Bragg's Law and Miller Indices

Understanding Crystallography and Diffraction

CCCW24

May 28, 2024

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Learning Objectives

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

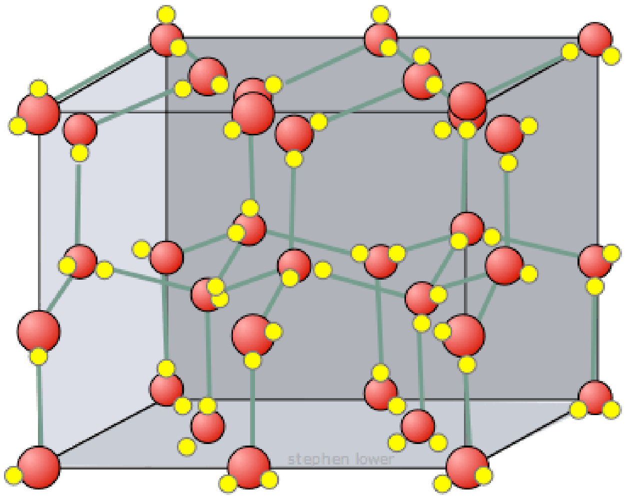
- Explain the principle of X-ray diffraction and its role in studying crystal structures.
- Describe and derive Bragg’s Law.
- Introduce Miller Indices as a notation system for describing crystal planes and directions.
- Understand the process of determining Miller Indices for crystal planes.
- Encourage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

Introduction

Understanding the Structure of Materials

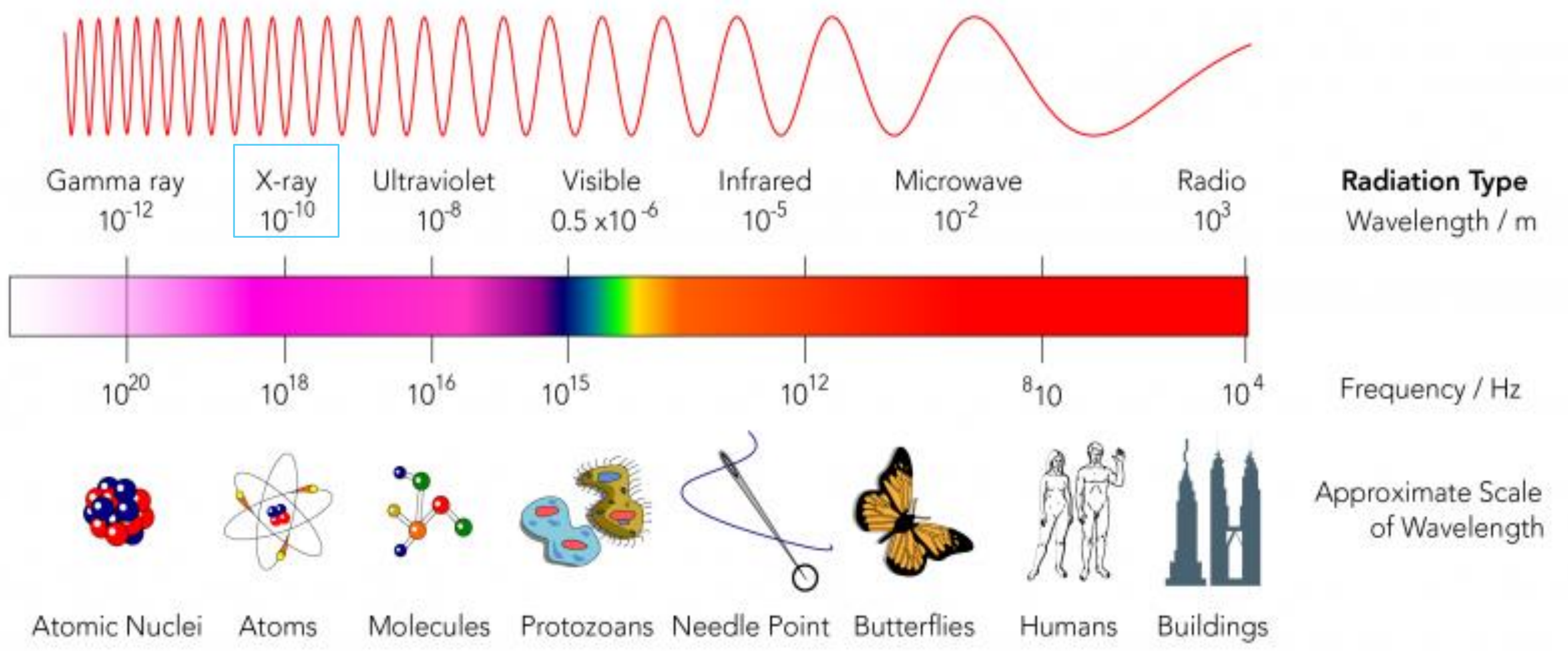
- We use **crystallography** to understand the structure of **crystalline** solids.
    - Crystallography: The study of *crystal structures*.
    - Crystal structure: A description of the ordered arrangement of atoms, ions, or molecules in a crystalline solid.

- 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.

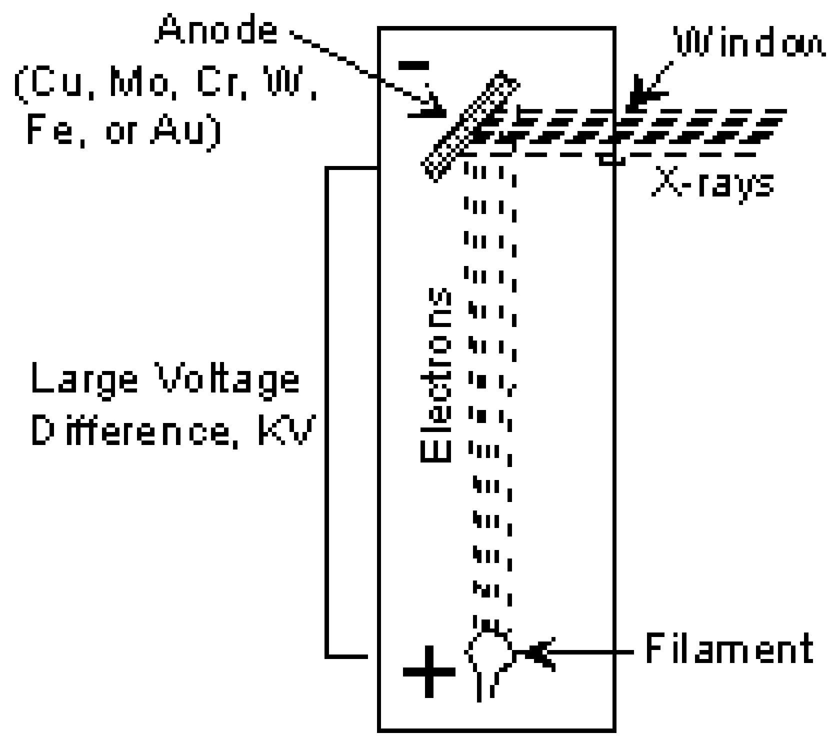
X-Ray Tube

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

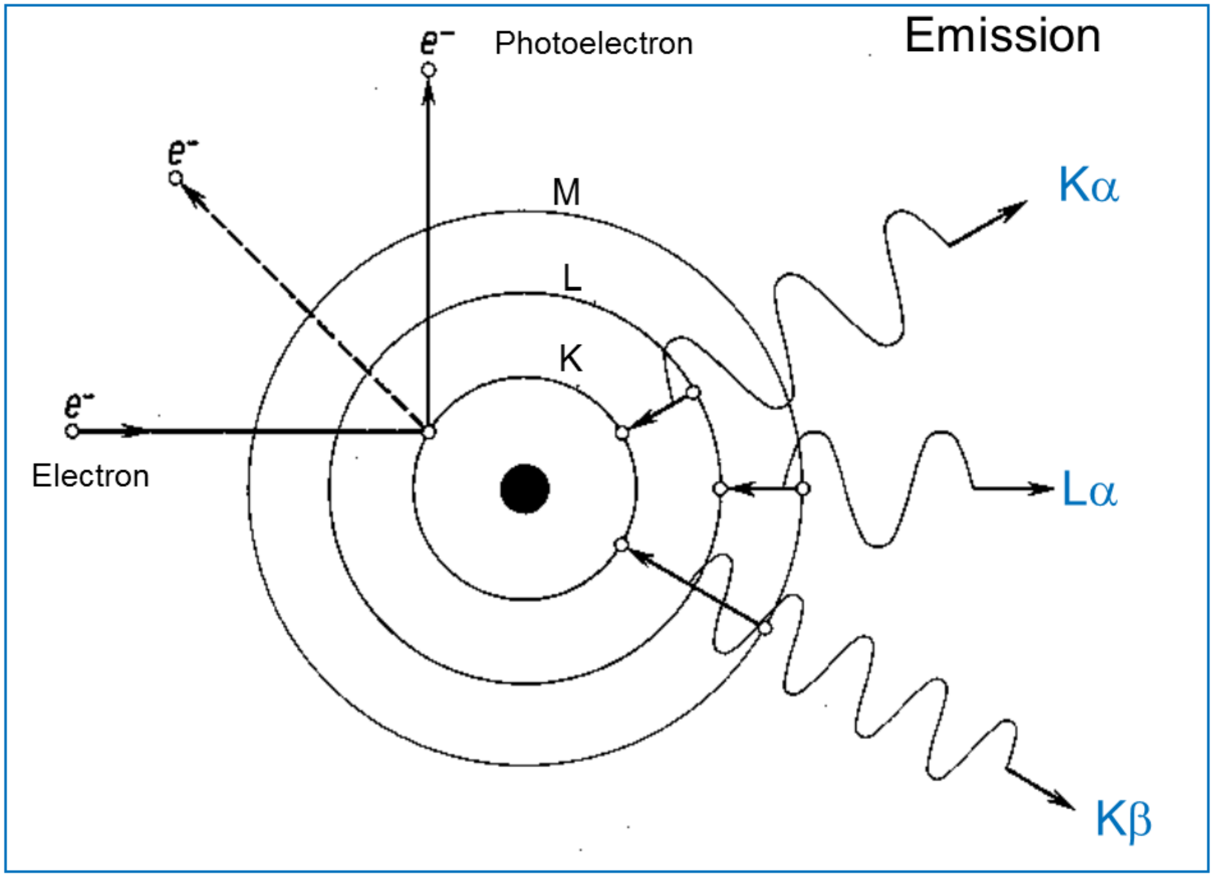
- Electrons are generated at the cathode, and directed to the anode by placing a large difference in voltage between the two sites.

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

- Target materials produce X-rays of specific wavelength.

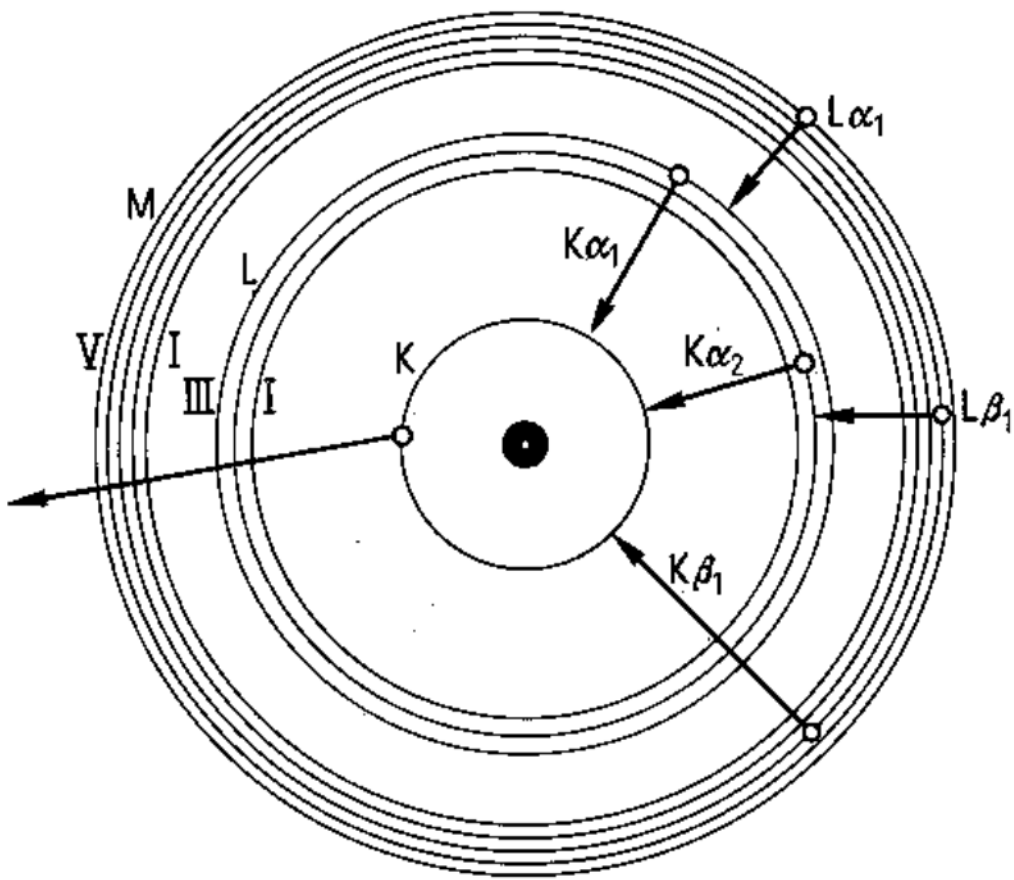


Generation of Characteristic Radiation



- Incoming electron knocks out an electron from the inner shell of an atom.
- Designation K,L,M correspond to shells with a different principal quantum number.

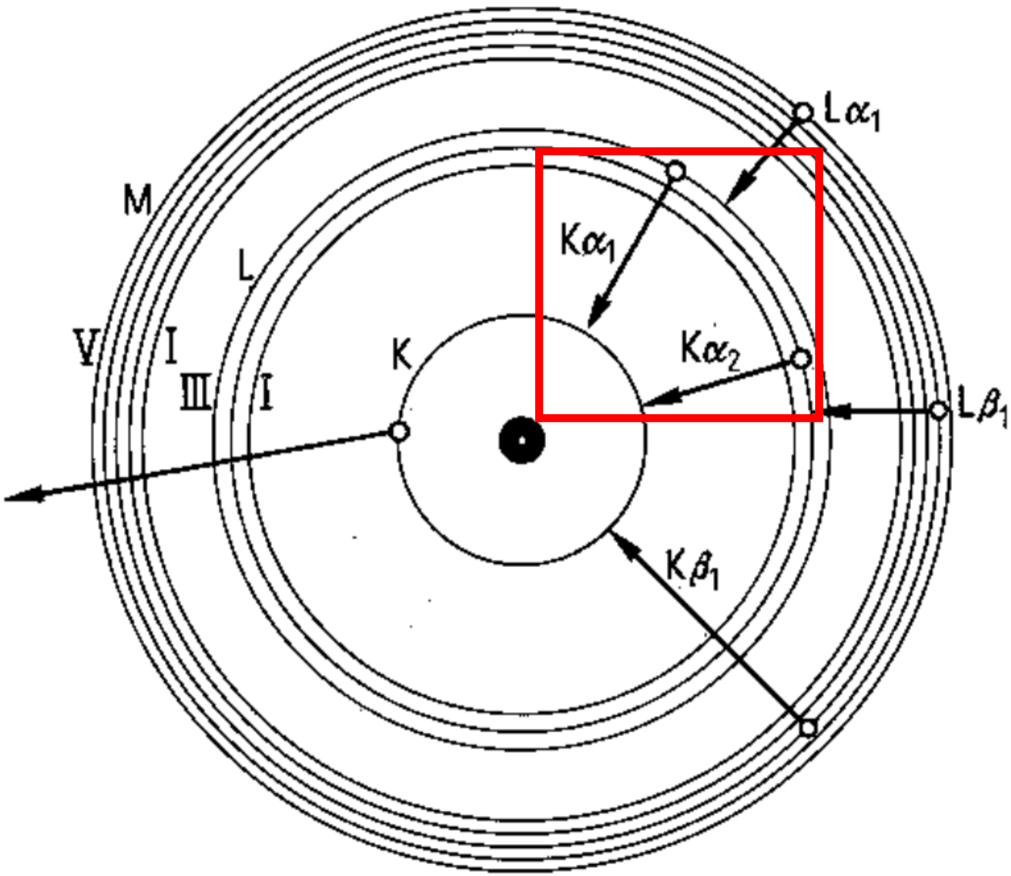
Generation of Characteristic Radiation



Bohr`s model

- Not every electron in each of these shells has the same energy. The shells must be further divided.
- K-shell vacancy can be filled by electrons from 2 orbitals in the L shell, for example.
- The electron transmission and the characteristic radiation emitted is given a further numerical subscript.

Generation of Characteristic Radiation



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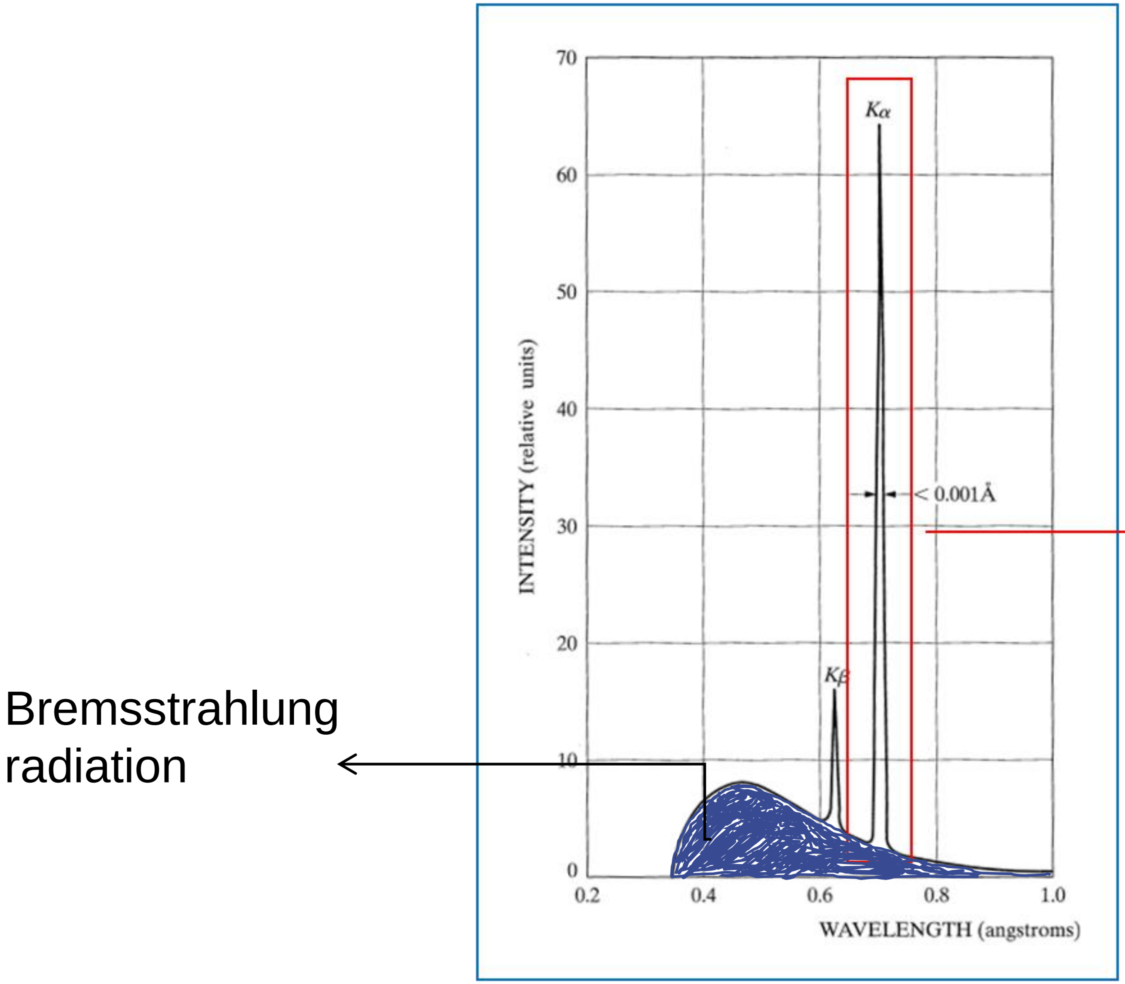
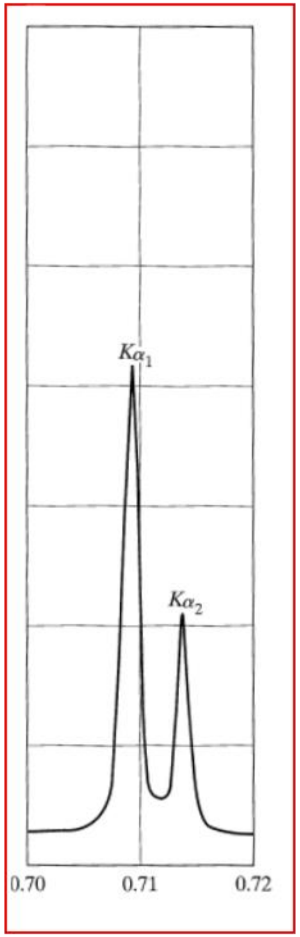
Emission Spectrum of an X-Ray Tube: Close-up of Kα





Cullity, B.D. and Stock, S.R., 2001, Elements of X-Ray Diffraction, 3rd Ed., Addison-Wesley

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.

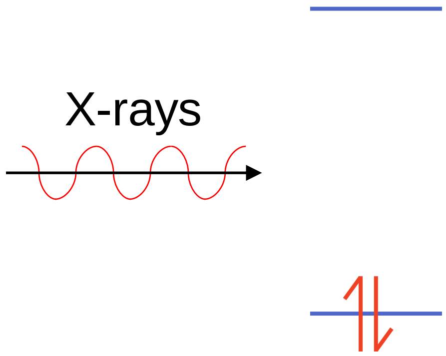
Element	Wavelength (λ) Å ($K\alpha_1$)
Ag	**0.5594**
Mo	**0.7097**
Cu	**1.5405**
Co	1.7889
Fe	1.9360
Cr	2.2896

PXRD Analysis

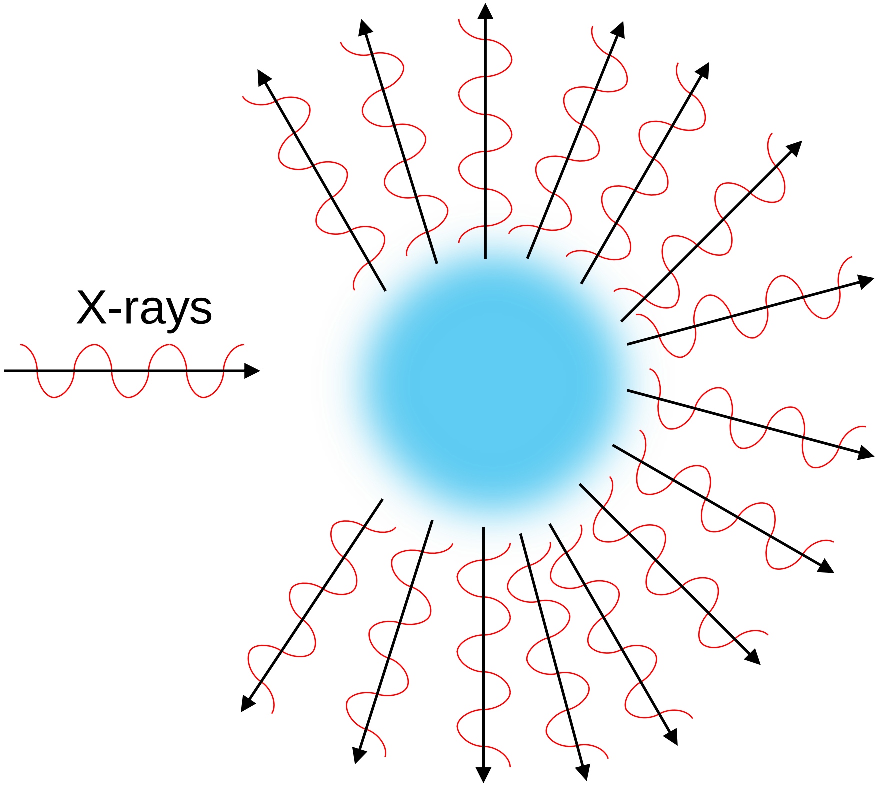
Electromagnetic Radiation

How does electromagnetic radiation interaction with matter?

Absorption

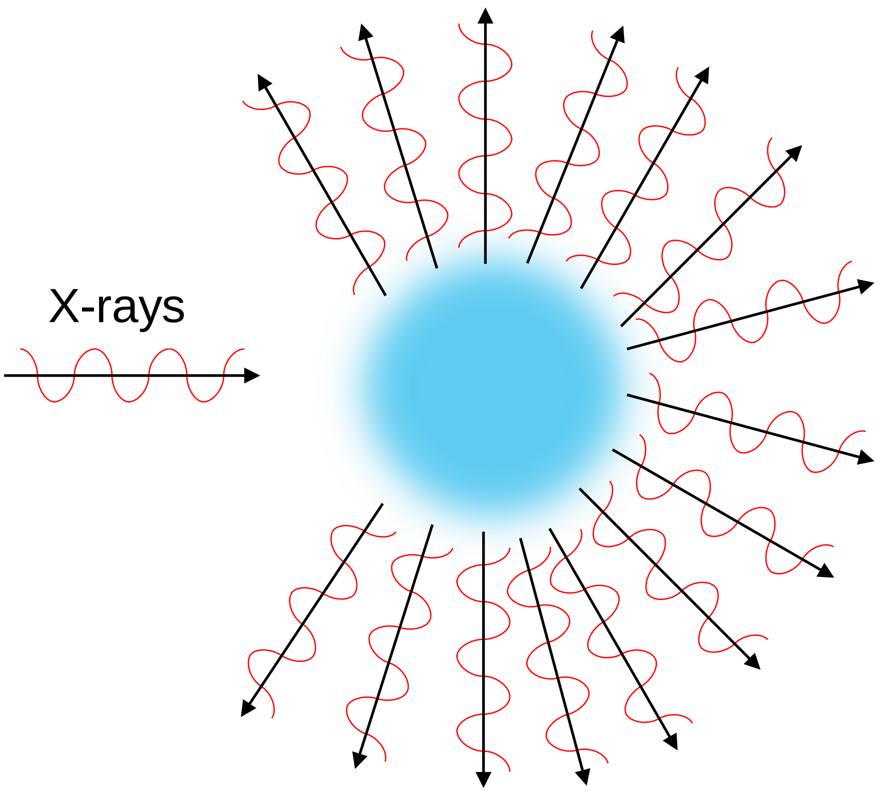


Scattering



X-Ray Scattering

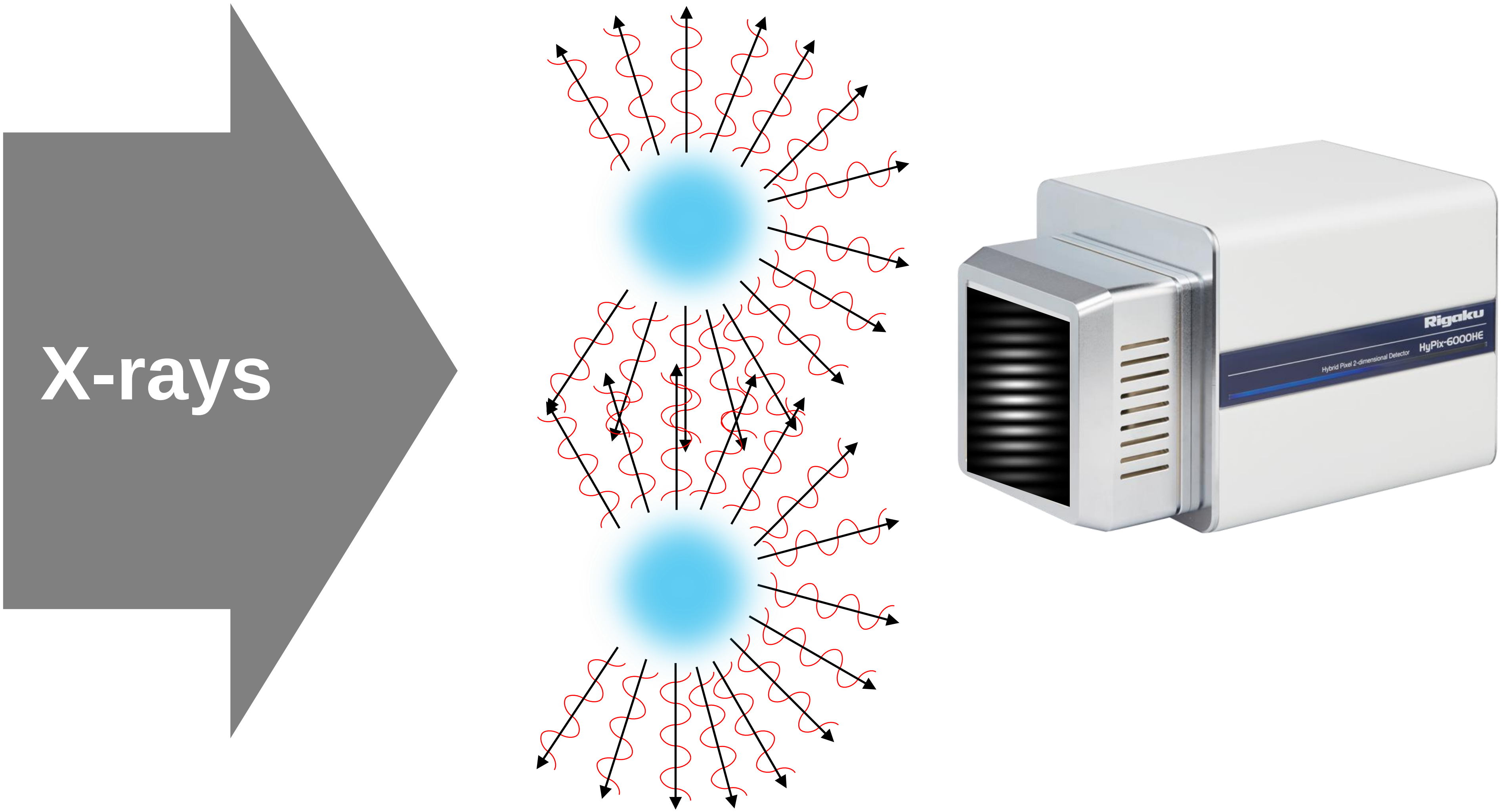
X-ray scattering is what we care about!



- 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

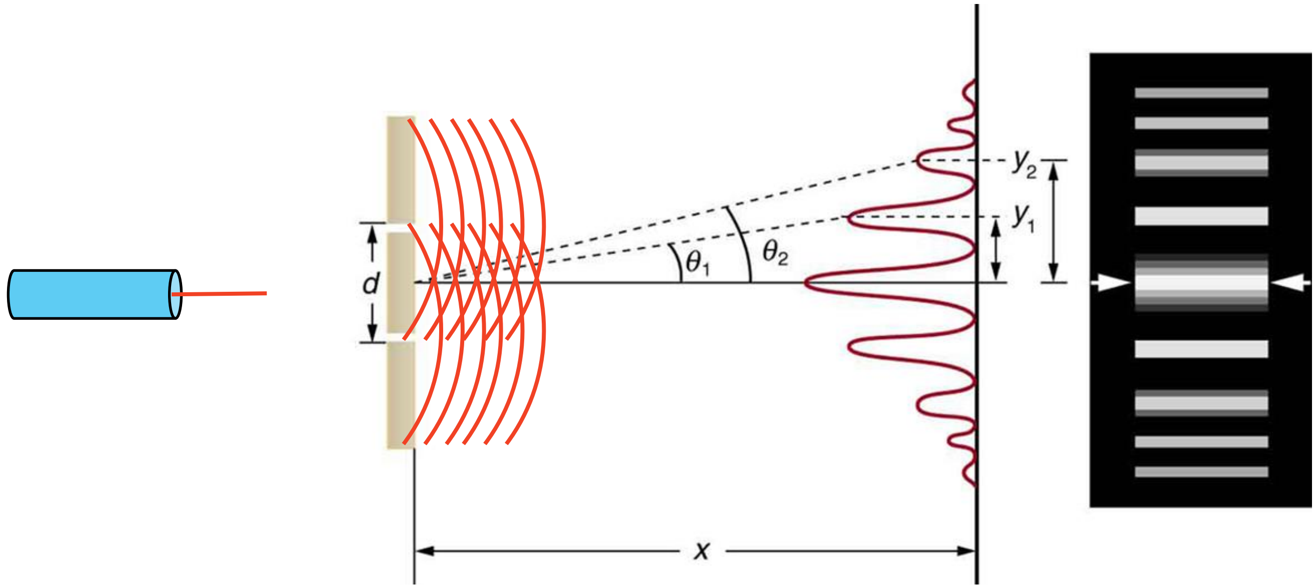
What happens when we have more than one atom?



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.

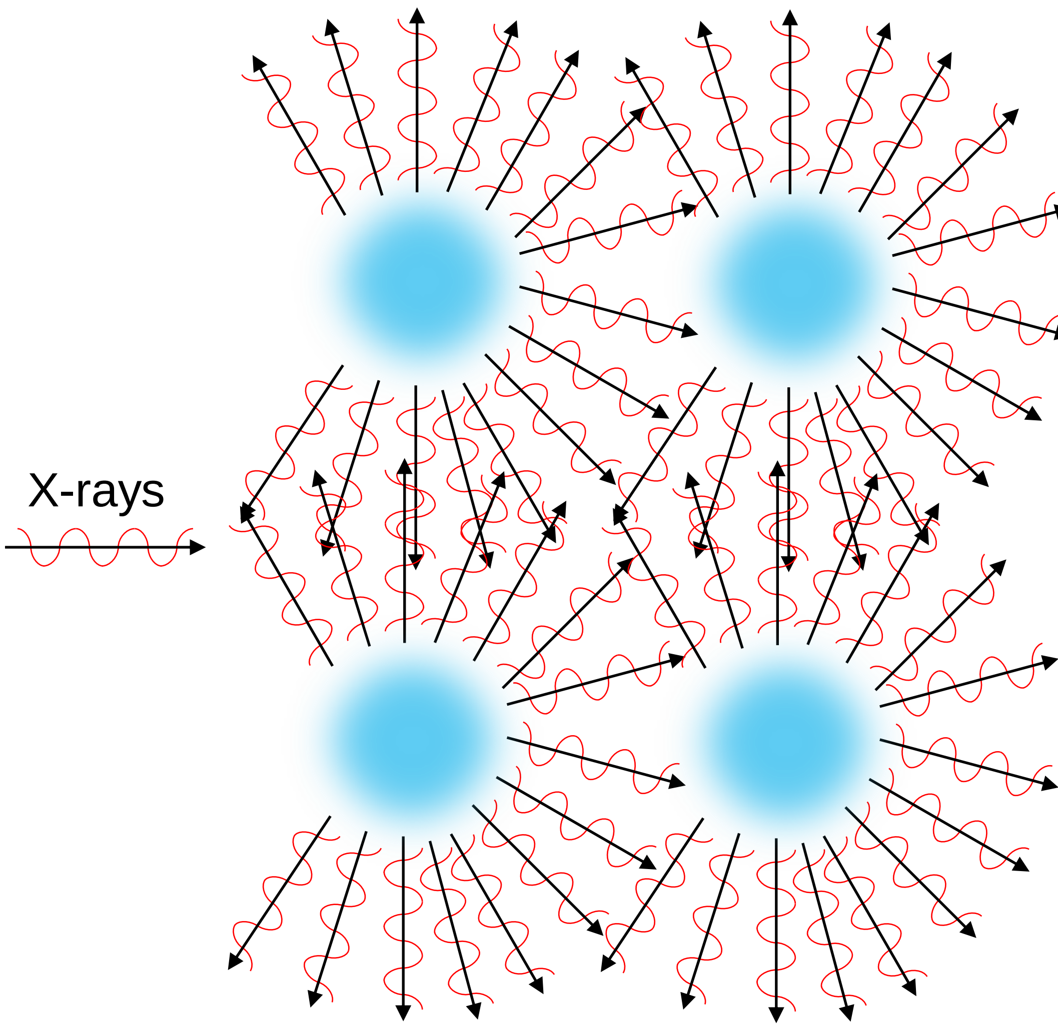
X-Ray Diffraction

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.

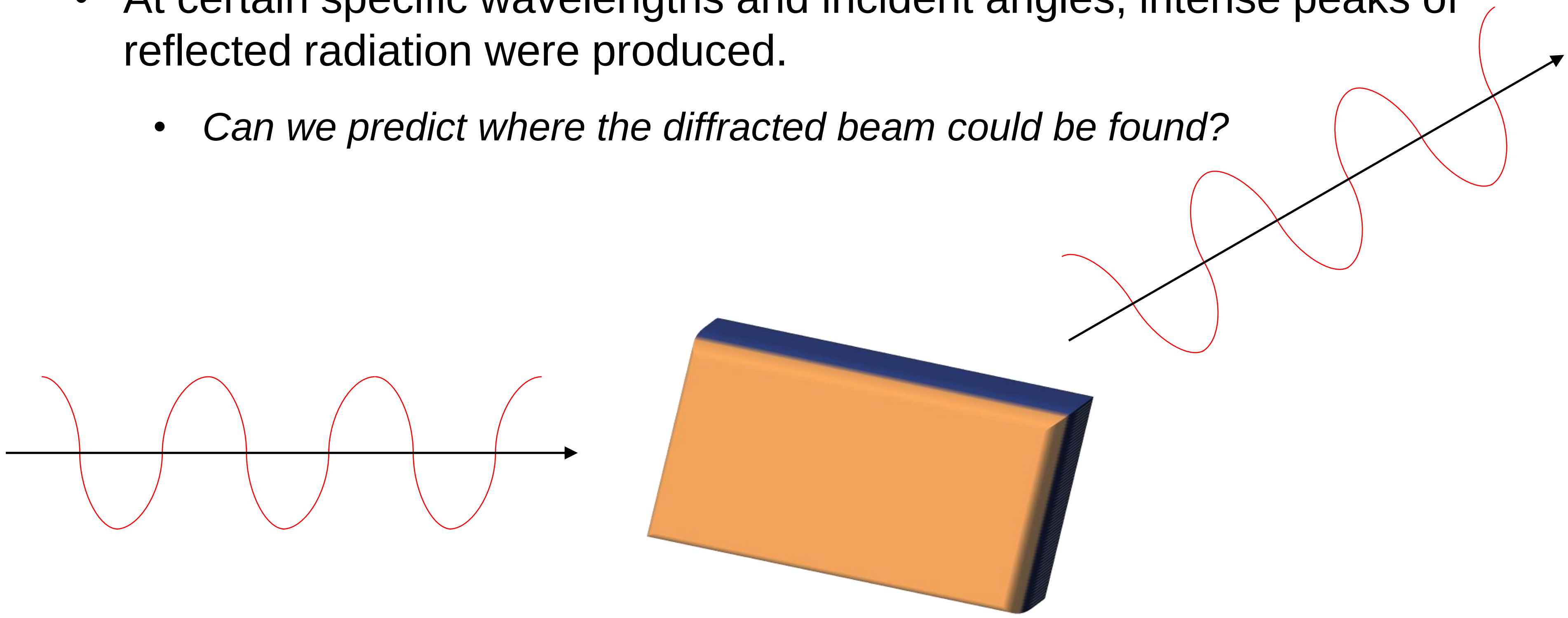
- The diffraction pattern consists of bright spots, or diffraction peaks, that correspond to a specific set of crystal planes.



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

Diffraction by a Crystal…Recap…

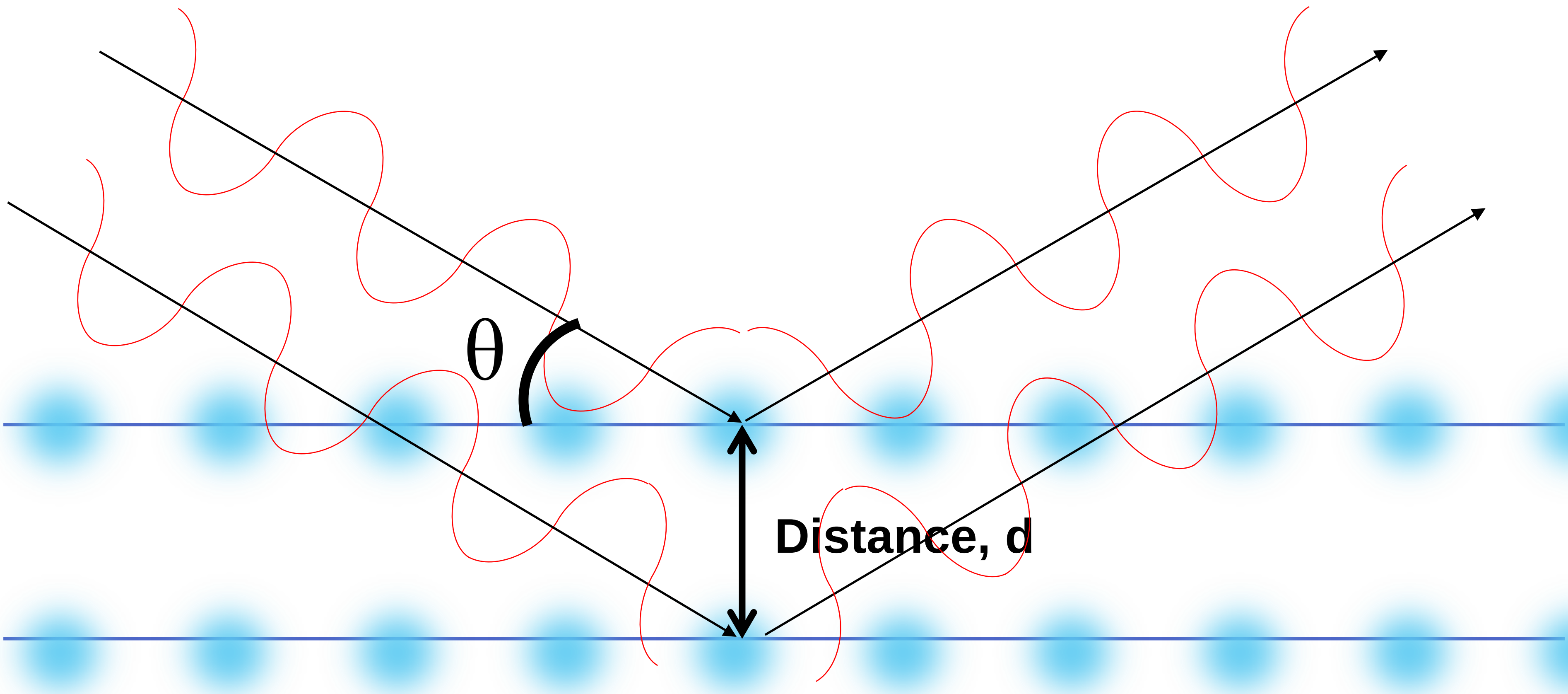
- X-ray diffraction is a technique that involves the scattering of X-rays by the atoms in a crystalline material
- The ordered array of atoms in the crystal acts like a new point source of X-rays, which constructively and destructively interfere to result in a pattern.
- At certain specific wavelengths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



Bragg's Law

Model

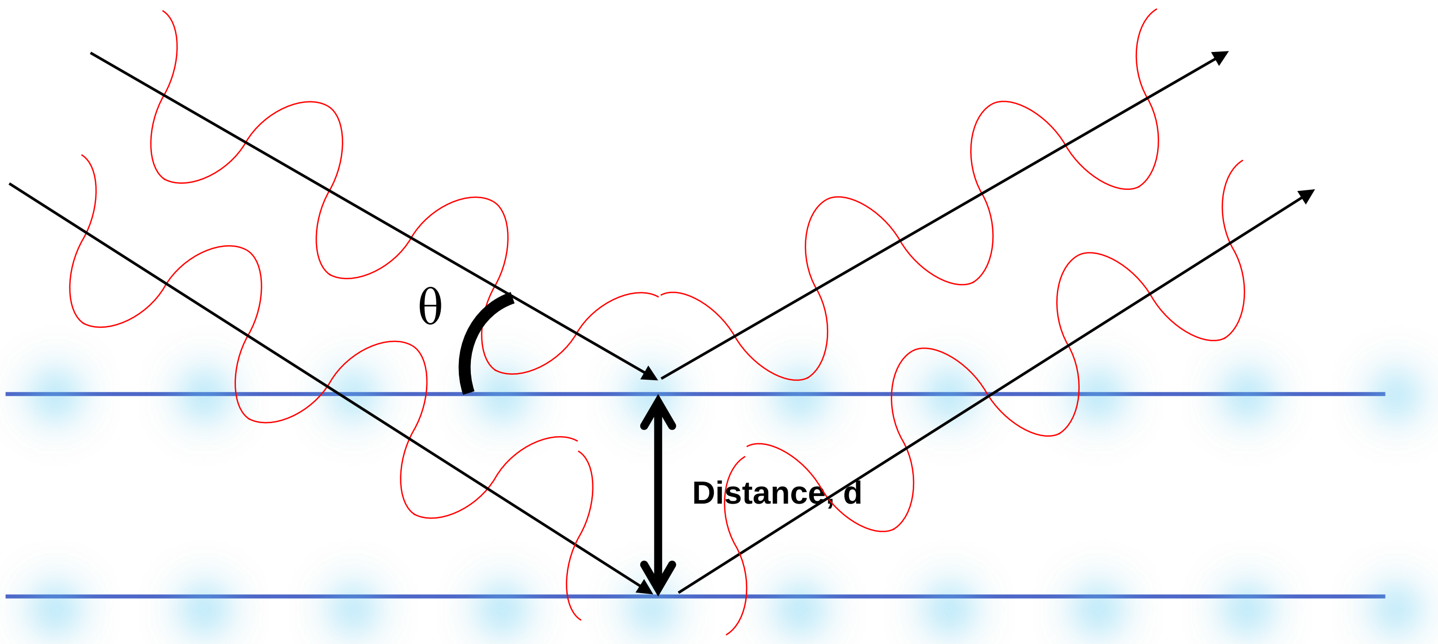
- Crystal is a set of discrete parallel planes.



Bragg's Law

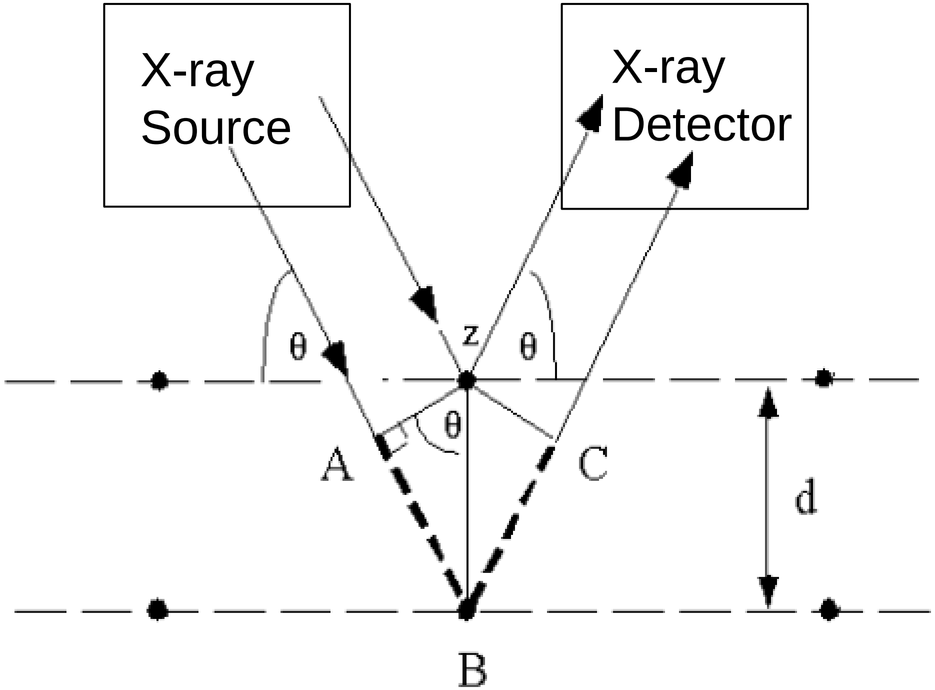
Conditions for Constructive Interference

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



Derivation of Bragg's Law

Derivation



$n\lambda = AB + BC$

$n\lambda = 2\ AB$

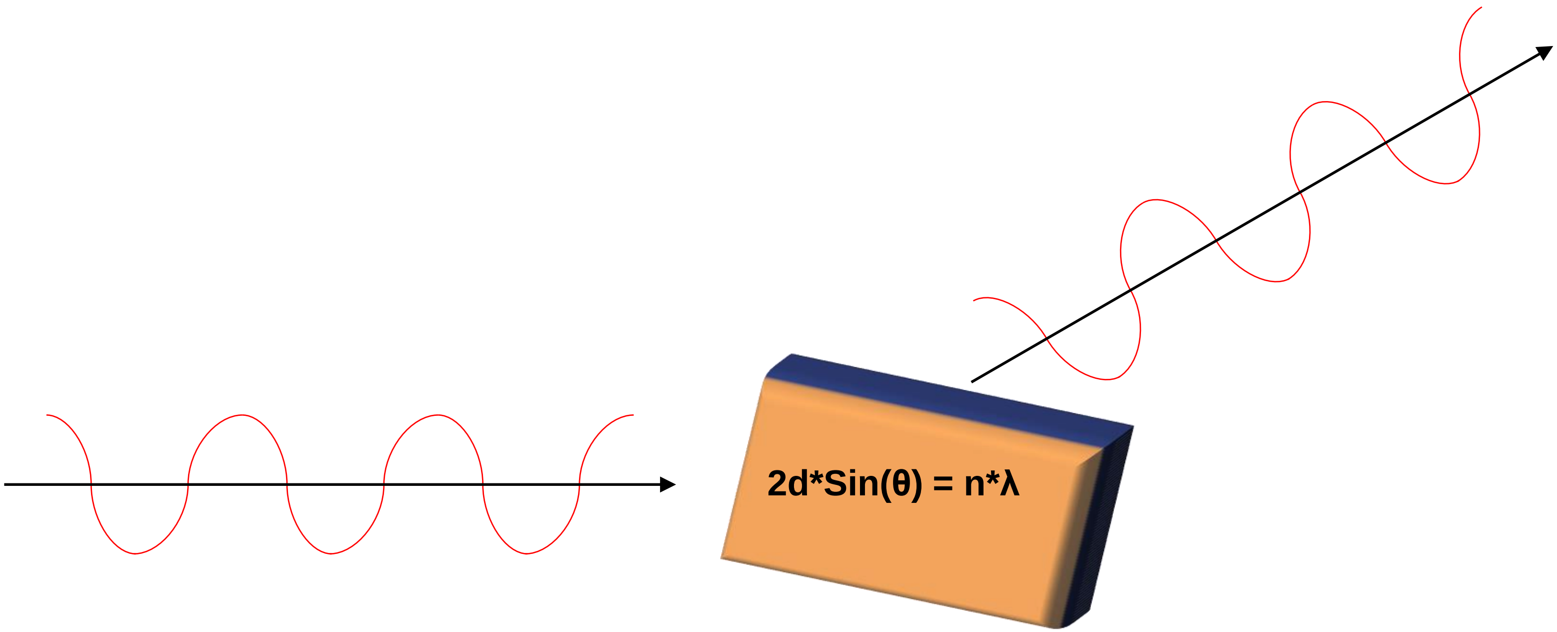
$AB = d \sin \theta$

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

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, 2AB, travelled by longer path is equal to nλ do we have constructive interference (diffraction).

Planes and Distances



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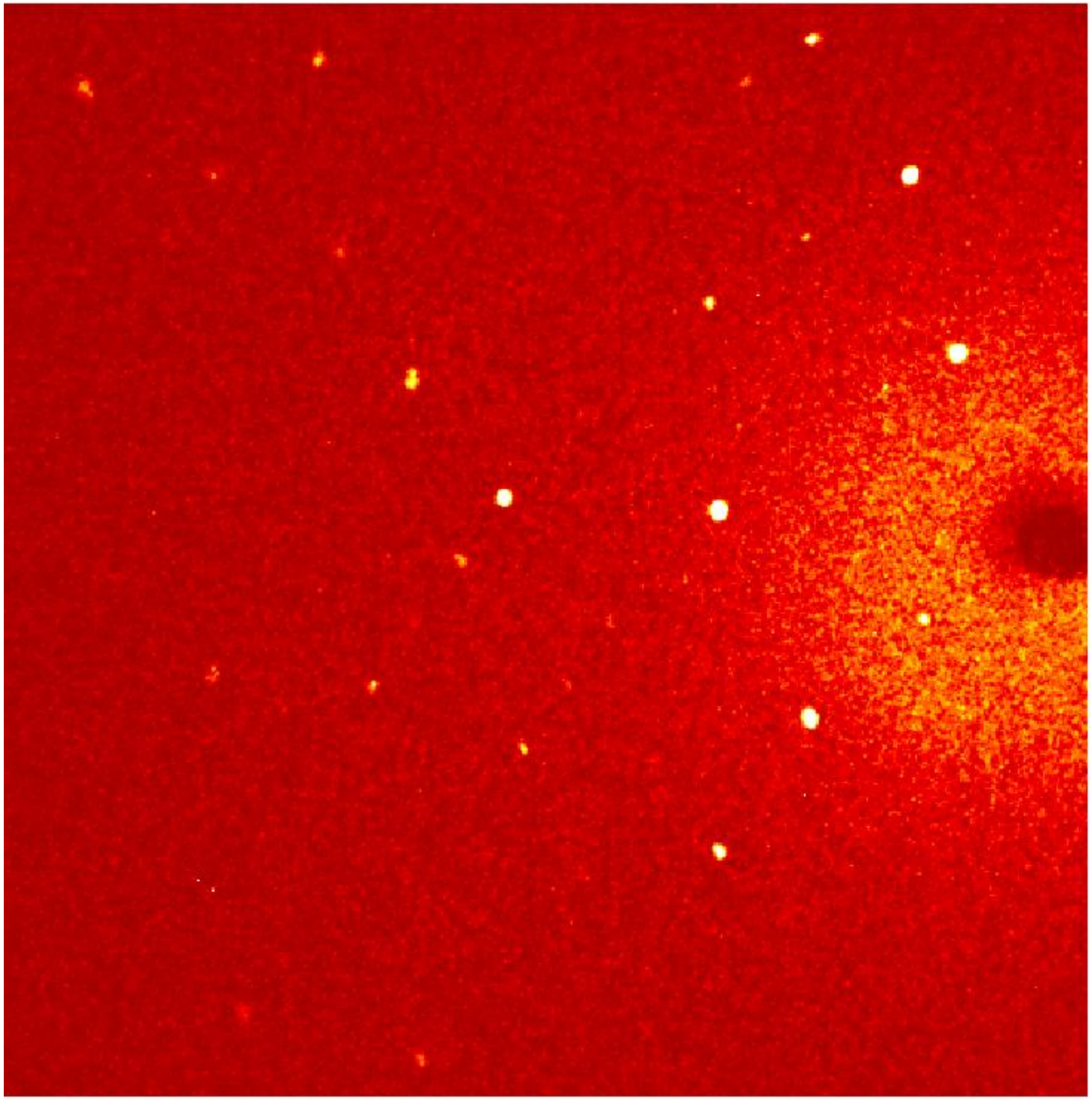
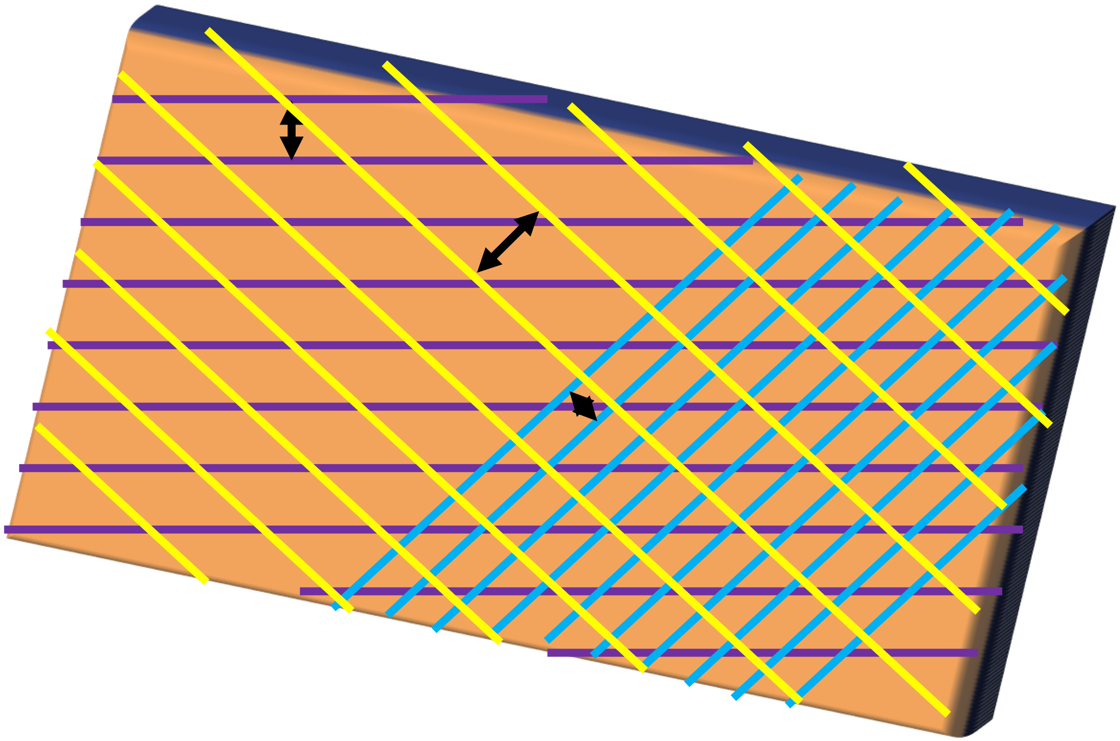


Each bright spot, or **reflection**, represents a plane that has satisfied Bragg’s condition for diffraction.

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.

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

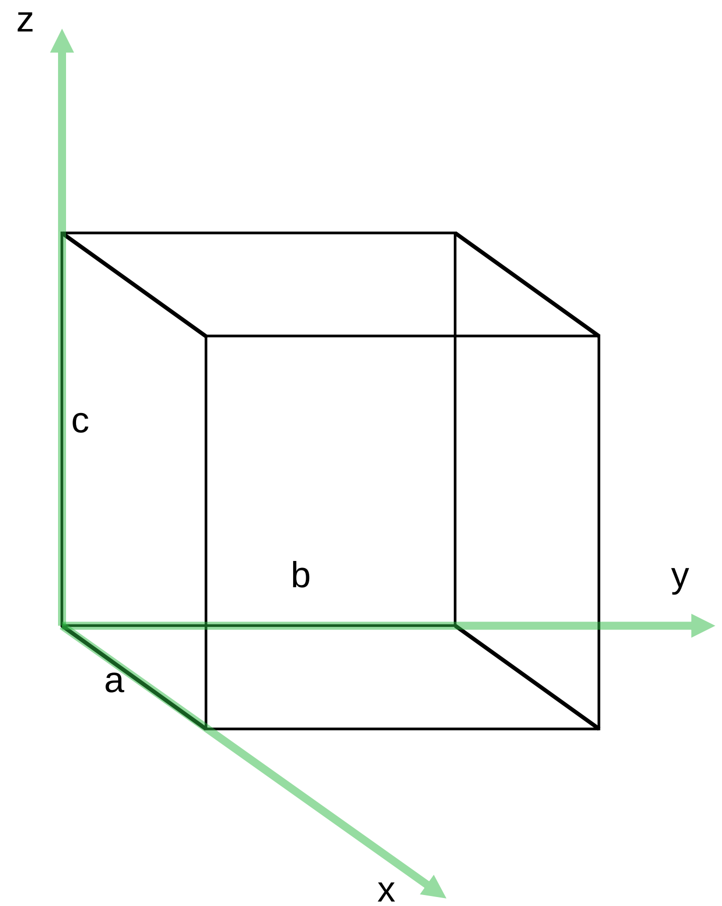
Planes and Distances

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

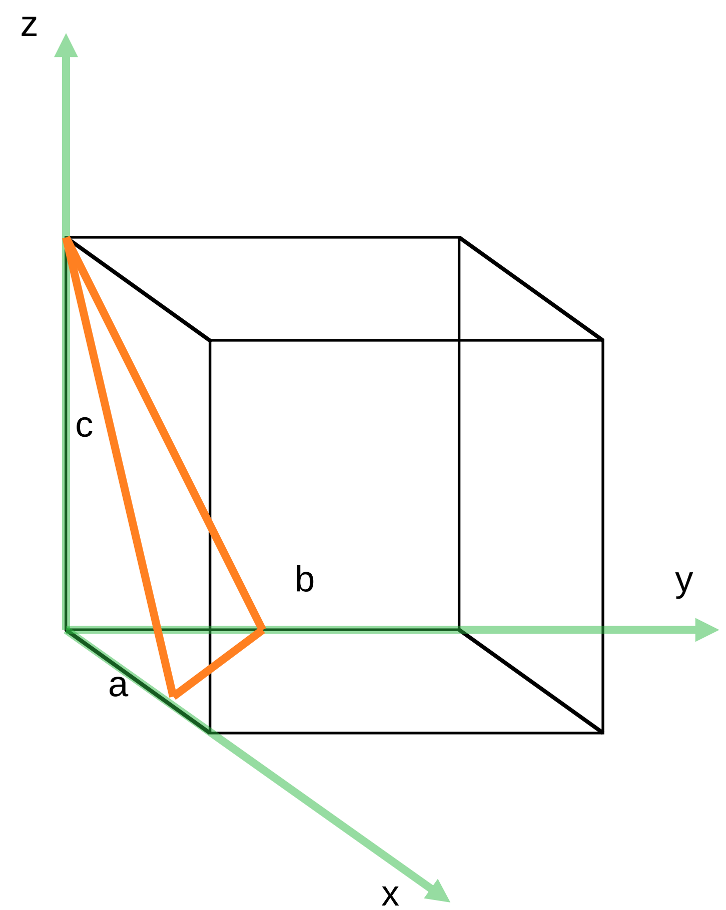
Miller Planes

- 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

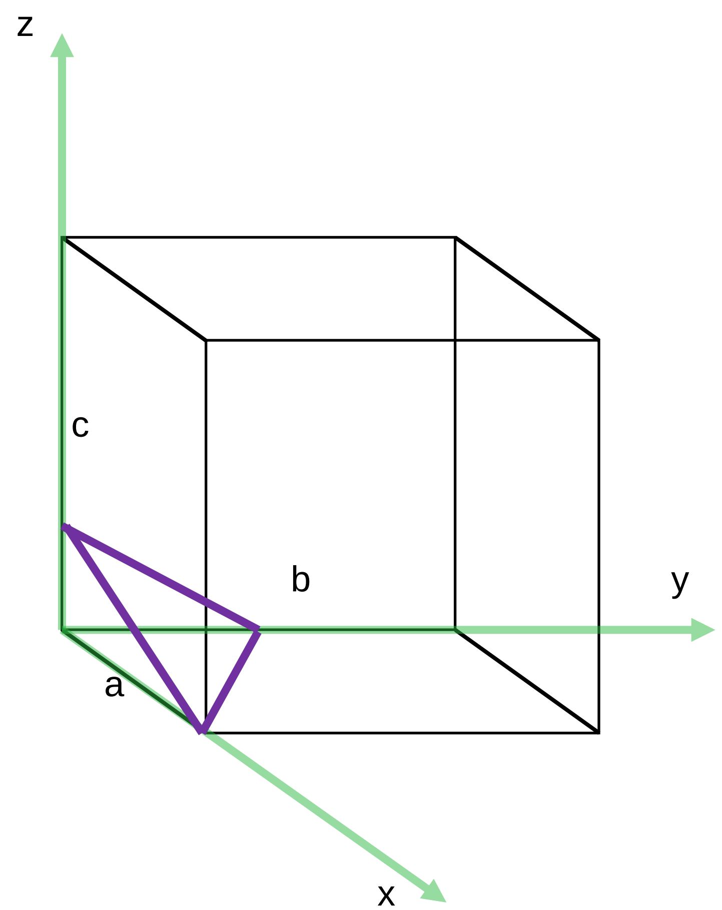
Miller Planes

- 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



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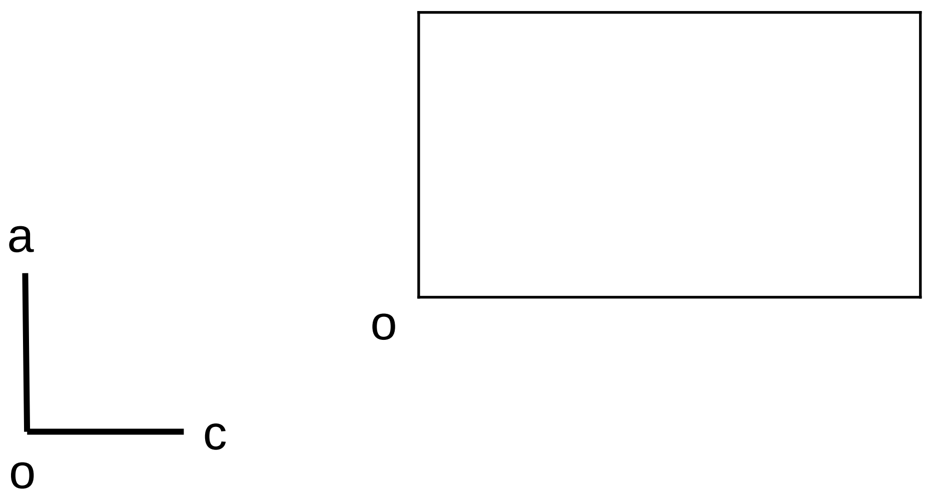
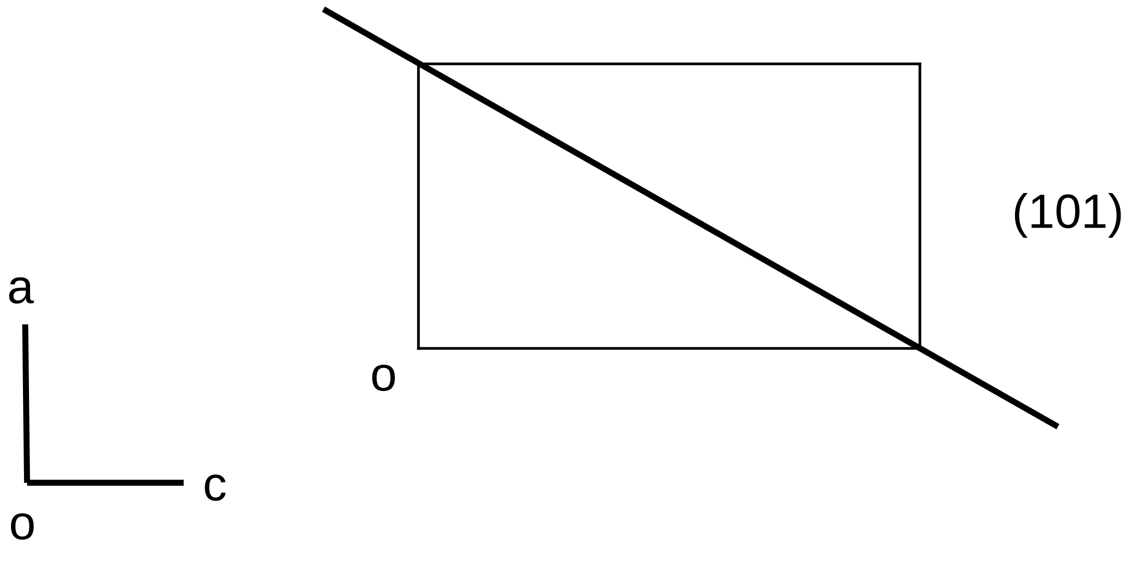
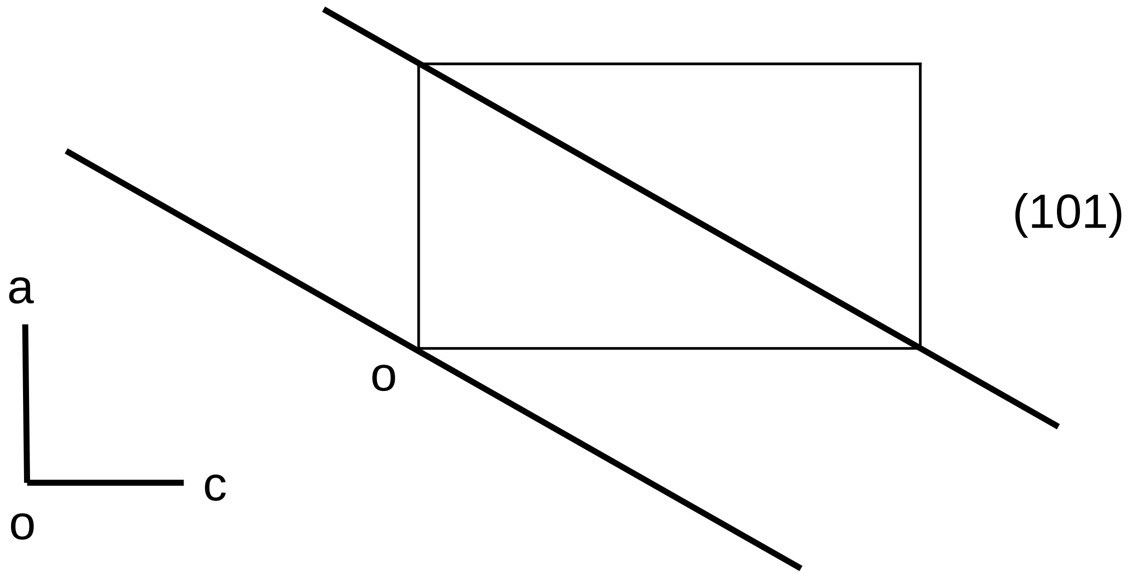

a
o
c
o


(101)
a
o
c
o


(101)
a
o
c
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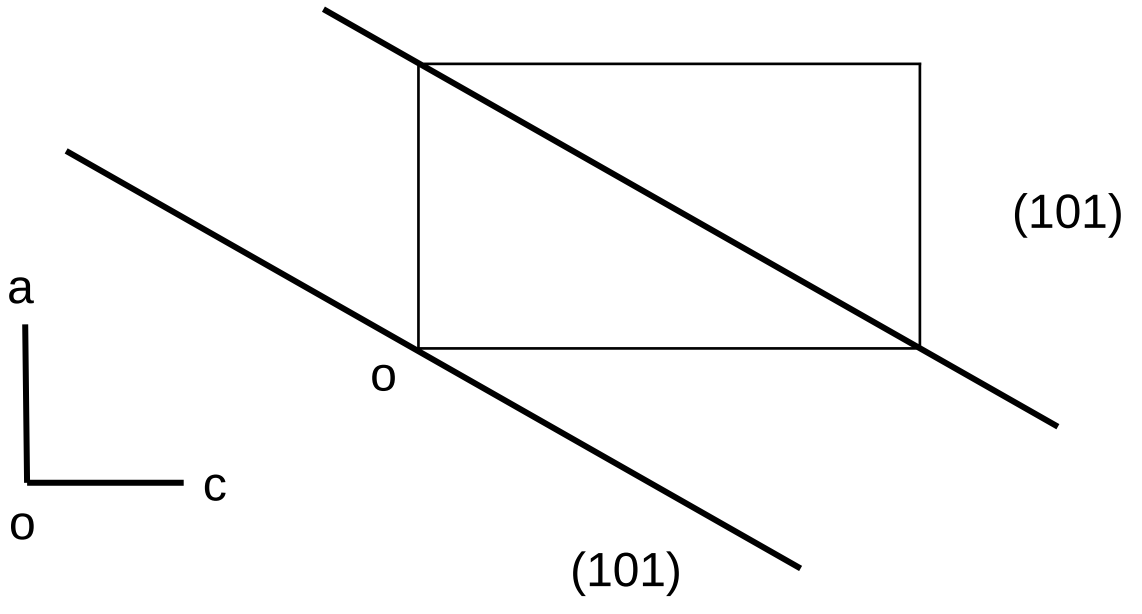
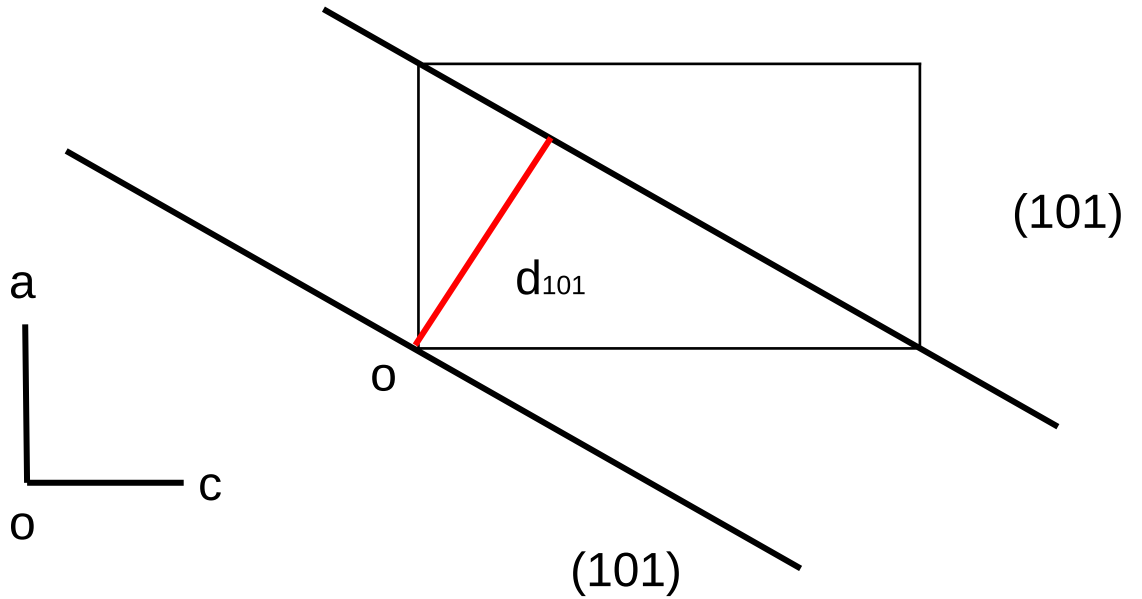


(101)
a
o
c
o
(101)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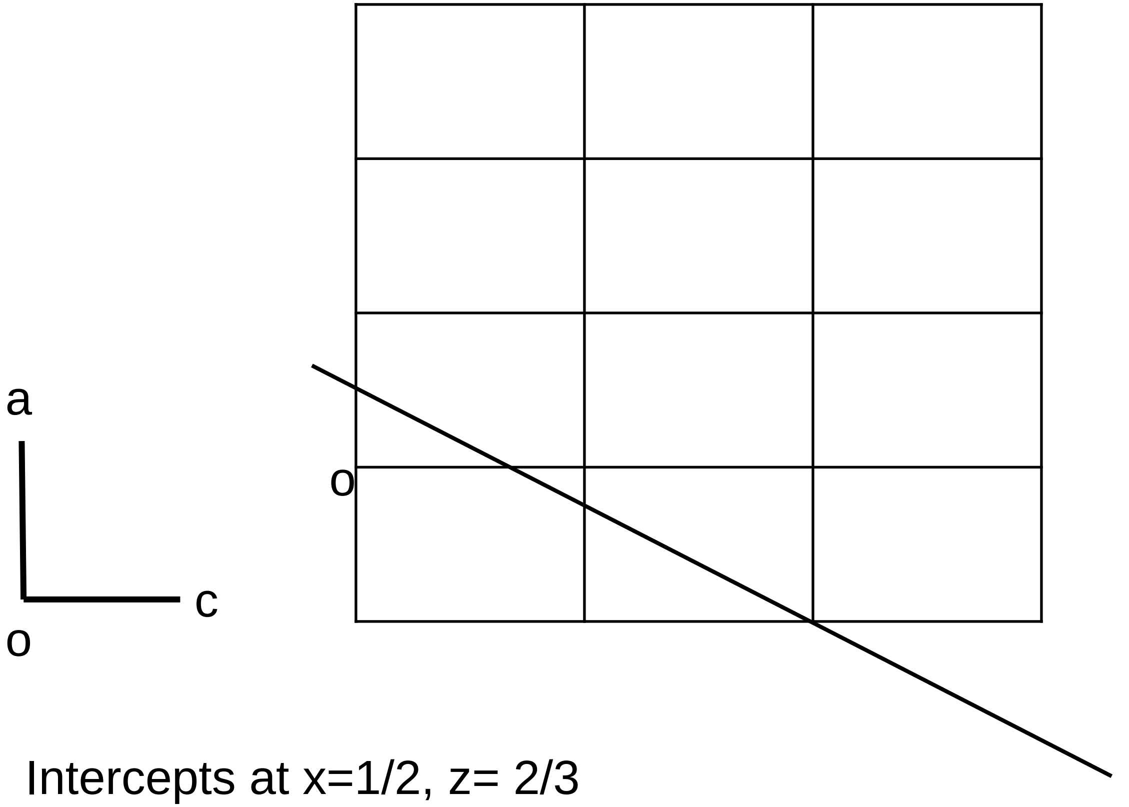
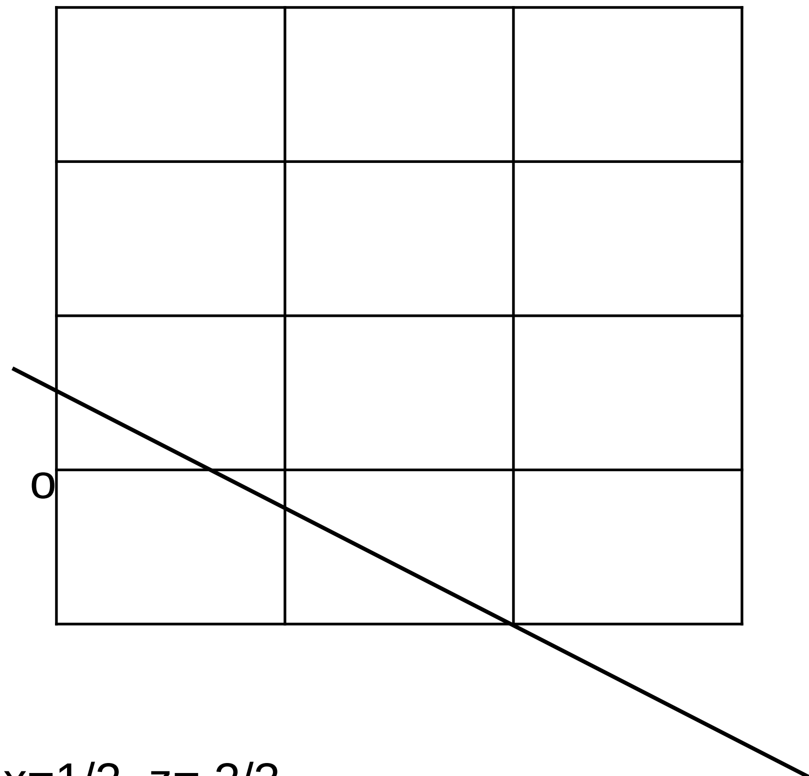
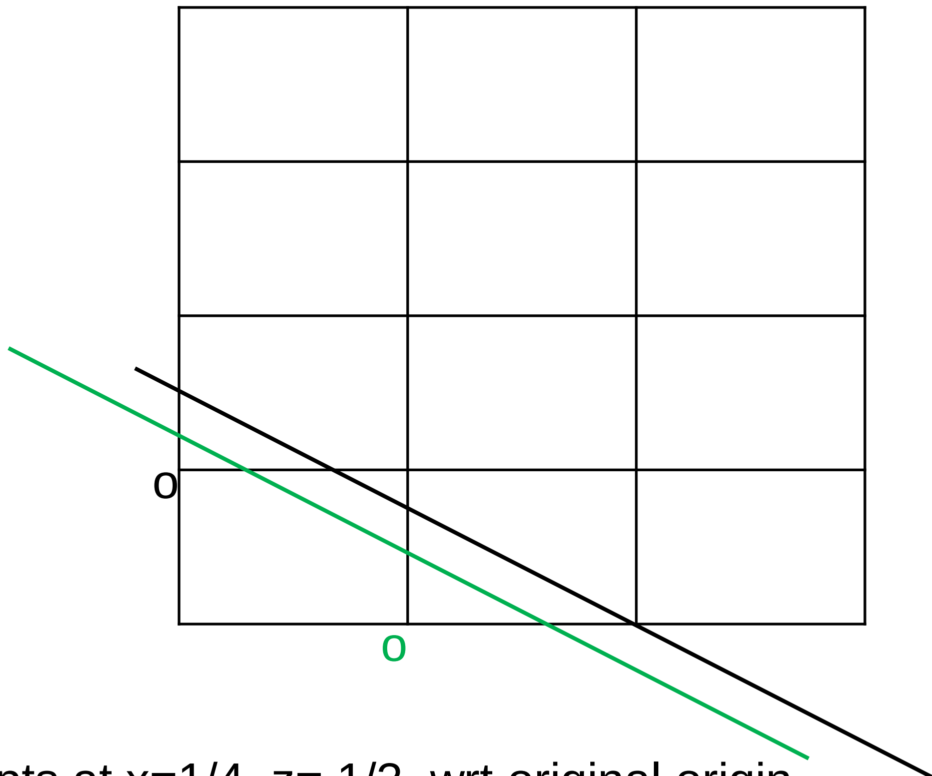


Intercepts at x=1/2, z= 2/3



Intercepts at x=1/2, z= 2/3

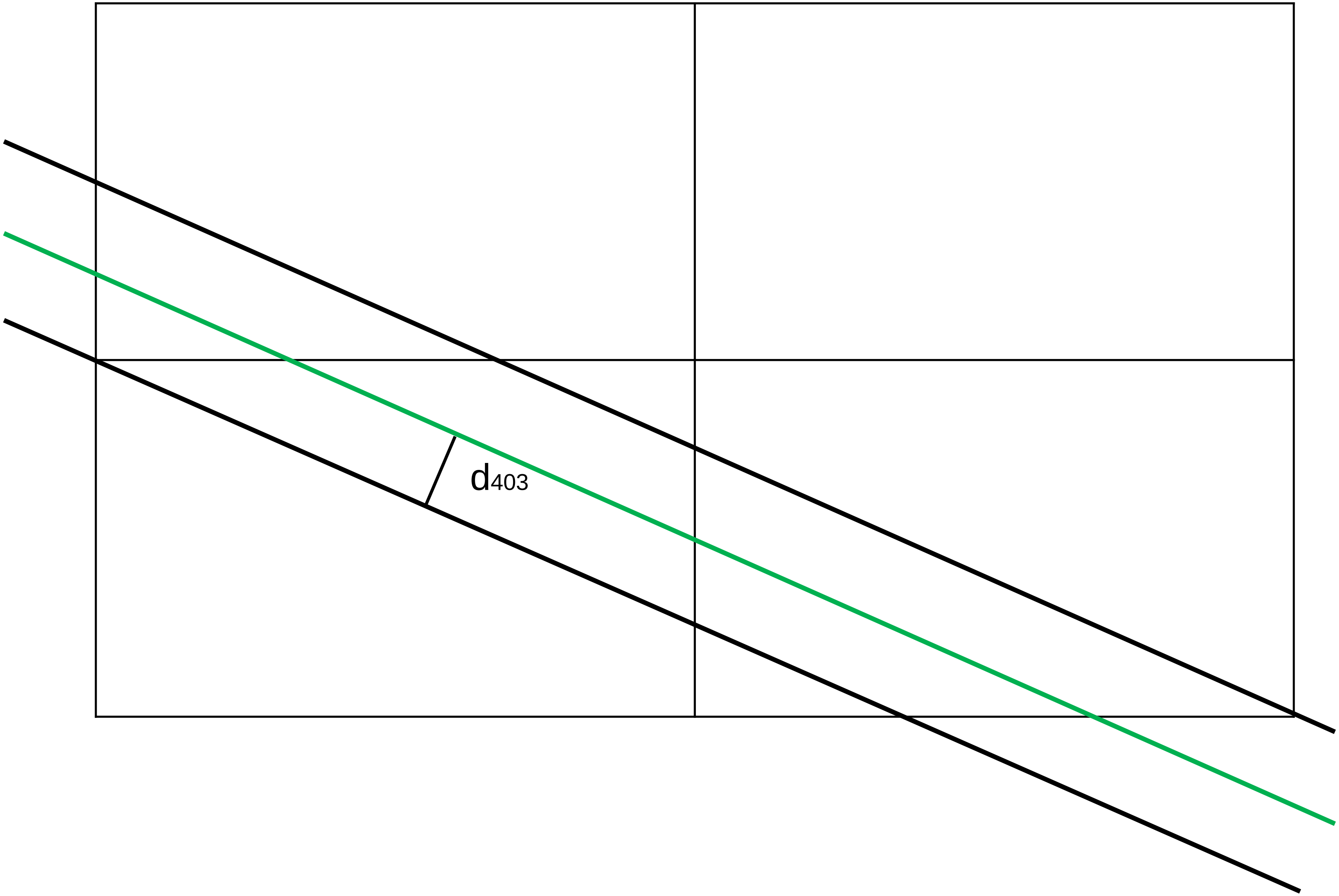
(2 0 3/2) Miller index, however indices should be integers!



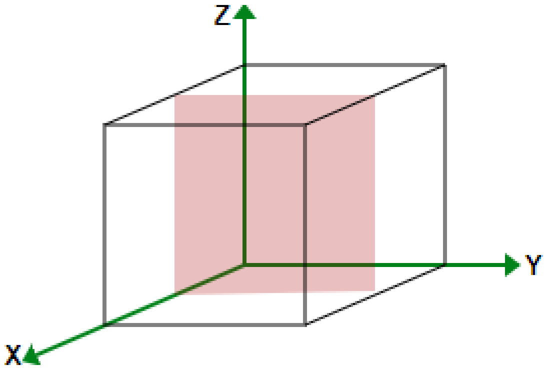
Intercepts at x=1/4, z= 1/3, wrt original origin

Miller index is now (4 0 3)

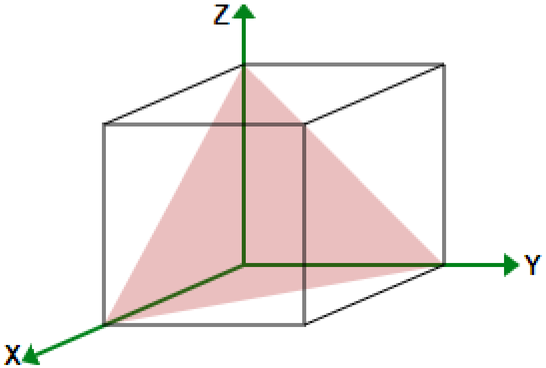
Plane in green is a (403) plane from an adjacent unit cell


d403

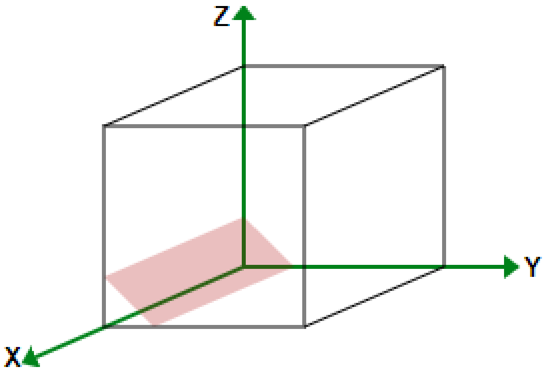
Practice



(200)



(111)

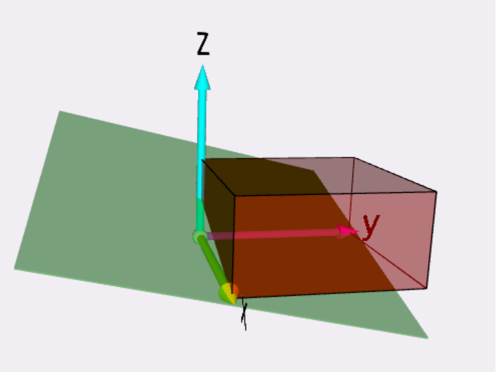


(044)

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 $(00\bar{1})$.

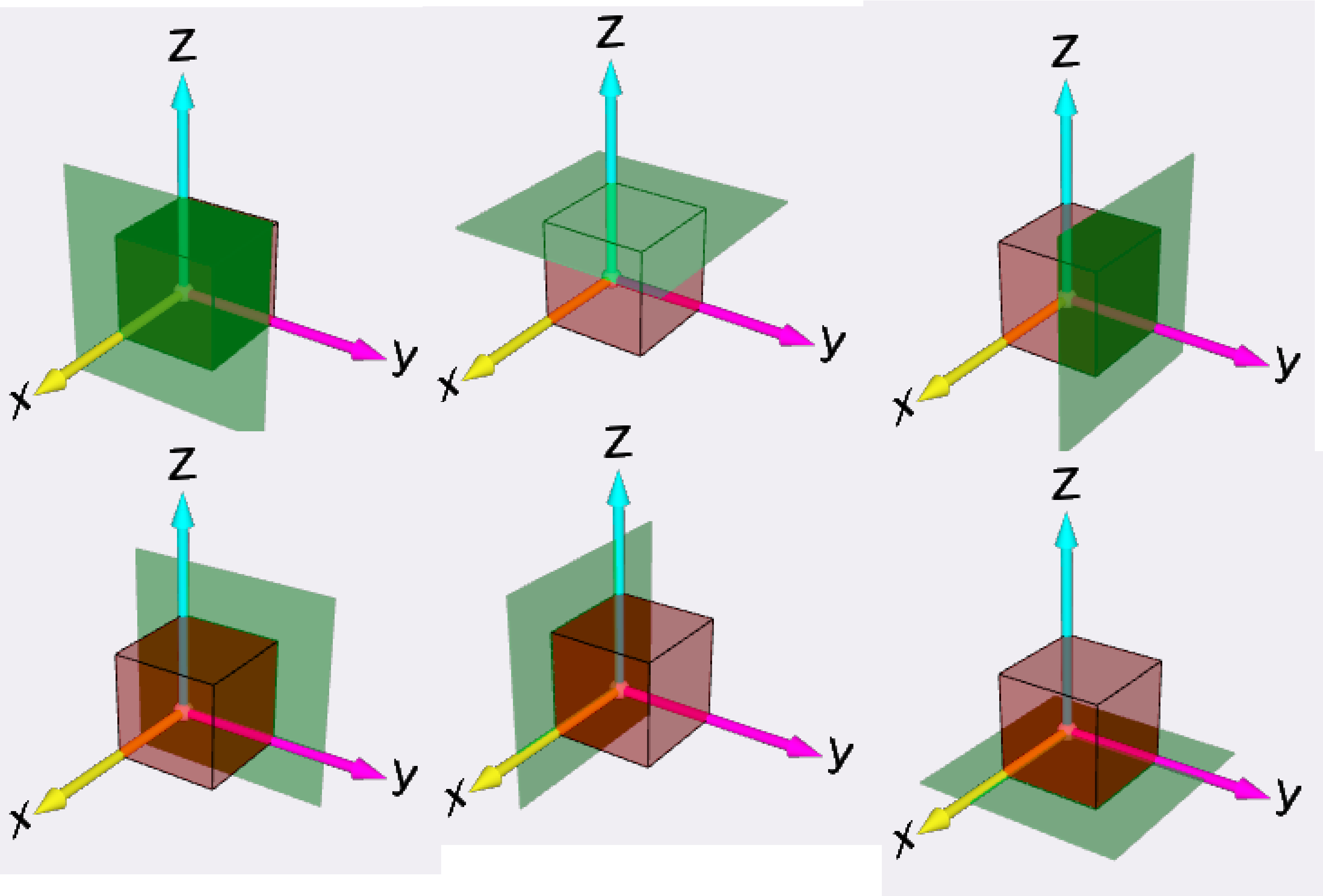
Planes and Distances

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=90º



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…

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

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?