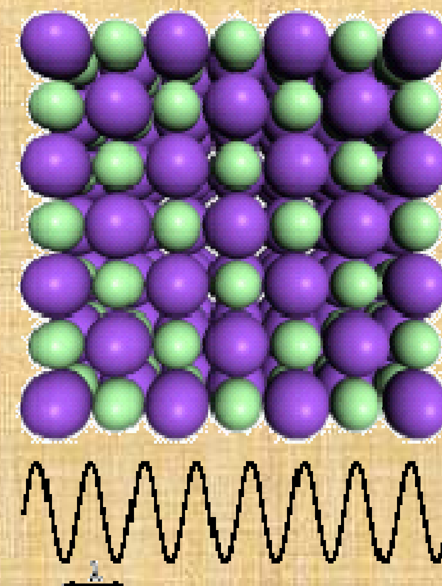
X-RAY CRYSTALLOGRAPHY

- **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.

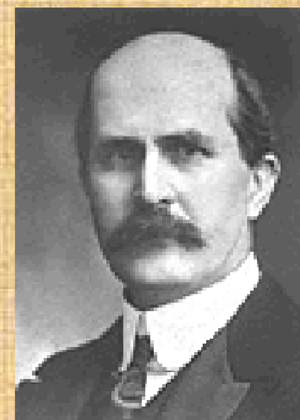
X-Ray Diffraction

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)

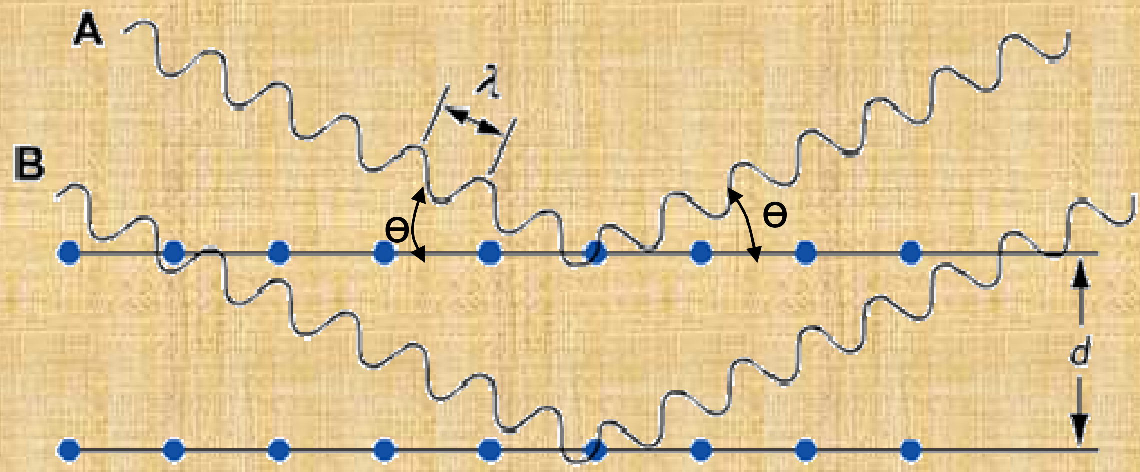
- 1915, the father and son were awarded the Nobel prize for physics *"for their services in the analysis of crystal structure by means of Xrays".*

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.

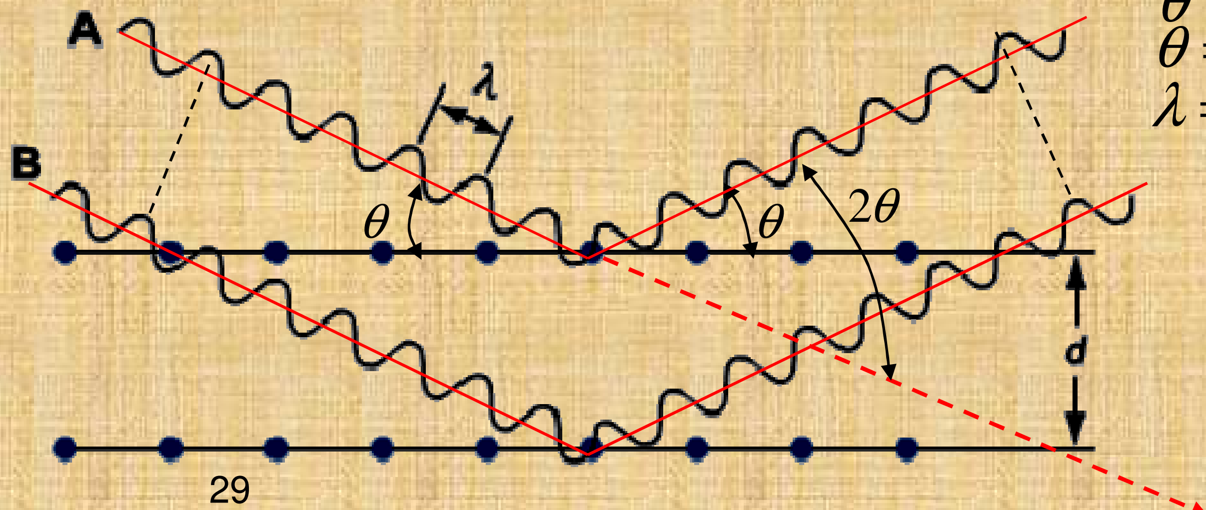


Diffraction Condition

- 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.



θ =***Incident angle***

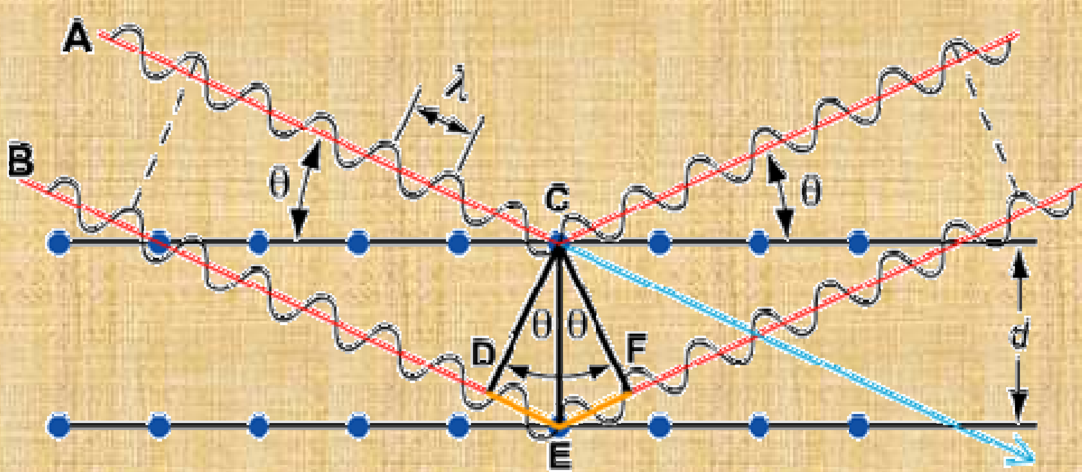
θ =***Reflected angle***

λ =***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.

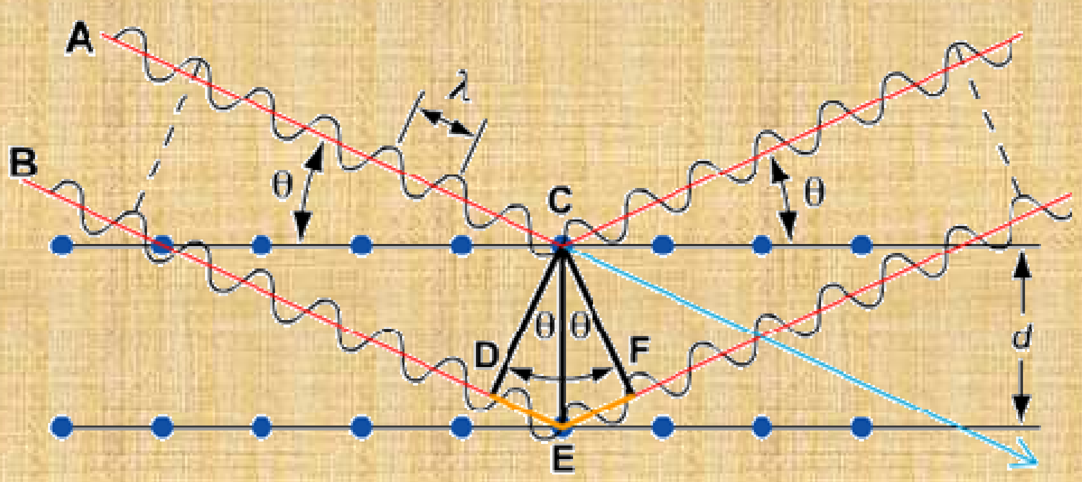


The line CE is equivalent to the distance between the two layers (d)

$$DE = d \sin\theta$$

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

$$n\lambda \leq 2d$$

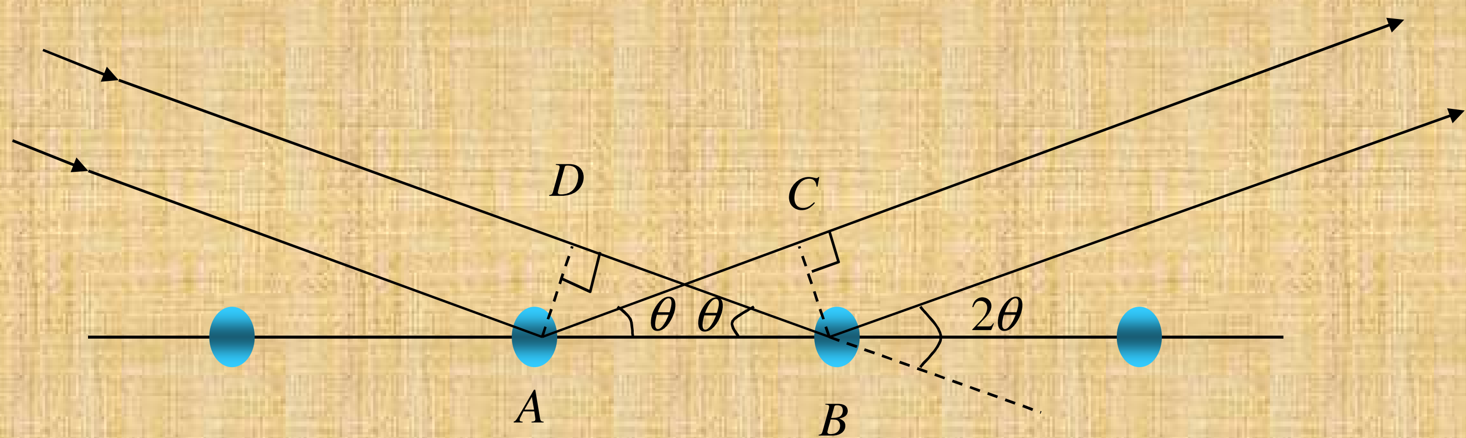
- This is why we cannot use visible light. No diffraction occurs when the above condition is not satisfied.

- 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)

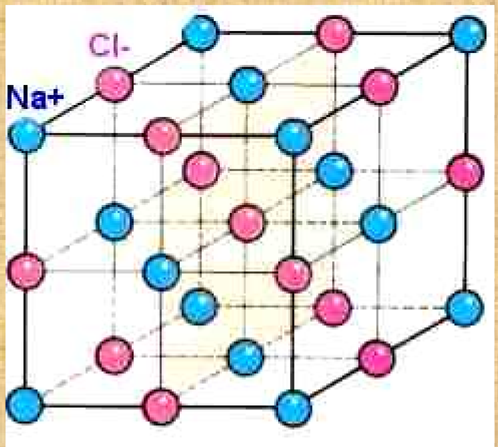
- By repeating the experiment with a different crystal face he could use his eqn. to find for example the ratio of (100) and (111) plane spacings, information that confirmed the cubic symmetry of the atomic arrangement.

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

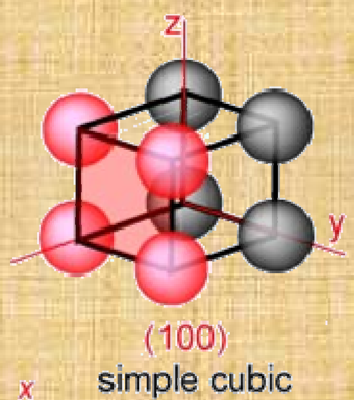
Since Bragg's Law applies to all sets of crystal planes, the lattice can be deduced from the diffraction pattern, making use of general expressions for the spacing of the planes in terms of their Miller indices. For cubic structures

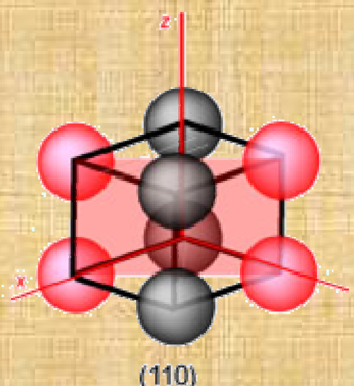
$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

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





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