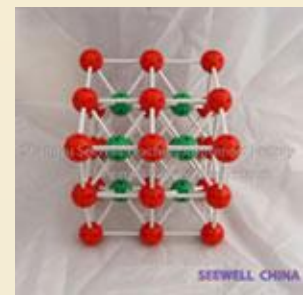


# CHAPTER 3: CRYSTAL STRUCTURES

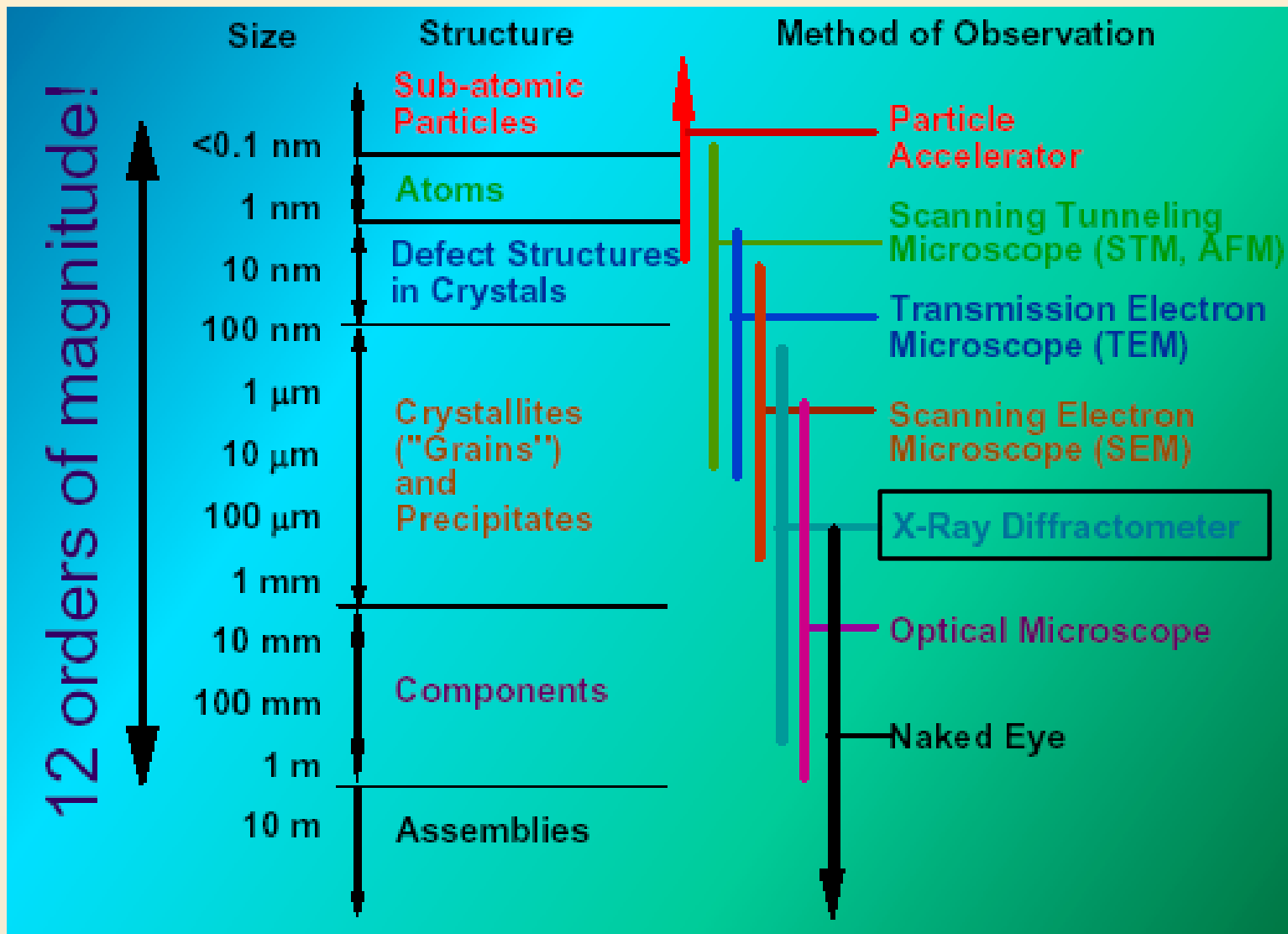
## X-Ray Diffraction (XRD)

### ISSUES TO ADDRESS...

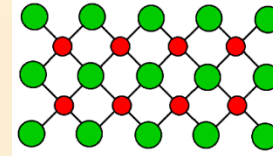
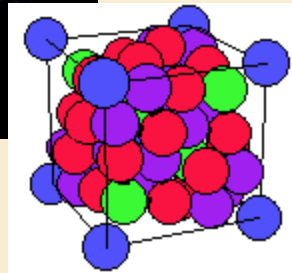
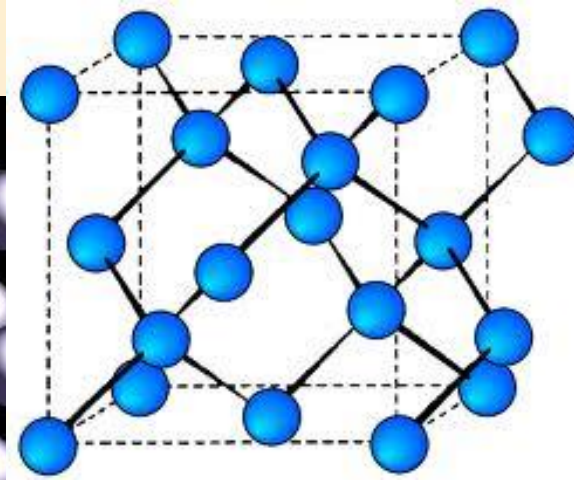
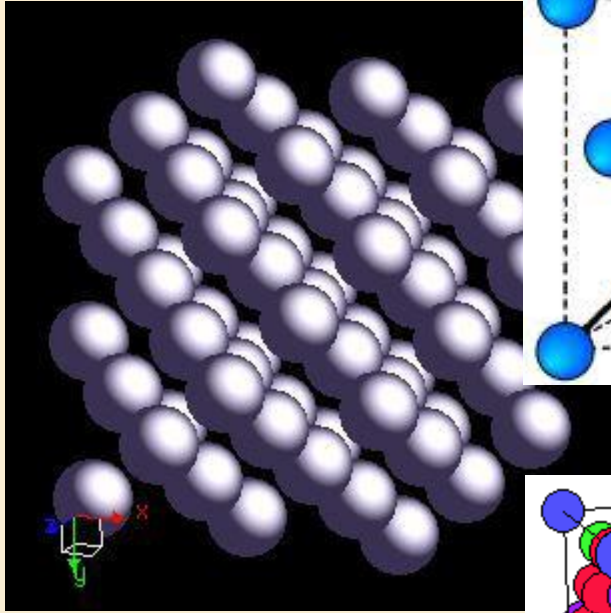
- Historical retrospective
- Henry Bragg Equation
- XRD-analysis
- How to read XRD patterns?
- Exclusions
- What questions can be answered by XRD method?



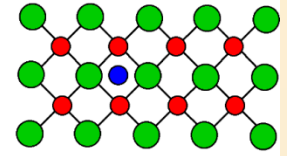
# Scale of Structure Organization



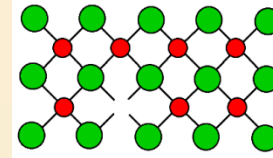
# Crystal Structure



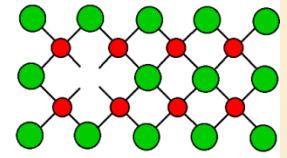
(a) perfect lattice



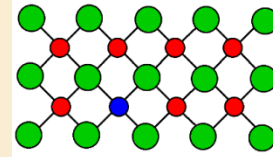
(b) interstitial impurity



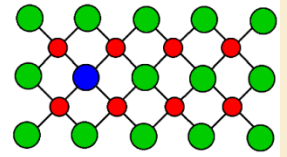
(c) cation vacancy



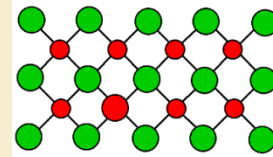
(d) anion vacancy



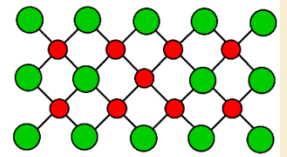
(e) substitution of cation



(f) substitution of anion



(g)  $B_A$  antisite defect



(h)  $A_B$  antisite defect

**Practical questions to address:**

**How to define what crystal structure do we have?**

**Or in another words: what phases do we have?**

**Do we have defects or strain in our structure?**

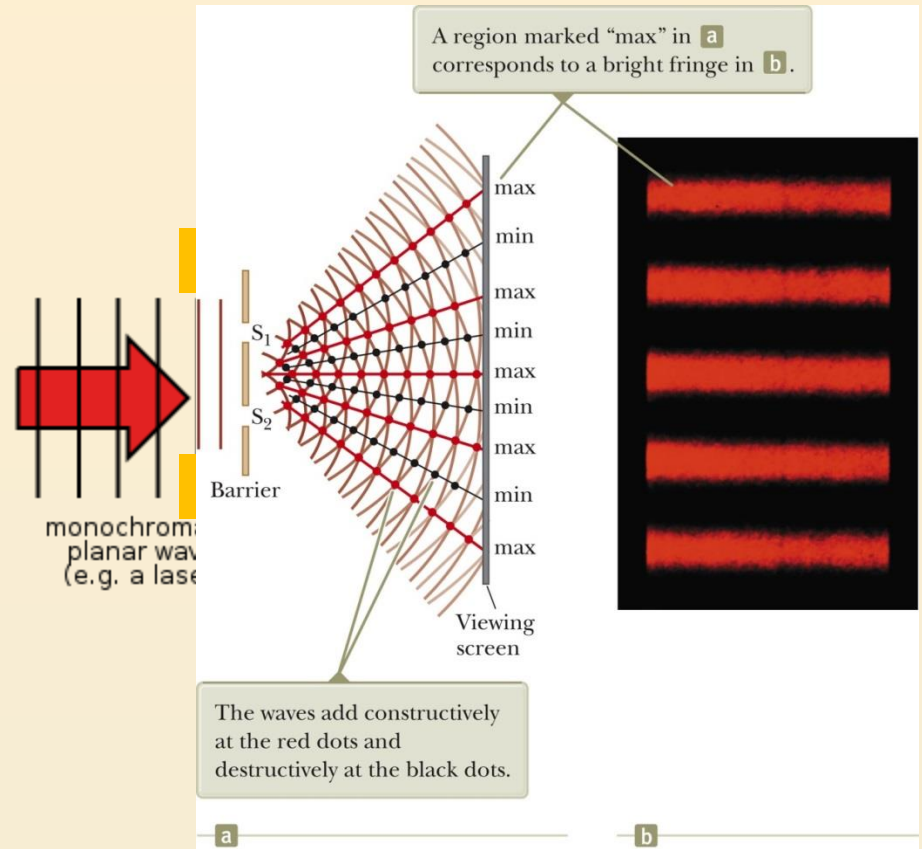
*From art  
to science*

*Materials science became a real science due to the development of modern analysis and imaging techniques.*

**Modern analysis** and imaging techniques become possible due to developments in the materials science .....

# Nature of light

- **Newton:** particles (*corpuscles*)
- **Huygens:** waves
- **Thomas Young** double slit experiment (1801)
- Path difference  $\Rightarrow$  phase difference
- Light consists of waves !
- Wave-particle duality



Schematic diagram of Young's double slit experiment. Slits  $S_1$  and  $S_2$  behave as coherent source of light waves that produce *interference pattern* on the viewing screen

See additional file **Interference of Light Waves** on my website

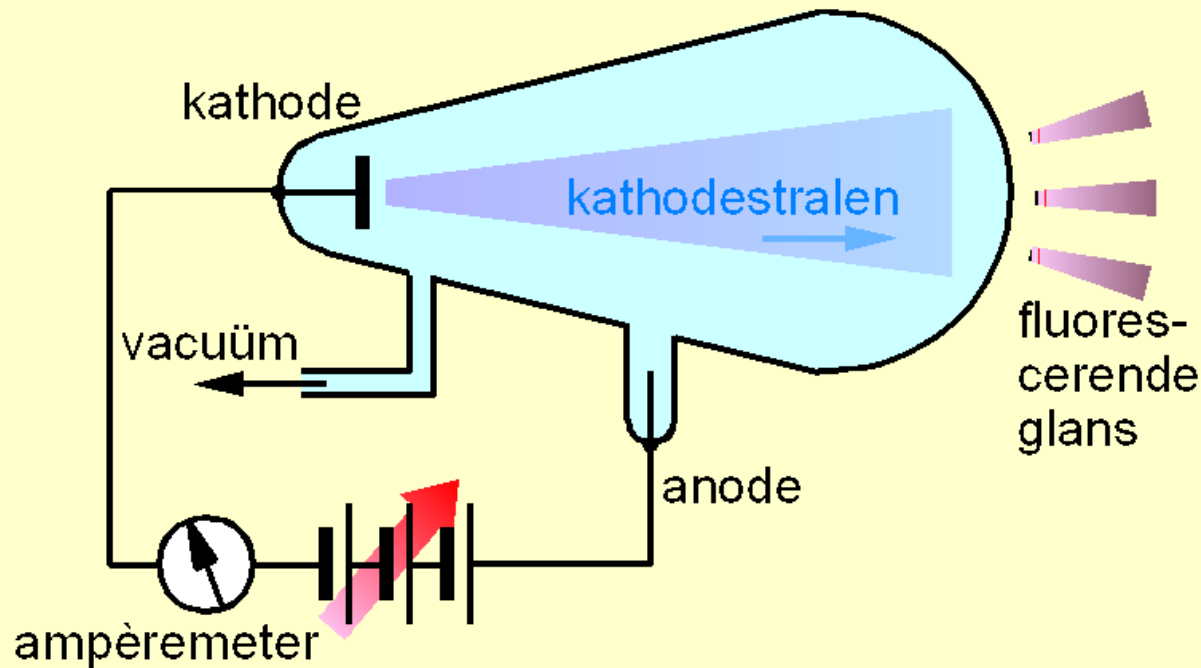
# Wilhelm Conrad Röntgen

Discovered the 'Röntgen' rays in 1895. Named these 'X-rays'.

**X-radiation** (composed of **X-rays**) is a form of **electromagnetic radiation**.

Most X-rays have a wavelength in the range of 0.01 to 10 nm, corresponding to frequencies in the range 30 petahertz to 30 exahertz ( $3 \times 10^{16}$  Hz to  $3 \times 10^{19}$  Hz) and energies in the range 100 eV to 100 keV.

*Invisible  
rays*



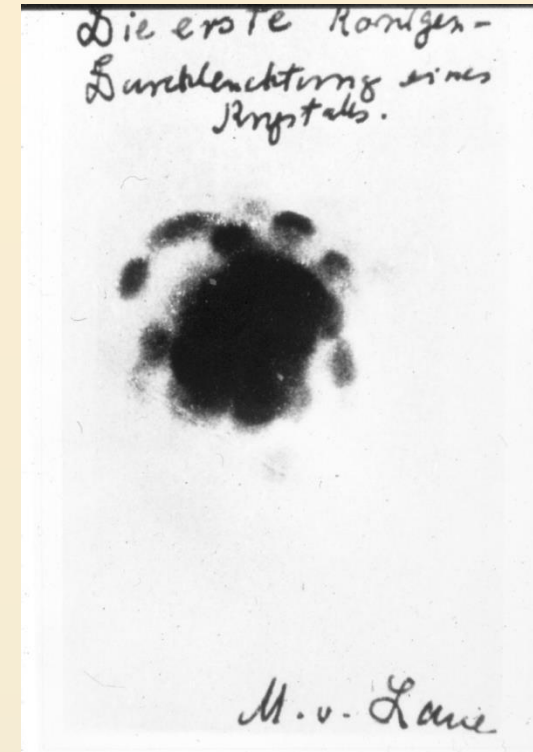
Nobel prize  
1901

Radiation went straight through a closed, black carton, hitting a fluorescent screen.



## Max von Laue

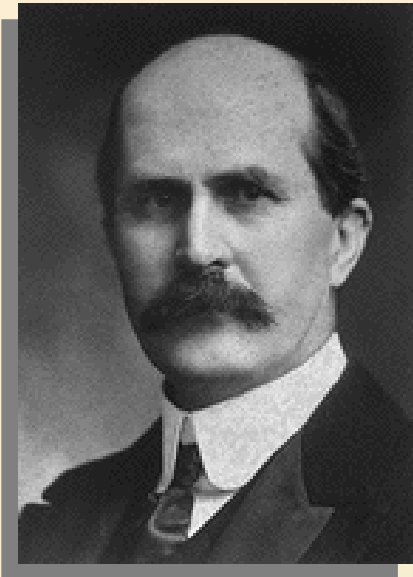
- The periodicity and interatomic spacing of crystals had been deduced earlier (e.g. Auguste Bravais).
- von Laue realized that if X-rays were waves with short wavelength, interference phenomena should be observed like in Young's double slit experiment.
- Experiment in 1912, Nobel Prize in 1914



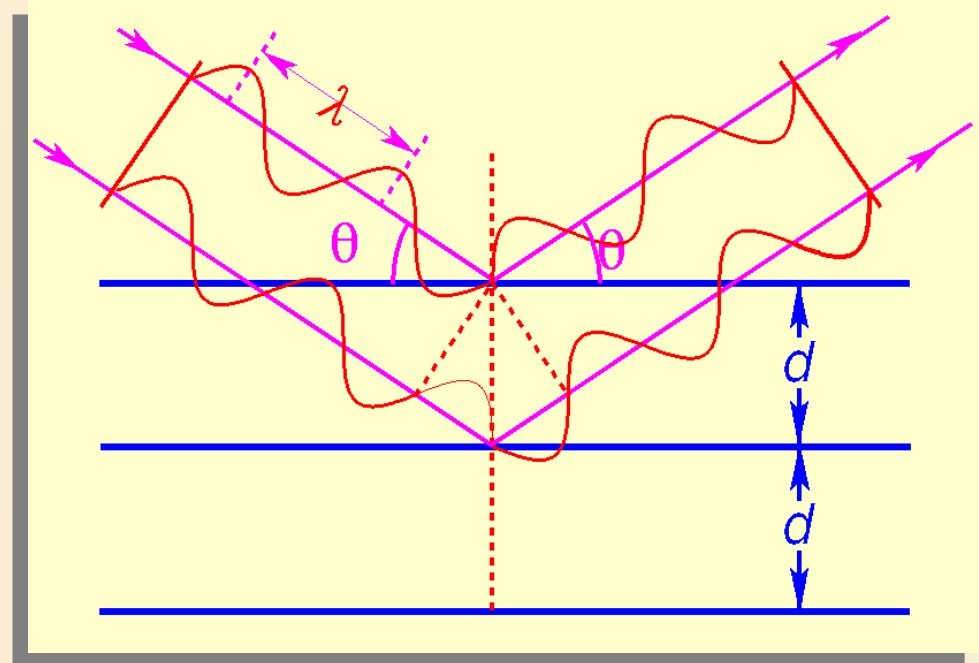
# Sir William Henry Bragg:

- William Henry and William Lawrence Bragg (father and son) found a simple interpretation of von Laue's experiment.
- They assume that each crystal plane reflects radiation as a mirror and analyze this situation for cases of constructive and destructive interference.

## *Bragg's law*



**Noble  
prize  
1915!**



Conditions for reflection:

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

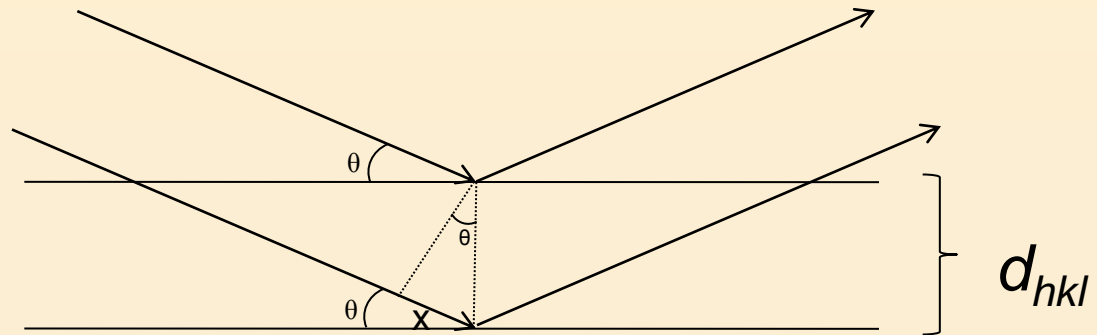
The most important thing in science is not so much to obtain new facts as to discover new ways of thinking about them.



# Derivation of Bragg's law

$$\sin(\theta) = \frac{x}{d_{hkl}}$$

$$\Rightarrow x = d_{hkl} \sin(\theta)$$



Path difference  $\Delta = 2x \Rightarrow$  phase shift

Constructive interference if  $\Delta = n\lambda$

This gives the criterion for constructive interference:

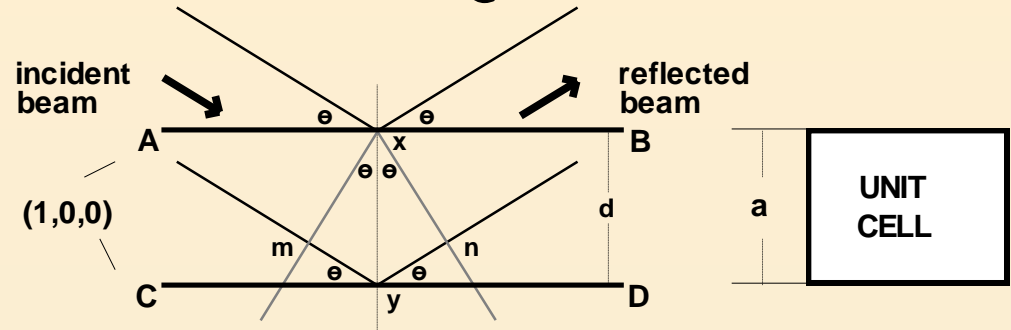
$$\Rightarrow \Delta = 2d_{hkl} \sin(\theta) = n\lambda$$

Bragg's law tells you at which angle  $\theta_B$  to expect maximum diffracted intensity for a particular family of crystal planes. For large crystals, all other angles give zero intensity.

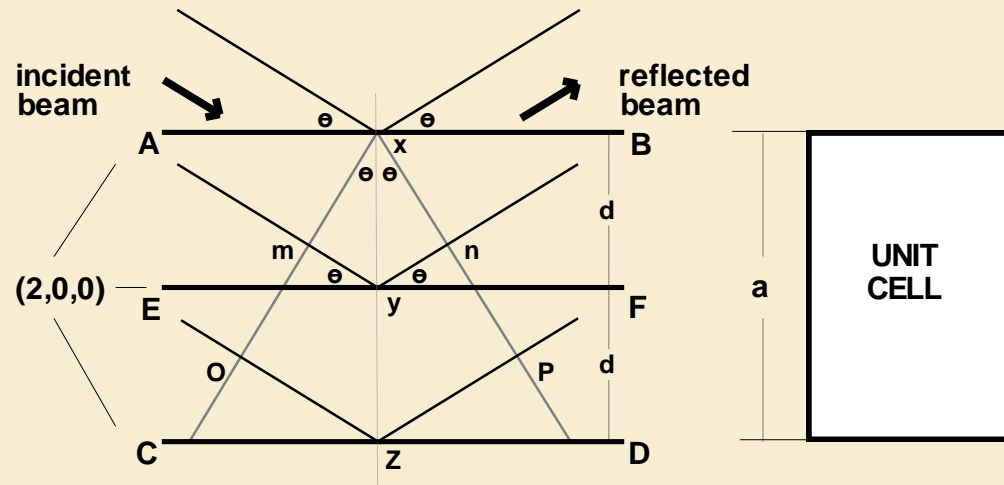
# Conclusions:

## DIFFRACTION AND THE BRAGG EQUATION

**Max von Laue** was the first to suggest that crystals might diffract X-rays and he also provided the first explanation for the diffraction observed. However, it is the explanation provided by Bragg that is simpler and more popular.



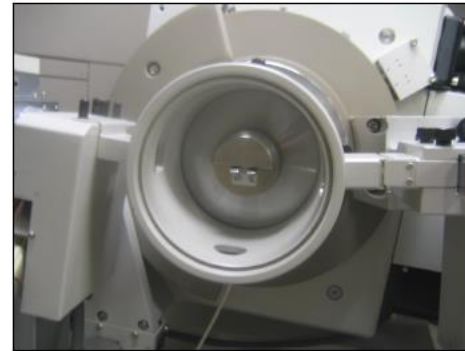
$$2d_{(1,0,0)} \sin \theta = \lambda \quad \text{This is a first order reflection}$$



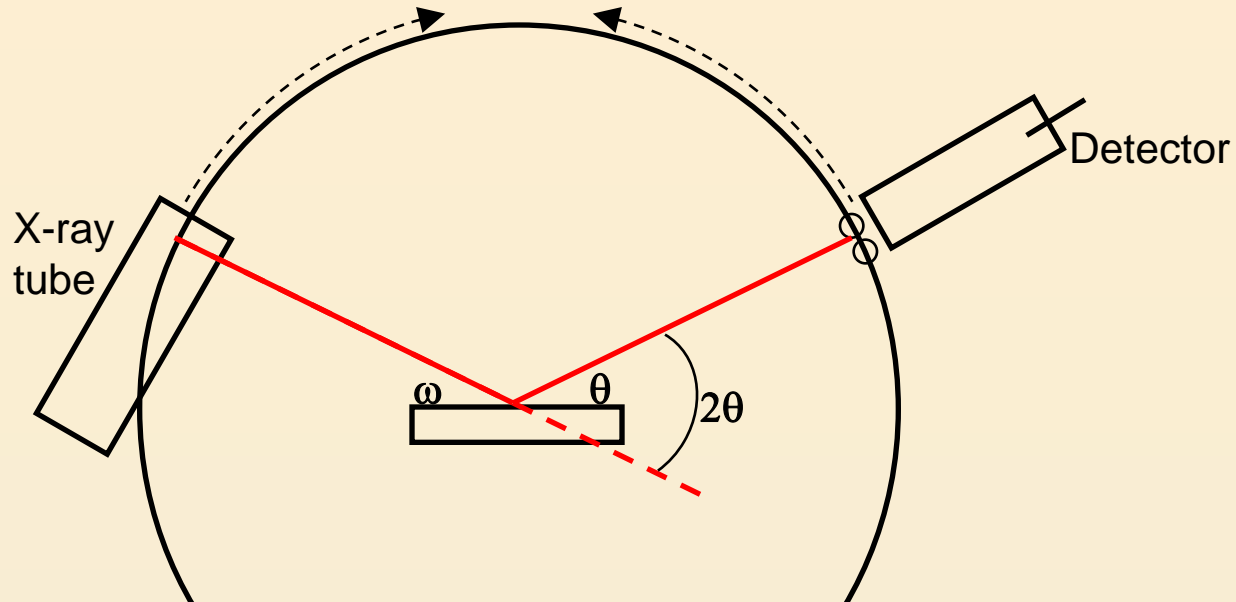
$$2d_{(1,0,0)} \sin \theta = 2\lambda \quad \text{This is a second order reflection}$$

In the **Bragg** view crystal planes act as mirrors. Constructive interference is observed when the path difference between the two reflected beams is  $n\lambda$ . The path difference is  $2d \sin \theta$ . Since  $\sin \theta = \frac{m}{d}$ ,  $2d \sin \theta = 2m$ .  $2m = n\lambda$  where d is the interplanar spacing.

# Typical View of X-ray Diffractometer



# The powder diffractometers typically use the Bragg-Brentano geometry

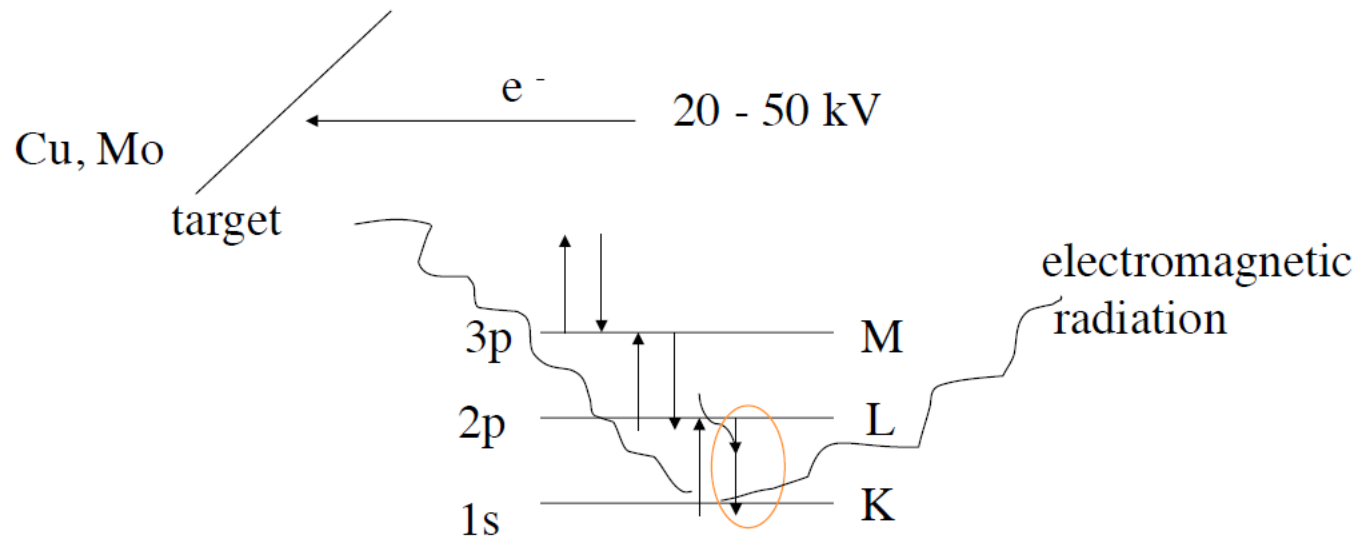


- The incident angle,  $\omega$ , is defined between the X-ray source and the sample.
- The diffracted angle,  $2\theta$ , is defined between the incident beam and the detector angle.
- The incident angle  $\omega$  is always  $\frac{1}{2}$  of the detector angle  $2\theta$ .
- In a  $\theta:2\theta$  instrument (e.g. Rigaku RU300), the tube is fixed, the sample rotates at  $\theta$  °/min and the detector rotates at  $2\theta$  °/min.
- In a  $\theta:\theta$  instrument (e.g. PANalytical X'Pert Pro), the sample is fixed and the tube rotates at a rate  $-\theta$  °/min and the detector rotates at a rate of  $\theta$  °/min.

## Production of X-rays

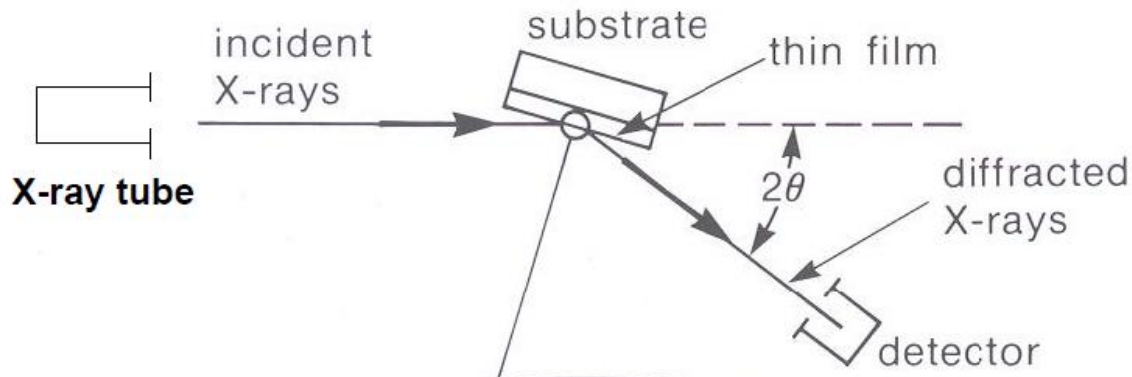
- ★ X-rays are produced by bombarding a metal target (Cu, Mo usually) with a beam of electrons emitted from a hot filament (often tungsten). The incident beam will ionize electrons from the K-shell (1s) of the target atom and X-rays are emitted as the resultant vacancies are filled by electrons dropping down from the L (2p) or M (3p) levels. This gives rise to  $K_a$  and  $K_b$  lines.

# X-rays



$\text{Cu } K_{\alpha} = 1.5418 \text{ \AA}$   
 $\text{Mo } K_{\alpha} = 0.7107 \text{ \AA}$

# Basic Features of Typical XRD Experiment

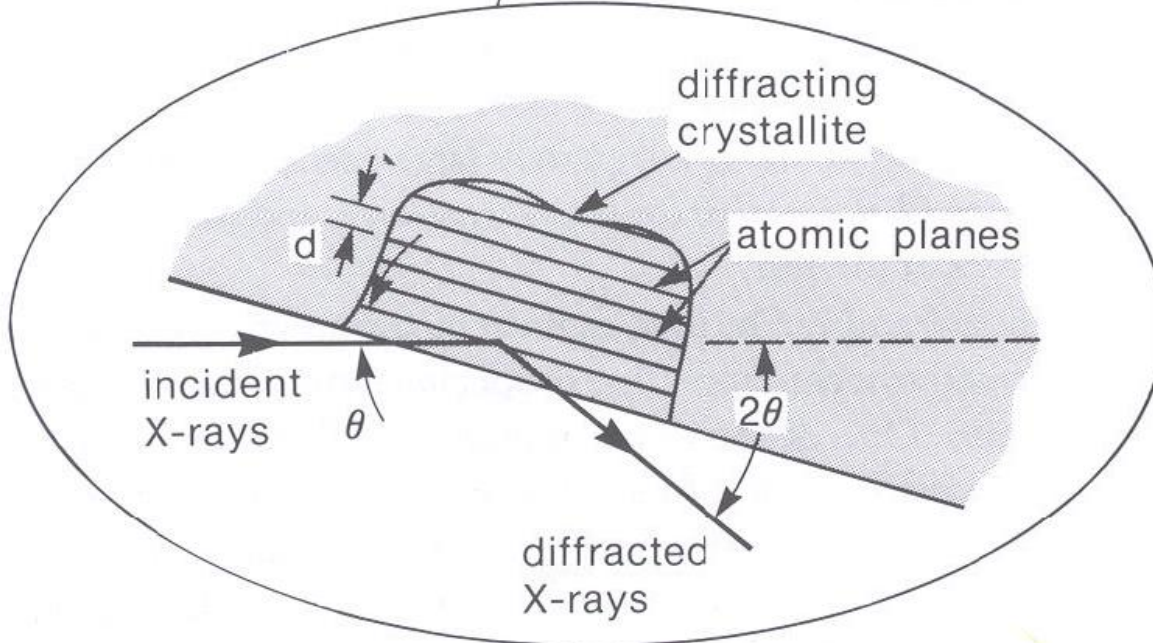


1) Production

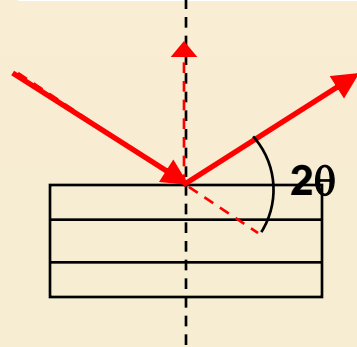
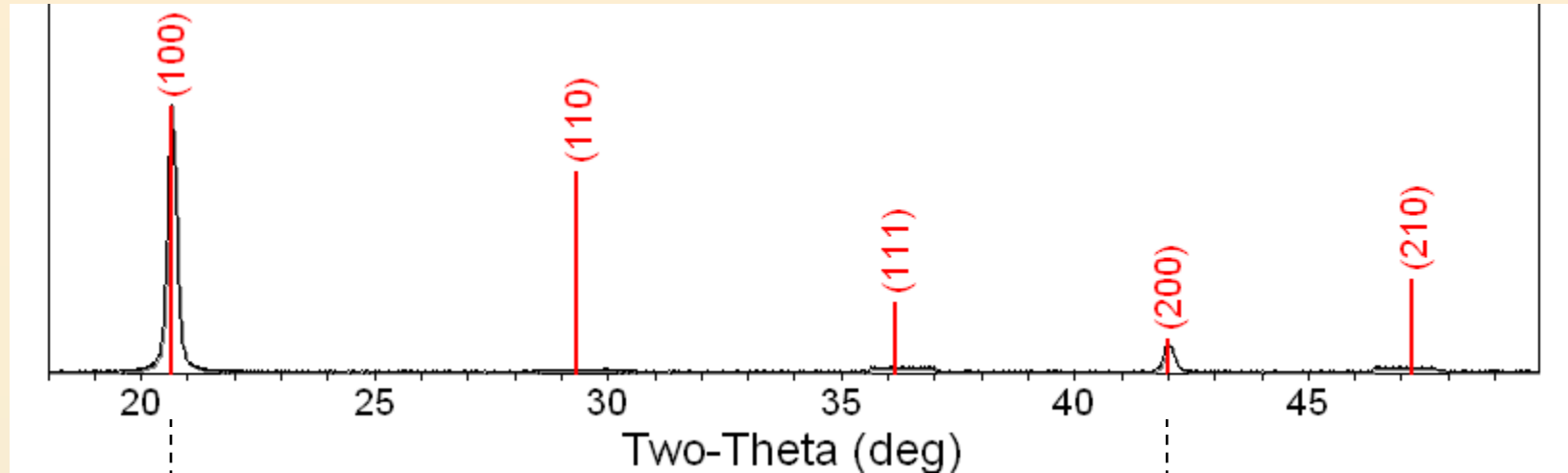
2) Diffraction

3) Detection

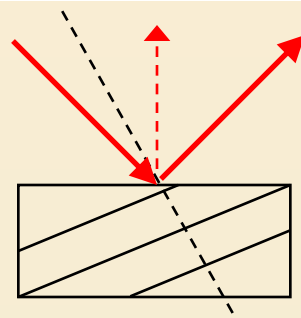
4) Interpretation



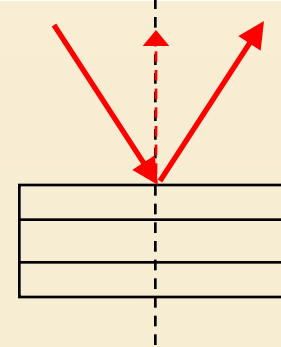
A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.



At  $20.6^\circ 2\theta$ , Bragg's law fulfilled for the (100) planes, producing a diffraction peak.



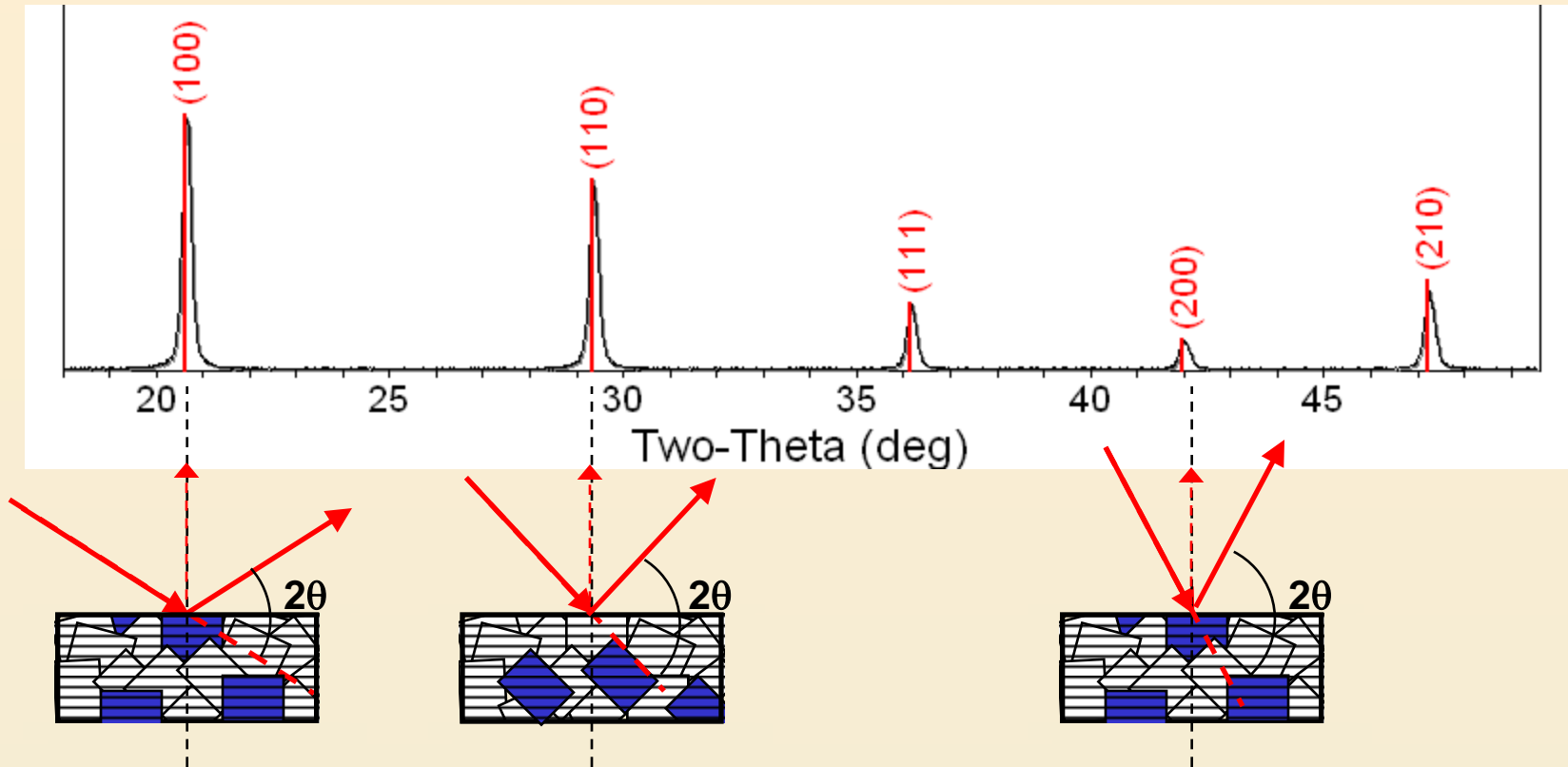
The (110) planes would diffract at  $29.3^\circ 2\theta$ ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.



The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since  $d_{200}$  is  $\frac{1}{2} d_{100}$ , they appear at  $42^\circ 2\theta$ .



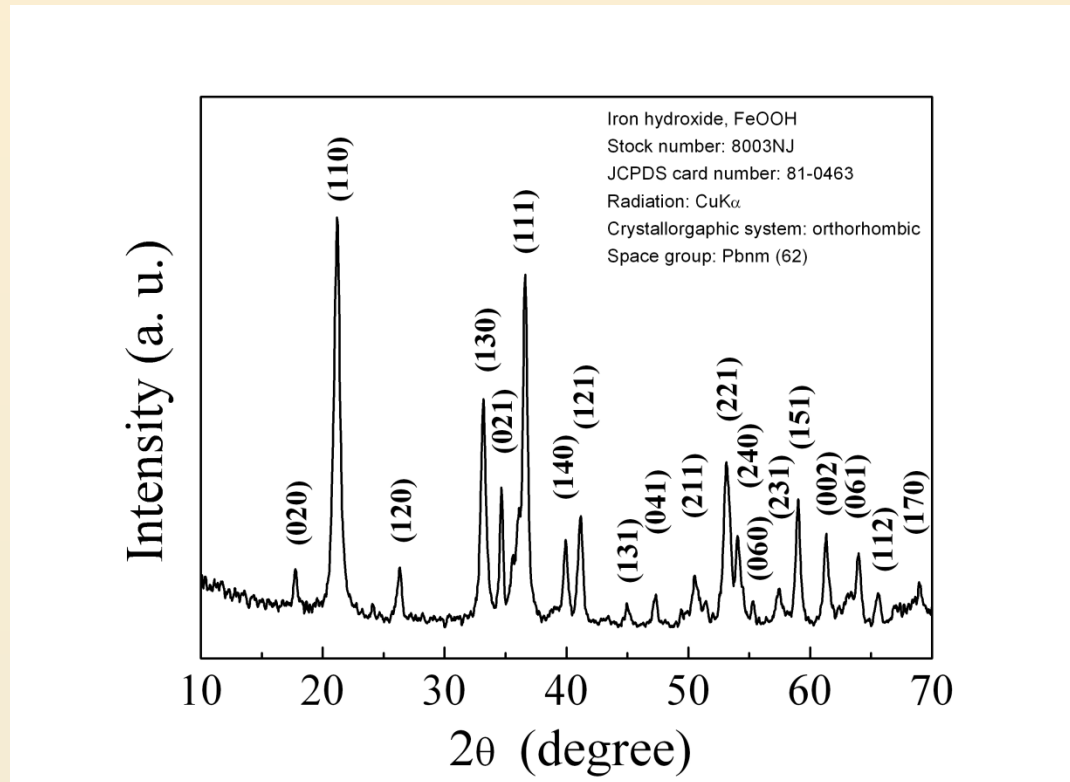
A polycrystalline sample should contain thousands of crystallites. Therefore, all possible diffraction peaks should be observed.



- For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).
- Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.

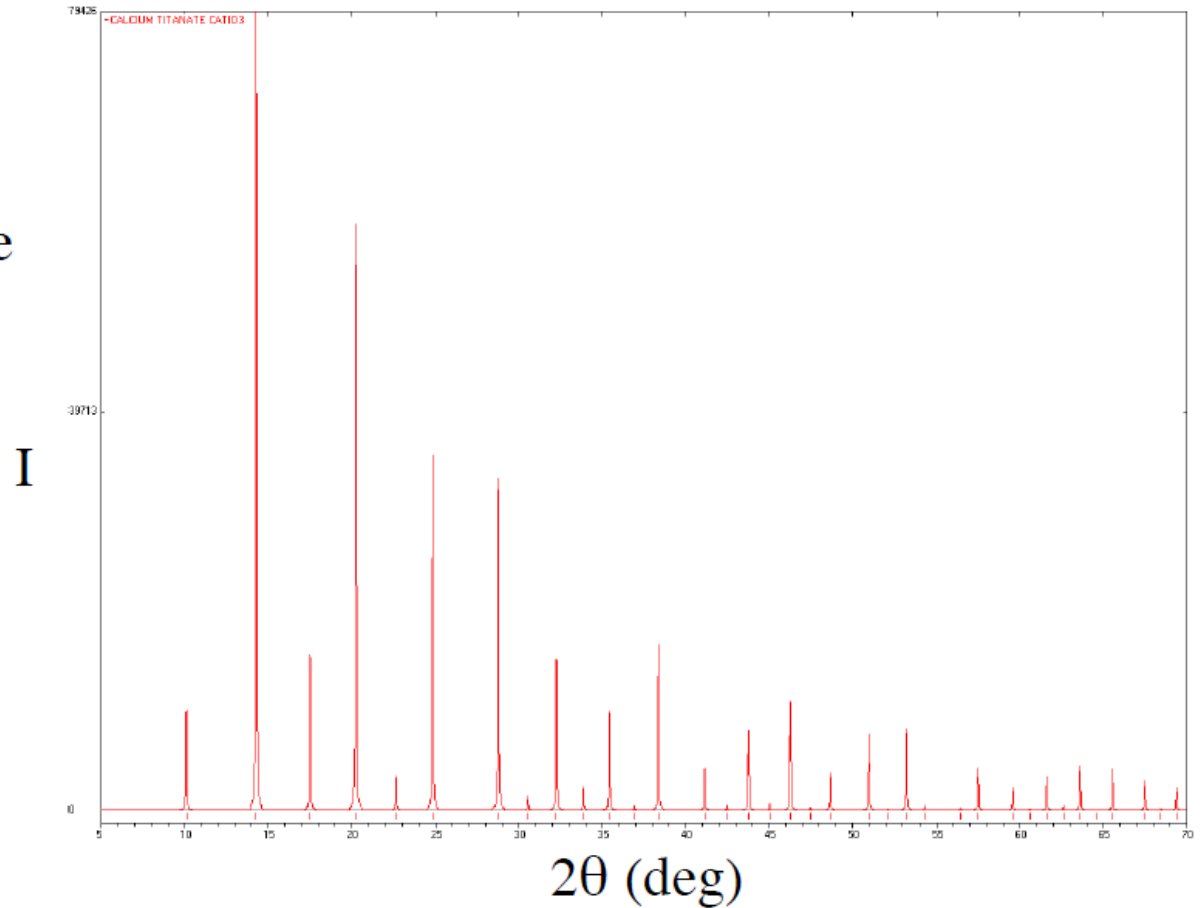
# Example: Diffraction Patterns

- Each peak represents the solution to Bragg's law for known radiation wavelength ( $\lambda = 0.154\text{nm}$ )
- The unique relationship between such patterns and crystal structures provide a powerful tool for identification of the phase composition of powders and polycrystalline materials.



# Diffraction pattern

- Intensity (I) is the total area under a peak



## d-spacing in different crystal systems

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- ★ Cubic  $\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$
- ★ Tetragonal  $\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
- ★ Orthorhombic  $\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
- ★ Hexagonal  $\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$
- ★ Monoclinic  $\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$
- ★ Triclinic -  $\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$

## Powder Preparation

- ★ It needs to be a powder
- ★ It needs to be a pure powder
- ★ Its nice to have about 1/2 g of sample, but one can work with less
- ★ The powder needs to be packed tightly in the sample holder. Loose powders will give poor intensities.

## Data Collection

- ★ The scattering intensity drops as  $1/2(1+\cos^2 2\theta)$
- ★ This means that you don't get much intensity past  $70^\circ 2\theta$ . A good range is  $10-70^\circ 2\theta$ .
- ★ How long should you collect (time per step)?
- ★ Depends on what you want to do!
  - ★ Routine analysis may only take 30-60 min.
  - ★ Data for Rietveld analysis may take 12-18 hours to collect

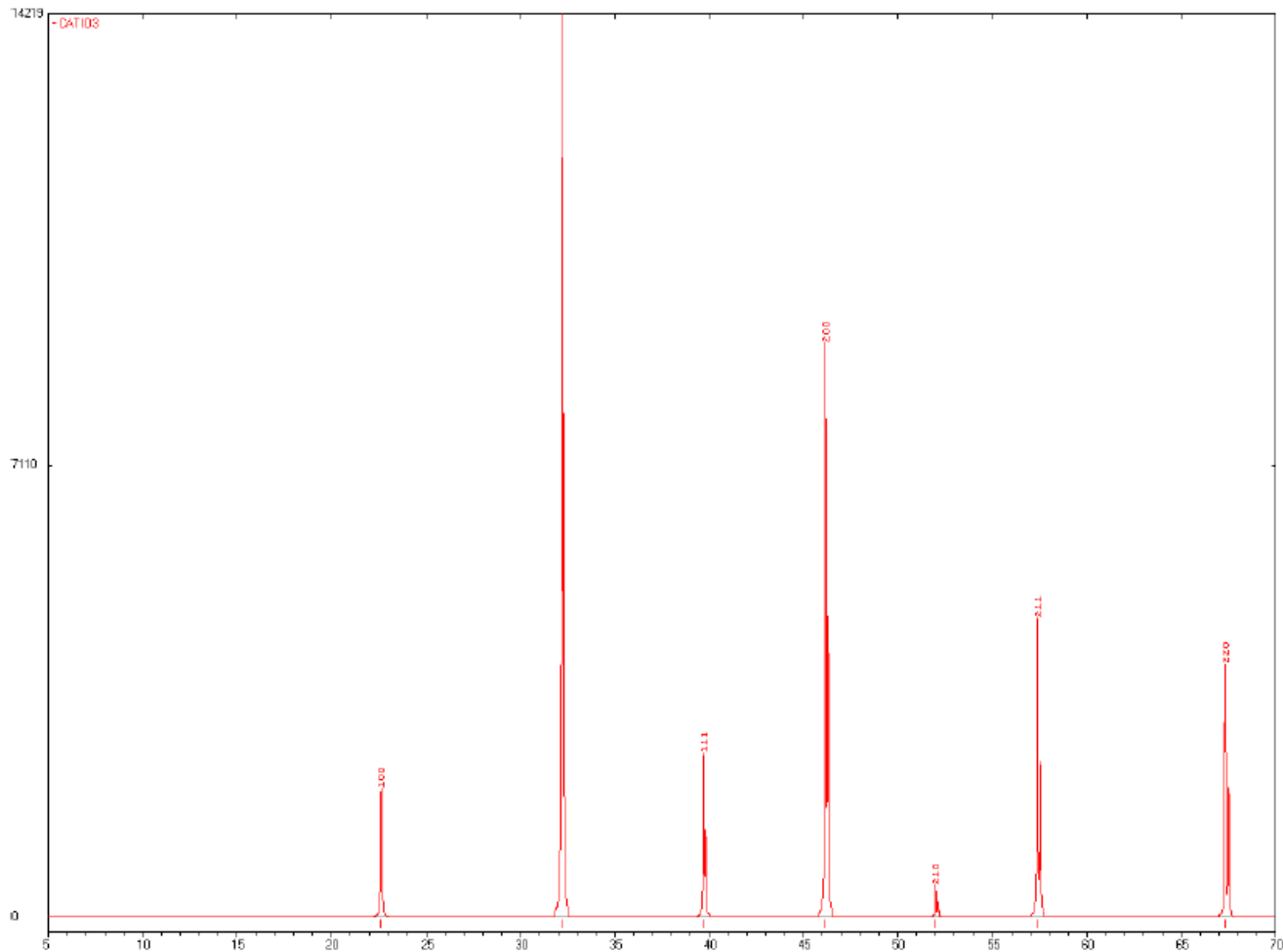
# Indexing Patterns

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- ★ Indexing is the process of determining the unit cell dimensions from the peak positions
  - ★ Manual indexing (time consuming...but still useful)
  - ★ Pattern matching/auto indexing (JADE or other computer based indexing software)

# Cubic pattern

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# Relationship between diffraction peaks, miller indices and lattice spacings

Simple cubic material  $a = 5.0 \text{ \AA}$

hkl	d(Å)	2 $\Theta$
100	5.00	17.72
110	3.54	25.15
111	2.89	30.94

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

Bragg Equation:  $n\lambda = 2d\sin\theta$

How many lattice planes are possible?

How many d-spacings? The number is large but finite.

$n\lambda = 2d\sin\theta$  so if  $\theta = 180$ , then  $d = \lambda/2$ . For Cu radiation that means that we can only see d-spacings down to  $0.77 \text{ \AA}$  for Mo radiation, down to about  $0.35 \text{ \AA}$



# Structure Factor

The general expression for :

$$F \equiv \sum_{n=1}^N f_n e^{2\pi i(hu_n + kv_n + lw_n)}$$

Now we apply this to various crystals. First, consider examples of crystals with a basis group of just one atom per lattice point, with atomic scattering factor  $f$ . The results are valid *for any crystal system*.

## Primitive Cells

This is really simple!  $N = 1$ , so

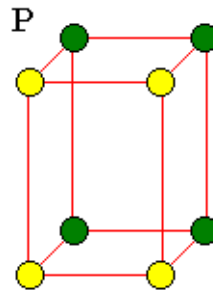
$$F \equiv \sum_{n=1}^N f_n e^{2\pi i(hu_n + kv_n + lw_n)} = f e^{2\pi i(hu + kv + lw)}$$

Define the position of the cell so that our atom is at  $uvw = 000$ ; then  $(hu + kv + lw) = 0$ , and we get just

$$F = f e^{2\pi i(0)} = f$$

so

$$F = f$$



# ***Basis and Bravais Structure Factor Terms***

$$F = \sum_{n=1}^{N_p} e^{2\pi i \mathbf{g} \cdot \mathbf{r}_n} \sum_{m=1}^{N_b} f_m e^{2\pi i \mathbf{g} \cdot \mathbf{r}_m} = F_{BR} F_{BA}$$

The following simple table giving the integer values of  $F_{BR}$  for the different types of centering translations. Keep in mind that these are valid for any crystal system.

Centering type	Missing Reflections ( $F_{BR} = 0$ )	Possible Reflections ( $F_{BR} \neq 0$ )	Bravais Term $F_{BR}$ for possible reflections
P (primitive)	None	All	1
I (body-centered)	( $h + k + l$ ) odd	( $h + k + l$ ) even	2
A (base-centered on A face)	( $k + l$ ) odd	( $k + l$ ) even	2
B (base-centered on B face)	( $h + l$ ) odd	( $h + l$ ) even	2
C (base-centered on C face)	( $h + k$ ) odd	( $h + k$ ) even	2
F (face-centered)	hkl mixed	hkl unmixed	4

# What Information Do We Get or Can We Get From Powder X-ray Diffraction

- ★ Lattice parameters
- ★ Phase identity
- ★ Phase purity
- ★ Crystallinity
- ★ Crystal structure
- ★ Percent phase composition

# What Information Do We NOT Get From Powder X-ray Diffraction

- ★ Elemental analysis -
  - ★ How much lithium is in this sample?
  - ★ Is there iron in this sample
  - ★ What elements are in this sample
- ★ Tell me what this sample is ????
  - ★ Unless you know something about this sample, powder XRD won't have answers !!!

# Summary

**X-rays are electromagnetic radiation of wavelength about 1 Å ( $10^{-10}$  m), which is about the same size as an atom.**

The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. X-ray diffraction has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a "fingerprint" for its identification. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle are etc. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science.

We can determine the size and the shape of the unit cell for any compound most easily using X-ray diffraction.