X-ray Diffraction Techniques (XRD)

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What is crystallography?

- the study of macroscopic crystal forms
- “Crystal”: has been usually defined in terms of the structure and symmetry of these forms.
- Modern crystallography has been redefined by x-ray diffraction. By the study of atomic arrangements in crystalline materials
- The definition of a crystal has become that of Buerger (1956): “a region of matter within which the atoms are arranged in a three-dimensional translational periodic pattern.”
- This orderly arrangement in a crystalline material is known as the crystal structure.
- X-ray crystallography is disturbed with discover and describing this structure (using diffraction as a tool).
- Automatic processing of diffraction data often effectively distances the analyst from the crystallographic

What Crystallographic Principles are most important to understand?

- lattice description, unit cells, lattice planes, d-spacing and Miller indices,
- crystal structure and symmetry elements,
- the joint lattice

Description of Crystal Structure

- Three-dimensional pattern (groups of atoms or molecules) is the “core” constant unit
- The pattern is repeated in space by movement operations – translation, rotation and reflection
- Crystal structures are “created” in a two-step process:
  - Point-group operations create the pattern
  - Translation operation produce the crystal structure
- “Infinite” repetition is necessary for XRD to determine the structure

The Lattice

- Lattice: is "an imaginary pattern of points (or nodes) in which every point (node) has a location that is the same to that of any other point (node) in the pattern. A lattice has no particular origin, as it can be shifted parallel to itself." (Klein, 2002)

- The lattice must be described in terms of 3-dimensional coordinates related to the translation directions. Lattice points, Miller indices, Lattice planes (and the "d-spacing" between them) are conventions that facilitate description of the lattice.

- Although it is an imaginary construct, the lattice is used to describe the structure of real materials.

$\bar{1}$

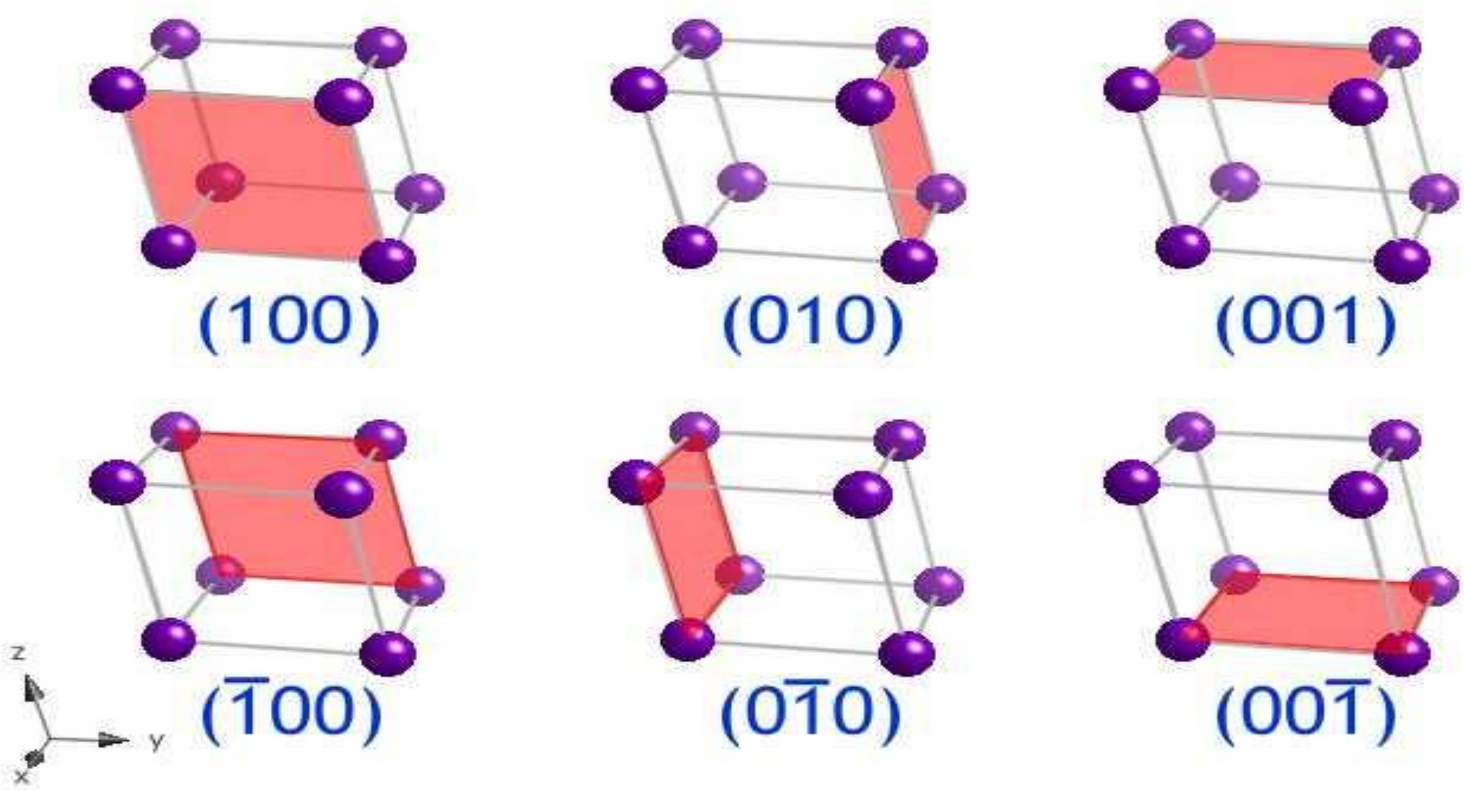
Symmetry Operations

- Crystal structure is "created" by replicating a 3-d pattern with a variety of replication (or movement) operations:
    - Rotation (symbols R: **1,2,3,4,6** = n of times form is repeated in a 360º rotation)
    - Reflection (symbol: **m** Form replicated across a mirror plane)
    - Inversion (symbol: ***i***. Form replicated by projection through a point of inversion)

$\bar{1}$

    - Rotation-inversion (symbol: $\bar{1}$ for single rotation with inversion. $\bar{3}$ for 3-fold rotation w. inversion at each rotation)

Miller indices(hkl): form a notation system in crystallography for planes in crystal (Bravais) lattices. In particular, a family of lattice planes is determined by three integers *h*, *k*, and *ℓ*, the *Miller indices*



X-RAY

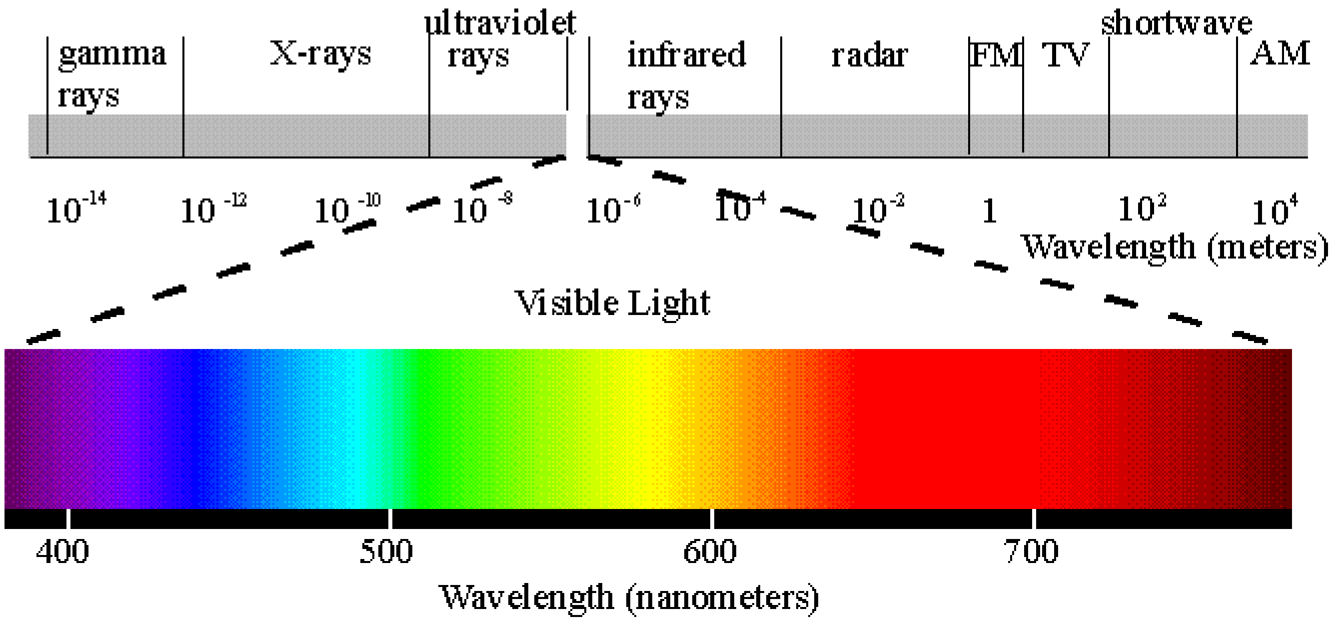
- X-rays were discovered in 1895 by the German physicist (Wilhelm Conrad Röntgen) and were so named because their nature was unknown at the time.

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

Wilhelm Conrad Röntgen
(1845-1923)

X-RAY properties

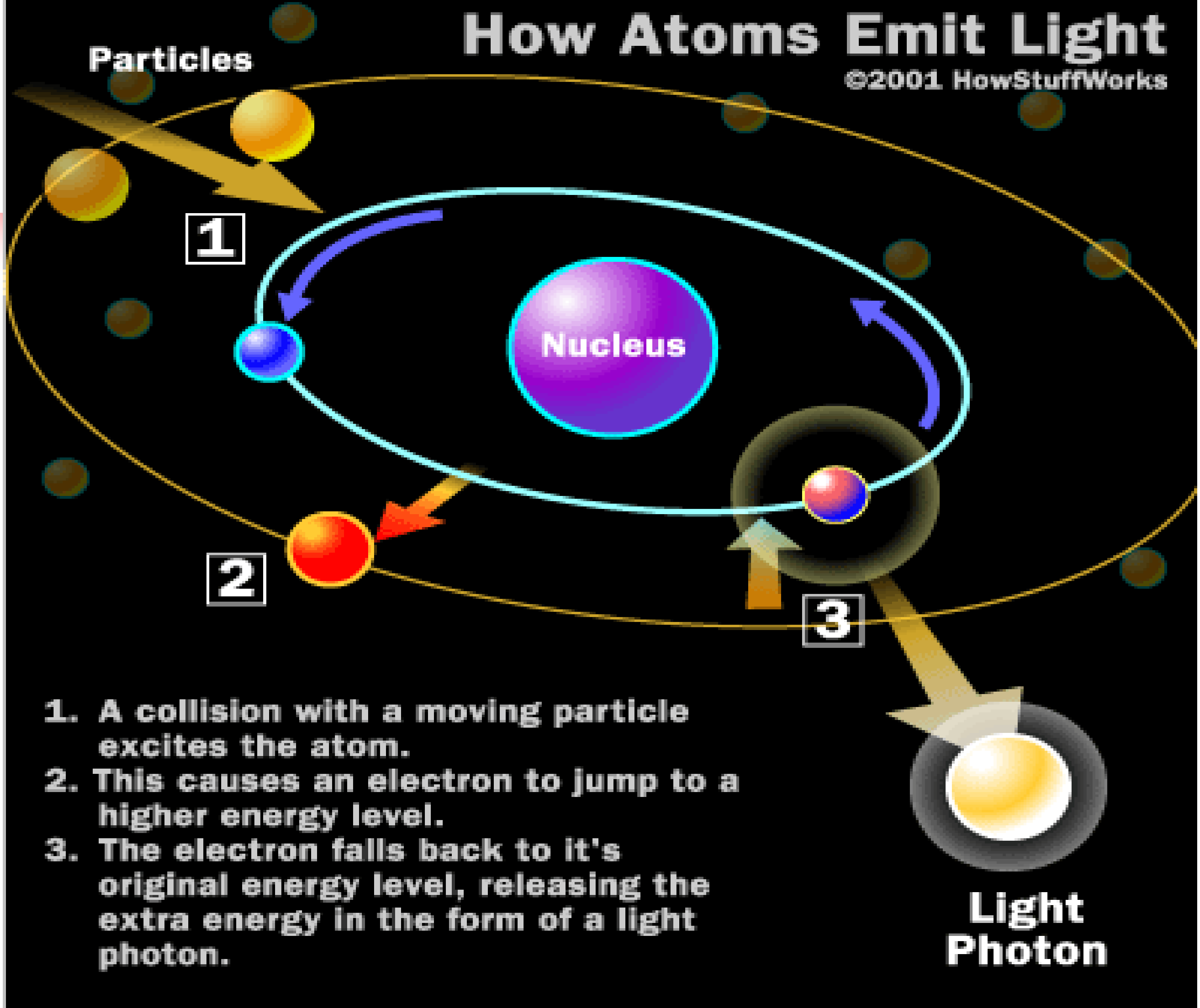
X ray, invisible, highly penetrating electromagnetic radiation of much shorter wavelength (higher frequency) than visible light. The wavelength range for X rays is from about 10^{-8} m to about 10^{-11} m, the corresponding frequency range is from about 3×10^{16} Hz to about 3×10^{19} Hz.



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

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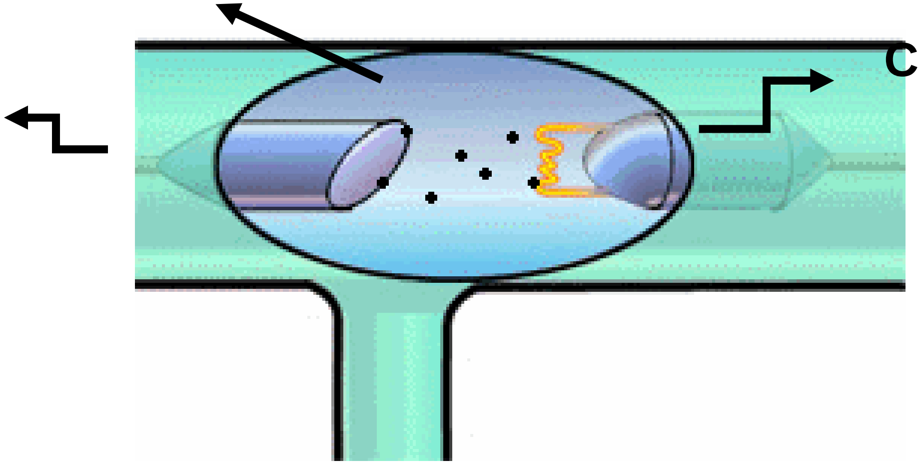
1. A collision with a moving particle excites the atom.
2. This causes an electron to jump to a higher energy level.
3. The electron falls back to it's original energy level, releasing the extra energy in the form of a light photon.

X-RAY TUBE

- X rays can be produced in a highly empty glass tuber,bulk, called an X-ray tube, that contains really 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.



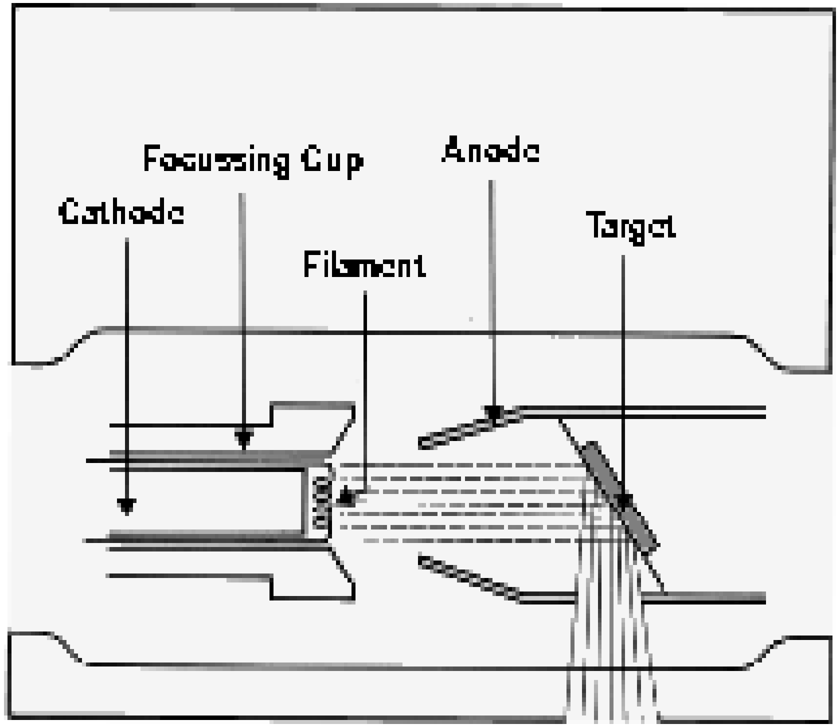
Evacuated glass bulb

Anode

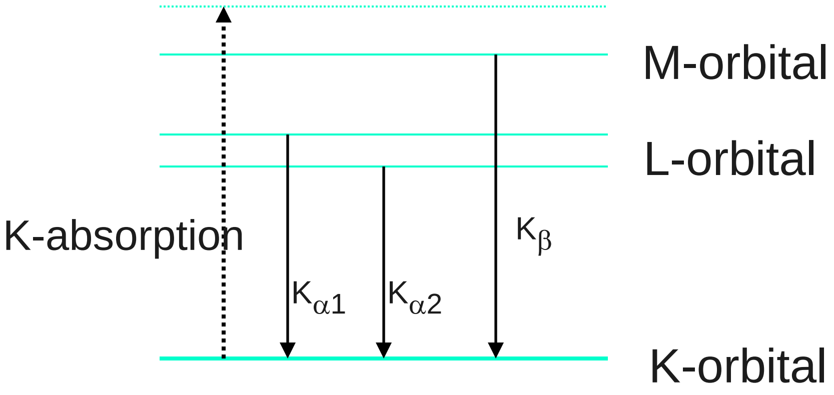
Cathode

X-ray Sources for Crystallographic Studies

Home Source – Rotating Anode



X-Ray Tube



M-orbital

L-orbital

K-absorption

K_β

$K_{\alpha 1}$ $K_{\alpha 2}$

K-orbital

Wave-lengths

Cu($K_{\alpha 1}$)= 1.54015 Å

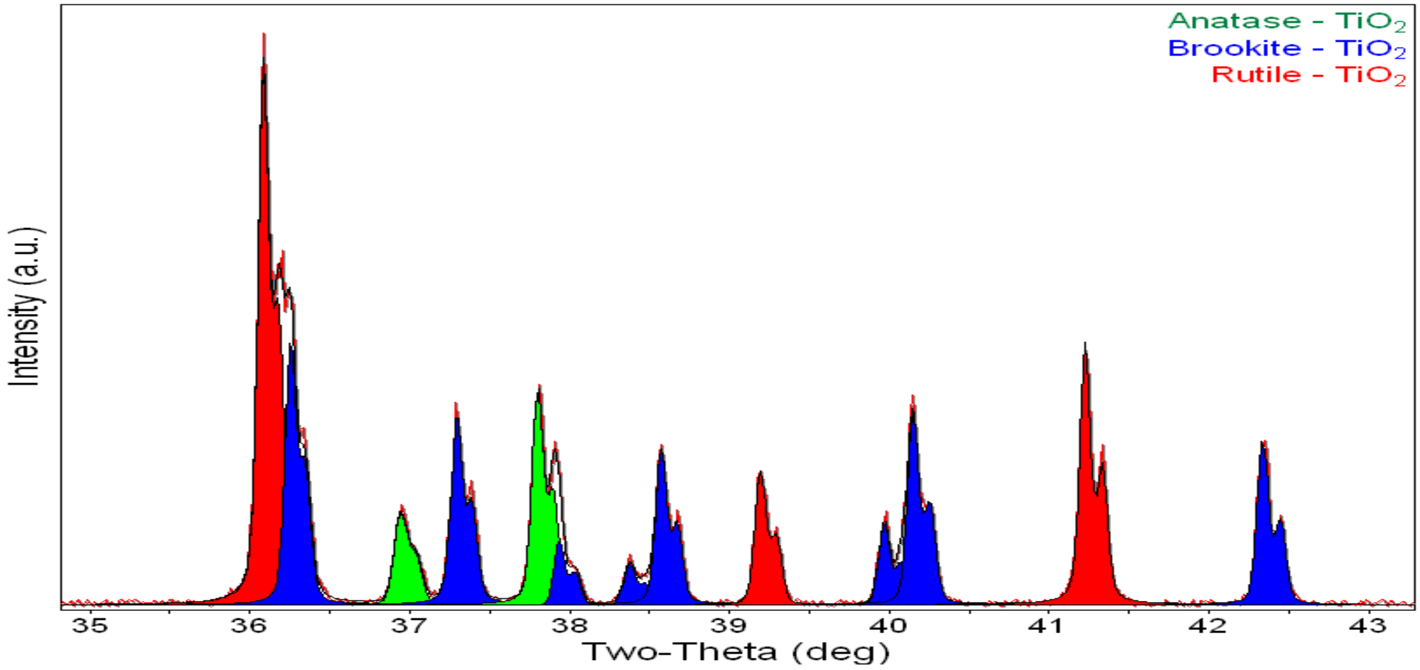
Cu($K_{\alpha 2}$)= 1.54433 Å

Cu(K_{α})= 1.54015 Å

Cu(K_{β})= 1.39317 Å

X-Ray Powder Diffraction (XRPD) uses information about the position, intensity, width, and shape of diffraction peaks in a pattern from a polycrystalline sample.

The x-axis, 2theta, corresponds to the angular position of the detector that rotates around the sample.



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.

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.

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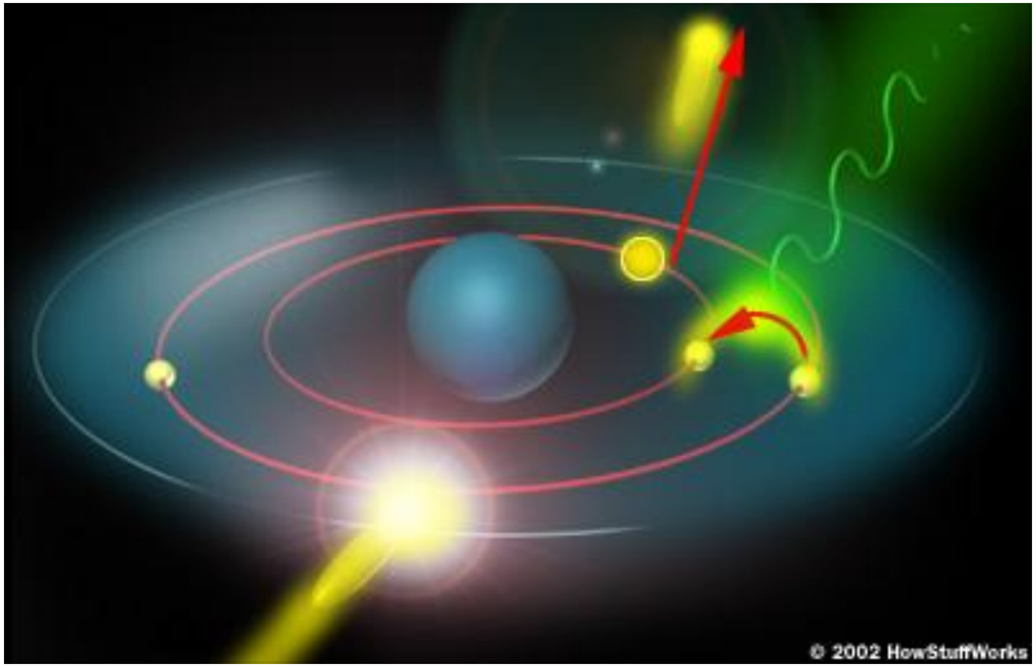
X-ray

Generation of X-rays (K-Shell)

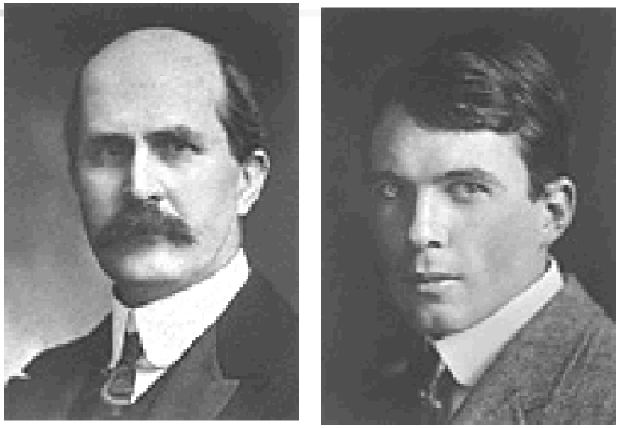
An electron in a higher orbital immediately falls to the lower energy level, releasing its extra energy in the form of a photon. It's a big drop, so the photon has a high energy level; it is an X-ray photon.



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.

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 distinguished 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

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

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

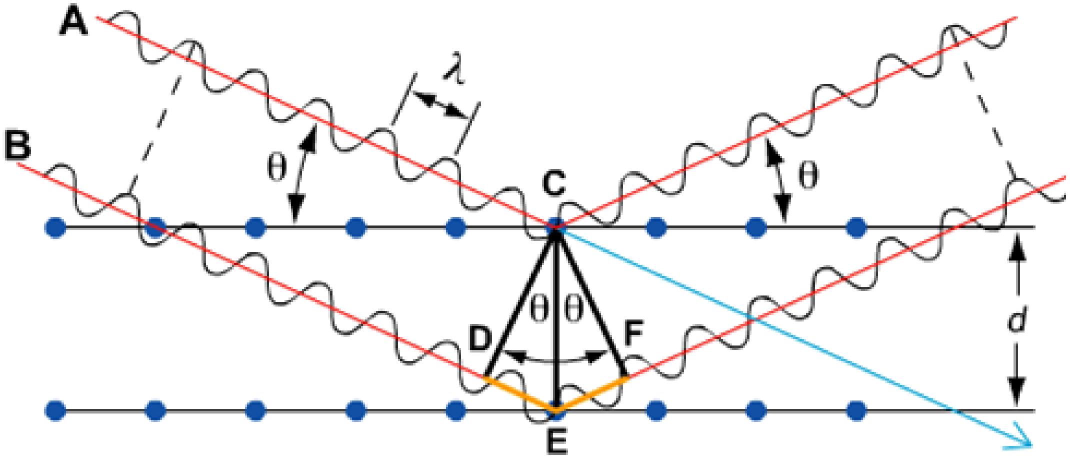
- Bragg reflection can only occur for wavelength

$$n\lambda \le 2d$$

- 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.

Bragg Law

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



$$EF = d \sin\theta$$

$$DE = d \sin\theta$$

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

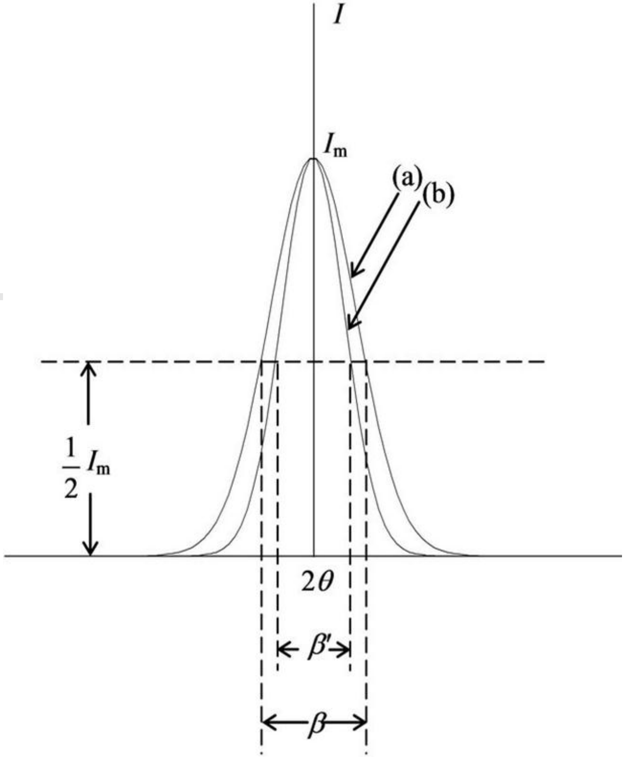
$$\boxed{n\lambda = 2d \sin\theta}$$

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

SCHERRER EQUATION

The **Scherrer equation** ,in X-ray diffraction and crystallography ,is a formula that
The Scherrer equation can be written as:

$$\tau = \frac{\kappa\lambda}{\beta \cos\theta}$$



where:

τ =is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size;

K= is a dimensionless **shape factor** ,with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite;

λ= is the X-ray wavelength;

β= is the line broadening at half the maximum intensity) FWHM ,(after subtracting the instrumental line broadening, in radians .This quantity is also sometimes denoted as $\Delta(2\theta)$,,,,Θ =is the Bragg angle.

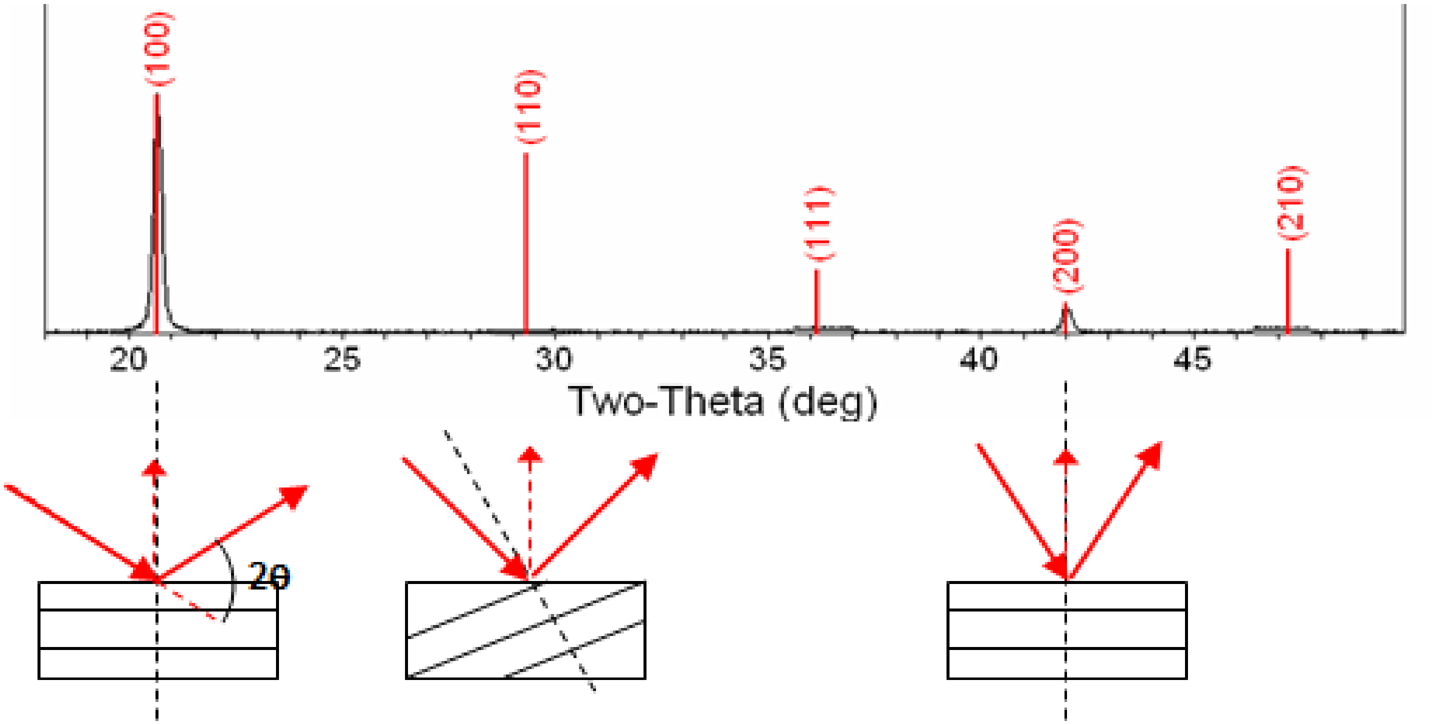
Applicability

[The Scherrer equation is limited to nano-scale particles. It is not applicable to grains larger than about 0.1 to 0.2 μm, which precludes those observed in most metallographic and ceramographic microstructures.

It is important to realize that the Scherrer formula provides a lower bound on the particle size. The reason for this is that a variety of factors can contribute to the width of a diffraction peak besides instrumental effects and crystallite size; the most important of these are usually inhomogeneous strain and crystal lattice imperfections. The following sources of peak broadening are listed in reference:dislocations, stacking faults, twinning, microstresses, grain boundaries, sub-boundaries, coherency strain, chemical heterogeneities, and crystallite smallness. (Some of the those and other imperfections may also result in peak shift, peak asymmetry, anisotropic peak broadening, or affect peak shape.)

If all of these other contributions to the peak width were zero, then the peak width would be determined solely by the crystallite size and the Scherrer formula would apply. If the other contributions to the width are non-zero, then the crystallite size can be larger than that predicted by the Scherrer formula, with the "extra" peak width coming from the other factors. The concept of crystallinity can be used to collectively describe the effect of crystal size and imperfections on peak broadening.

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

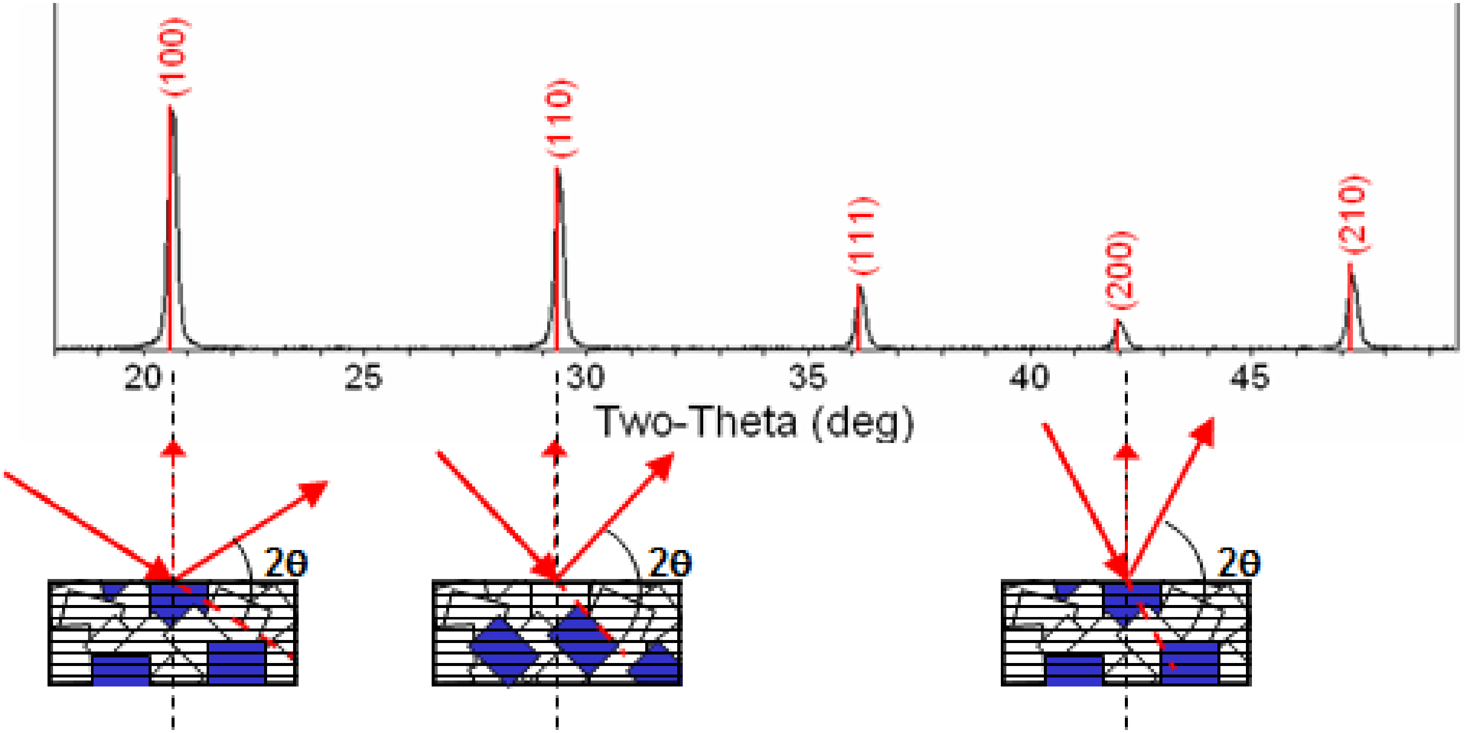


At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.

The (110) planes would diffract at 29.3 °2θ; 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 ½ d_{100}, they appear at 42 °2θ.

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.

- Bragg's equation is a negative law
  - If Bragg's eq. is NOT satisfied → NO reflection can occur
  - If Bragg's eq. is satisfied → reflection *MAY* occur
- Diffraction = Reinforced Coherent Scattering

Reflection versus Scattering

Reflection	Diffraction
Occurs from surface	Occurs throughout the bulk
Takes place at any angle	Takes place only at Bragg angles
~100 % of the intensity may be reflected	Small fraction of intensity is diffracted

X-rays can be reflected at very small angles of incidence

Summary:

Which information does a powder pattern offer?

peak position → dimension of the simple cell

peak intensity → content of the simple cell

peak broadening → strain/crystallite size

scaling factor→ quantitative phase amount

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

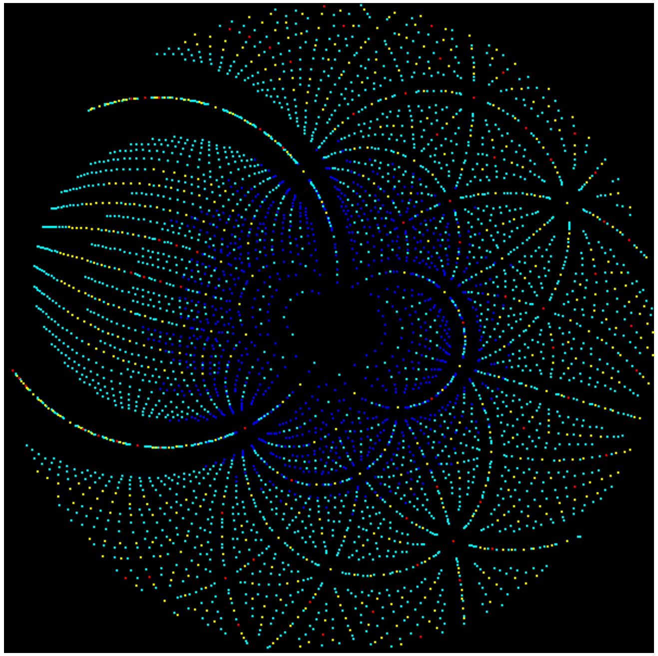
X-RAY DIFFRACTION METHODS

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

1- LAUE METHOD

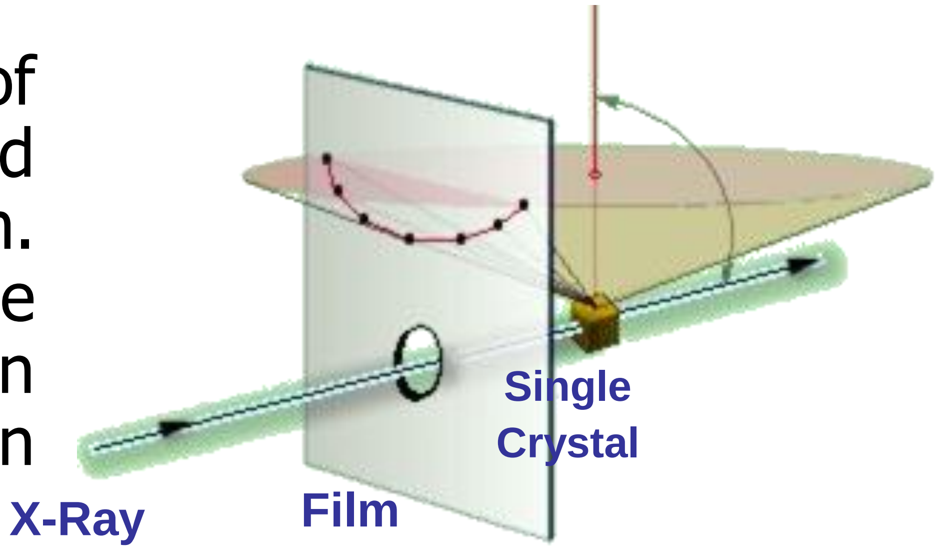
- The Laue method is mainly used to determine the orientation of large single crystals while radiation is reflected from, or transmitted through a fixed crystal.
- The diffracted beams form arrays of spots, that lie on curves on the film.
- The Bragg angle is fixed for every set of planes in the crystal. 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.



A-Back-reflection Laue Method

- the film is placed **between** the (x-ray source) and (the crystal). The beams which are diffracted in a backward direction are recorded.

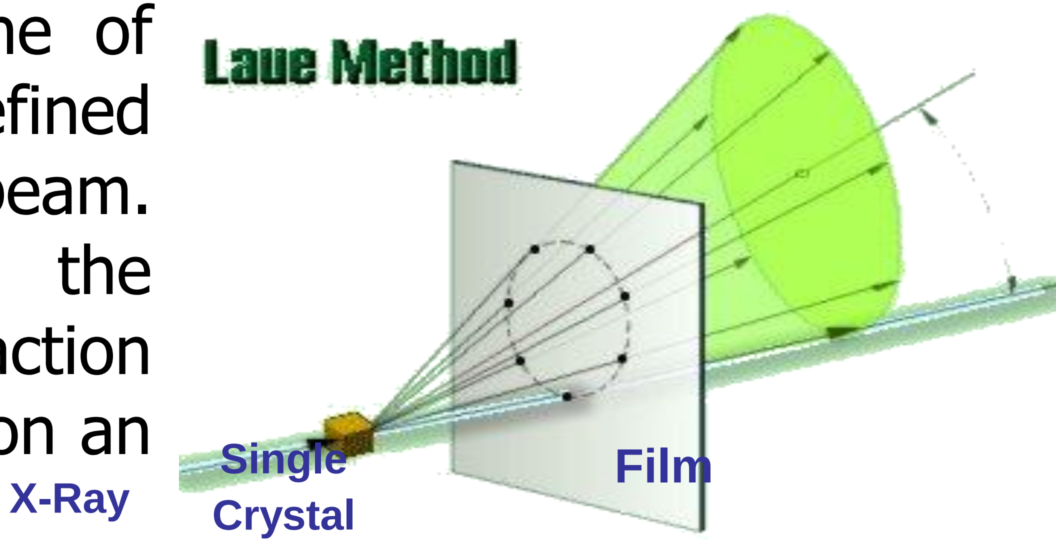
- One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an hyperbola.



B-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.



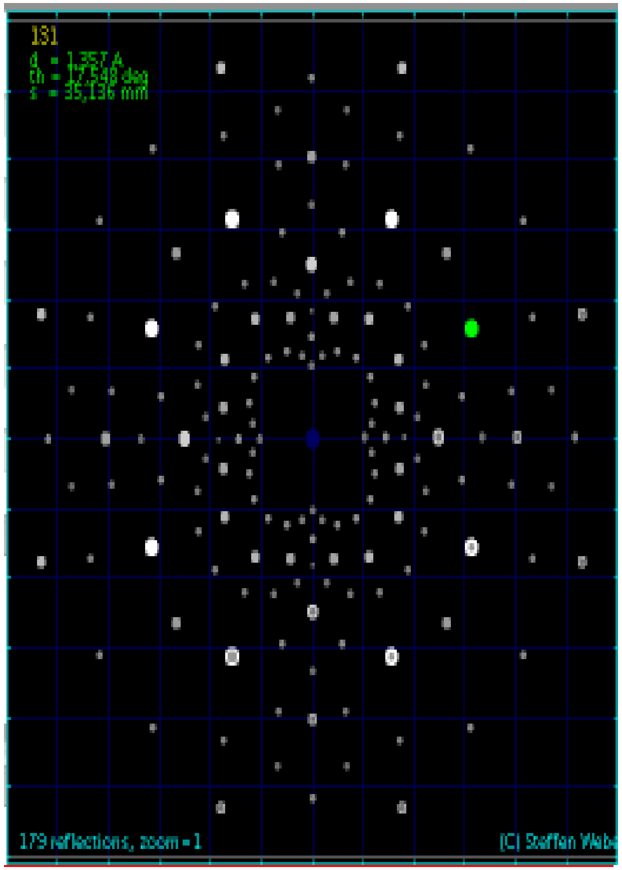
C-Laue Pattern

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.

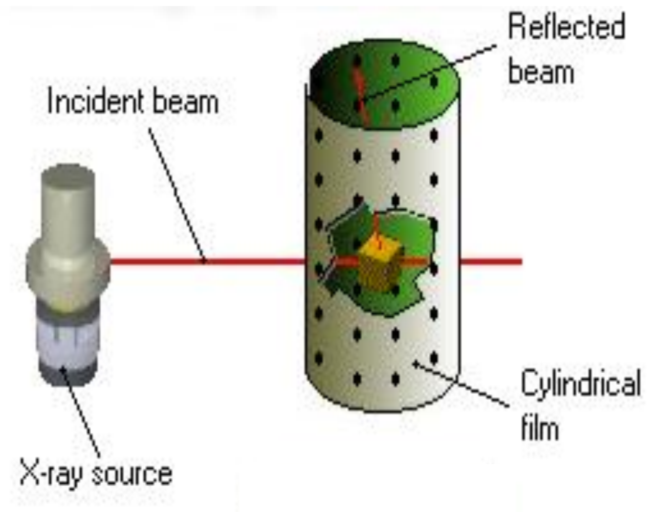
Although the Laue method can also be used to determine the crystal structure, several wavelengths can reflect in different orders from the same set of planes, with the different order reflections superimposed on the same spot in the film.

This makes crystal structure determination by spot intensity diffucult.

so Rotating crystal method overcomes this problem. How?

2- 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.

3- 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

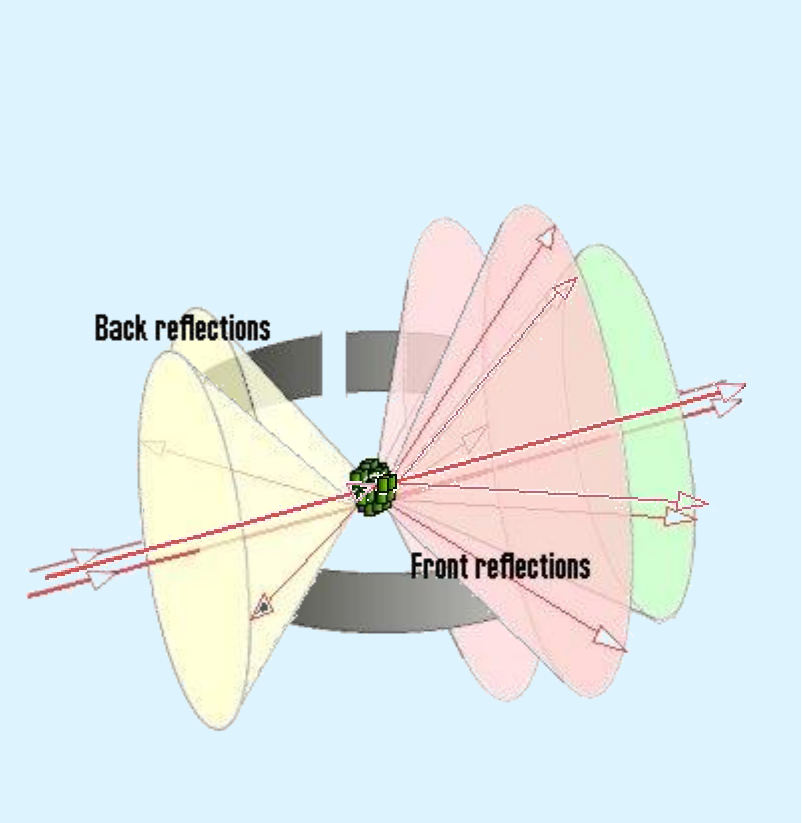
The powder method is used to determine the value of the lattice parameters accurately. Lattice parameters are the magnitudes of the unit vectors **a**, **b** and **c** which define the unit cell for the crystal.

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 able 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

- 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.

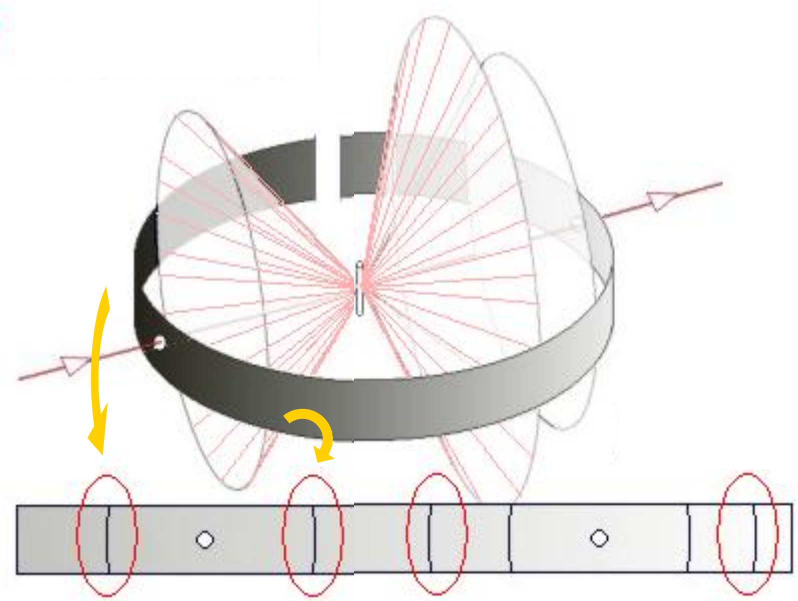
If the sample consists of some tens of randomly orientated single crystals, the diffracted beams are seen to lie on the surface of several cones. The cones may emerge in all directions, forwards and backwards.



Debye Scherrer Camera

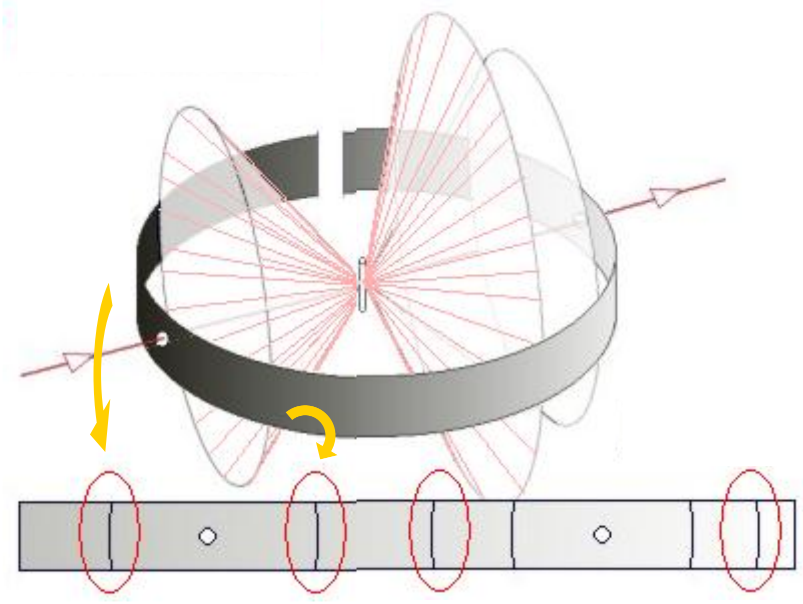
A very small amount of powdered material is conserved into a fine tube tube made from glass that does not diffract x-rays.

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.



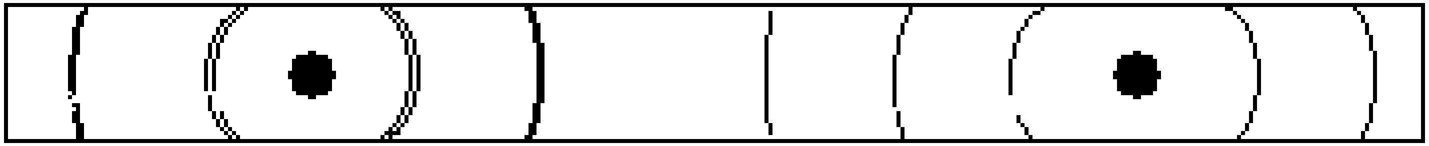
Debye Scherrer Camera

The powder diffracts the x-rays in accordance with Braggs law to produce cones of diffracted beams. These cones intersect a band 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, compressed 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 surface of polygrained materials;
6. Measurement of strain and small grain size…..etc

Advantages and disadvantages of X-rays

Advantages;

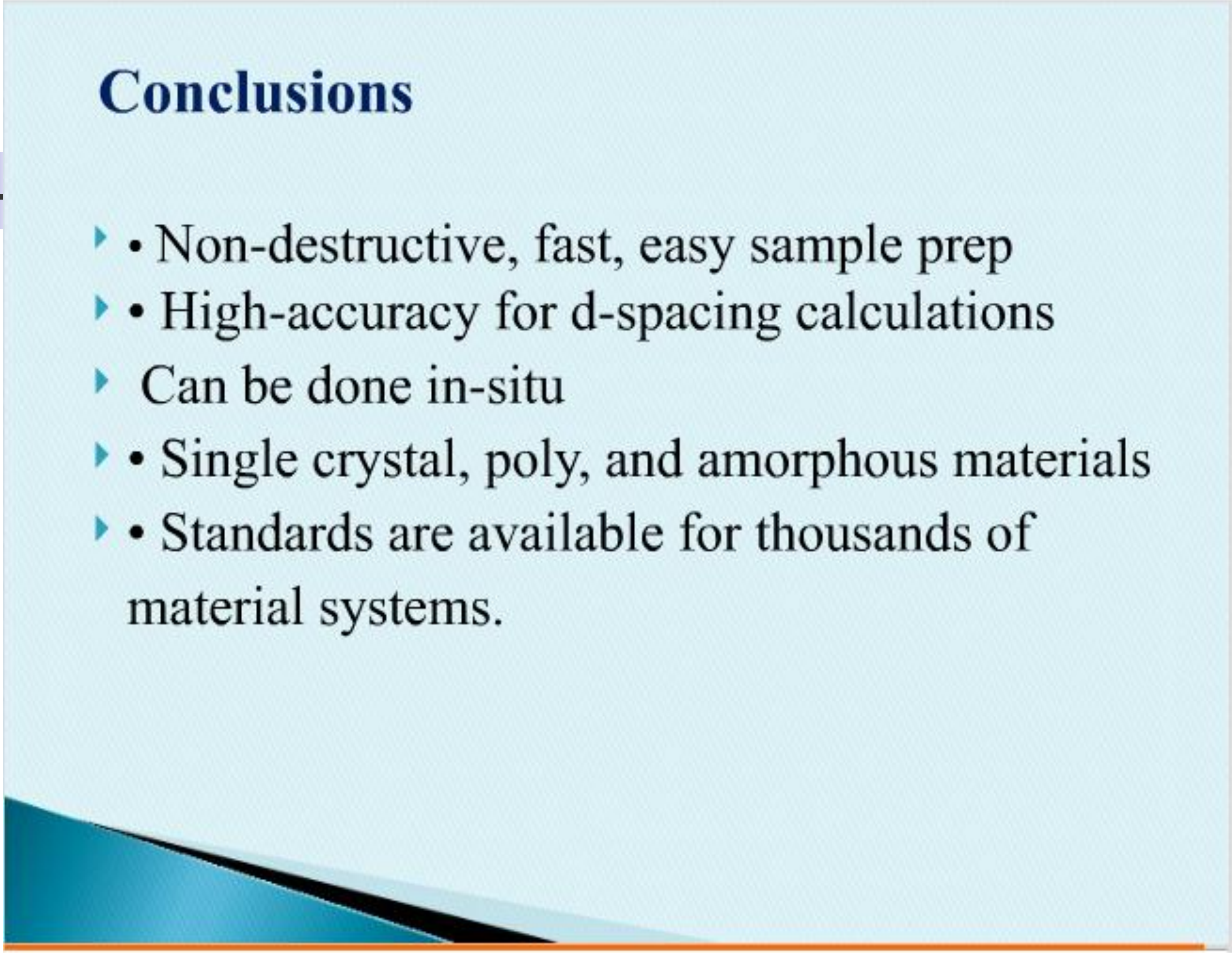
- X-ray is the cheapest, the most convenient and widely used method.
- X-rays are not absorbed very much by air, so the specimen need not be in an evacuated chamber.

Disadvantage;

- They do not interact very strongly with lighter elements(have small atomic number).

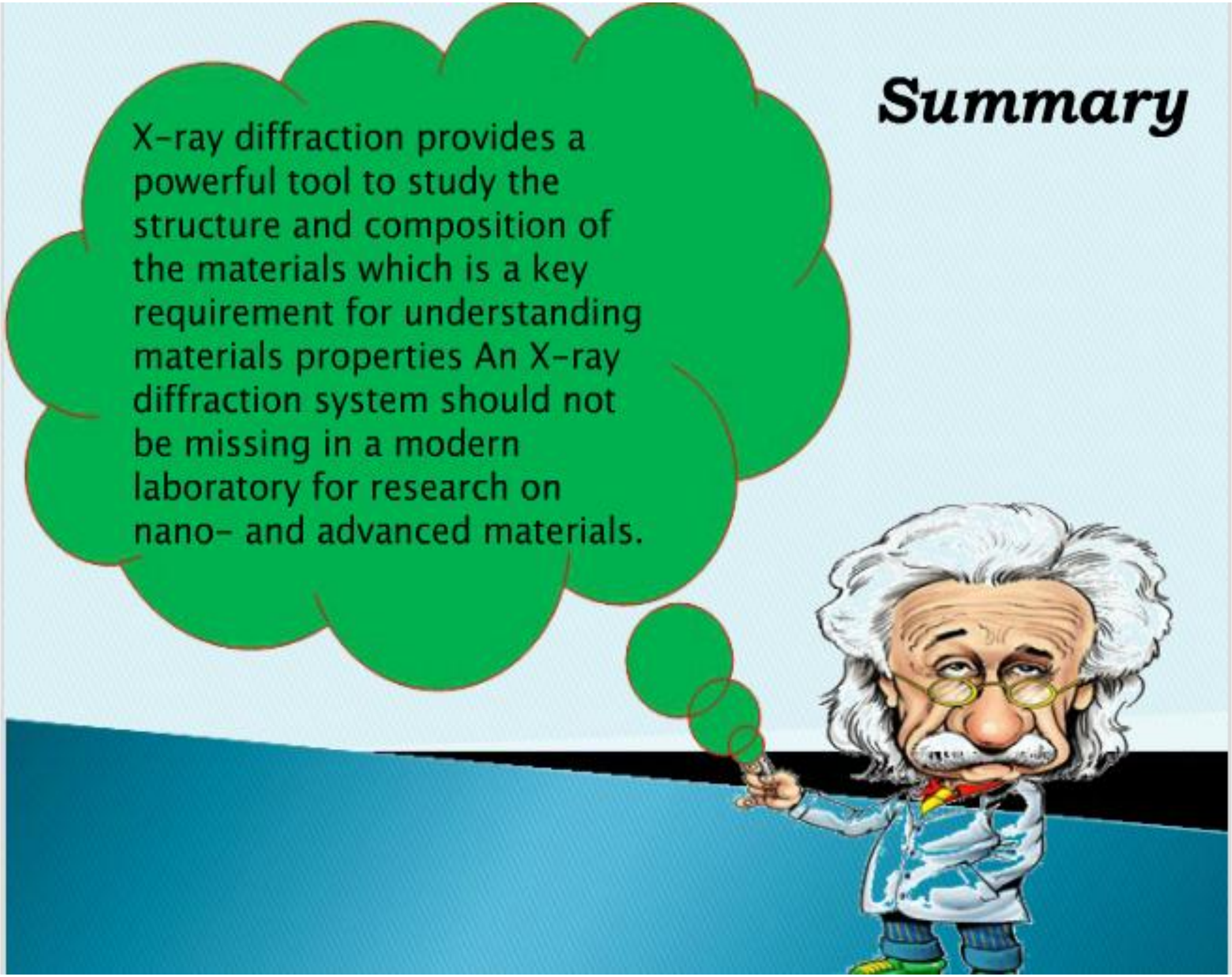
Application areas of X-ray analysis

- Chemicals
  - Catalysts, pigments, nanopowders, wide variety of anorganic/organic complexes
- Pharmaceuticals
  - From API to full drug
  - Drug delivery systems
- Semiconductors
  - Epitaxial thin films, quantum dots, etc.
- Biomaterials



Conclusions

- • Non-destructive, fast, easy sample prep
- • High-accuracy for d-spacing calculations
- Can be done in-situ
- • Single crystal, poly, and amorphous materials
- • Standards are available for thousands of material systems.

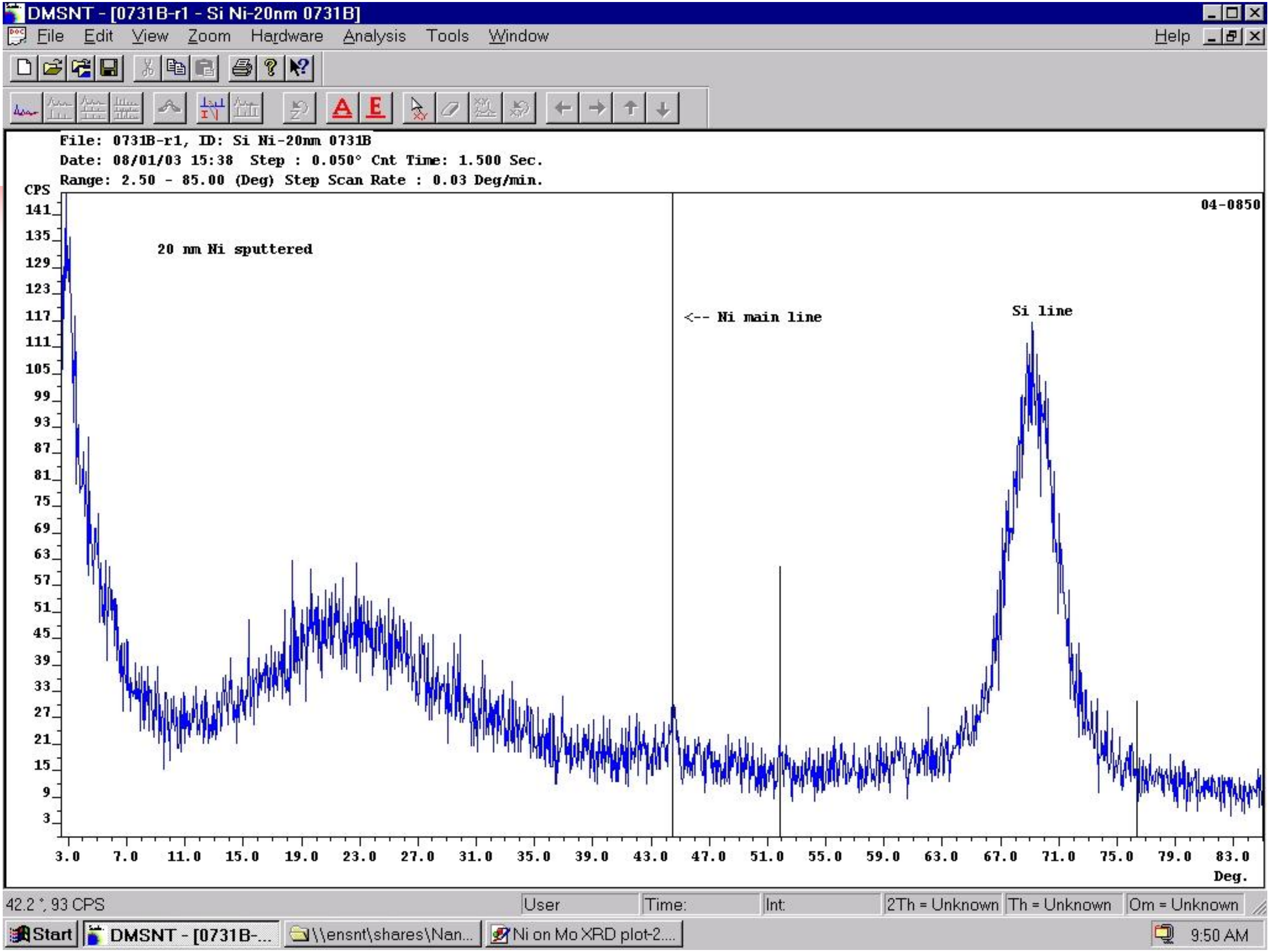


Summary

X-ray diffraction provides a powerful tool to study the structure and composition of the materials which is a key requirement for understanding materials properties An X-ray diffraction system should not be missing in a modern laboratory for research on nano- and advanced materials.


CCD CONTROL
FRAME GRABBER
MERCURY
RADIATION SHIELD

SIEMENS



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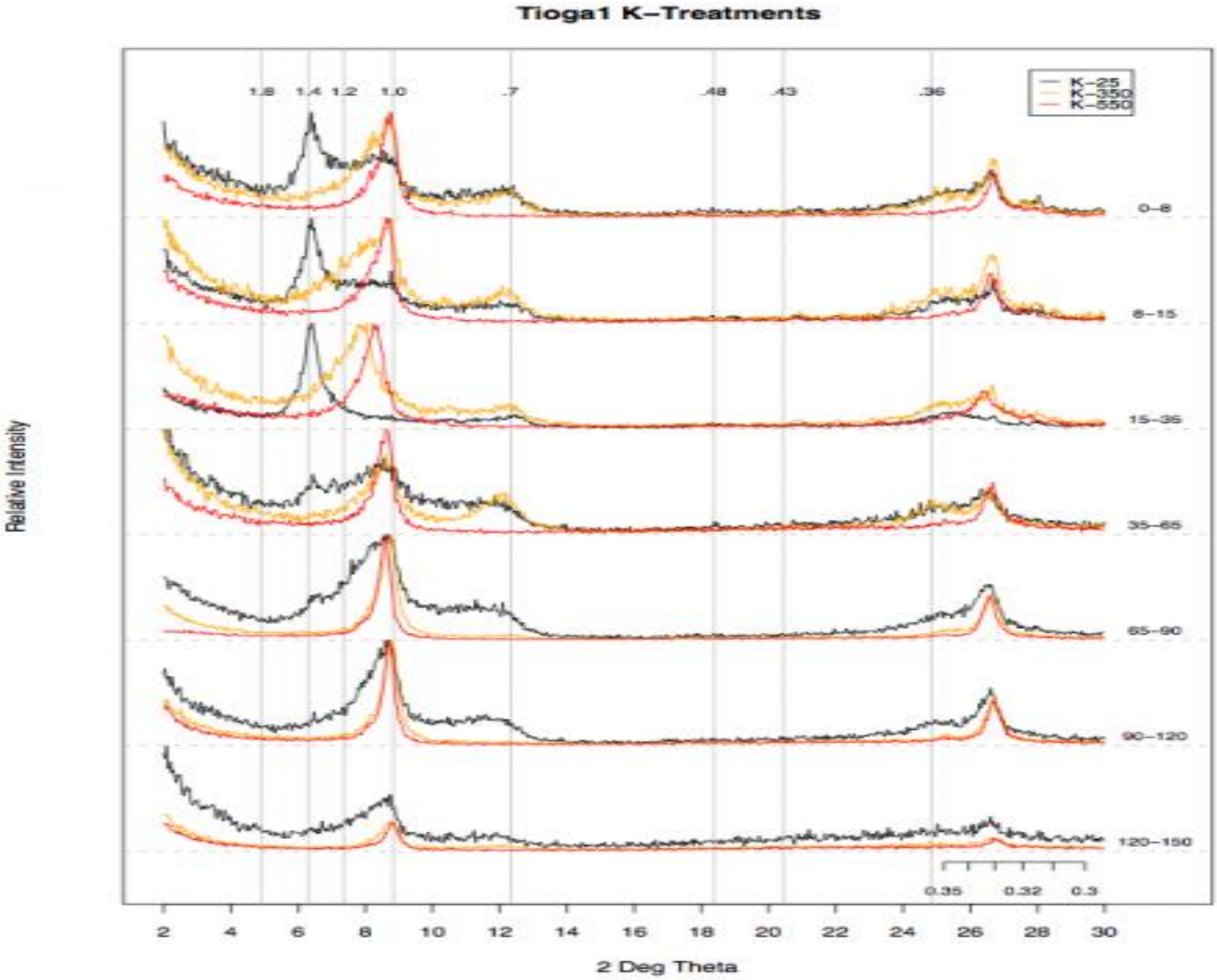
Tioga1 K−Treatments
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