CHAPTER 3
X-RAY DIFFRACTION IN CRYSTAL

I. X-Ray
II. Diffraction
III. Diffraction of Waves by Crystals
IV. X-Ray Diffraction
V. Bragg Equation
VI. X-Ray Methods
VII. Neutron & Electron Diffraction

Bertha Röntgen's Hand 8 Nov, 1895

X-RAY

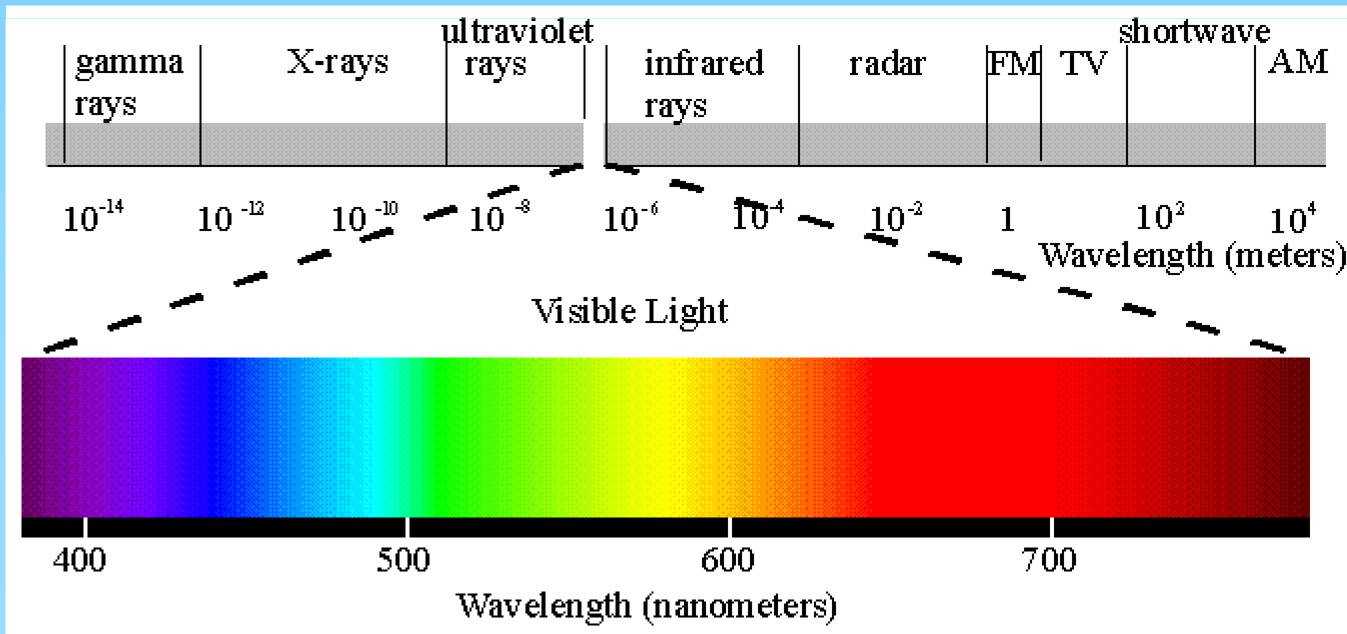
- X-rays were discovered in 1895 by the German physicist Wilhelm Conrad Röntgen and were so named because their nature was unknown at the time.

- He was awarded the Nobel prize for physics in 1901.

Wilhelm Conrad Röntgen
(1845-1923)

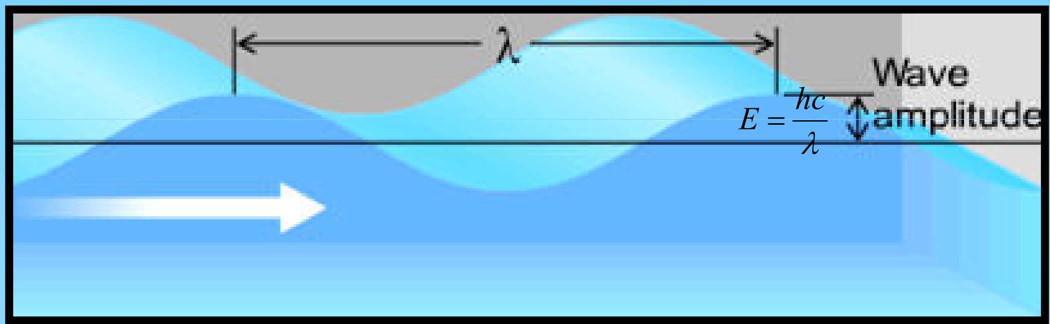
X-RAY PROPERTIES

- X ray, invisible, highly penetrating electromagnetic radiation of much shorter wavelength (higher frequency) than visible light. The wavelength range for X rays is from about 10^{-8} m to about 10^{-11} m, the corresponding frequency range is from about 3×10^{16} Hz to about 3×10^{19} Hz.



X-RAY ENERGY

- Electromagnetic radiation described as having packets of energy, or photons. The energy of the photon is related to its frequency by the following formula:



λ=Wavelength , ν = Frequency , c = Velocity of light

$$E = h\nu$$

$$\nu = \frac{c}{\lambda}$$

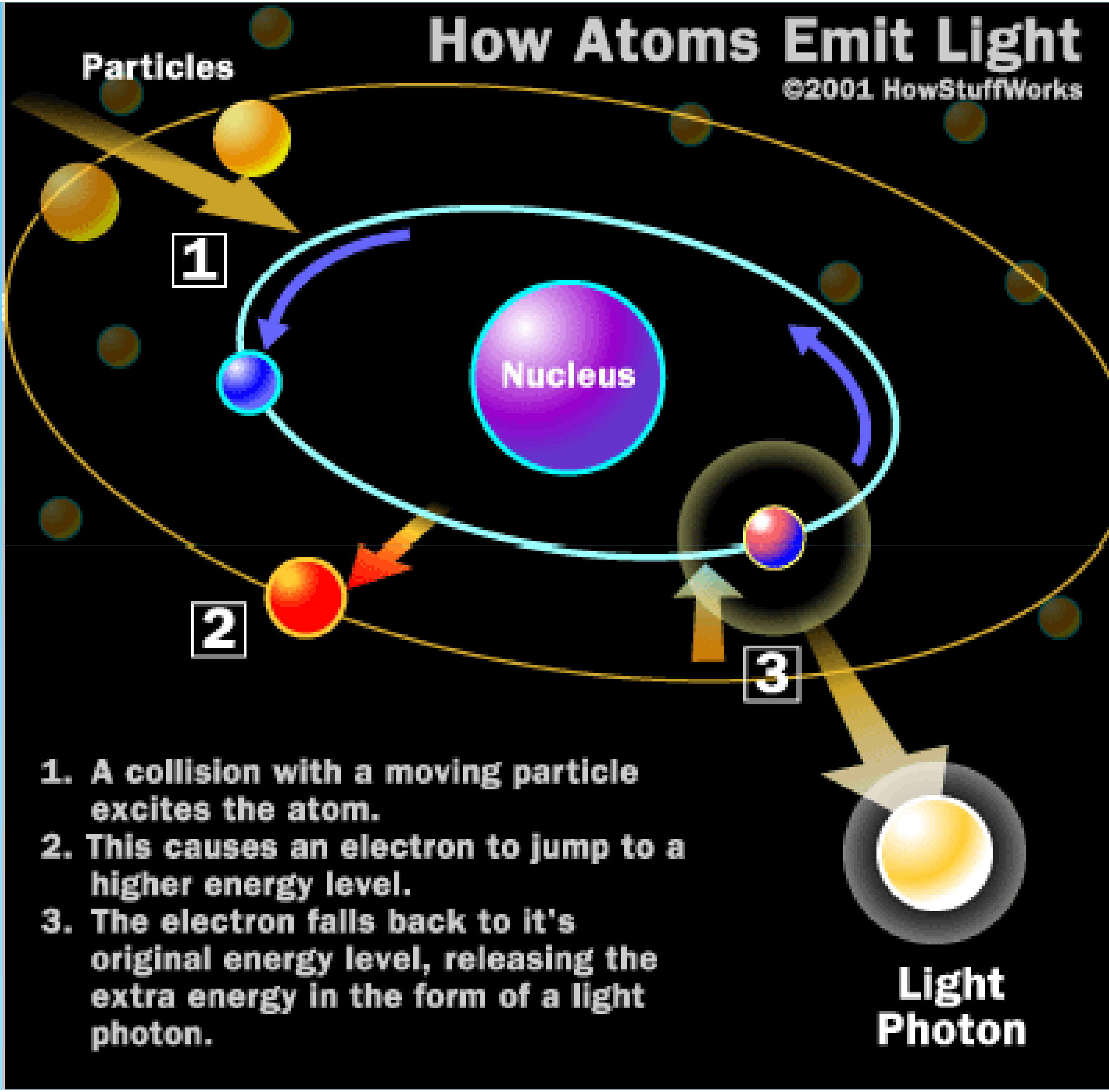
$$E = \frac{hc}{\lambda}$$

$$\lambda_{x\text{-ray}} \approx 10^{-10} \approx 1A^{\circ} \longrightarrow E \simeq 10^{4}\ ev$$

PRODUCTION OF X-RAYS

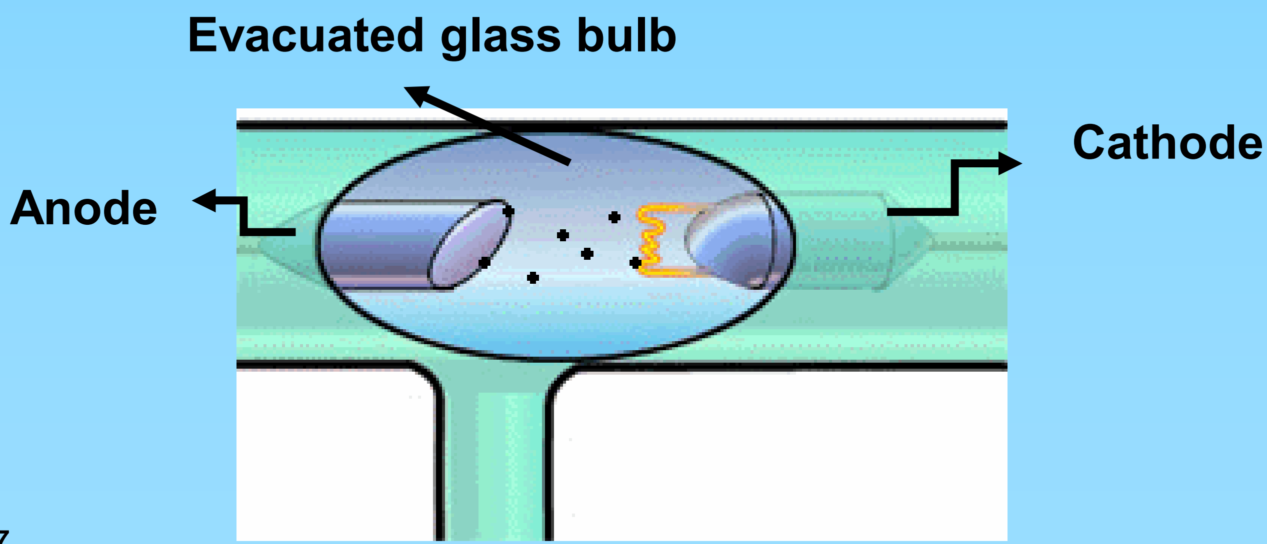
- Visible light photons and X-ray photons are both produced by the movement of **electrons** in atoms. Electrons occupy different energy levels, or orbitals, around an atom's nucleus.

- When an electron drops to a lower orbital, it needs to release some energy; it releases the extra energy in the form of a photon. The energy level of the photon depends on how far the electron dropped between orbitals.


How Atoms Emit Light
©2001 HowStuffWorks
Particles
Nucleus
1
2
3
Light Photon
1. A collision with a moving particle excites the atom.
2. This causes an electron to jump to a higher energy level.
3. The electron falls back to it's original energy level, releasing the extra energy in the form of a light photon.

X-RAY TUBE

- X rays can be produced in a highly evacuated glass bulb, called an X-ray tube, that contains essentially two electrodes—an anode made of platinum, tungsten, or another heavy metal of high melting point, and a cathode. When a high voltage is applied between the electrodes, streams of electrons (cathode rays) are accelerated from the cathode to the anode and produce X rays as they strike the anode.



Monochromatic and Broad Spectrum of X-rays

- X-rays can be created by bombarding a metal target with high energy (> 10^4) electrons.
- Some of these electrons excite electrons from core states in the metal, which then recombine, producing highly monochromatic X-rays. These are referred to as characteristic X-ray lines.
- Other electrons, which are decelerated by the periodic potential of the metal, produce a broad spectrum of X-ray frequencies.
- Depending on the diffraction experiment, either or both of these X-ray spectra can be used.

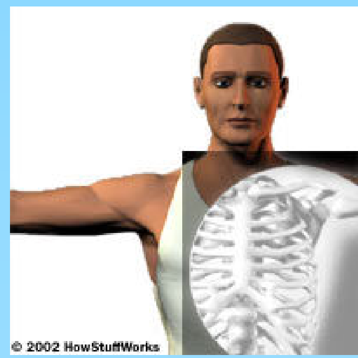
10^4

ABSORPTION OF X-RAYS

- The atoms that make up your body tissue absorb visible light photons very well. The energy level of the photon fits with various energy differences between electron positions.

...something you won't see very often (Visible Light)

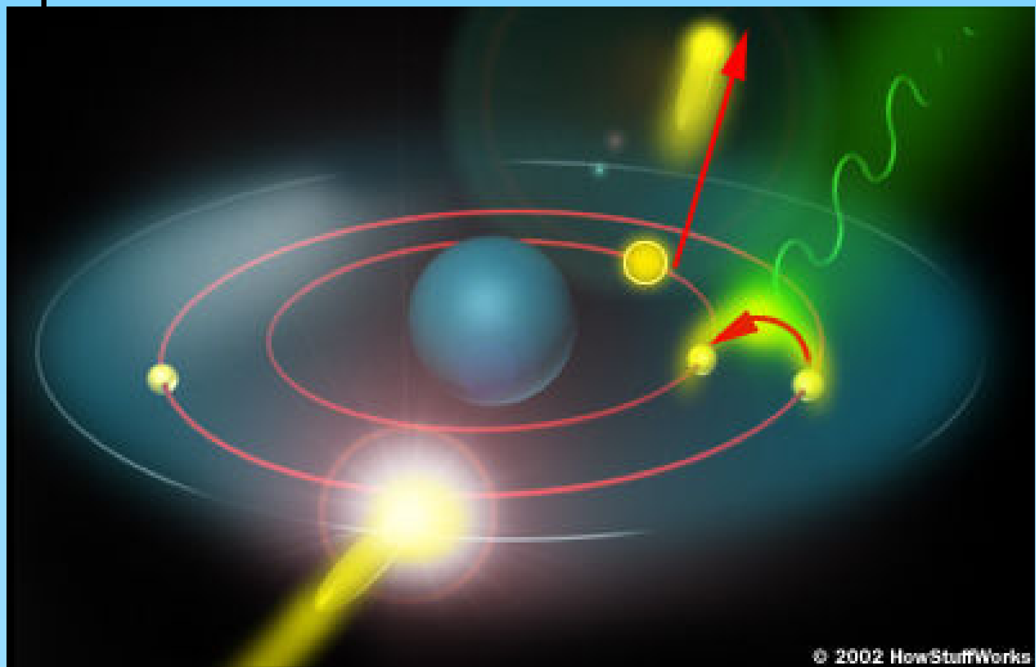
- Radio waves don't have enough energy to move electrons between orbitals in larger atoms, so they pass through most stuff. X-ray photons also pass through most things, but for the opposite reason: They have too much energy.



X-ray

Generation of X-rays (K-Shell Knockout)

An electron in a higher orbital immediately falls to the lower energy level, releasing its extra energy in the form of a photon. It's a big drop, so the photon has a high energy level; it is an X-ray photon.



The free electron collides with the tungsten atom, knocking an electron out of a lower orbital. A higher orbital electron fills the empty position, releasing its excess energy as a photon.

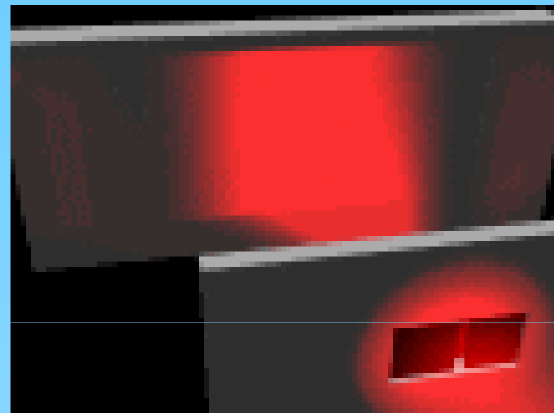
Absorption of X-rays

- A larger atom is more likely to absorb an X-ray photon in this way, because larger atoms have greater energy differences between orbitals -- the energy level more closely matches the energy of the photon. Smaller atoms, where the electron orbitals are separated by relatively low jumps in energy, are less likely to absorb X-ray photons.

- The soft tissue in your body is composed of smaller atoms, and so does not absorb X-ray photons particularly well. The calcium atoms that make up your bones are much larger, so they are better at **absorbing X-ray photons**.

DIFFRACTION

- Diffraction is a wave phenomenon in which the apparent bending and spreading of waves when they meet an obstruction.
- Diffraction occurs with electromagnetic waves, such as light and radio waves, and also in sound waves and water waves.
- The most conceptually simple example of diffraction is double-slit diffraction, that’s why firstly we remember light diffraction.



Width b Variable
(500-1500 nm)

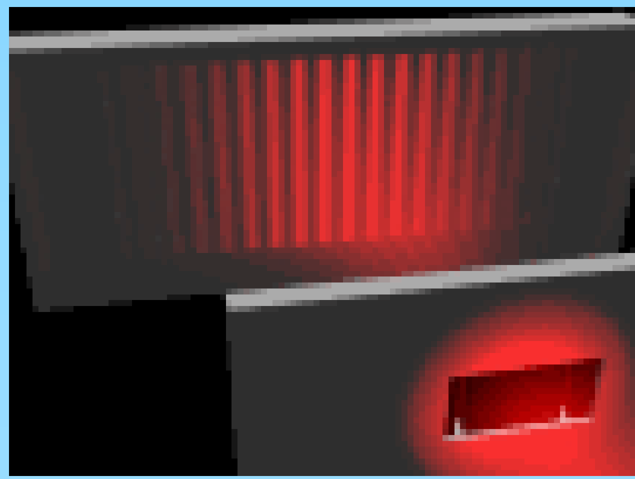
Wavelength Constant
(600 nm)

Distance d = Constant

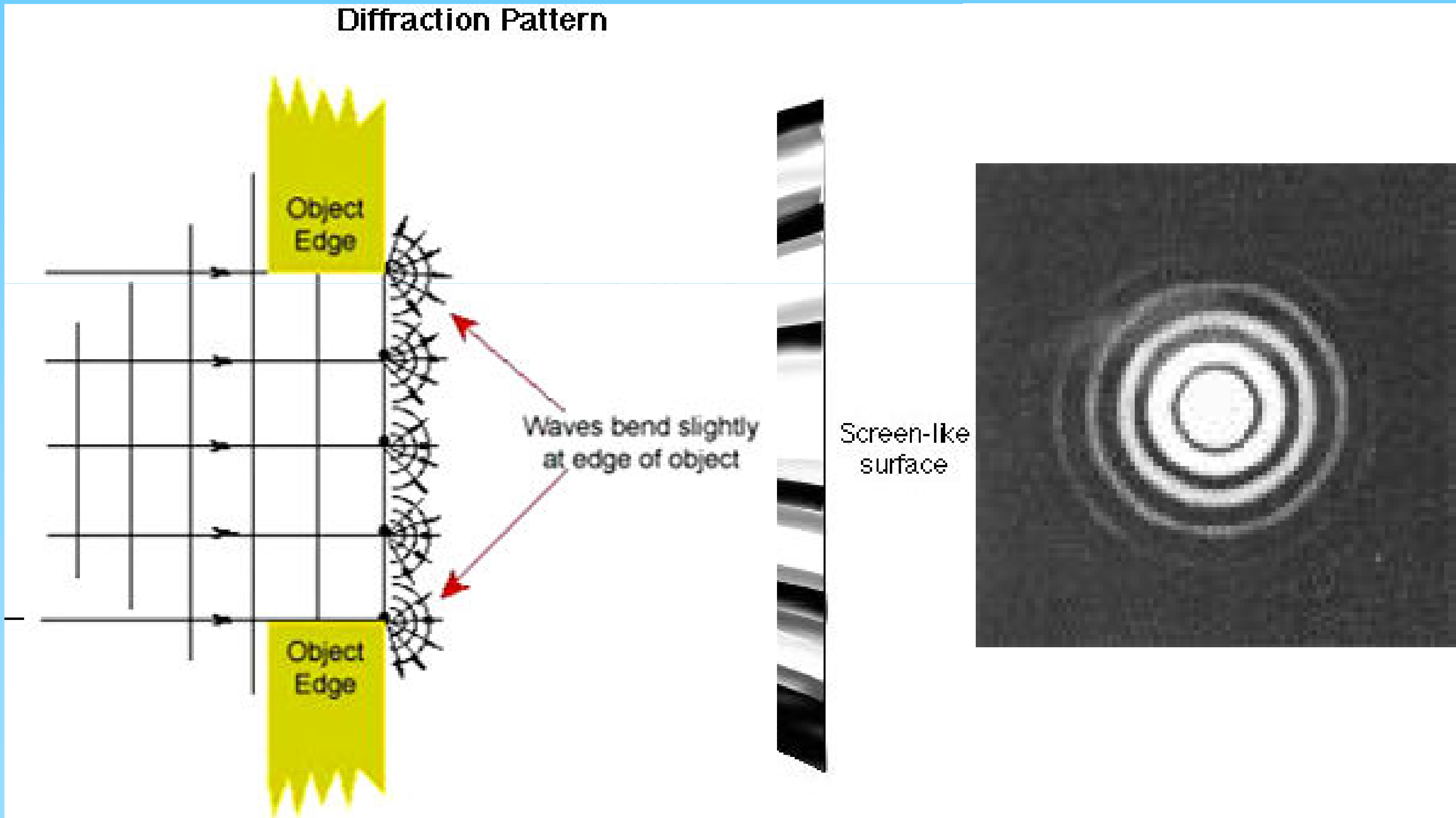
LIGHT DIFFRACTION

- Light diffraction is caused by light bending around the edge of an object. The interference pattern of bright and dark lines from the diffraction experiment can only be explained by the additive nature of waves; wave peaks can add together to make a brighter light, or a peak and a through will cancel each other out and result in darkness.

Thus Young's light interference experiment proves that light has wavelike properties.

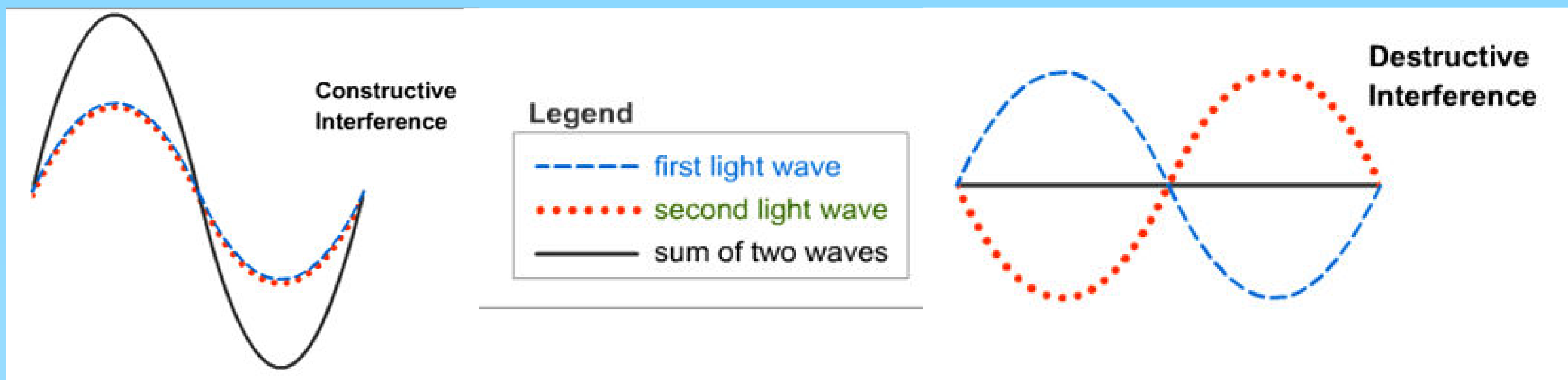


LIGHT INTERFERENCE

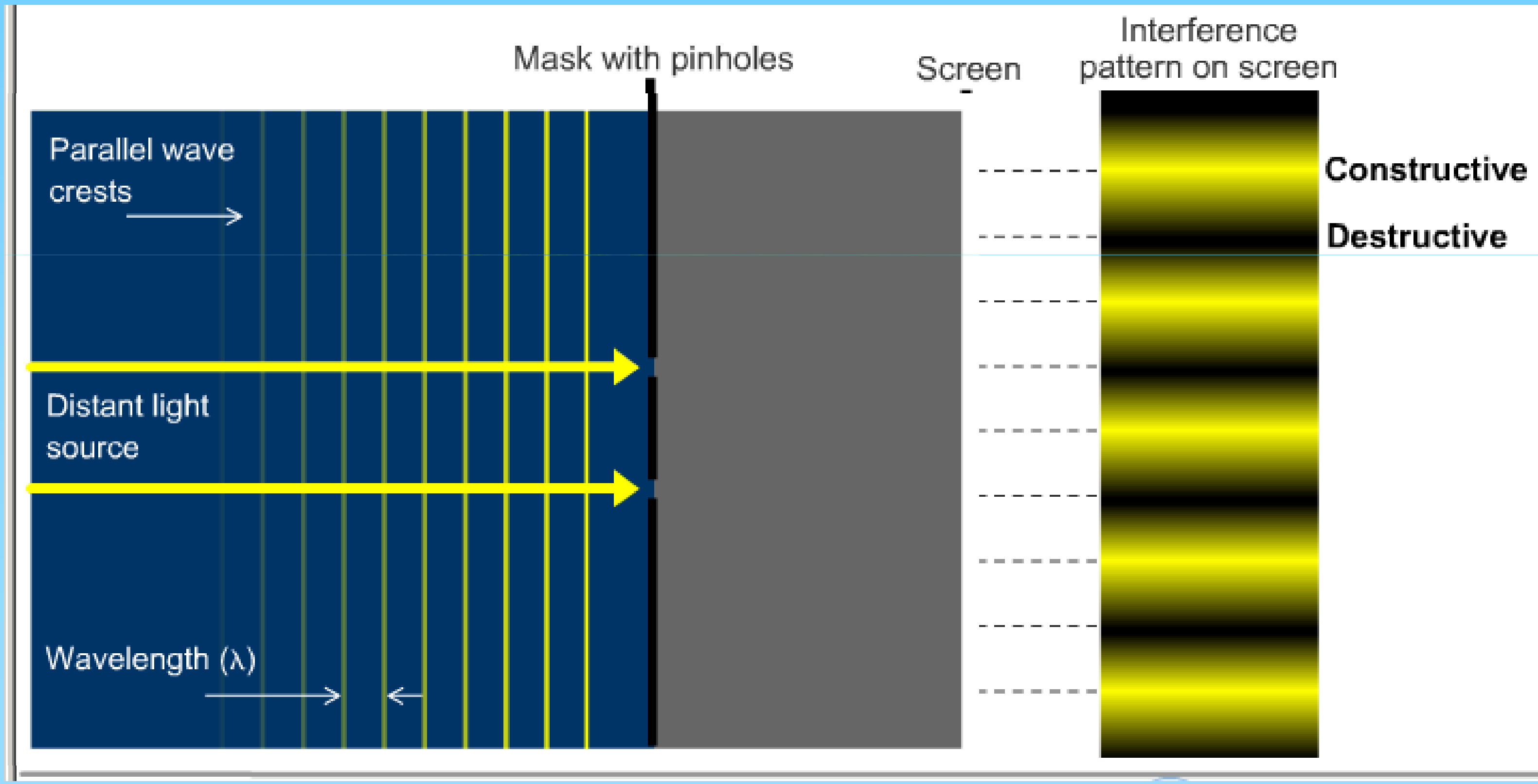


Constructive & Destructive Waves

- **Constructive interference is the result of synchronized light waves that add together to** increase **the light intensity.**
- **Destructive İnterference . results when two out-of-phase light waves cancel each other out, resulting in darkness.**



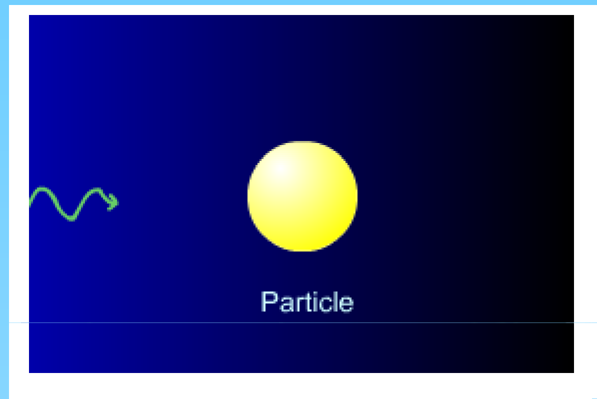
Light Interference



Diffraction from a particle and solid

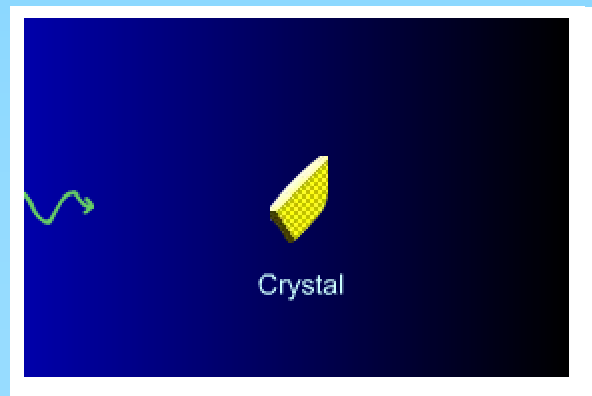
Single particle

- To understand diffraction we also have to consider what happens when a wave interacts with a single particle**.** The particle scatters the incident beam uniformly in **all** directions



Solid material

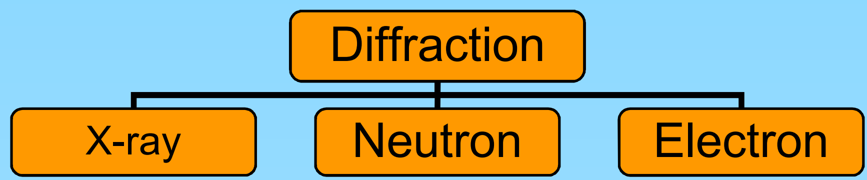
- What happens if the beam is incident on solid material? If we consider a crystalline material, the scattered beams may add together in a few directions and reinforce each other to give **diffracted** beams



Diffraction of Waves by Crystals

A crystal is a periodic structure
(unit cells are repeated regularly)

Solid State Physics deals how the waves are propagated through such periodic structures. In this chapter we study the crystal structure through the diffraction of photons (X-ray), nuetrons and electrons.



The general princibles will be the same for each type of waves.

Diffraction of Waves by Crystals

- The diffraction depends on the crystal structure and on the wavelength.
- At optical wavelengths such as 5000 angstroms the superposition of the waves scattered elastically by the individual atoms of a crystal results in ordinary optical refraction.
- When the wavelength of the radiation is comparable with or smaller than the lattice constant, one can find diffracted beams in directions quite different from the incident radiation.

Diffraction of Waves by Crystals

- ***The structure of a crystal*** can be determined by studying the ***diffraction pattern of a*** beam of radiation incident on the crystal.

- Beam diffraction takes place ***only in certain specific directions***, much as light is diffracted by a grating.

- By measuring the ***directions of the diffraction*** and the ***corresponding intensities***, one obtains information concerning the ***crystal structure*** responsible for diffraction.

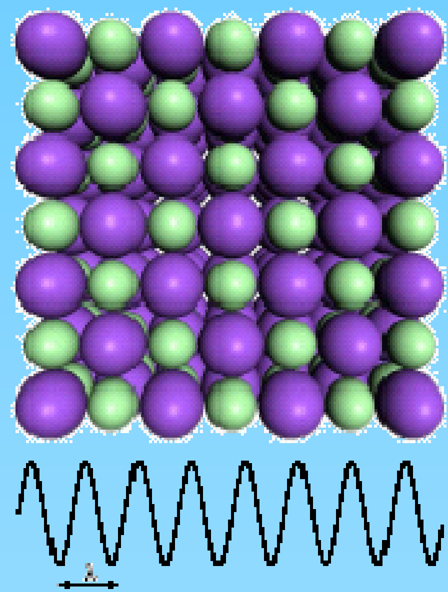
X-RAY CRYSTALLOGRAPHY

- **X-ray crystallography** is a technique in crystallography in which the pattern produced by the diffraction of x-rays through the closely spaced lattice of atoms in a crystal is recorded and then analyzed to reveal the nature of that lattice.

- X-ray diffraction = (XRD)

X-Ray Crystallography

- The wavelength of X-rays is typically 1 A°, comparable to the interatomic spacing (distances between atoms or ions) in solids.



- We need X-rays:

$$E_{x-ray} = \hbar\omega = h\upsilon = \frac{hc}{\lambda} = \frac{hc}{1x10^{-10}m} = 12.3x10^{3} eV$$

Crystal Structure Determination

A crystal behaves as a 3-D diffraction grating for x-rays

- In a diffraction experiment, the spacing of lines on the grating can be deduced from the separation of the diffraction maxima Information about the structure of the lines on the grating can be obtained by measuring the relative intensities of different orders
- Similarly, measurement of the separation of the X-ray diffraction maxima from a crystal allows us to determine the size of the unit cell and from the intensities of diffracted beams one can obtain information about the arrangement of atoms within the cell.

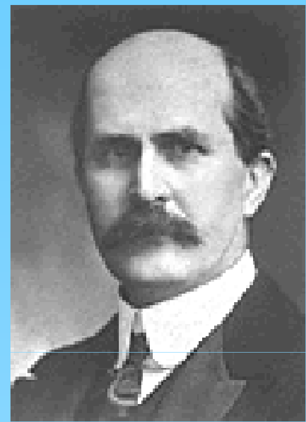
X-Ray Diffraction

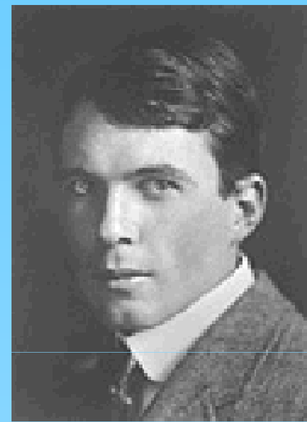
W. L. Bragg presented a simple explanation of the diffracted beams from a crystal.

The Bragg derivation is simple but is convincing only since it reproduces the correct result.

X-Ray Diffraction & Bragg Equation

- English physicists Sir W.H. Bragg and his son Sir W.L. Bragg developed a relationship in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (theta, θ).This observation is an example of X-ray **wave interference**.





Sir William Henry Bragg (1862-1942), William Lawrence Bragg (1890-1971)

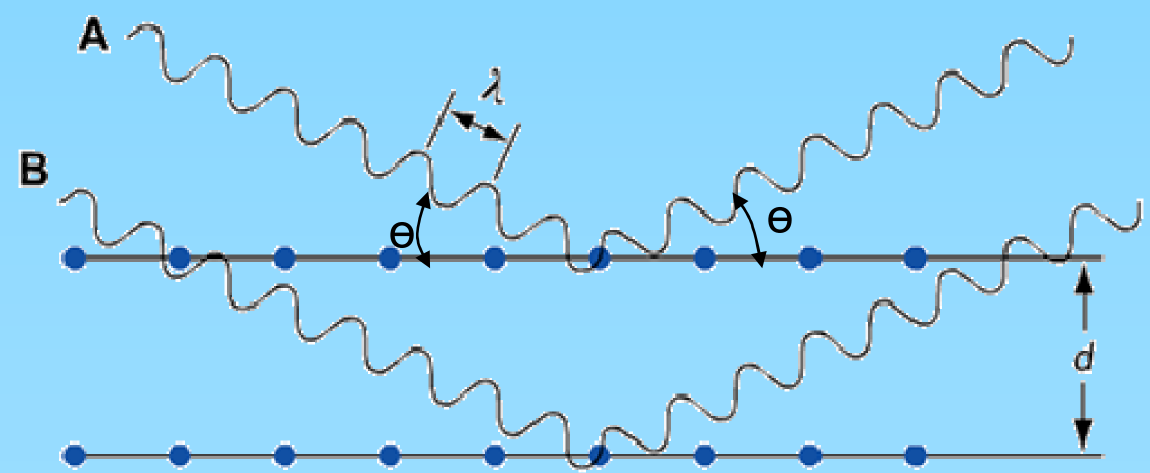
- 1915, the father and son were awarded the Nobel prize for physics *"for their services in the analysis of crystal structure by means of Xrays".*

Bragg Equation

- Bragg law identifies the angles of the incident radiation relative to the lattice planes for which diffraction peaks occurs.
- Bragg derived the condition for constructive interference of the X-rays scattered from a set of parallel lattice planes.

BRAGG EQUATION

- W.L. Bragg considered crystals to be made up of parallel planes of atoms. Incident waves are reflected specularly from parallel planes of atoms in the crystal, with each plane is reflecting only a very small fraction of the radiation, like a lightly silvered mirror.
- In mirrorlike reflection the angle of incidence is equal to the angle of reflection.

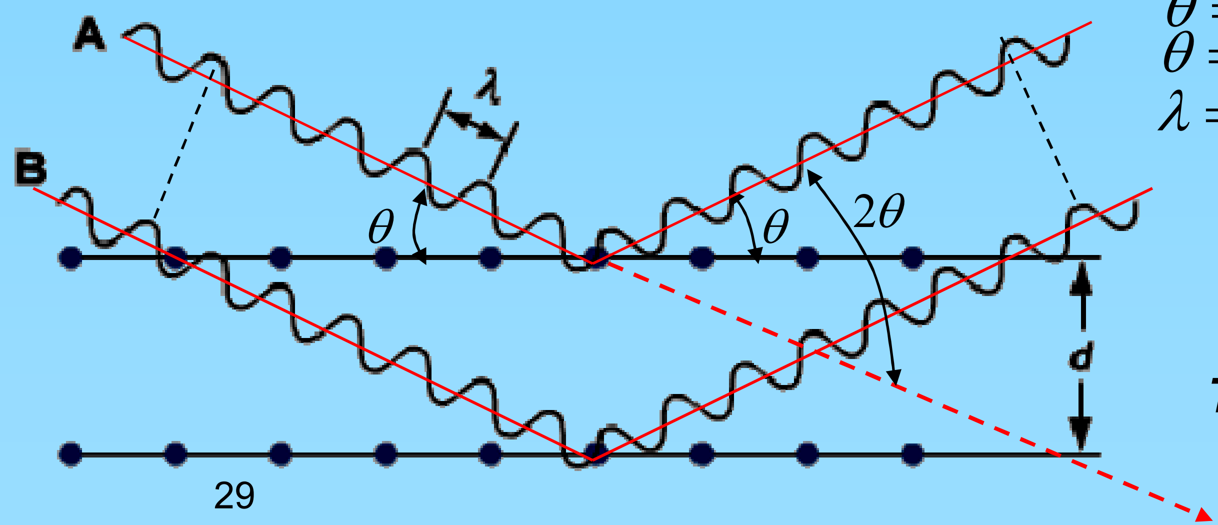


Diffraction Condition

- The diffracted beams are found to occur when the reflections from planes of atoms interfere constructively.
- We treat elastic scattering, in which the energy of X-ray is not changed on reflection.

Bragg Equation

- When the X-rays strike a layer of a crystal, some of them will be reflected. We are interested in X-rays that are in-phase with one another. X-rays that add together constructively in x-ray diffraction analysis in-phase before they are reflected and after they reflected.

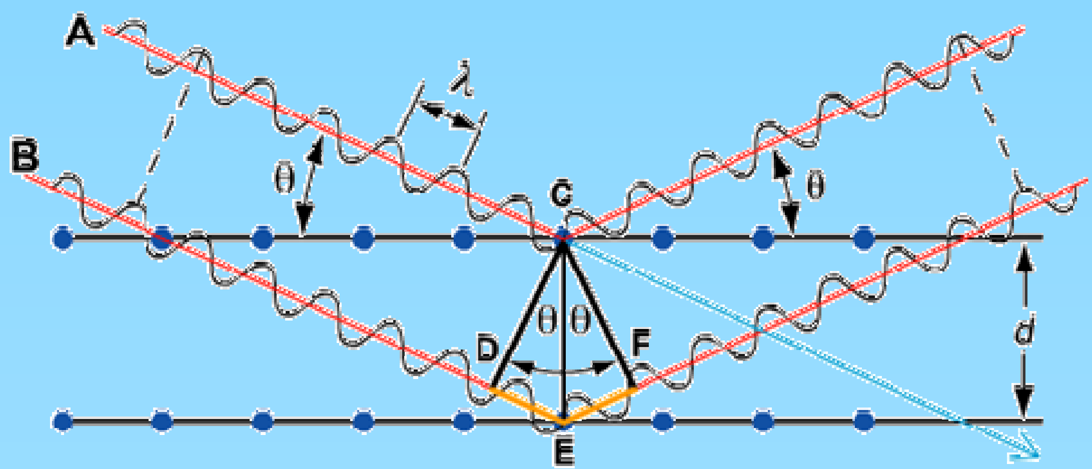


$\theta =$ ***Incident angle***
$\theta =$ ***Reflected angle***
$\lambda =$ ***Wavelength of X-ray***

Total Diffracted Angle $= 2\theta$

Bragg Equation

- These two x-ray beams travel slightly different distances. The difference in the distances traveled is related to the distance between the adjacent layers.
- Connecting the two beams with perpendicular lines shows the difference between the top and the bottom beams.

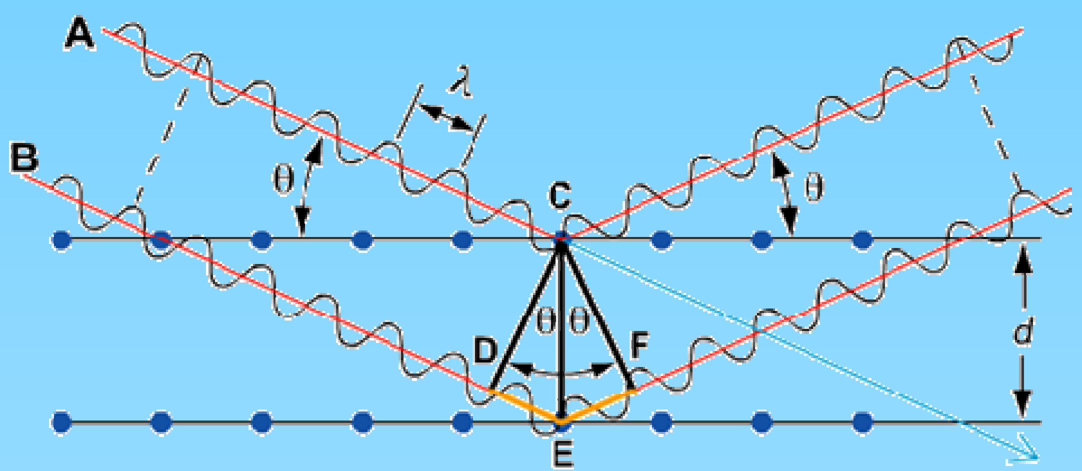


The line CE is equivalent to the distance between the two layers (d)

$$DE = d \sin\theta$$

Bragg Law

- The length DE is the same as EF, so the total distance traveled by the bottom wave is expressed by:



$$EF = d \sin \theta$$

$$DE = d \sin \theta$$

$$DE + EF = 2d \sin \theta$$

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

- Constructive interference of the radiation from successive planes occurs when the path difference is an integral number of wavelenghts. This is the **Bragg Law.**

Bragg Equation

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

where, d is the spacing of the planes and n is the order of diffraction.

- Bragg reflection can only occur for wavelength

$$n\lambda \leq 2d$$

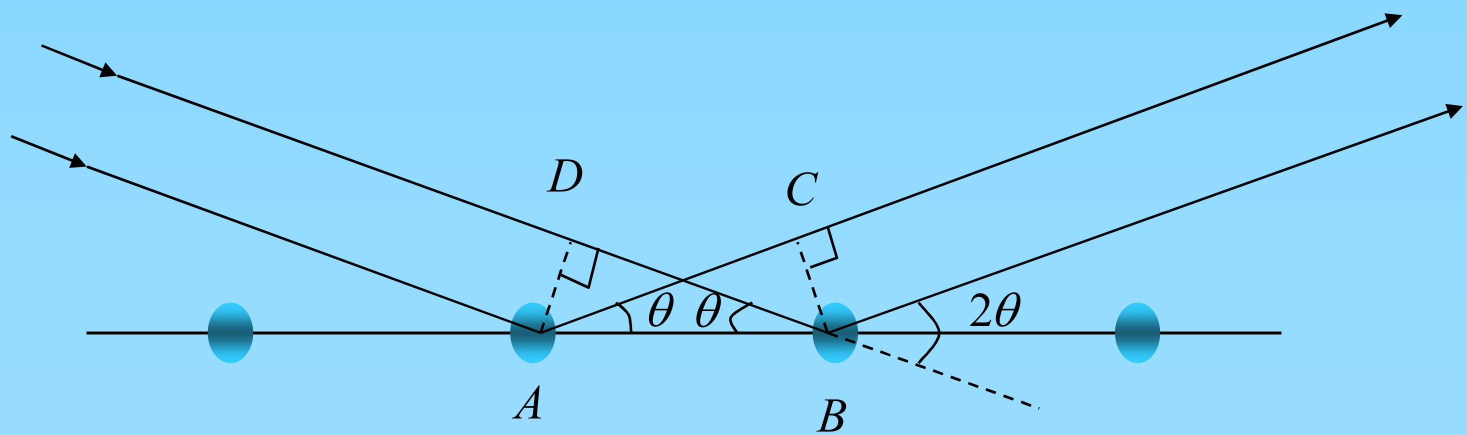
- This is why we cannot use visible light. No diffraction occurs when the above condition is not satisfied.

- The diffracted beams (reflections) from any set of lattice planes can only occur at particular angles pradicted by the Bragg law.

Scattering of X-rays from adjacent lattice points A and B

X-rays are incident at an angle θ on one of the planes of the set.

There will be constructive interference of the waves scattered from the two successive lattice points A and B in the plane if the distances AC and DB are equal.



Constructive interference of waves scattered from the same plane

If the scattered wave makes the same angle to the plane as the incident wave

↓

The diffracted wave looks as if it has been reflected from the plane

We consider the scattering from lattice points rather than atoms because it is the basis of atoms associated with each lattice point that is the true repeat unit of the crystal; The lattice point is analoque of the line on optical diffraction grating and the basis represents the structure of the line.

Diffraction maximum

Coherent scattering from a single plane is not sufficient to obtain a diffraction maximum. It is also necessary that successive planes should scatter in phase

- This will be the case if the path difference for scattering off two adjacent planes is an integral number of wavelengths

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

Labelling the reflection planes

- To label the reflections, Miller indices of the planes can be used.
- A beam corresponding to a value of $n>1$ could be identified by a statement such as ‘the nth-order reflections from the (hkl) planes’.
- (nh nk nl) reflection

Third-order reflection from (111) plane

↓

(333) reflection

n-th order diffraction off (hkl) planes

- Rewriting the Bragg law

$$2\left(\frac{d}{n}\right)\sin\ \theta = \lambda$$

which makes n-th order diffraction off (hkl) planes of spacing ‘d’ look like first-order diffraction off planes of spacing d/n.

- Planes of this reduced spacing would have Miller indices (nh nk nl).

X-ray structure analysis of NaCl and KCl

The GENERAL PRINCIBLES of X-RAY STRUCTURE ANALYSIS to DEDUCE the STRUCTURE of NaCl and KCl

Bragg used an ordinary spectrometer and measured the intensity of specular reflection from a cleaved face of a crystal

found six values of θ for which a sharp peak in intensity occurred, corresponding to three characteristics wavelengths (K,L and M x-rays) in first and second order (n=1 and n=2 in Bragg law)

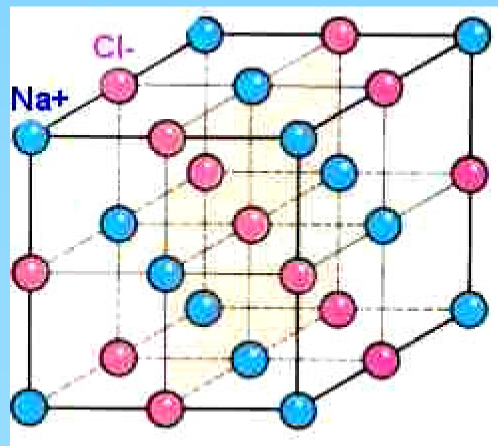
- By repeating the experiment with a different crystal face he could use his eqn. to find for example the ratio of (100) and (111) plane spacings, information that confirmed the cubic symmetry of the atomic arrangement.

Details of structure

Details of structure were than deduced from the differences between the diffraction patterns for NaCl and KCl.

- ***Major difference;*** absence of (111) reflection in KCl compared to a weak but detectable (111) reflection in NaCl.

- This arises because the K and Cl ions both have the argon electron shell structure and hence scatter x-rays almost equally whereas Na and Cl ions have different scattering strengths. (111) reflection in NaCl corresponds to one wavelength of path difference between neighbouring (111) planes.



Experimental arrangements for x-ray diffraction

- Since the pioneering work of Bragg, x-ray diffraction has become into a routine technique for the determination of crsytal structure.

Bragg Equation

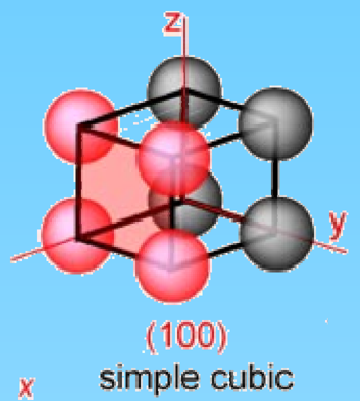
Since Bragg's Law applies to all sets of crystal planes, the lattice can be deduced from the diffraction pattern, making use of general expressions for the spacing of the planes in terms of their Miller indices. For cubic structures

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

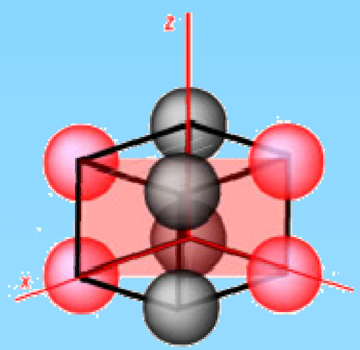
Note that the smaller the spacing the higher the angle of diffraction, *i.e.* the spacing of peaks in the diffraction pattern is inversely proportional to the spacing of the planes in the lattice. The diffraction pattern will reflect the symmetry properties of the lattice.

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

Bragg Equation



(100)
simple cubic



(110)

A simple example is the ***difference between the series of (n00) reflections for a simple cubic and a body centred cubic lattice***. For the simple cubic lattice, all values of *n* will give Bragg peaks.

However, for the body centred cubic lattice the (100) planes are interleaved by an equivalent set at the halfway position. At the angle where Bragg's Law would give the (100) reflection the interleaved planes will give a reflection exactly out of phase with that from the primary planes, which will exactly cancel the signal. There is no signal from (*n*00) planes with odd values of *n*. This kind of argument leads to rules for identifying the lattice symmetry from "missing" reflections, which are often quite simple.

Types of X-ray camera

There are many types of X-ray camera to sort out reflections from different crystal planes. We will study only three types of X-ray photograph that are widely used for the simple structures.

1. Laue photograph
2. Rotating crystal method
3. Powder photograph

X-RAY DIFFRACTION METHODS

X-Ray Diffraction Method

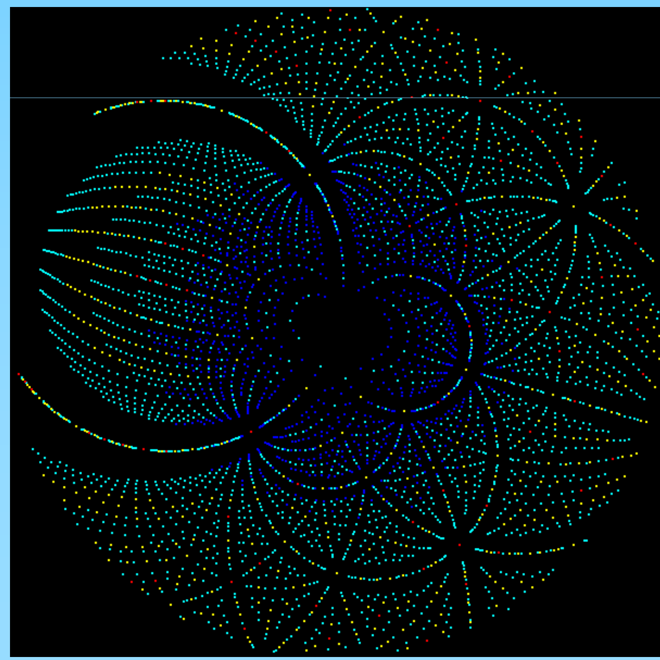
Laue	Rotating Crystal	Powder
Orientation	Lattice constant	Lattice Parameters
Single Crystal	Single Crystal	Polycrystal (powdered)
Polychromatic Beam	Monochromatic Beam	Monochromatic Beam
Fixed Angle	Variable Angle	Variable Angle

LAUE METHOD

- The Laue method is mainly used to determine the orientation of large single crystals while radiation is reflected from, or transmitted through a fixed crystal.

- The diffracted beams form arrays of spots, that lie on curves on the film.

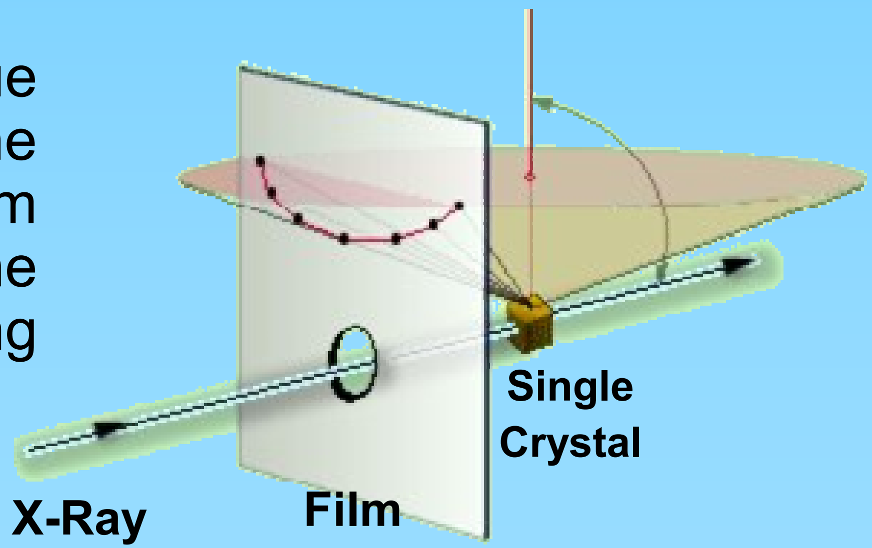
- The Bragg angle is fixed for every set of planes in the crystal. Each set of planes picks out and diffracts the particular wavelength from the white radiation that satisfies the Bragg law for the values of d and θ involved.



Back-reflection Laue Method

- In the back-reflection method, the film is placed **between** the x-ray source and the crystal. The beams which are diffracted in a backward direction are recorded.

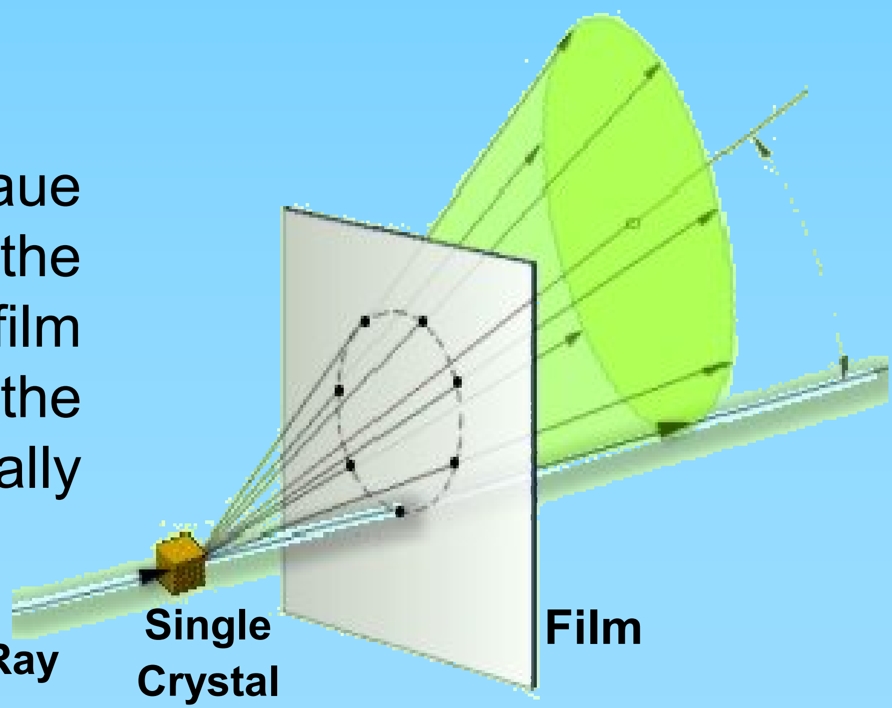
- One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an hyperbola.



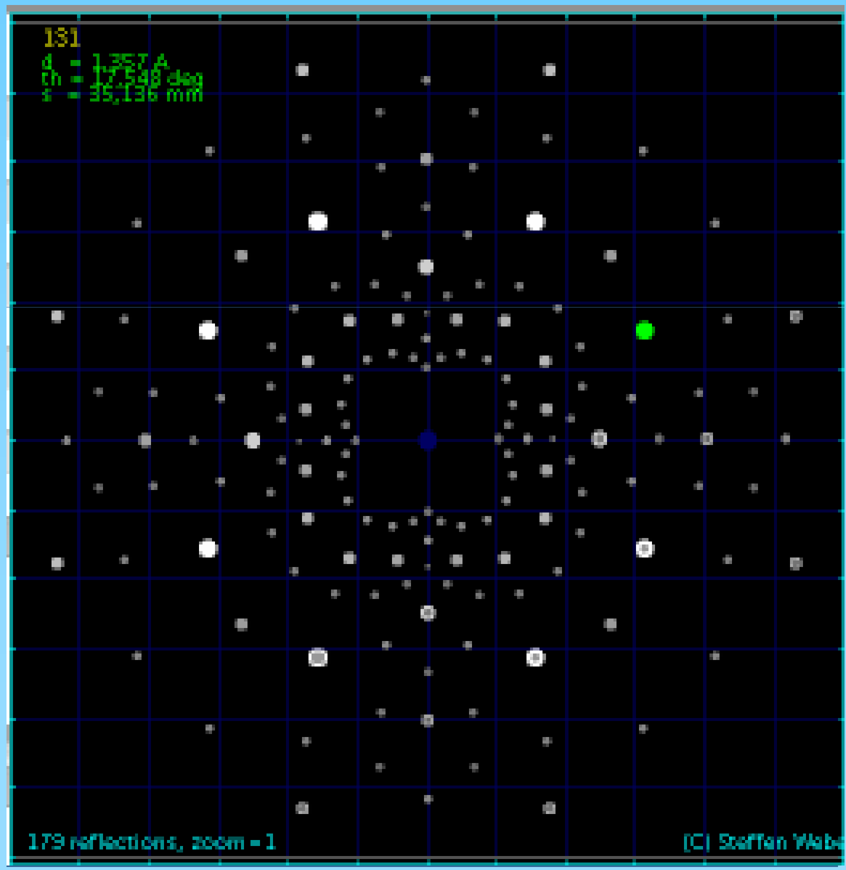
Transmission Laue Method

- In the transmission Laue method, the film is placed **behind** the crystal to record beams which are transmitted through the crystal.

- One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an ellipse.



Laue Pattern



The symmetry of the spot pattern reflects the symmetry of the crystal when viewed along the direction of the incident beam. Laue method is often used to determine the orientation of single crystals by means of illuminating the crystal with a continuos spectrum of X-rays;

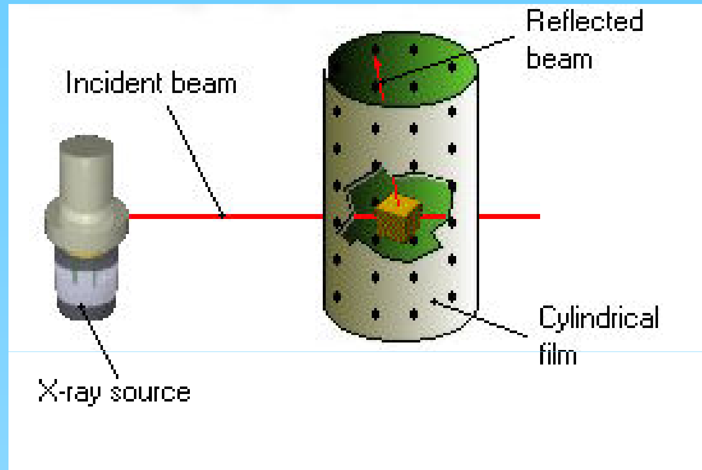
- ☑ ***Single crystal***
- ☑ ***Continous spectrum of x-rays***
- ☑ ***Symmetry of the crystal; orientation***

Crystal structure determination by Laue method

- Therefore, the Laue method is mainly used to determine the crystal orientation.
- Although the Laue method can also be used to determine the crystal structure, several wavelengths can reflect in different orders from the same set of planes, with the different order reflections superimposed on the same spot in the film. This makes crystal structure determination by spot intensity diffucult.
- Rotating crystal method overcomes this problem. How?

ROTATING CRYSTAL METHOD

- In the rotating crystal method, a single crystal is mounted with an axis normal to a monochromatic x-ray beam. A cylindrical film is placed around it and the crystal is rotated about the chosen axis.



- As the crystal rotates, sets of lattice planes will at some point make the correct Bragg angle for the monochromatic incident beam, and at that point a diffracted beam will be formed.

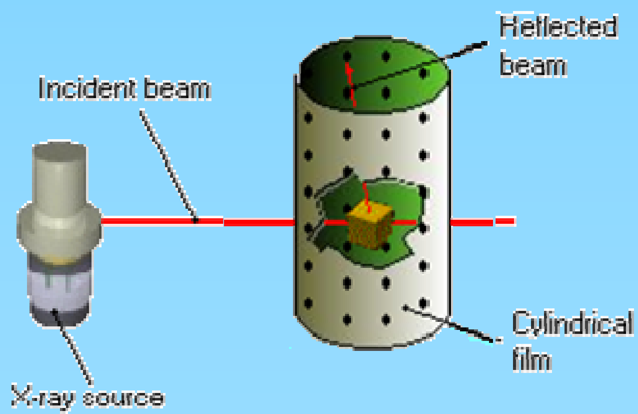
ROTATING CRYSTAL METHOD

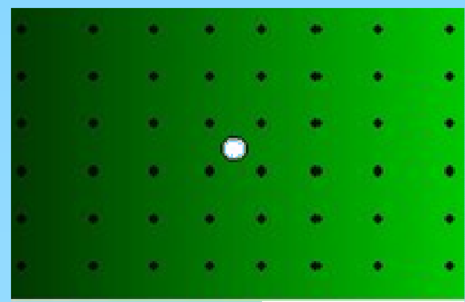
Lattice constant of the crystal can be determined by means of this method; for a given wavelength if the angle θ at which a reflection occurs is known, d_{hkl} can be determined.

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

Rotating Crystal Method

The reflected beams are located on the surface of imaginary cones. By recording the diffraction patterns (both angles and intensities) for various crystal orientations, one can determine the shape and size of unit cell as well as arrangement of atoms inside the cell.





Film

THE POWDER METHOD

If a powdered specimen is used, instead of a single crystal, then there is ***no need to rotate*** the specimen, because there will always be some crystals at an orientation for which diffraction is permitted. Here a monochromatic X-ray beam is incident on a powdered or polycrystalline sample.

This method is useful for samples that are difficult to obtain in single crystal form.

THE POWDER METHOD

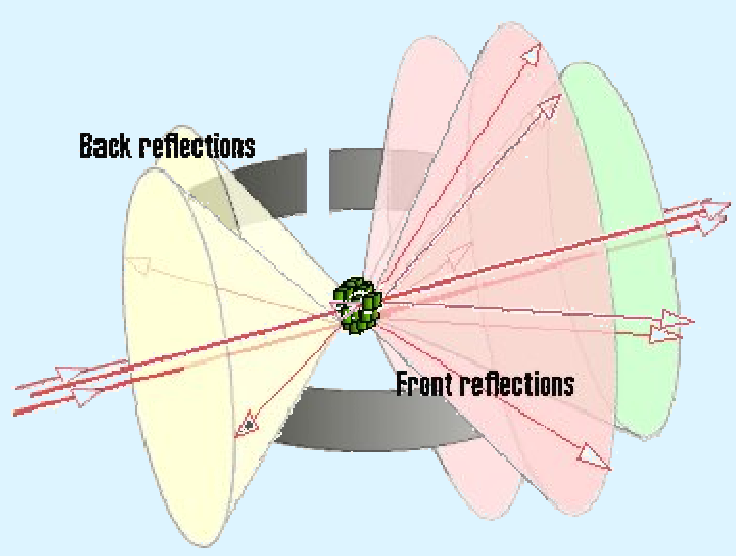
The powder method is used to determine the value of the lattice parameters accurately. Lattice parameters are the magnitudes of the unit vectors **a**, **b** and **c** which define the unit cell for the crystal.

For every set of crystal planes, by chance, ***one or more crystals*** will be in the ***correct orientation*** to give the correct Bragg angle to satisfy Bragg's equation. Every crystal plane is thus capable of diffraction. Each diffraction line is made up of a large number of small spots, each from a separate crystal. Each spot is so small as to give the appearance of a continuous line.

The Powder Method

- If a sample consists of some tens of randomly oriented single crystals, the diffracted beams are seen to lie on the surface of several cones. The cones may emerge in all directions, forwards and backwards.

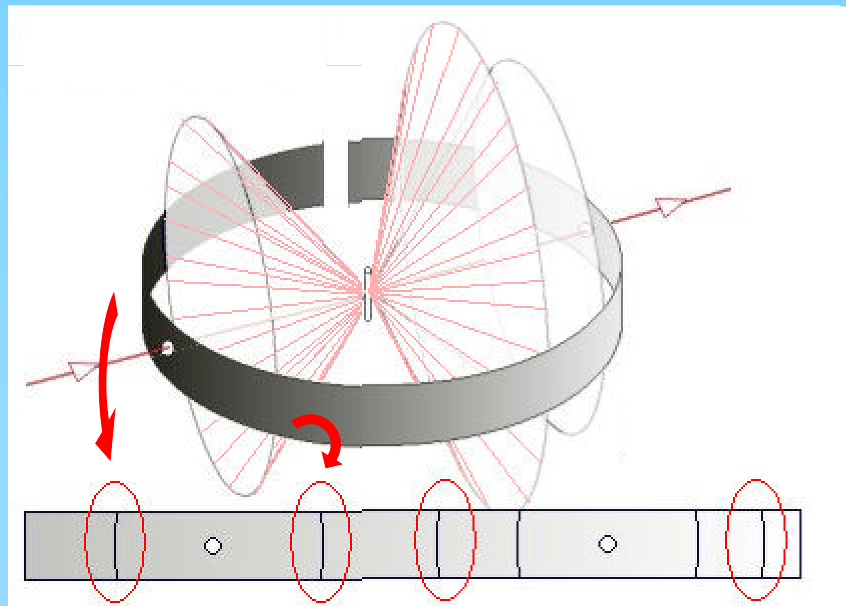
- A sample of some hundreds of crystals (i.e. a powdered sample) show that the diffracted beams form continuous cones. A circle of film is used to record the diffraction pattern as shown. Each cone intersects the film giving diffraction lines. The lines are seen as arcs on the film.



Debye Scherrer Camera

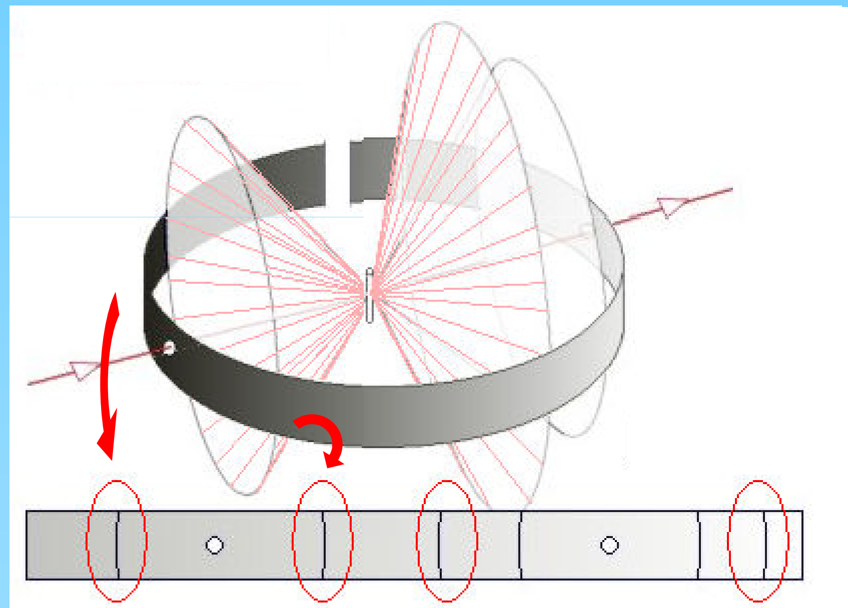
A very small amount of powdered material is sealed into a fine capillary tube made from glass that does not diffract x-rays.

The specimen is placed in the **Debye Scherrer** camera and is accurately aligned to be in the centre of the camera. X-rays enter the camera through a collimator.



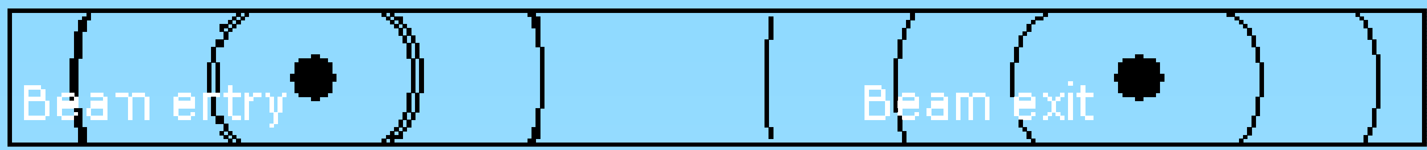
Debye Scherrer Camera

The powder diffracts the x-rays in accordance with Braggs law to produce cones of diffracted beams. These cones intersect a strip of photographic film located in the cylindrical camera to produce a characteristic set of arcs on the film.



Powder diffraction film

When the film is removed from the camera, flattened and processed, it shows the diffraction lines and the holes for the incident and transmitted beams.



Application of XRD

XRD is a nondestructive technique. Some of the uses of x-ray diffraction are;

1. Differentiation between crystalline and amorphous materials;
2. Determination of the structure of crystalline materials;
3. Determination of electron distribution within the atoms, and throughout the unit cell;
4. Determination of the orientation of single crystals;
5. Determination of the texture of polygrained materials;
6. Measurement of strain and small grain size…..etc

Advantages and disadvantages of X-rays

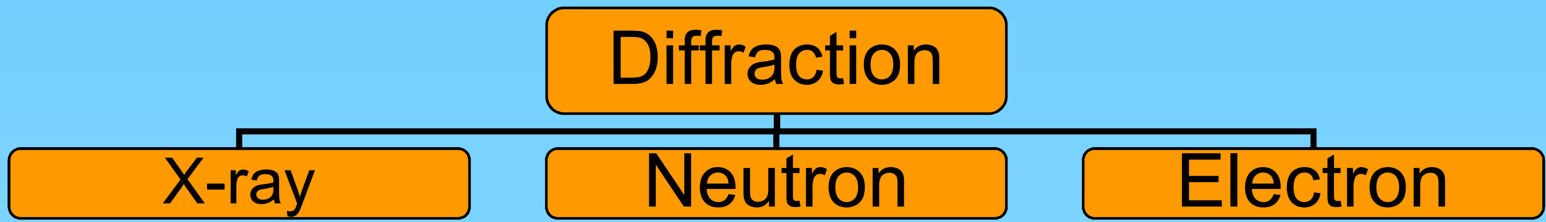
Advantages;

- X-ray is the cheapest, the most convenient and widely used method.
- X-rays are not absorbed very much by air, so the specimen need not be in an evacuated chamber.

Disadvantage;

- They do not interact very strongly with lighter elements.

Difraction Methods



Different radiation source of neutron or electron can also be used in diffraction experiments.

The physical basis for the diffraction of electron and neutron beams is the same as that for the diffraction of X rays, the only difference being in the mechanism of scattering.

Neutron Diffraction

- Neutrons were discovered in 1932 and their wave properties was shown in 1936.

$$E = p^2/2m \qquad p = h/\lambda$$

E=Energy λ=Wavelength

p=Momentum

m_n=Mass of neutron = $1,67.10^{-27}$kg

- λ ~1A°; Energy E~0.08 eV. This energy is of the same order of magnitude as the thermal energy kT at room temperature, 0.025 eV, and for this reason we speak of thermal neutrons.

Neutron Diffraction

- Neutron does not interact with electrons in the crystal. Thus, unlike the x-ray, which is scattered entirely by electrons, the neutron is scattered entirely by nuclei

- Although uncharged, neutron has an intrinsic magnetic moment, so it will interact strongly with atoms and ions in the crystal which also have magnetic moments.

- Neutrons are more useful than X-rays for determining the crystal structures of solids containing light elements.

- Neutron sources in the world are limited so neutron diffraction is a very special tool.

Neutron Diffraction

Neutron diffraction has several advantages over its x-ray counterpart;

- Neutron diffraction is an important tool in the investigation of magnetic ordering that occur in some materials.

- Light atoms such as H are better resolved in a neutron pattern because, having only a few electrons to scatter the X ray beam, they do not contribute significantly to the X ray diffracted pattern.

Electron Diffraction

Electron diffraction has also been used in the analysis of crystal structure. The electron, like the neutron, possesses wave properties;

$$E = \frac{\hbar^2 k^2}{2m_e} = \frac{h^2}{2m_e \lambda^2} = 40eV \qquad \lambda \approx 2A^0$$

Electrons are ***charged particles*** and interact strongly with all atoms. So electrons with an energy of a few eV would be completely ***absorbed by the specimen***. In order that an electron beam can penetrate into a specimen , it necessitas a beam of very high energy (50 keV to 1MeV) as well as the specimen must be thin (100-1000 nm)

Electron Diffraction

If low electron energies are used, the penetration depth will be very small (only about 50 A°), and the beam will be reflected from the surface. Consequently, electron diffraction is a useful technique for surface structure studies.

Electrons are scattered strongly in air, so diffraction experiment must be carried out in a high vacuum. This brings complication and it is expensive as well.

Diffraction Methods

X-Ray	Neutron	Electron
$\lambda = 1A°$	$\lambda = 1A°$	$\lambda = 2A°$
$E \sim 10^4$ eV	$E \sim 0.08$ eV	$E \sim 150$ eV
interact with electron Penetrating	interact with nuclei Highly Penetrating	interact with electron Less Penetrating