EE113FZ
Solid State Electronics
Lecture 9: X-Ray Diffraction

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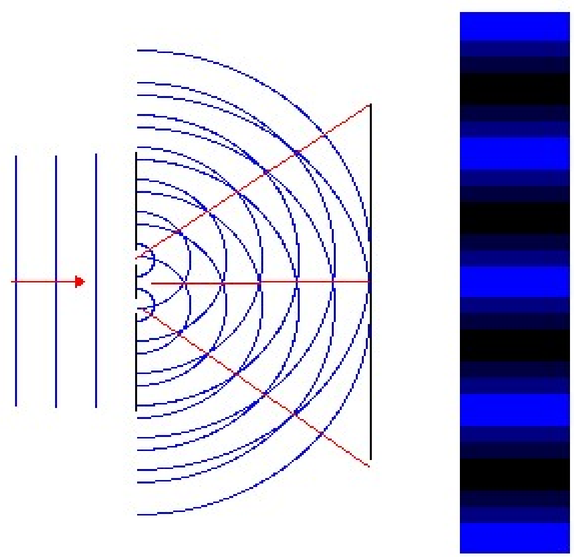
What is to be Discussed Today?

- How do we ‘see’ the various types of unit cells?
- Tell you what x-ray diffraction is.
- Interference -> diffraction -> x-ray diffraction.
- A nice little equation (Bragg’s law).
- Applications of X-ray diffraction in crystallography.
- Some sample data.

Interference

- If light is incident onto an obstacle which contains two very small slits a distance *d* apart, then the wavelets emanating from each slit will interfere behind the obstacle.



Interference

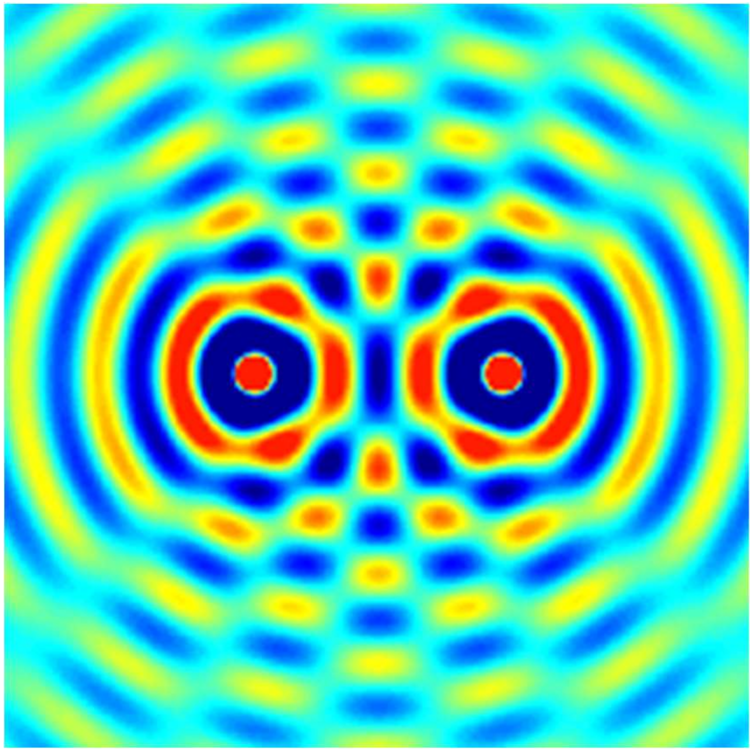
- Interference describes the phenomenon in which two waves superpose to form a resultant wave of greater, lower, or the same amplitude;
- The interaction of waves that are correlated or coherent with each other gives rise to areas of CONSTRUCTIVE and DESTRUCTIVE interaction;
- Constructive interaction gives areas of high amplitudes;
- Destructive interaction gives areas of low amplitudes;
- Interference effects can be observed with all types of waves, e.g., light, radio, acoustic, surface water waves, gravitational waves, and matter waves.

Principle of Superposition

- The principle of superposition (of waves) states that when two propagating waves of the same type are incident on the same point, the resultant amplitude at that point is equal to the vector sum of the amplitudes of the individual waves;
- If a crest (maximum) of a wave meets the crest of another wave at the same point, this is constructive interference. It occurs when the phase difference between the waves is an even multiple of π (180°);
- If a crest of a wave meets a trough (minimum) of another wave, this is destructive interference. It occurs when the phase difference between the waves is an odd multiple of π (180°).

Interference

Interference of waves from two point sources



https://en.wikipedia.org/wiki/Wave_interference

Interference & Standing Waves

- A good example of interference are standing waves in a glass tube:

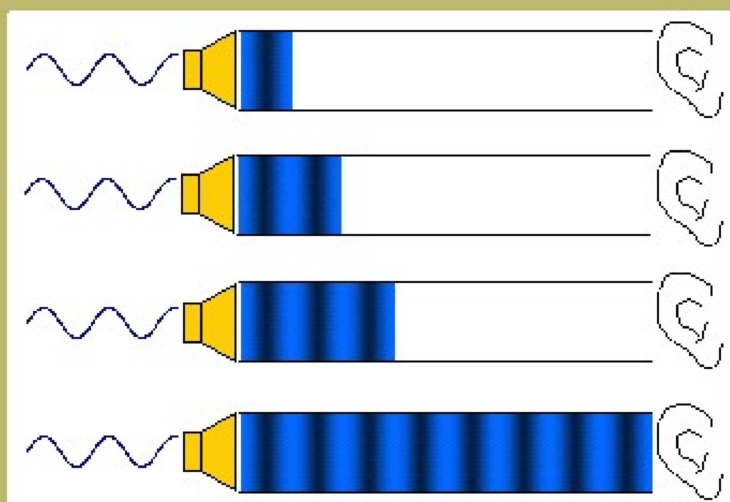


Figure 1. An alternating signal into a speaker creates sound waves which propagate away from the speaker. Here the sound waves pumped into a resonance tube are confined to move in one direction. The dark bands represent areas of high pressure, where the light bands represent areas of relatively low pressure.

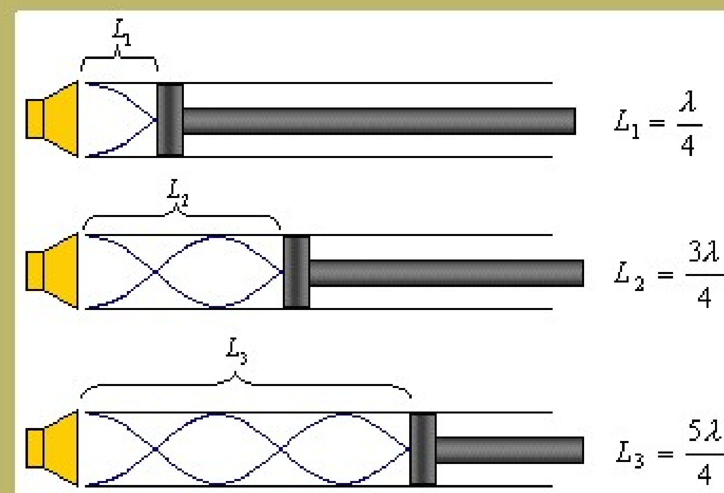


Figure 2. By moving the piston, the resonant modes may be detected. Note the relationship between the tube length and the sound's wavelength is given by

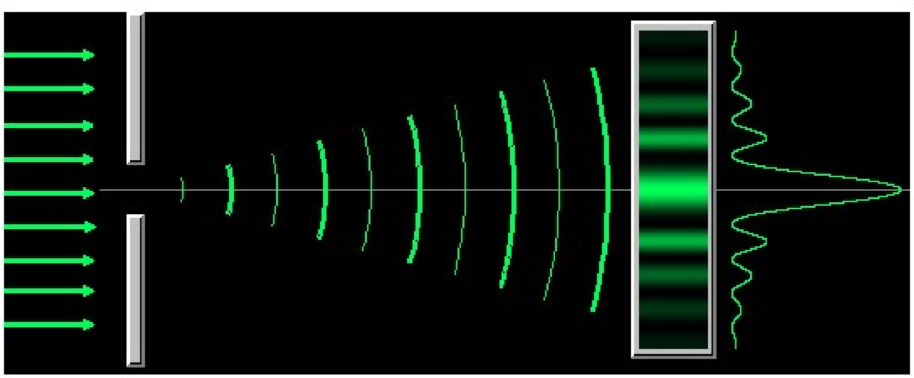
$$L = \frac{n\lambda}{4}, \quad n = 1, 3, 5, 7, \ldots$$

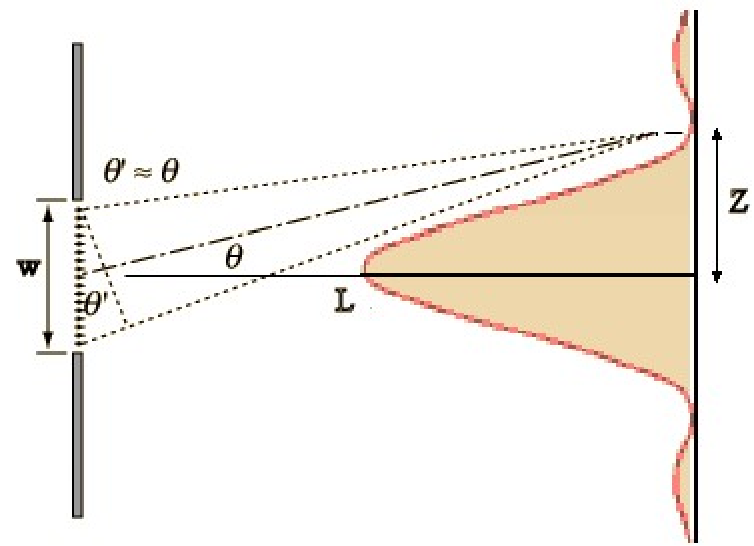
Interference

- The frequency of the sound wave is controlled by the signal fed into the loudspeaker;
- When the diaphragm of the loudspeaker moves in- and outwards, it creates a local volume of air with low/high pressures. This variation of local air pressure propagates to the right, and can be picked up by our ears;
- We can use a moving piston to close off the tube. Sound waves travelling to the right are reflected on the piston. The forward travelling wave and the reflected wave interfere with each other;
- When the effective tube length is $L = \frac{n\lambda}{4}$ in which n is an odd number, the standing waves created in the tube are in resonance.

Diffraction

- Diffraction is the tendency of a wave emitted from a finite source or passing through a finite aperture to spread out as it propagates.

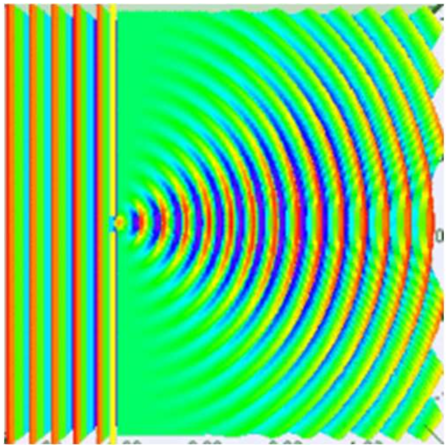




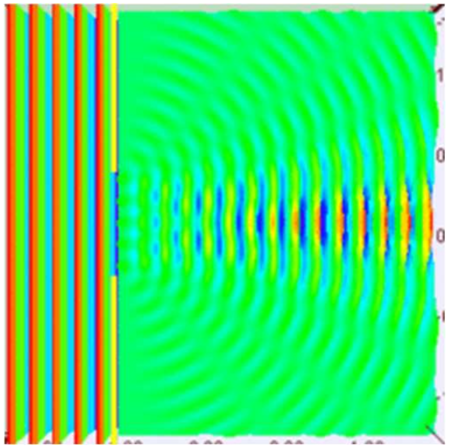
The diffracting object or the aperture effectively becomes a secondary source for the propagating wave.

Effects of Slit Width

- The same wavelength is used but the object is ‘different’:



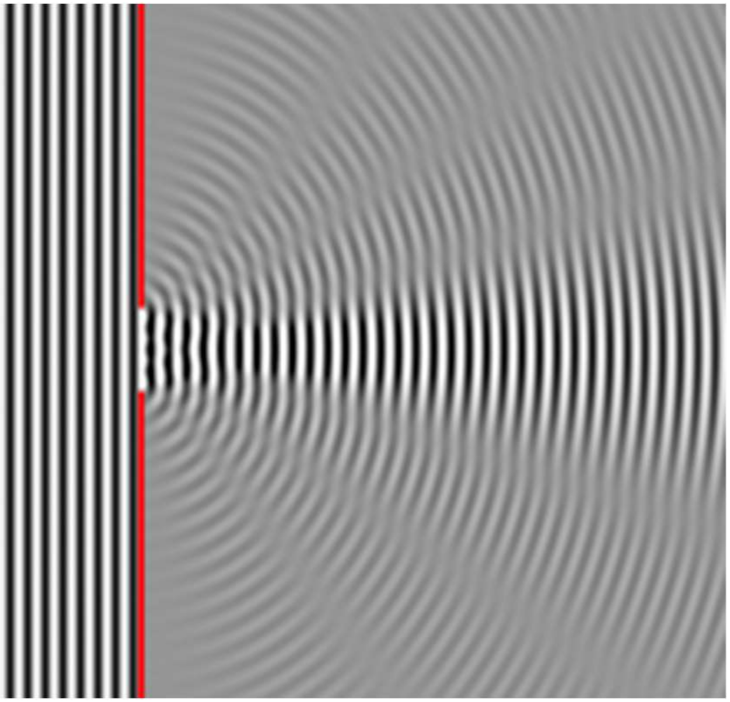
In this case the object is about the same size as the wavelength.



In this case the object is larger than the wavelength.

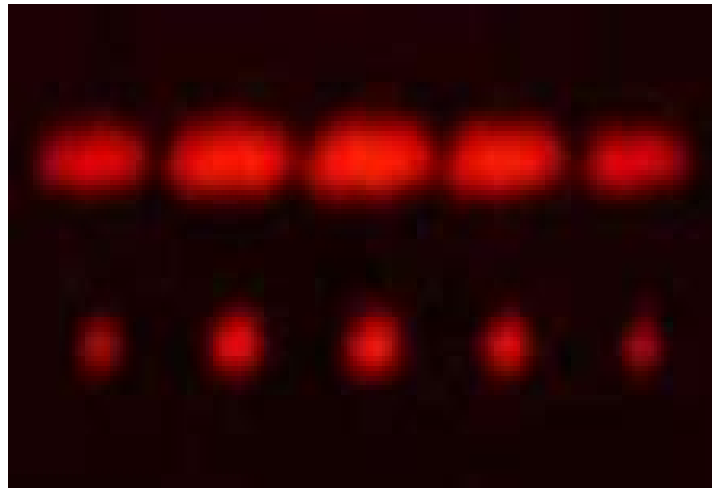
Diffraction is most pronounced when the wavelength of the wave is comparable to the linear dimensions of the obstacle.

Effects of Extra Slits



Same wavelength, with different sized object.

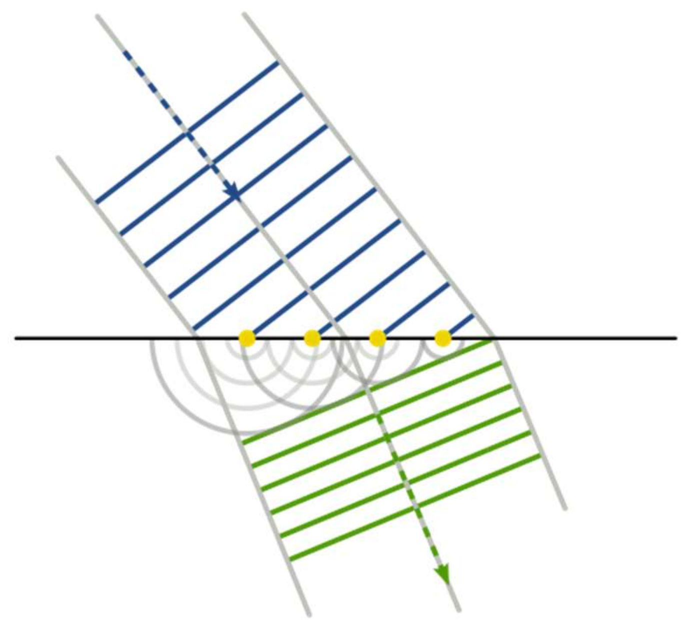
You can clearly see the 'flat' looking parts where destructive interference has taken place.



This image has 2 slits on the top line and 5 slits on the bottom line.

Huygens-Fresnel Principle

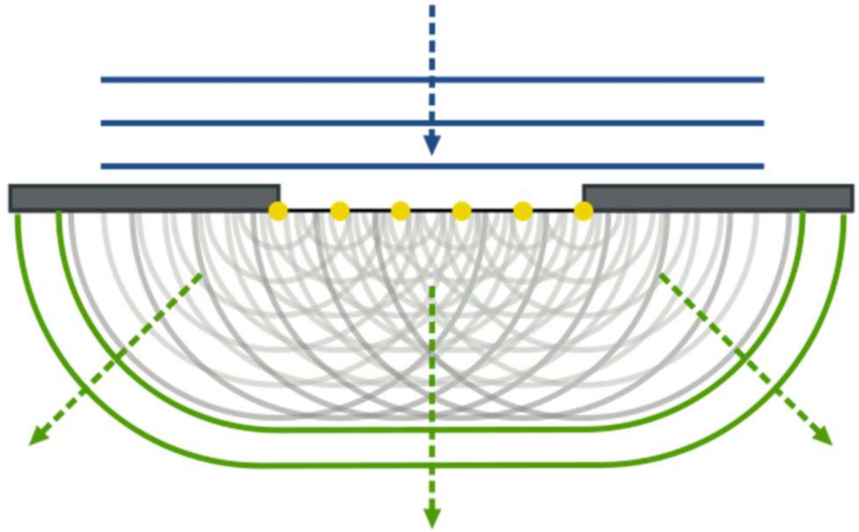
- Huygens-Fresnel principle is a method of analysing wave propagation problems that can be applied to both the far-field and the near-field regions;
- Every point on a wavefront is itself the source of spherical wavelets, and the secondary wavelets emanating from different points mutually interfere.



Wave refraction as interpreted by the Huygens-Fresnel principle.

https://en.wikipedia.org/wiki/Huygens%E2%80%93Fresnel_principle

What Happens During Diffraction?



https://en.wikipedia.org/wiki/Huygens%E2%80%93Fresnel_principle

- Diffraction occurs when a wave encounters an obstacle;
- This causes (secondary) waves to be produced;
- Secondary waves interfere with each other and form the diffraction pattern.

Single-Slit Diffraction

- Intensity minimum occurs when wave from a source at the very top of the slit interferences destructively with a source at the middle of the slit:

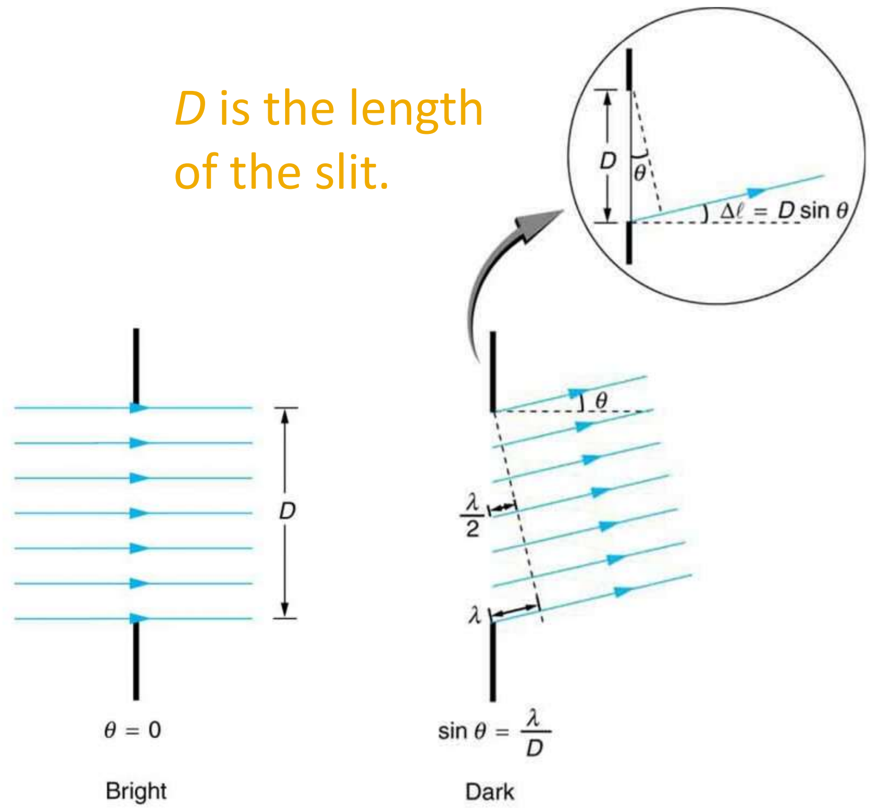
$$\frac{D}{2}\sin\theta = \frac{\lambda}{2}$$

- This relation can be extended to include higher-order minima:

$$D\sin\theta_n = n\lambda$$

n is a positive integer.

D is the length of the slit.



https://courses.lumenlearning.com/austincc-physics2/chapter/27-5-single-slit-diffraction/

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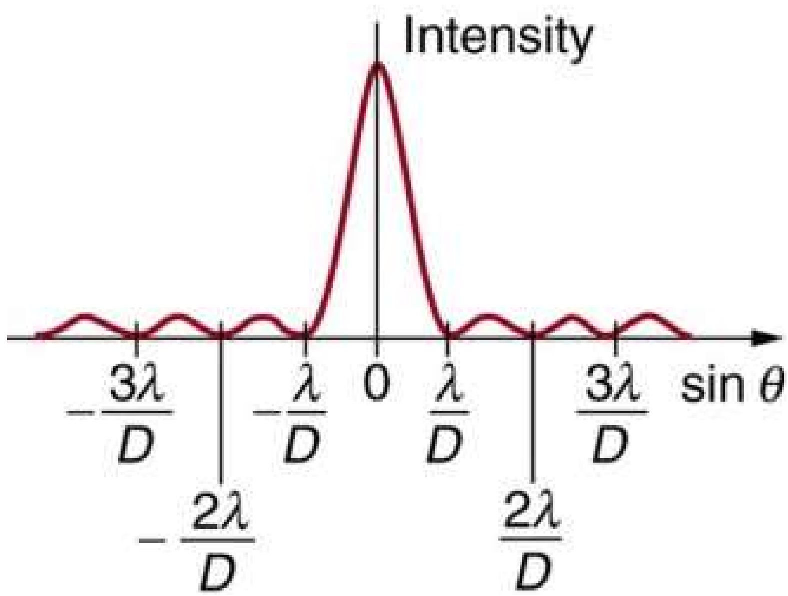


https://courses.lumenlearning.com/austincc-physics2/chapter/27-5-single-slit-diffraction/

Bragg Diffraction

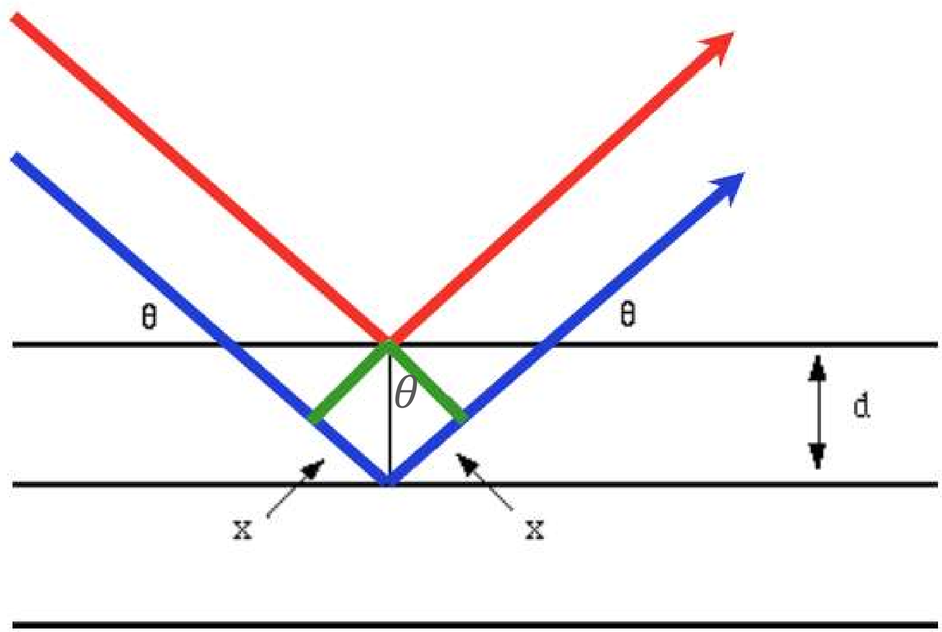
- The type of diffraction pattern from a 3D object like a crystal is called Bragg diffraction;
- From previous work we can predict at what angles there should be constructive interference (Bragg's law):

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

- λ is the wavelength, d is the distance between crystal planes, θ is the angle of the diffracted wave and n is the order of the diffracted beam;
- The order (n) is the integer number of wavelength differences that the reflected path takes.

X-Ray Diffraction in an Image

Bragg's Law



The path difference is $2d\sin\theta$.

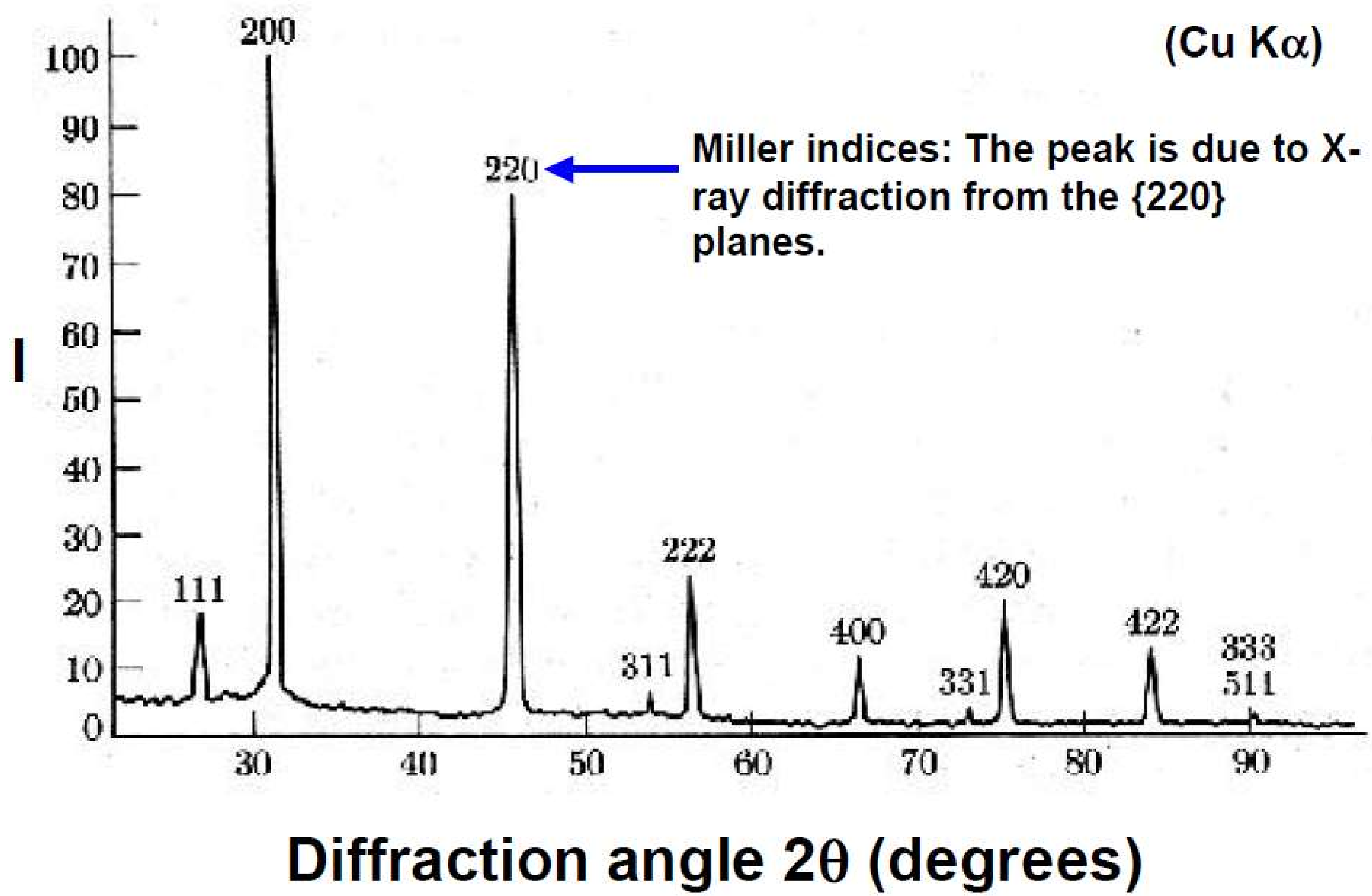
Why X-Rays?

- X-rays are used as the wavelength of them is usually smaller than the distance between the crystal planes (a commonly used source for laboratory x-rays, the Cu K-α line, has a wavelength of 1.54 Å);
- The crystal planes that diffract create sharp peaks in the intensity (think of the situation as diffraction from a very large number of regularly spaced slits);
- This allows the best angle of separation between the constructive interference areas making it easier to determine the location of the atoms.

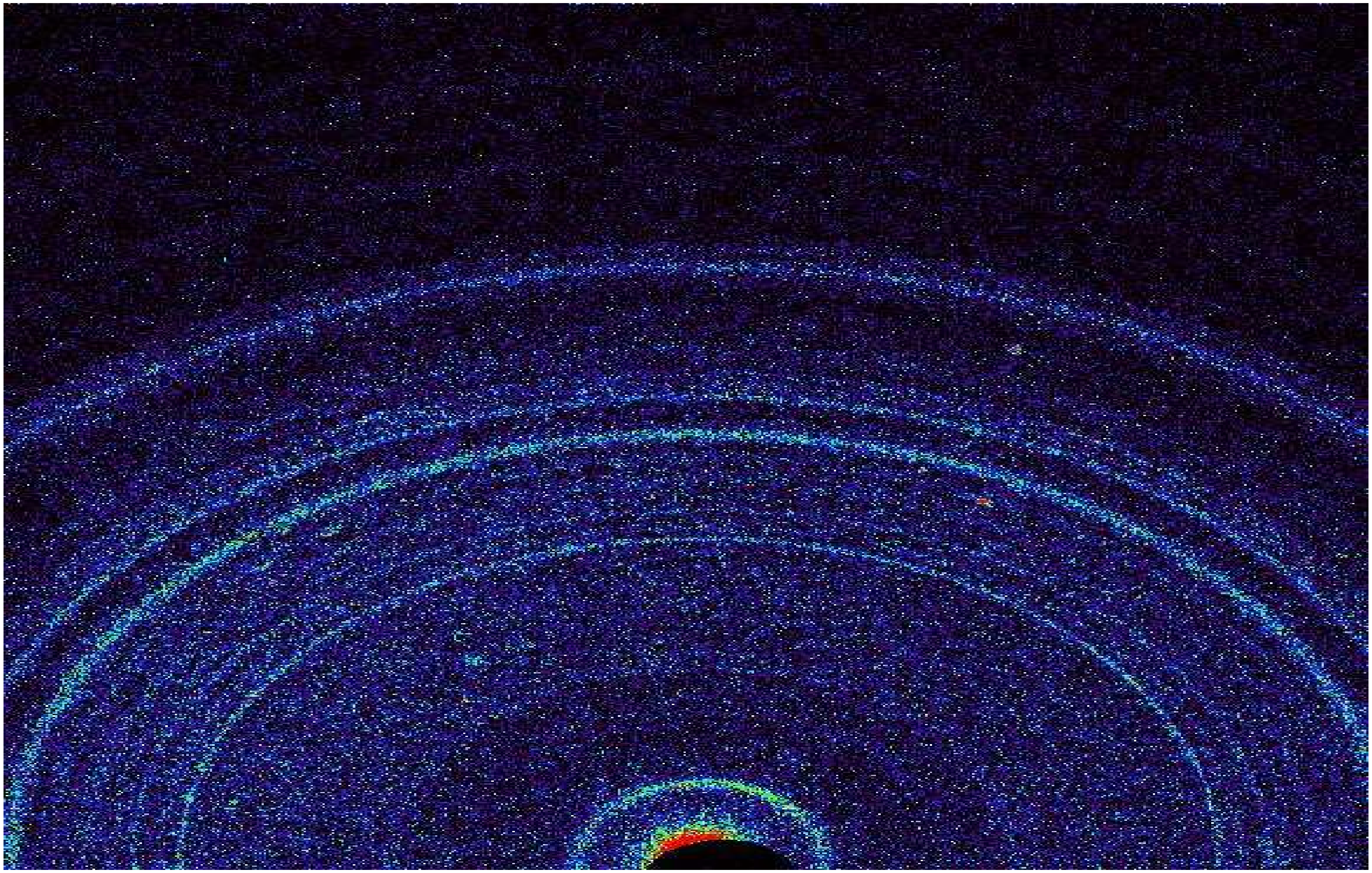
How X-Ray Diffraction (XRD) Works?

- Sample placed inside a diffractometer;
- The x-rays interact with the sample;
- A diffraction pattern is produced;
- The diffraction pattern is analysed by computer using FFT (Fast Fourier Transforms);
- The sample can be rotated to give additional information if needed.

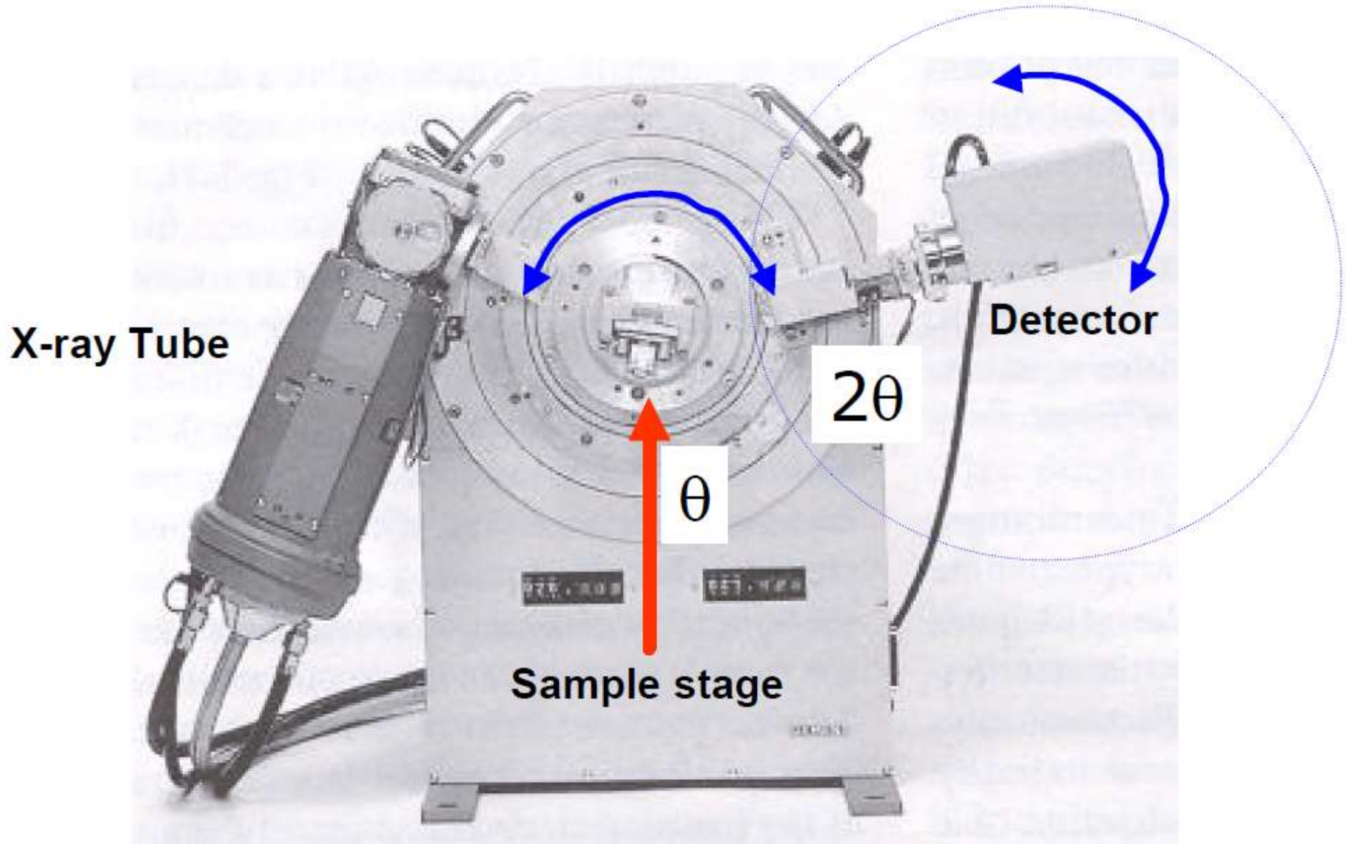
XRD Pattern of NaCl Powder



XRD of Soil From Mars



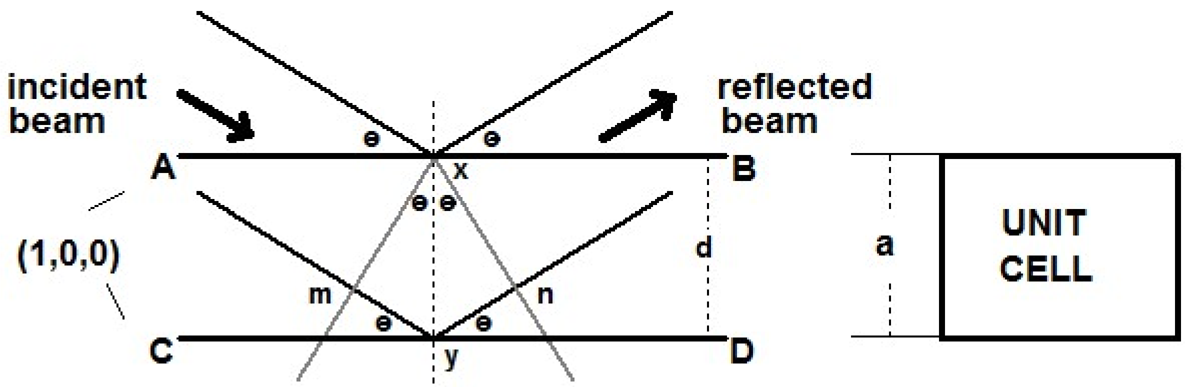
A Modern Automated X-Ray Diffractometer



Cost: $560K to 1.6M

Indices Calculation

- Remember that we mentioned Miller indices?
- We also mentioned (100) Miller indices?
- This is what it looks like:



- Remember that a crystal is 3D, so it has 3 coordinates.

X-Ray Diffraction in the Cubic Lattice System

- The interplanar distance *d* is the distance between two neighbouring parallel planes;
- In order to find the diffraction condition in the cubic lattice system, it is important to figure out *d*;
- In the cubic lattice system, the distance between neighbouring planes having Miller indices of (*hkl*) is

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

It can be proved through simple geometric analysis. For now, let's just take it as a readily known fact and use it.

X-Ray Diffraction in the Cubic Lattice System

- Bragg's law tells us: $n\lambda = 2d\sin\theta$;
- In a primitive cubic lattice, first-order diffraction peaks appear at

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

- The key observation is that for crystal planes with larger $(h^2 + k^2 + l^2)$, the interplanar distance d_{hkl} is smaller but the angle of diffraction of the first-order peak is higher.

Example: X-Ray Diffraction from Polonium

- Polonium (Z = 84), is the only known element with a primitive cubic structure. Its lattice parameter a = 3.35 Å. Calculate the angle of diffraction of the first-order x-ray diffraction peaks for its (100), (110), and (111) planes. Assume that the Cu K-α line with λ = 1.54 Å is used as the x-ray source.

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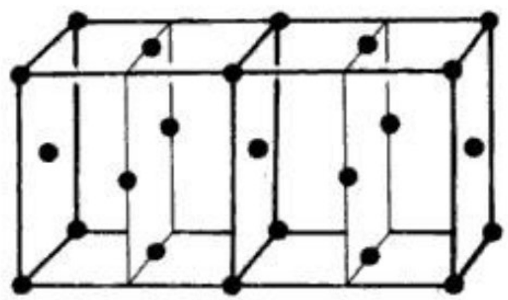
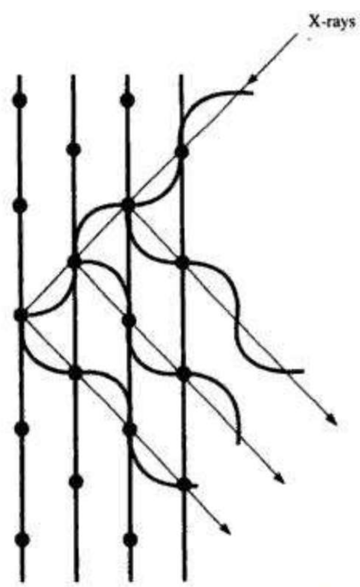
- (100): $\sin\theta = \frac{\lambda}{2a}\sqrt{1^2 + 0 + 0} = 0.230, \theta = 13.3°;$
- (110): $\sin\theta = \frac{\lambda}{2a}\sqrt{1^2 + 1^2 + 0} = 0.325, \theta = 19.0°;$
- (111): $\sin\theta = \frac{\lambda}{2a}\sqrt{1^2 + 1^2 + 1^2} = 0.398, \theta = 23.5°.$

Systematic Absences in BCC and FCC Lattice

- Additional atoms at body or face centres lead to destructive interference for some reflections.



Both (010) and (020) crystal planes are present in an FCC lattice.



Reflections from (200) planes are exactly out of phase with reflections from (100) planes.

- The missing reflections are called systematic absences or systematic extinction.

Systematic Absences in BCC and FCC Lattice

- For BCC and FCC structures, the following conditions have to be satisfied in order for a diffraction peak to be observed:
  - BCC: The sum of the Miller indices must be even, $h + k + l = 2n$ in which n is an integer number;
  - FCC: The Miller indices h, k, and l have to be either all even or all odd.

Summary: X-Ray Diffraction in Cubic Systems

Allowed list of $h^2 + k^2 + l^2$ for cubic crystals

Forbidden numbers	Primitive, P	Face Centered, F	Body Centered, I	Corresponding *hkl*
	1			*100*
	2		2	*110*
	3	3		*111*
	4	4	4	*200*
	5			*210*
	6		6	*211*
7				
	8	8	8	*220*
	9			*221, 300*
	10		10	*310*
	11	11		*311*
	12	12	12	*222*
	13			*320*
	14		14	*321*
15				
	16	16	16	*400*

Question: In the x-ray diffraction spectrum of an unknown material, if $\sin^2\theta$ follows a ratio of 1, 2, 3, 4, 5, 6, 8, … Can you take a guess on what crystal structure the material is in?