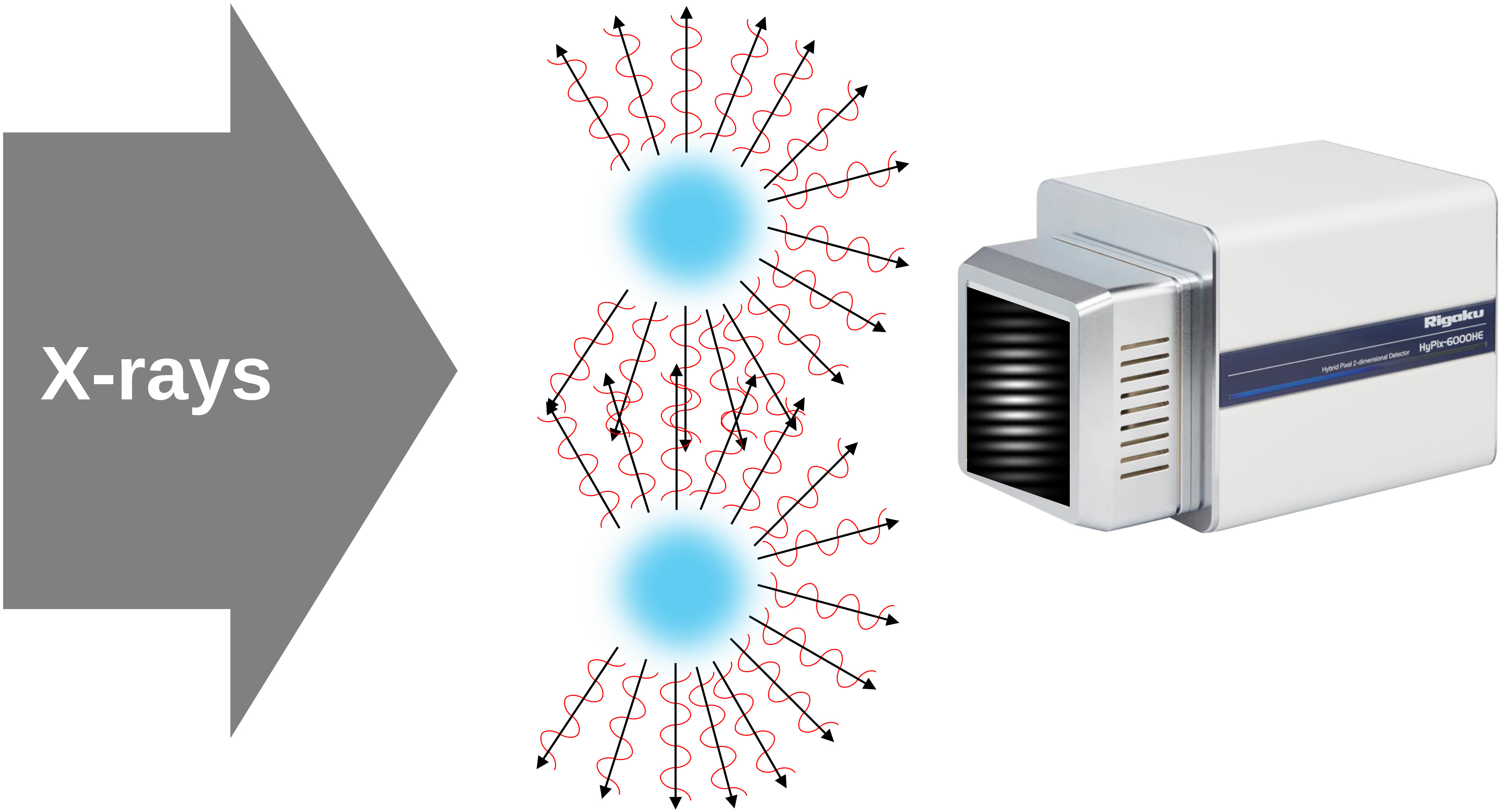


- X-rays interact with the electrons in an atom, causing them to change directions and scatter.
  - **Elastic**: Same wavelength and energy.
  - Inelastic: Different wavelength and energy.

- With multielectron atoms, the whole electron cloud oscillates.
  - The more electrons an atom has, the more it scatters X-rays.

X-Ray Scattering

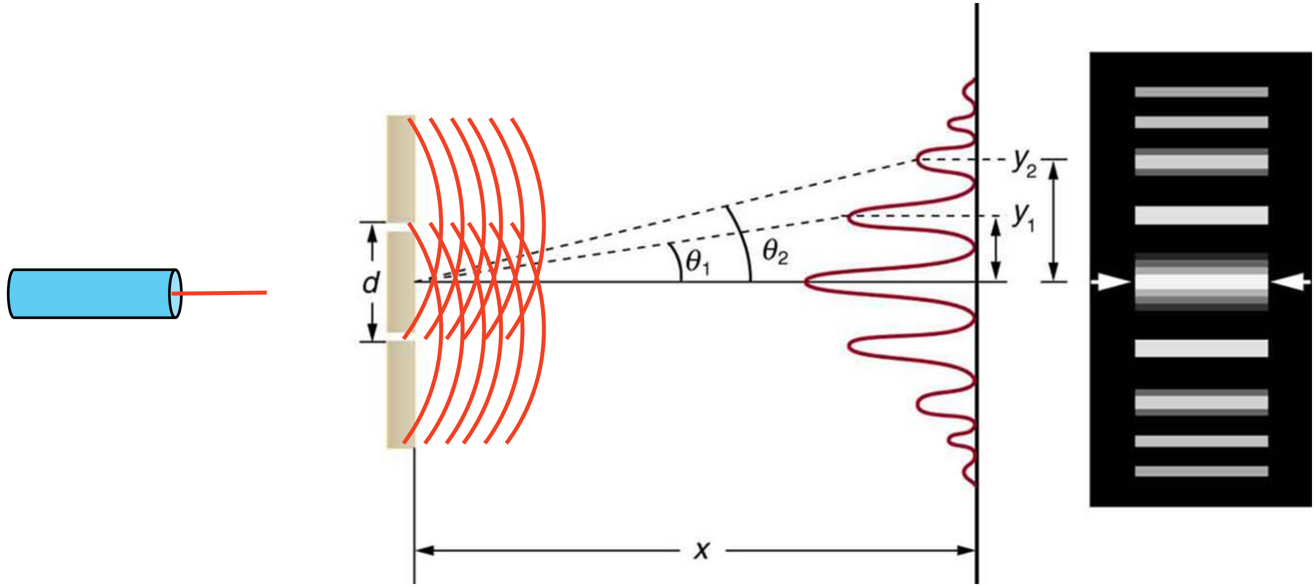
What happens when we have more than one atom?



The scattered waves from each atom can **interfere** with each other.

X-Ray Scattering

Young's Double Slit Experiment

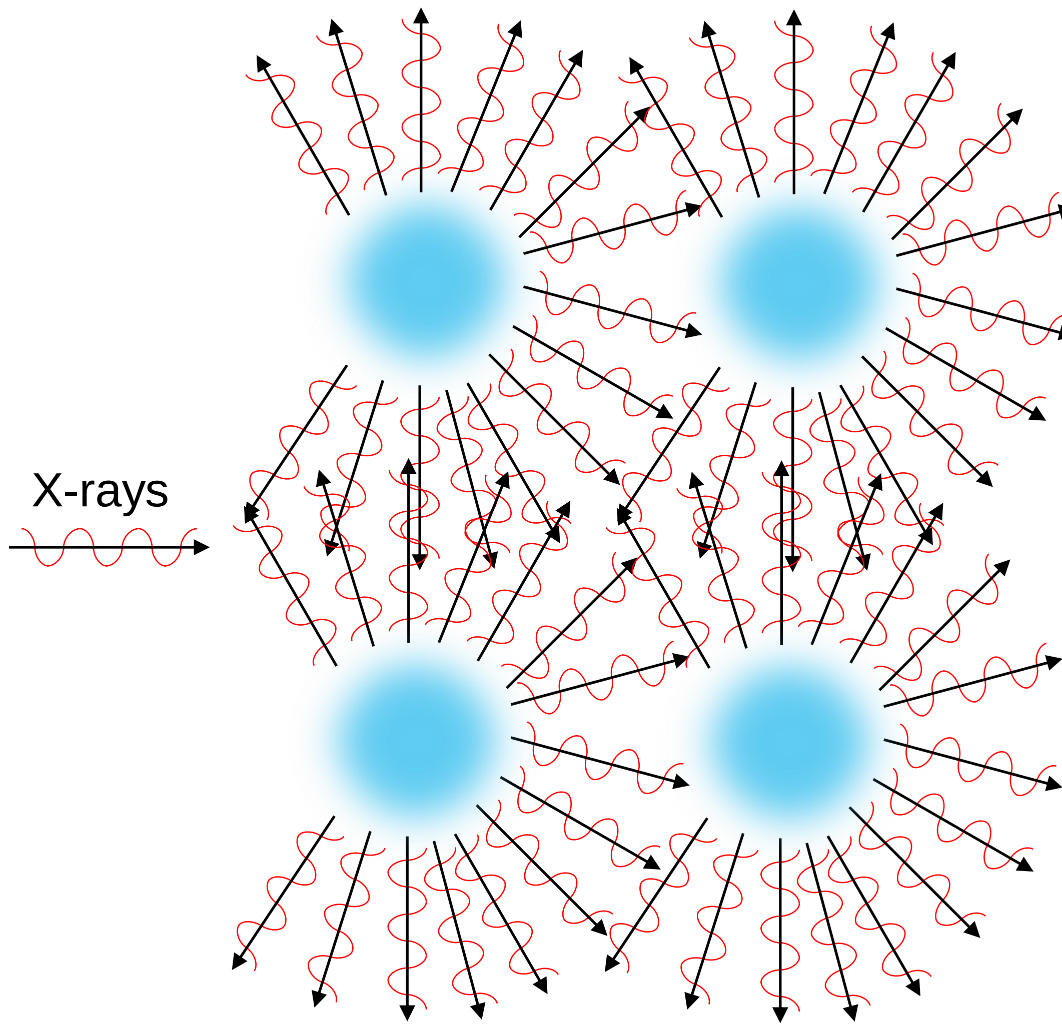


- Light passing through the slits creates two separate wavefronts that can interfere either:
  - Constructively (amplitudes of waves add).
  - Destructively (amplitudes of waves cancel).
- The wavelength of the light and the separation of the slits determines the spacing between the fringes.

X-Ray Diffraction

Bragg's "Double Slit" Experiment

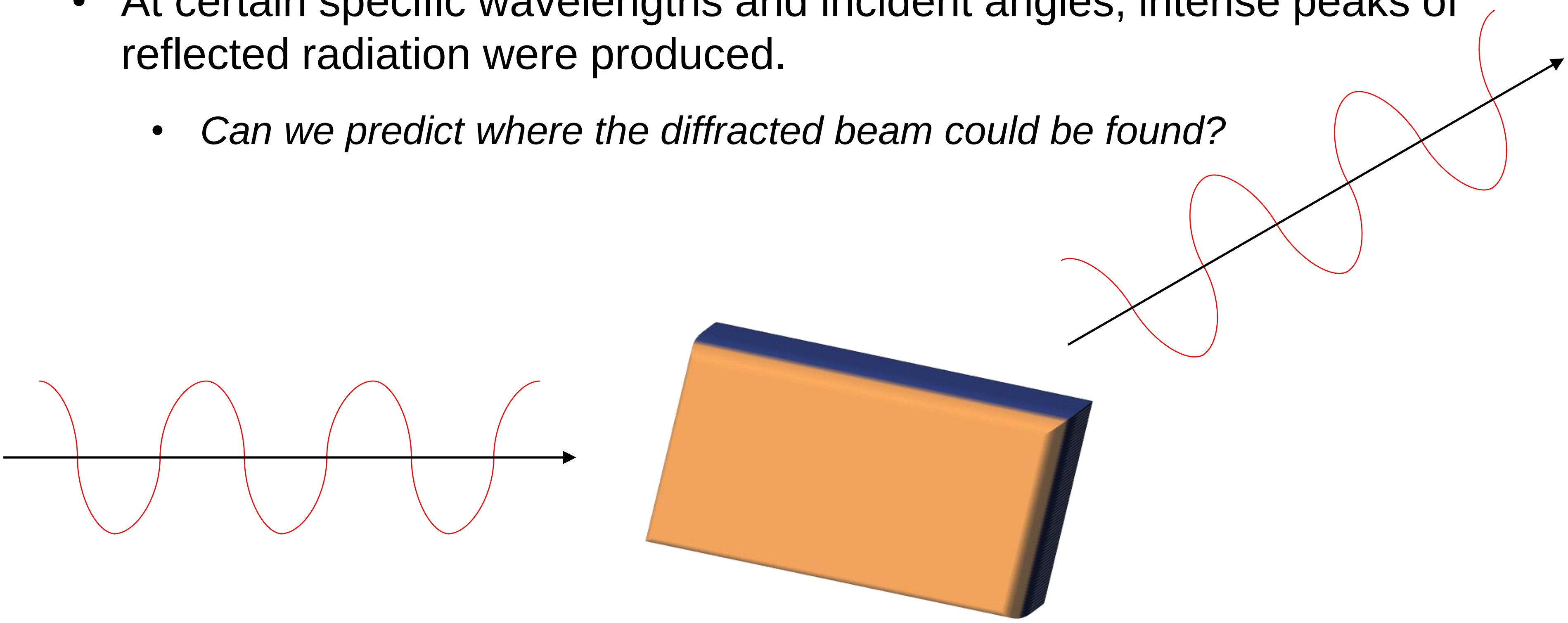
- The crystal is a 3D array of regularly spaced scattering centers (atoms).
- The X-rays diffract as they interact with these scattering centers and interfere with each other to produce a diffraction pattern.
- The diffraction pattern consists of bright spots, or diffraction peaks, that correspond to a specific set of crystal planes.



We still need to locate each diffraction peak and measure the intensity.

Diffraction by a Crystal…Recap…

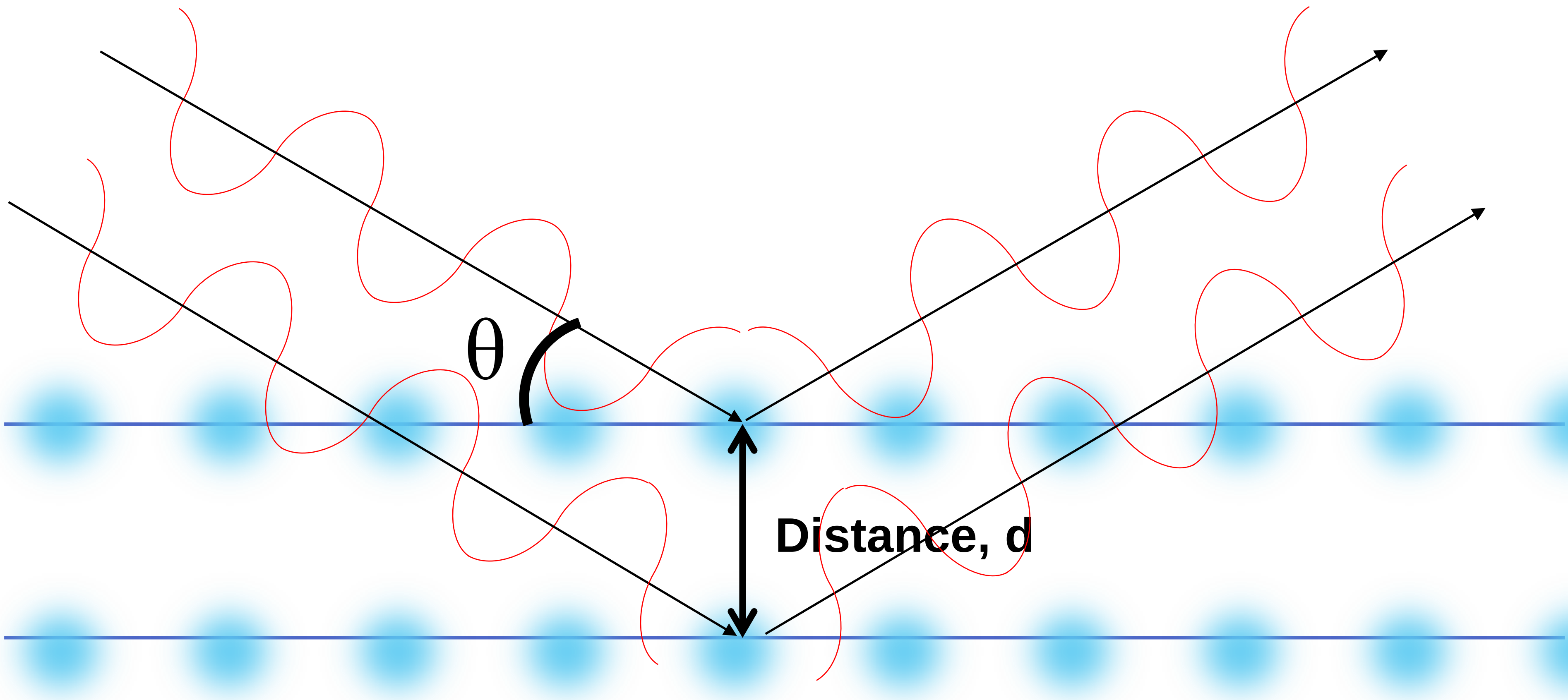
- X-ray diffraction is a technique that involves the scattering of X-rays by the atoms in a crystalline material
- The ordered array of atoms in the crystal acts like a new point source of X-rays, which constructively and destructively interfere to result in a pattern.
- At certain specific wavelengths and incident angles, intense peaks of reflected radiation were produced.
  - *Can we predict where the diffracted beam could be found?*



Derivation of Bragg's Law

Model

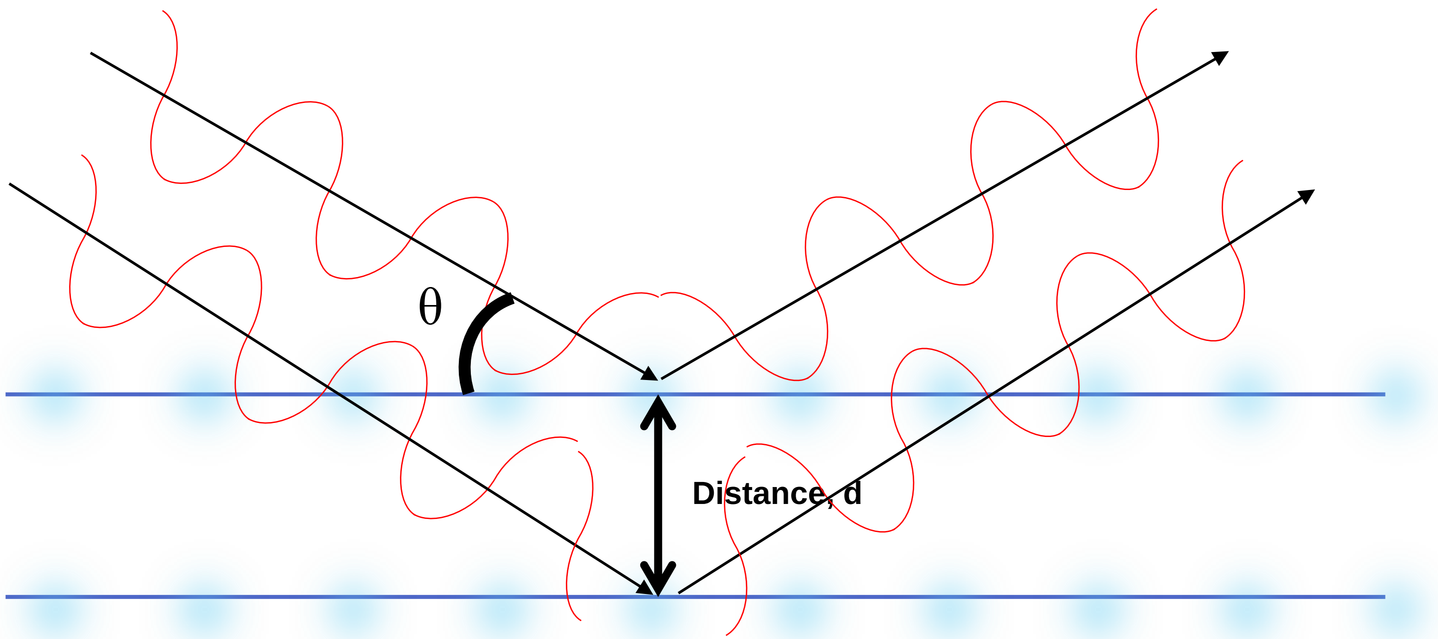
- Crystal is a set of discrete parallel planes.



Derivation of Bragg's Law

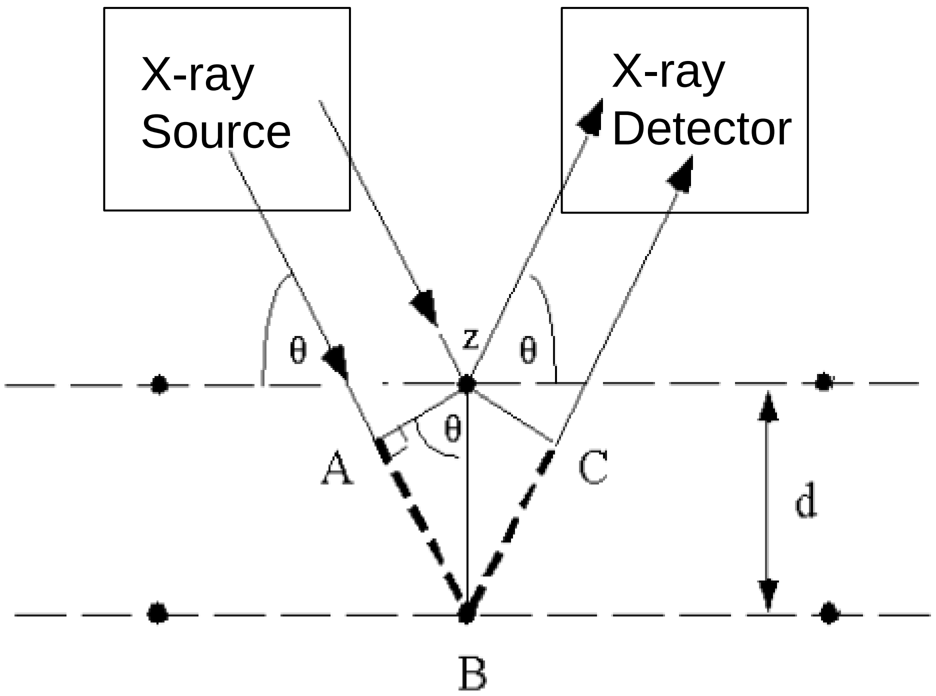
Conditions for Constructive Interference

- Beams must be in phase.
  - "Extra" distances MUST be some whole integer factor of the wavelength
    - 1λ, 2λ, 3λ, 4λ, … $n\lambda$
  - How much more one wavelength travels between the two planes depends on the distance between the two planes.



Derivation of Bragg's Law

Derivation



$n\lambda = AB + BC$

$n\lambda = 2\ AB$

$AB = \sin\theta\ d$

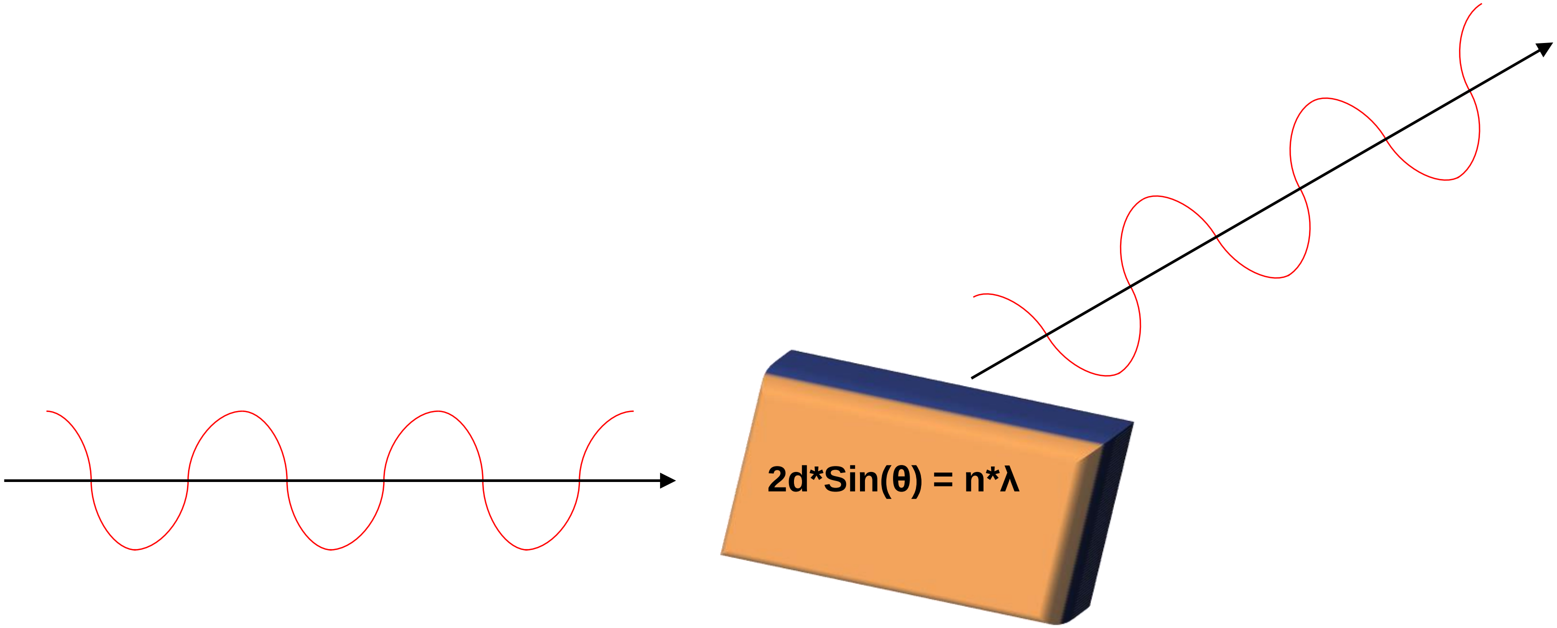
$\mathbf{n\lambda = 2d\sin\theta}$

Bragg's law

If we have parallel planes in a crystal a distance, d, apart, then only when the X-rays hit the plane at an angle, θ, where the extra distance, 2h, travelled by longer path is equal to nλ do we have constructive interference (diffraction).

Planes and Distances

Derivation



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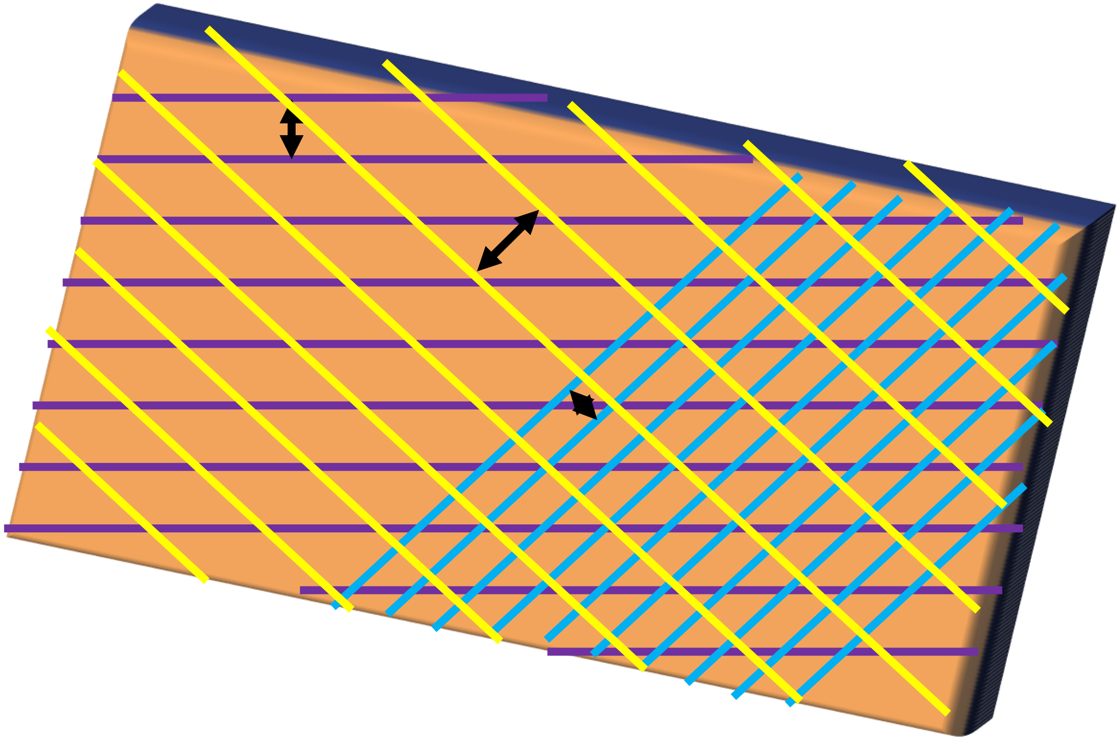
Planes and Distances



- We can draw an infinite number of parallel planes through a crystal.
- The family of planes are a distance d apart from each other.
- Only when we satisfy Bragg’s Law, do we see “diffraction” from the planes.

$$2d*\sin(\theta) = n*\lambda$$

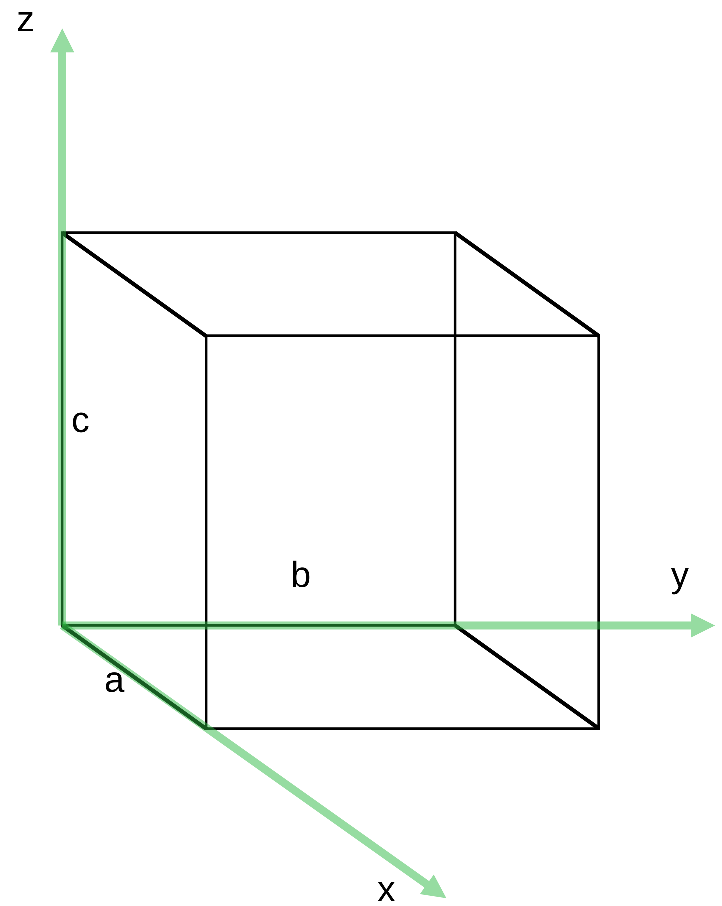
Planes and Distances

Miller Planes

- In 1839, William Hallowes Miller came up with a notation for these planes.

- We don't need to consider the whole crystal. We just need to look at the unit cell.

- We refer to these planes as (h k l).
  - h is the inverse of the fractional coordinate along a.
  - k is the inverse of the fractional coordinate along b.
  - l is the inverse of the fractional coordinate along c.



Planes and Distances

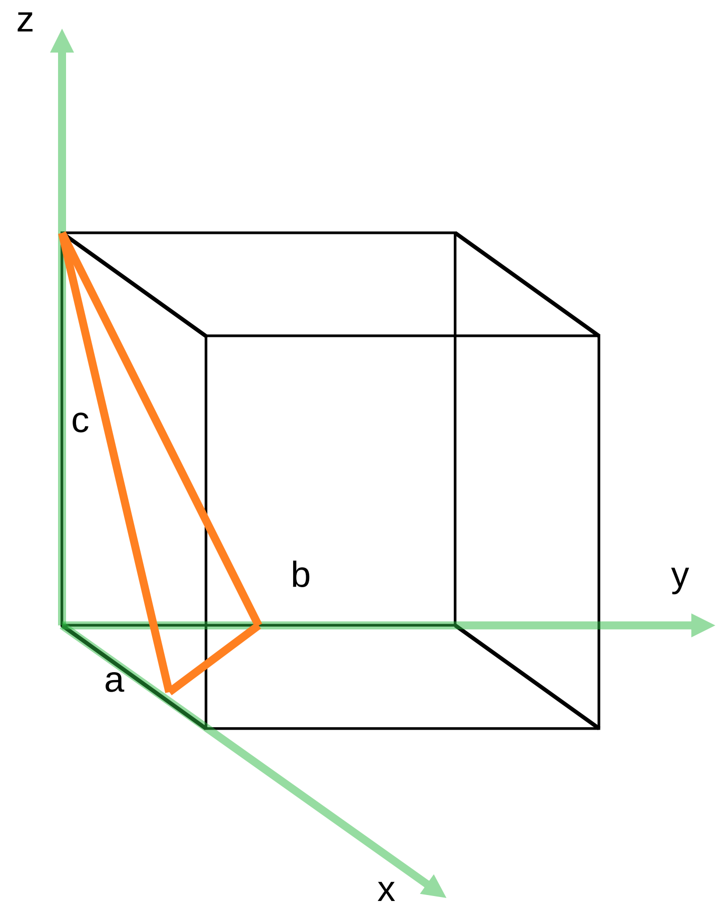
Miller Planes

- Every plane that we can draw in the unit cell, intersects at some fraction of the way along the unit cell axis (a, b, c).

The orange plane:

- Intersects a at 0.5
- Intersects b at 0.5
- Intersects c at 1

We call this the (221) plane



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Planes and Distances

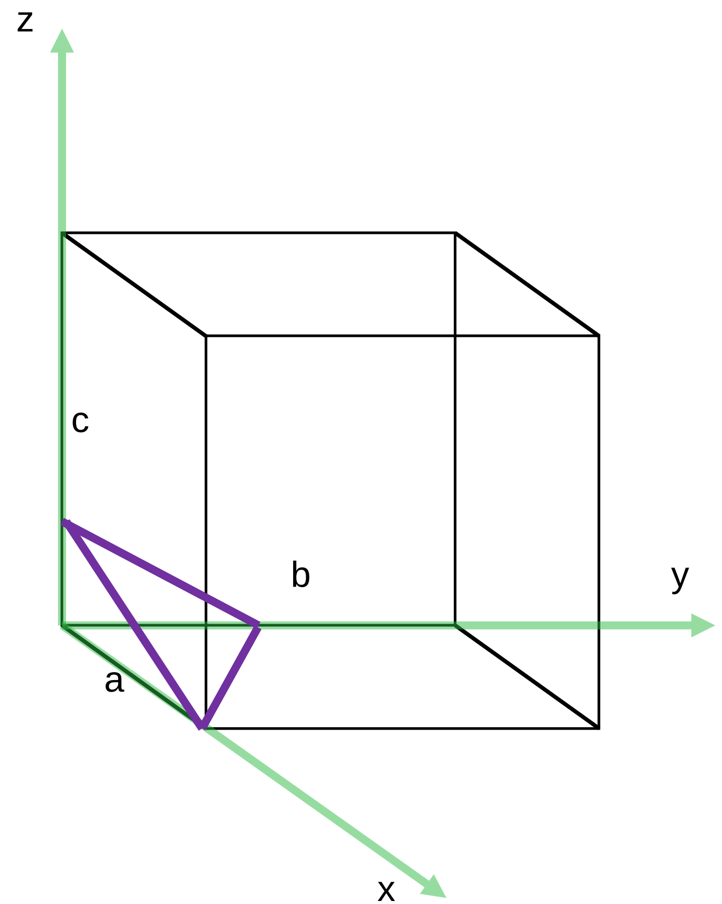
Miller Planes

- Every plane that we can draw in the unit cell, intersects at some fraction of the way along the unit cell axis (a, b, c).

The purple plane:

- Intersects a at 1
- Intersects b at 0.5
- Intersects c at 0.33

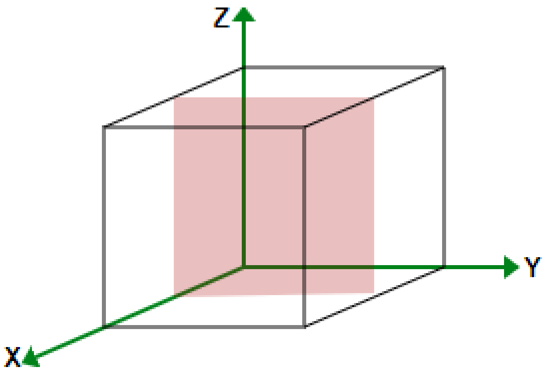
We call this the (123) plane



We refer to these planes as (h k l).

- h is the inverse of the fractional coordinate along a.
- k is the inverse of the fractional coordinate along b.
- l is the inverse of the fractional coordinate along c.

Practice



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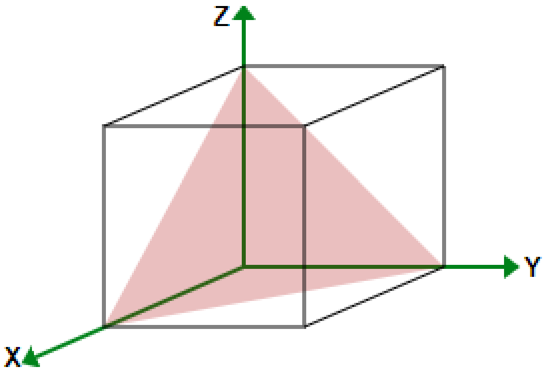

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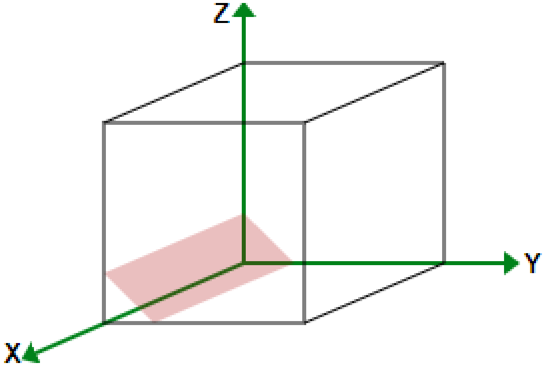

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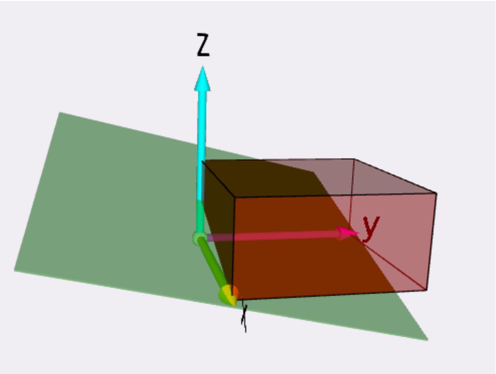
Planes and Distances

- The larger the indices, the smaller the d values.
- Negative numbers are denoted with a bar on top of the number.
  E.g. $(\bar{1}00)$.

http://KatzResearchGroup.com/Miller.html



- Notation:
  - Round brackets are used when referring to a specific plane.
    E.g. (100)
  - Curly brackets are used when referring to a set of planes related by symmetry.
    E.g. {100} family of planes in a cubic system consists of (100), (010), (001), $(\bar{1}00)$,$(0\bar{1}0)$ and $(00\bar{1})$.

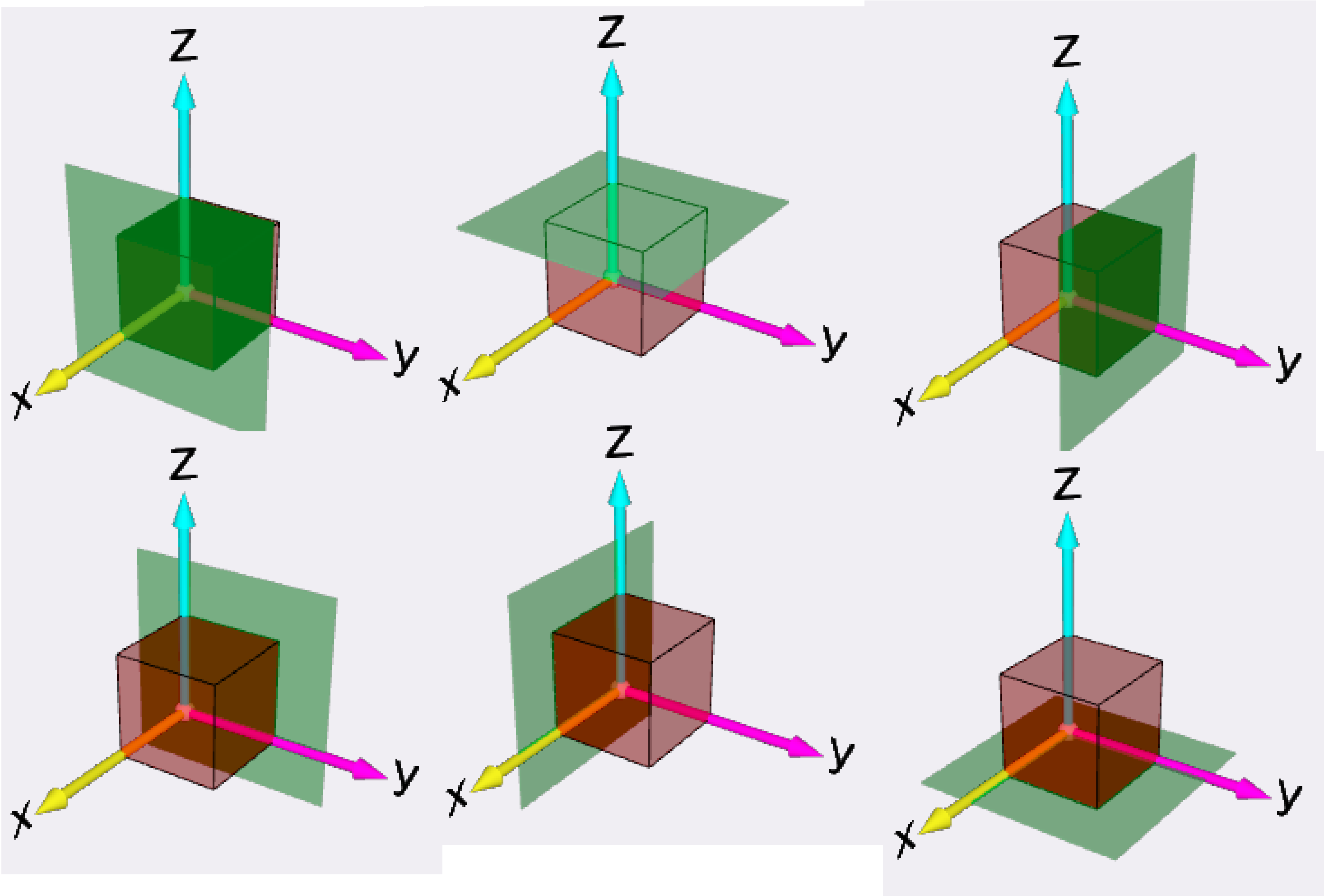
Planes and Distances

Family of Planes

E.g. {100} family of planes in a cubic system consists of (100), (010), (001), ($\bar{1}$00),(0$\bar{1}$0) and (00$\bar{1}$).

a=b=c

α=β=γ=90°



Planes and Distances

- If we know the unit cell length, then we can predict the distance between any parallel set of hkl planes.

General formula for determining the d-spacing…

$$\frac{1}{d^2} = \frac{1}{V^2}[h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta + l^2a^2b^2\sin^2\gamma + 2hkabc^2(\cos\alpha\cos\beta - \cos\gamma)$$
$$+ 2kla^2bc(\cos\beta\cos\gamma - \cos\alpha) + 2hlab^2c(\cos\alpha\cos\gamma - \cos\beta)].$$

Considering symmetry….

Cubic:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Orthorhombic:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Tetragonal:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{+l^2}{c^2}$$

Wrap-up

- Electrons scatter X-rays
- In an ordered array of atoms (a crystal), this leads to constructive and destructive interference.
  - Each type of atom has its own response to X-rays.
  - We observe a diffraction pattern.
    - **<u>Because all atoms are interacting with each other to form the diffraction pattern, every atom can contribute to every Bragg reflection we observe.</u>**
  - Bragg determined what conditions were necessary to get diffraction.
- Miller created a notation so that we can define any set of parallel planes.
  - Miller planes, hkl reflections, ….
- If we know the unit cell length, then we can predict the distance between any parallel set of hkl planes.
  - We can then determine at what angle we will see diffraction.
    - We can determine the intensity of that diffraction pattern.
      - We can reverse engineer the atoms and their positions that caused this.
        - We can get a crystal structure!!!!!

Learning Objectives

It is now the end of the lecture! Do you know…

- ✓ Explain the principle of X-ray diffraction and its role in studying crystal structures.
- ✓ Describe Bragg's Law and its role in studying crystal structures.
- ✓ Introduce Miller Indices as a notation system for describing crystal planes and directions.
- ✓ Understand the process of determining Miller Indices for crystal planes.
- ✓ Encourage further exploration and study of crystallography and diffraction.

???................Any questions???

Huge thank you to Mike Katz for sharing his slides!!

Questions?