X-ray Diffraction (XRD)

- 1.0 What is X-ray Diffraction
- 2.0 Basics of Crystallography
- 3.0 Production of X-rays
- 4.0 Applications of XRD
- 5.0 Instrumental Sources of Error
- 6.0 Conclusions

Bragg's Law

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

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). The variable *d* is the distance between atomic layers in a crystal, and the variable lambda λ is the **wavelength** of the incident X-ray beam; n is an integer. This observation is an example of X-ray **wave interference** (Roentgenstrahlinterferenzen), commonly known as X-ray diffraction (XRD), and was direct evidence for the periodic atomic structure of crystals postulated for several centuries.

The Nobel Prize in Physics 1915

"for their services in the analysis of crystal structure by means of X-rays"

Bragg's Law

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

Sir William Henry Bragg
1/2 of the prize
United Kingdom
London University
London, United Kingdom
b. 1862
d. 1942

William Lawrence Bragg
1/2 of the prize
United Kingdom
Victoria University
Manchester, United Kingdom
b. 1890
(in Adelaide, Australia)
d. 1971

The Braggs were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS and diamond.

Although Bragg's law was used to explain the interference pattern of X-rays scattered by crystals, diffraction has been developed to study the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest.

Deriving Bragg's Law: $n\lambda = 2d\sin\theta$

Constructive interference occurs only when

$n\lambda = AB + BC$

$AB = BC$

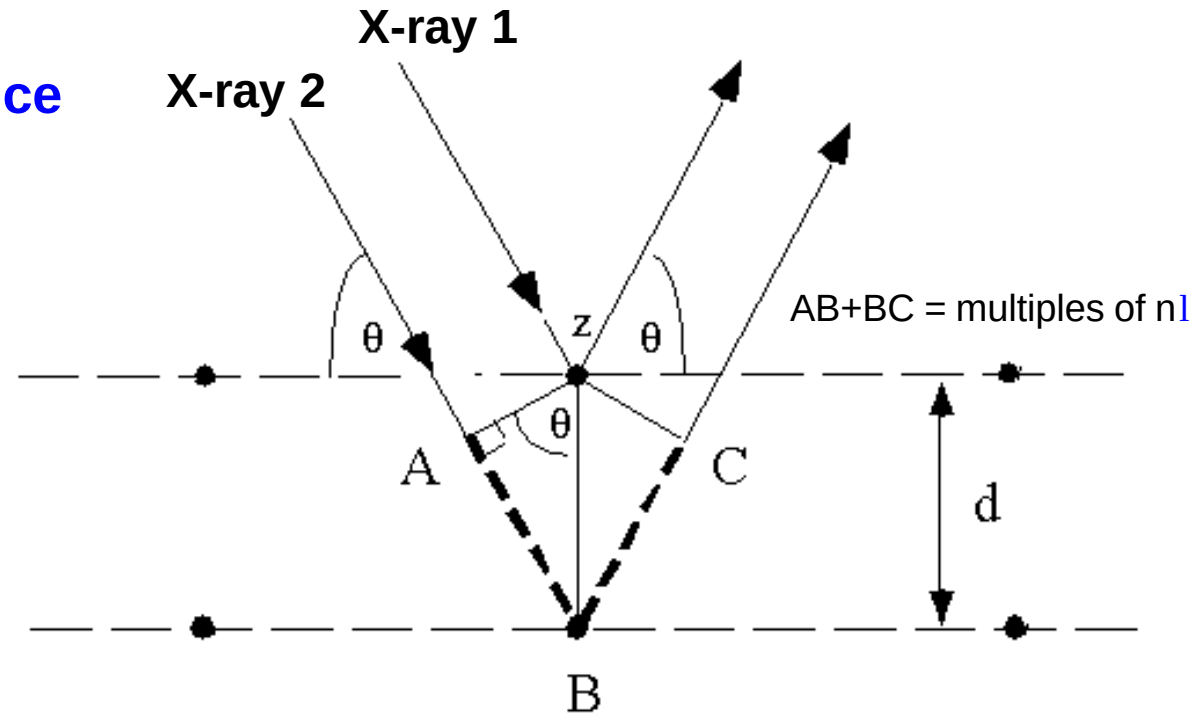
$n\lambda = 2AB$

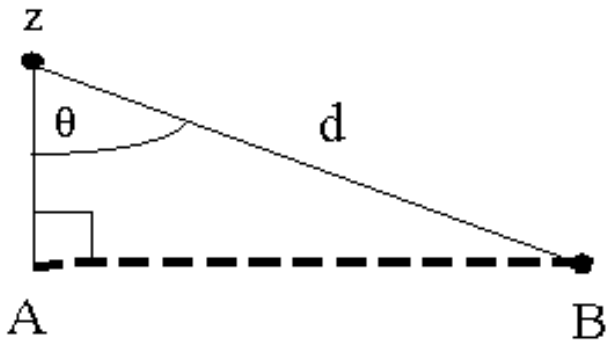
$\sin\theta = AB/d$

$AB = d\sin\theta$

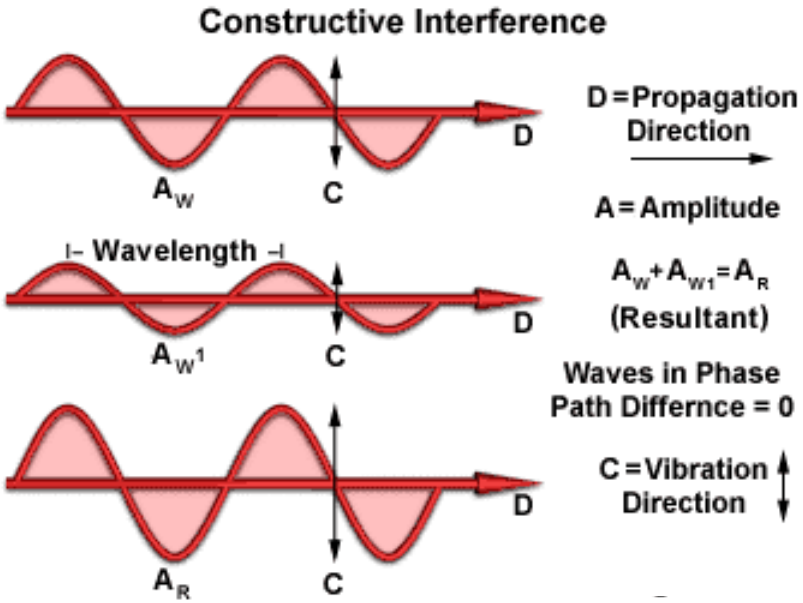
$n\lambda = 2d\sin\theta$

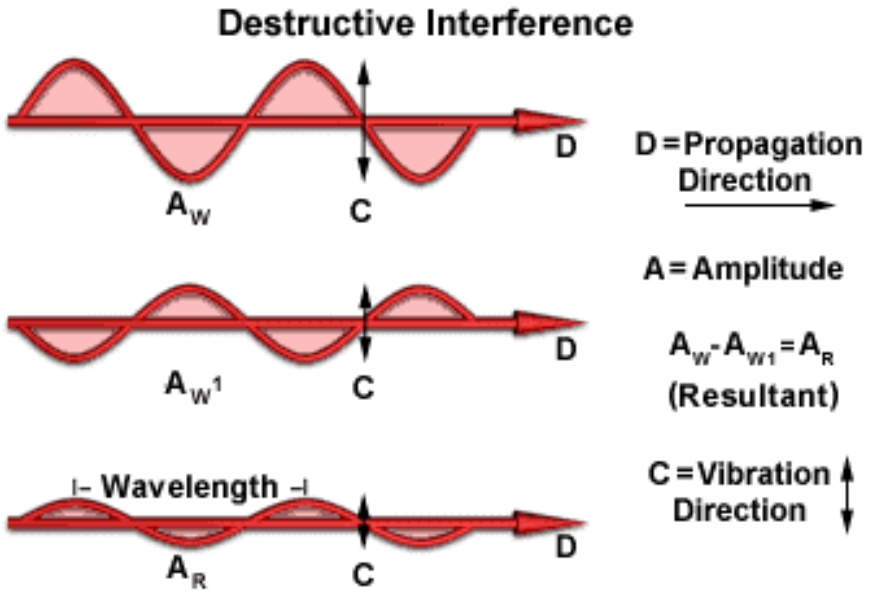
$\lambda = 2d_{hkl}\sin\theta_{hkl}$





Constructive and Destructive Interference of Waves



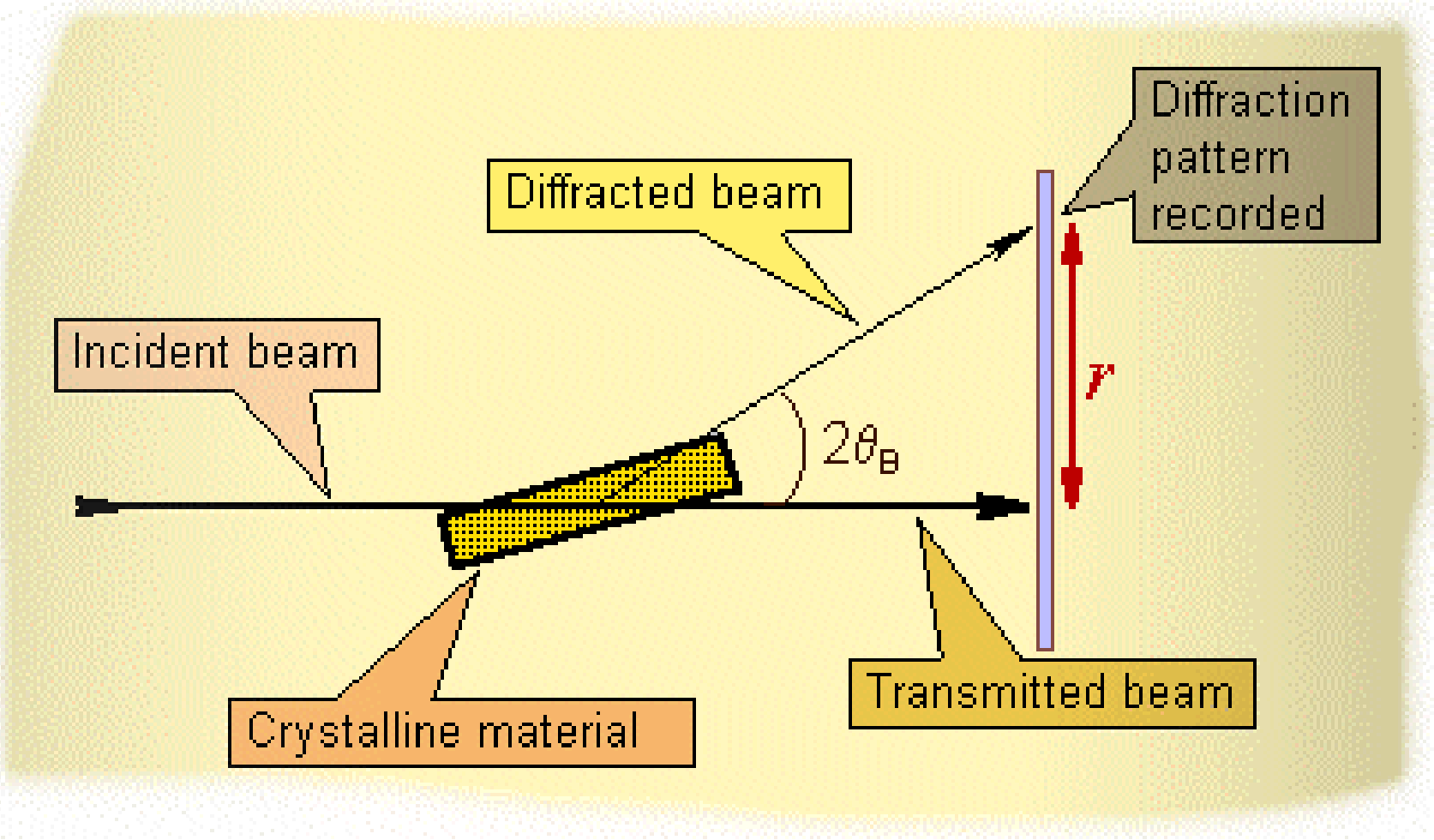


Constructive Interference
In Phase

Destructive Interference
Out of Phase

1.0 What is X-ray Diffraction ?

I



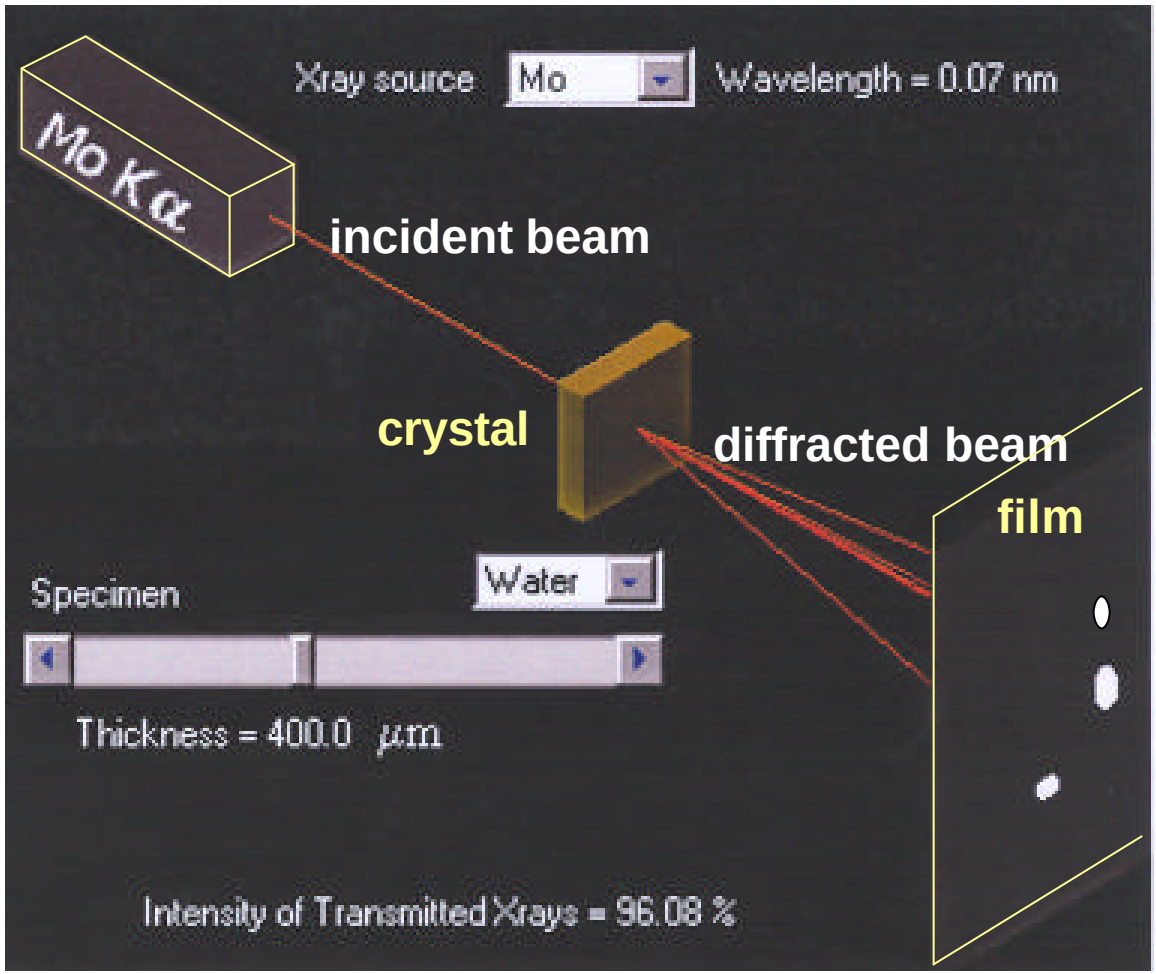
www.micro.magnet.fsu.edu/primer/java/interference/index.html

Why XRD?

- **Measure the average spacings between layers or rows of atoms**
- **Determine the orientation of a single crystal or grain**
- **Find the crystal structure of an unknown material**
- **Measure the size, shape and internal stress of small crystalline regions**

X-ray Diffraction (XRD)

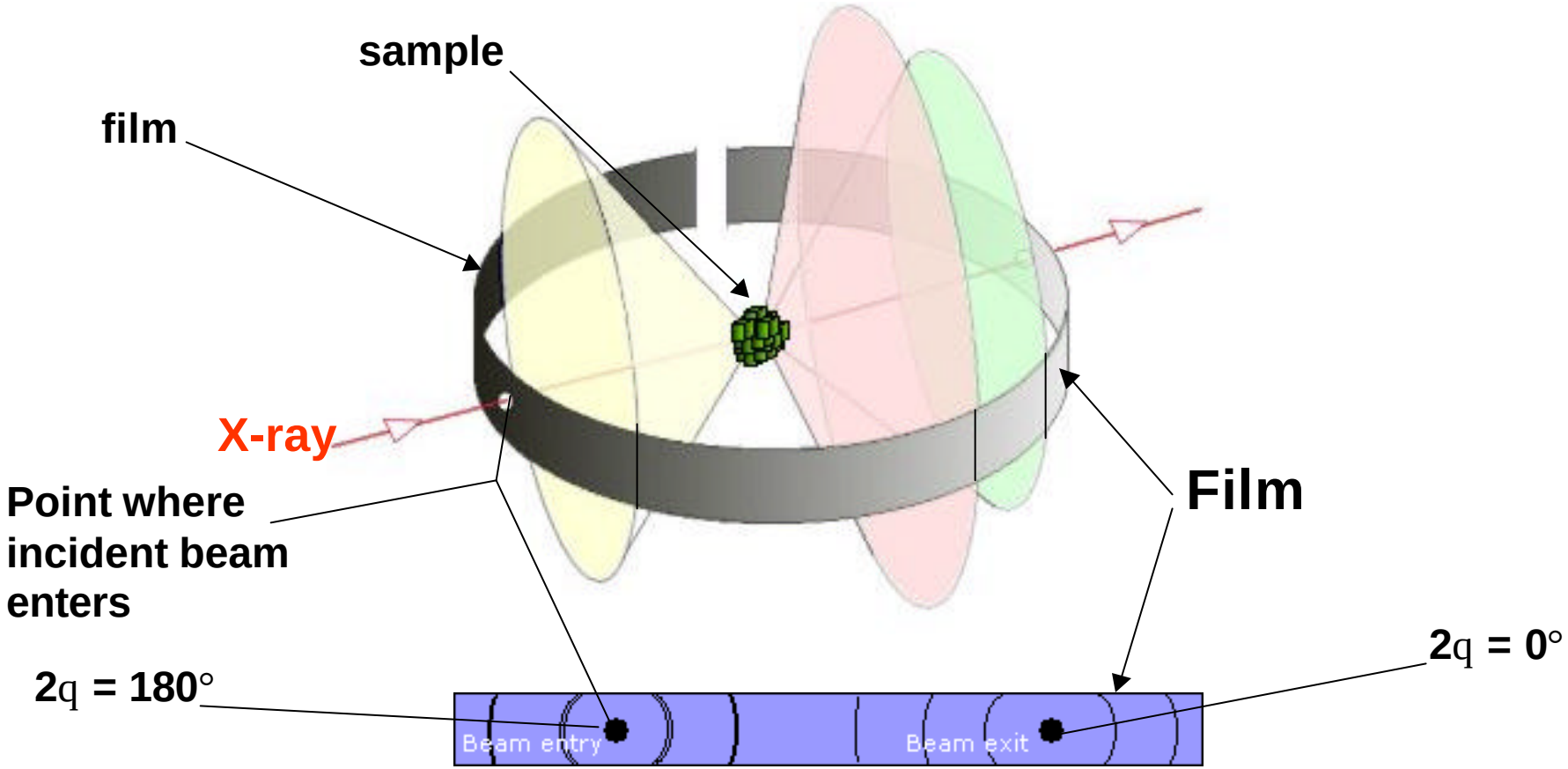
The atomic planes of a crystal cause an incident beam of X-rays to interfere with one another as they leave the crystal. The phenomenon is called X-ray diffraction.



Effect of sample thickness on the absorption of X-rays

http://www.matter.org.uk/diffraction/x-ray/default.htm

Detection of Diffracted X-rays
by Photographic film



Debye - Scherrer Camera

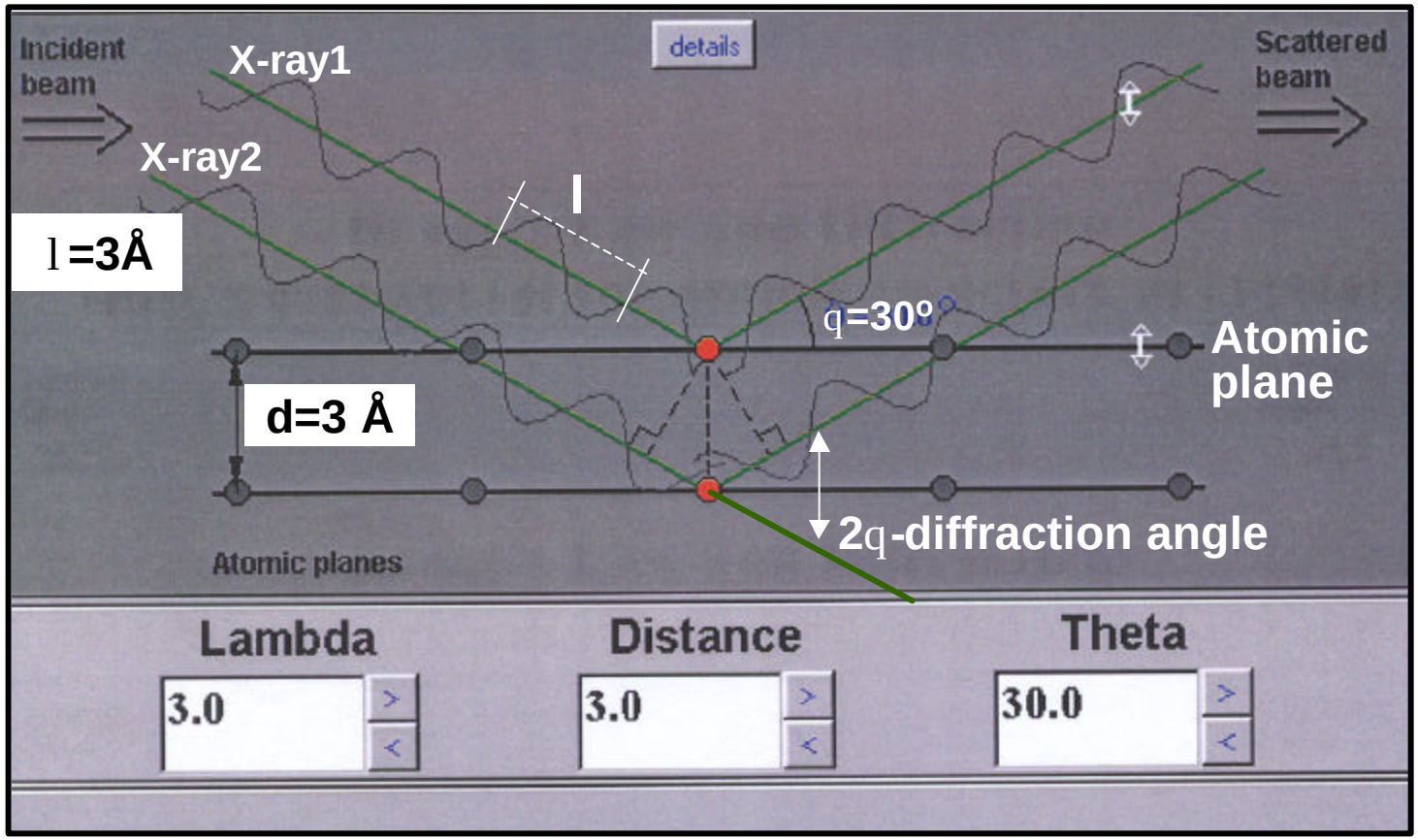
A sample of some hundreds of crystals (i.e. a powdered sample) show that the diffracted beams form continuous cones. A circle of film is used to record the diffraction pattern as shown. Each cone intersects the film giving diffraction lines. The lines are seen as arcs on the film.

Bragg's Law and Diffraction:

How waves reveal the atomic structure of crystals

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

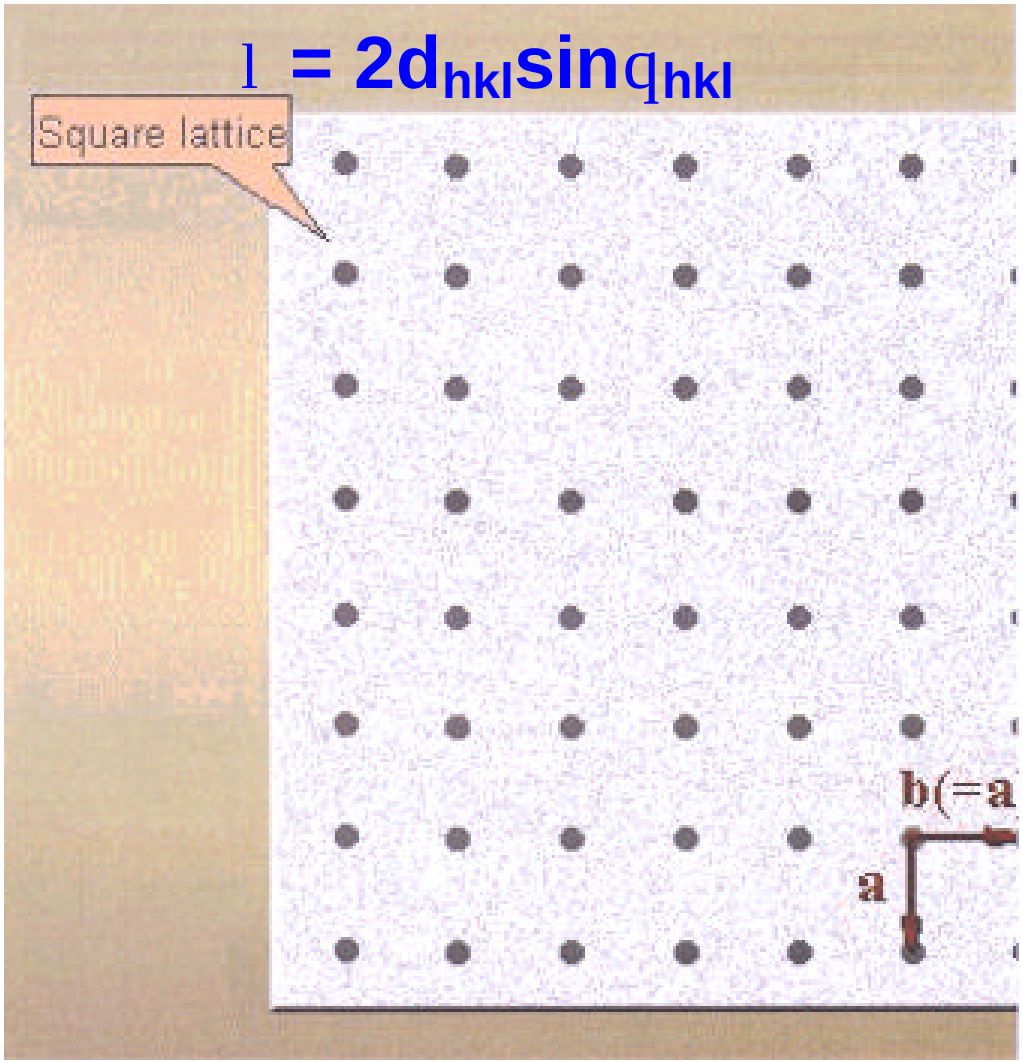
Diffraction occurs only when Bragg's Law is satisfied Condition for constructive interference (X-rays 1 & 2) from planes with spacing d



http://www.eserc.stonybrook.edu/ProjectJava/Bragg/

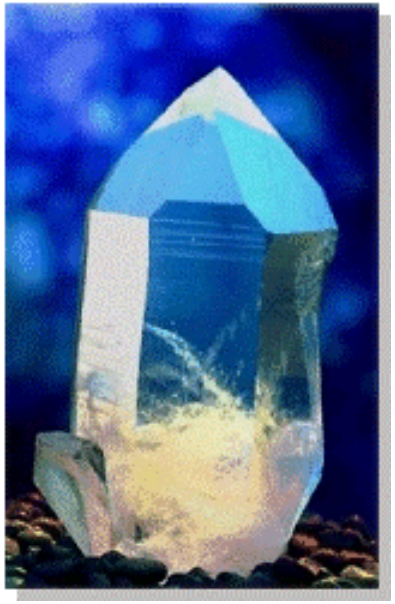
Planes in Crystals-2 dimension

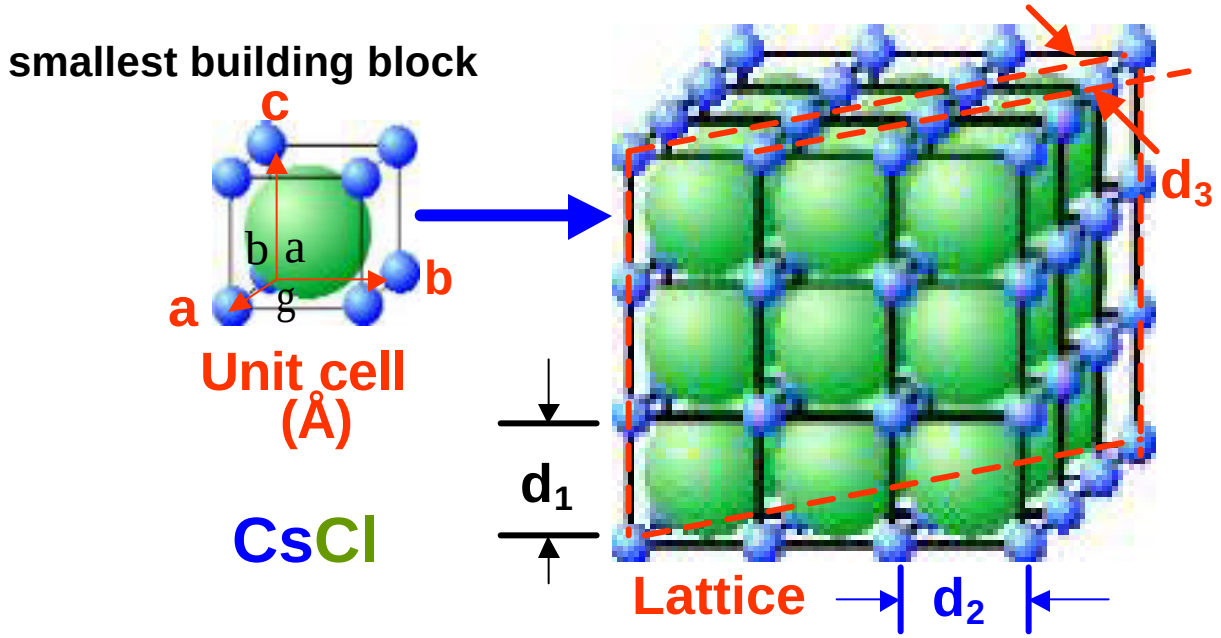
Different planes have different spacings



To satisfy Bragg's Law, θ must change as d changes e.g., θ decreases as d increases.

2.0 Basics of Crystallography





A crystal consists of a periodic arrangement of the unit cell into a lattice. The unit cell can contain a single atom or atoms in a fixed arrangement.

Crystals consist of planes of atoms that are spaced a distance d apart, but can be resolved into many atomic planes, each with a different d-spacing.

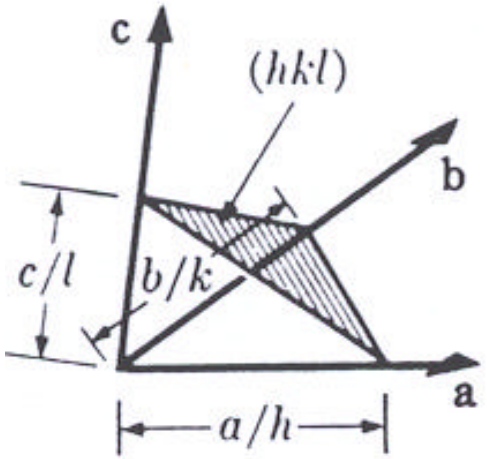
a,b and c (length) and α, β and γ angles between a,b and c are lattice constants or parameters which can be determined by XRD.

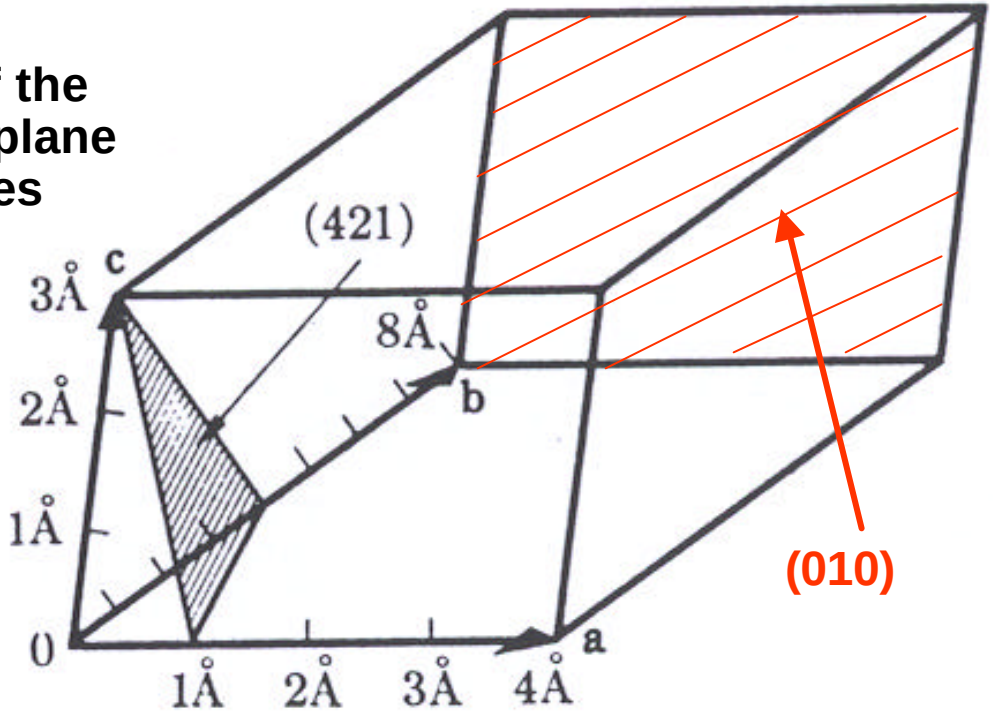
Seven Crystal Systems - Review

Crystal class	Axis system
Cubic	$a = b = c,\ \alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c,\ \alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c,\ \alpha = \beta = 90^\circ,\ \gamma = 120^\circ$
Rhombohedral	$a = b = c,\ \alpha = \beta = \gamma \neq 90^\circ$
Orthorhombic	$a \neq b \neq c,\ \alpha = \beta = \gamma = 90^\circ$
Monoclinic	$a \neq b \neq c,\ \alpha = \gamma = 90^\circ,\ \beta \neq 90^\circ$
Triclinic	$a \neq b \neq c,\ \alpha \neq \beta \neq \gamma \neq 90^\circ$

Miller Indices: hkl - Review

Miller indices-the reciprocals of the fractional intercepts which the plane makes with crystallographic axes





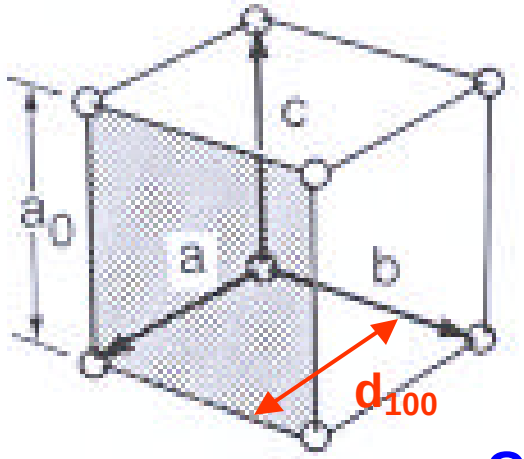
	a	b	c
Axial length	4Å	8Å	3Å
Intercept lengths	1Å	4Å	3Å
Fractional intercepts	¼	½	1
Miller indices	4	2	1
	h	k	l

a	b	c
4Å	8Å	3Å
¥	8Å	¥
0	1	0
0	1	0
h	k	l

4/ ¥ =0

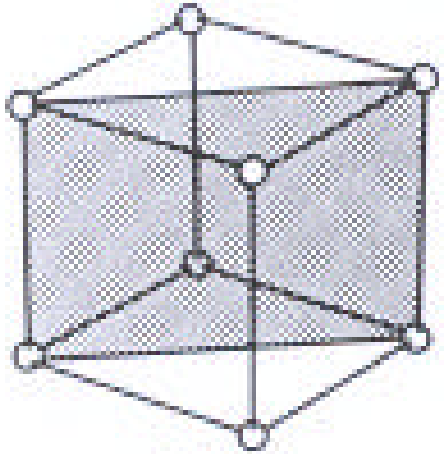
Several Atomic Planes and Their d-spacings in a Simple Cubic - Review

a b c
1 0 0
1 0 0



(100)

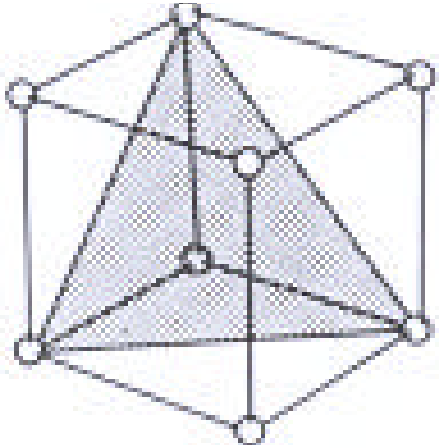
Cubic
$a=b=c=a_0$



(110)

a b c
1 1 0
1 1 0

a b c
1 1 1
1 1 1



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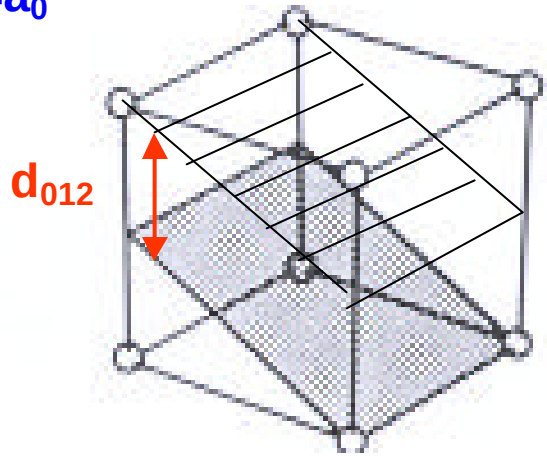
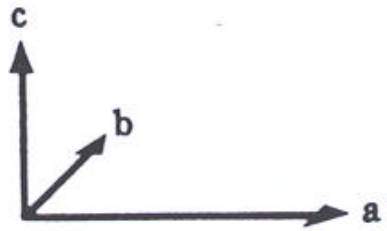


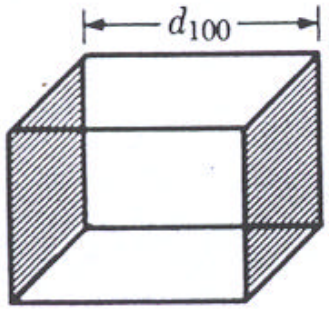
(012)

a b c
0 1 ½
0 1 2

Black numbers-fractional intercepts, Blue numbers-Miller indices

Planes and Spacings - Review





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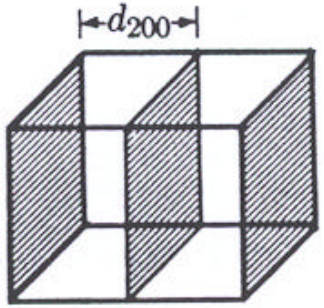

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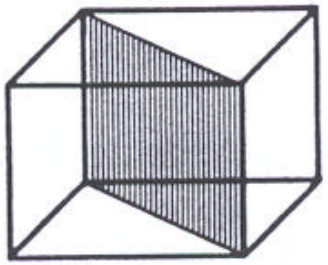

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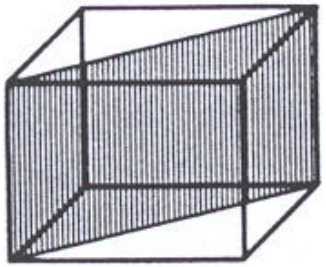
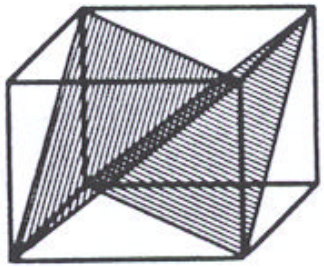
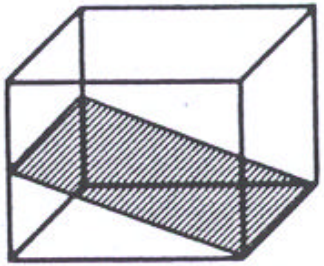


($\bar{1}10$)

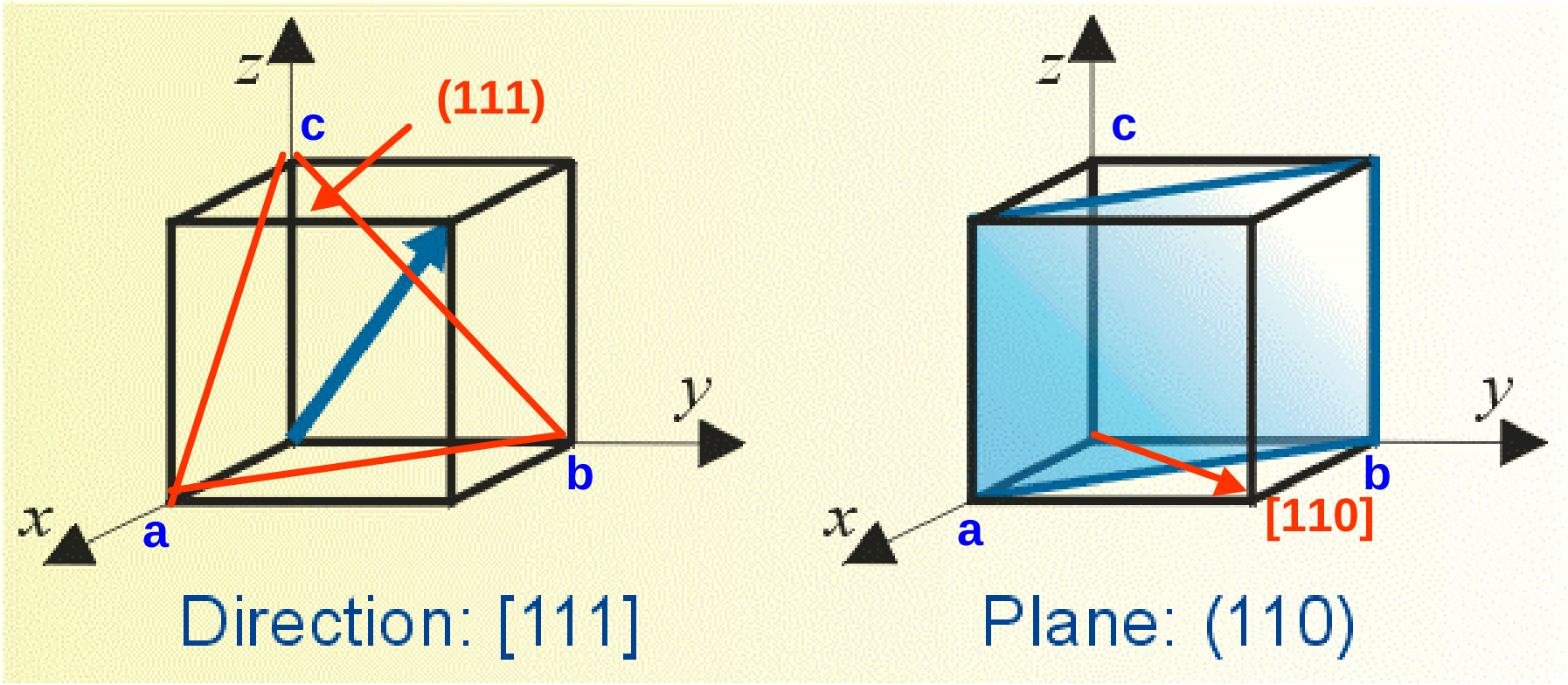


($11\bar{1}$)



(102)

Indexing of Planes and Directions - Review

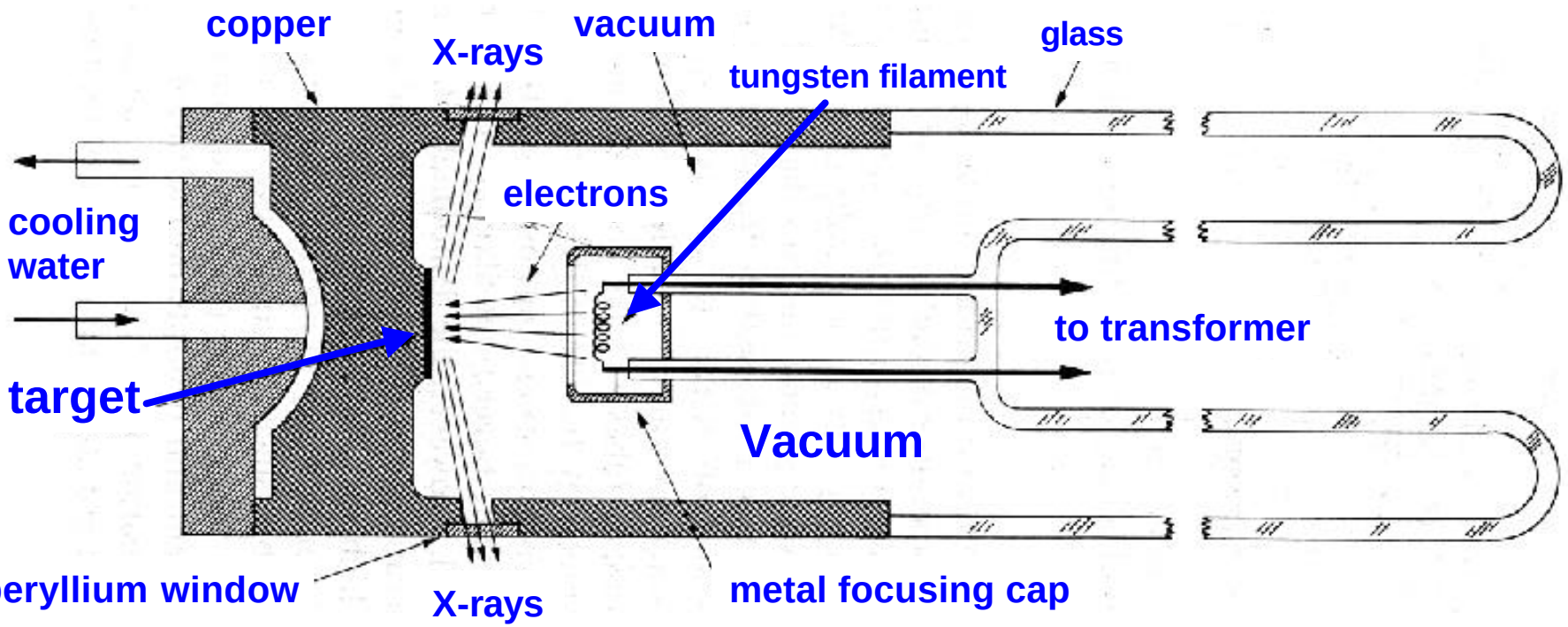


a direction: [uvw]
<uvw>: a set of equivalent directions

a plane: (hkl)
{hkl}: a set of equi-valent planes

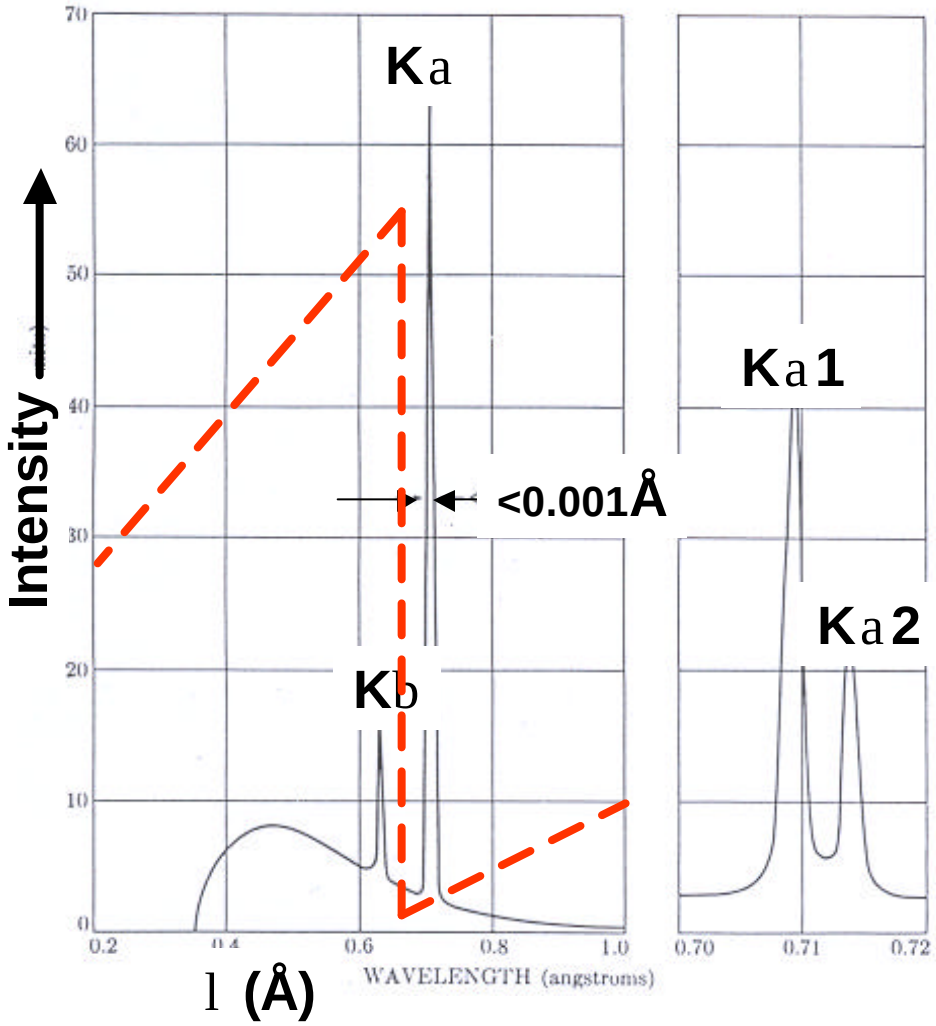
3.0 Production of X-rays

Cross section of sealed-off filament X-ray tube



X-rays are produced whenever high-speed electrons collide with a metal target. A source of electrons – hot W filament, a high accelerating voltage between the cathode (W) and the anode and a metal target, *Cu*, Al, Mo, Mg. The anode is a water-cooled block of Cu containing desired target metal.

Characteristic X-ray Lines



Spectrum of Mo at 35kV

Kb and Ka2 will cause extra peaks in XRD pattern, and shape changes, but can be eliminated by adding filters.

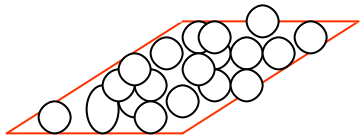
----- is the mass absorption coefficient of Zr.

Specimen Preparation

Powders: **0.1㎛m < particle size <40 ㎛m**

Peak broadening less diffraction occurring

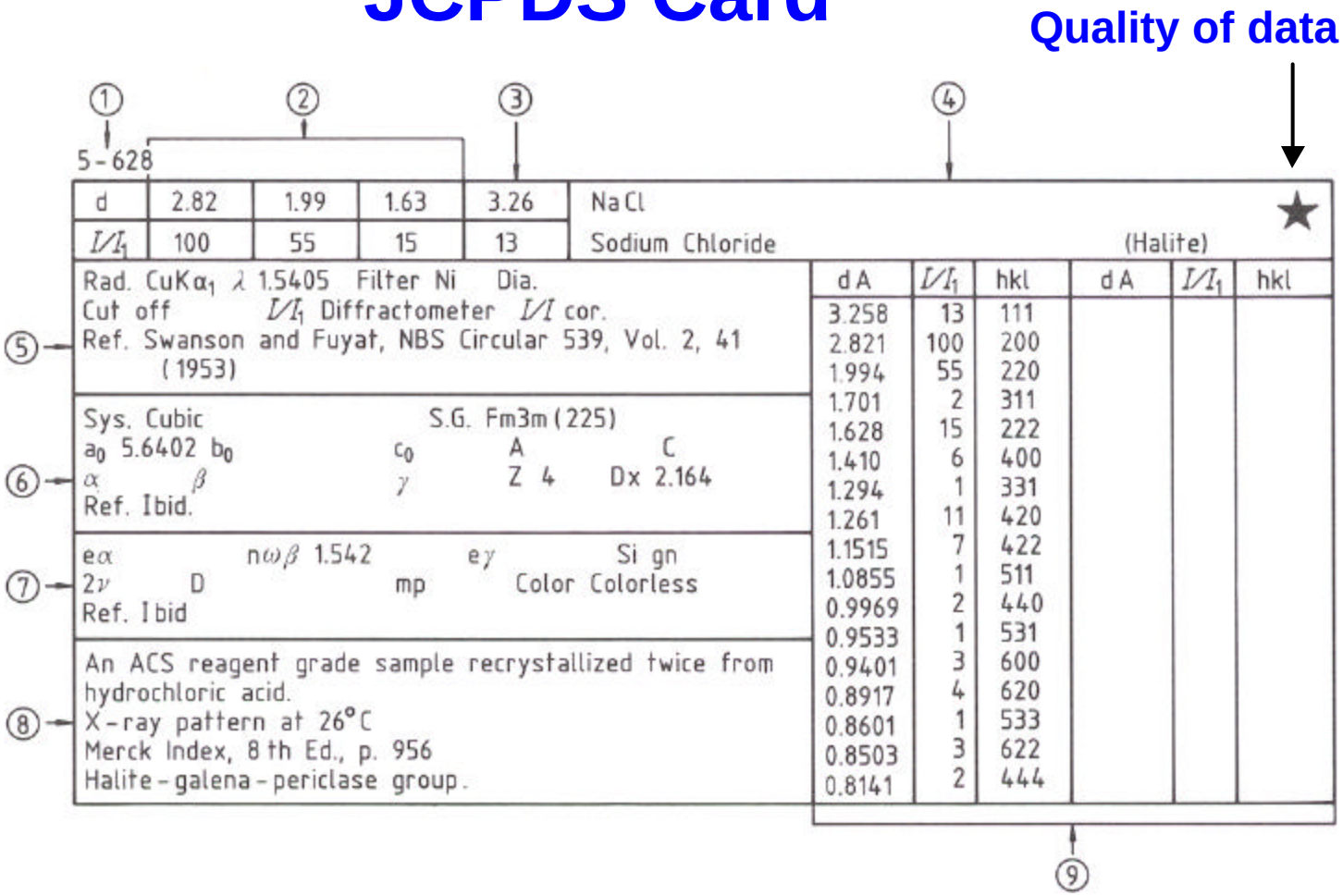
Double sided tape



Glass slide

Bulks: smooth surface after polishing, specimens should be thermal annealed to eliminate any surface deformation induced during polishing.

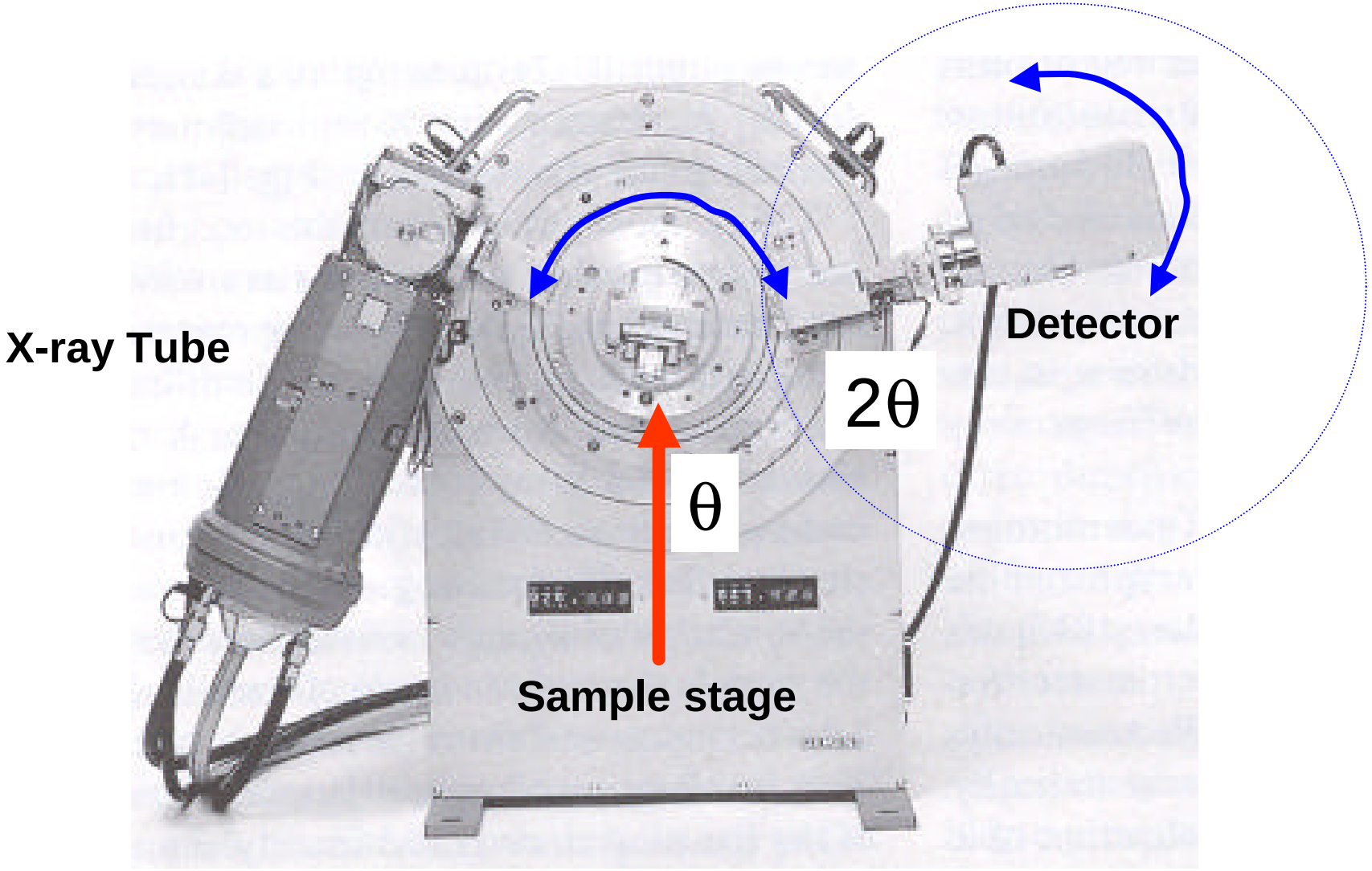
JCPDS Card



1.file number 2.three strongest lines 3.lowest-angle line 4.chemical formula and name 5.data on diffraction method used 6.crystallographic data 7.optical and other data 8.data on specimen 9.data on diffraction pattern.

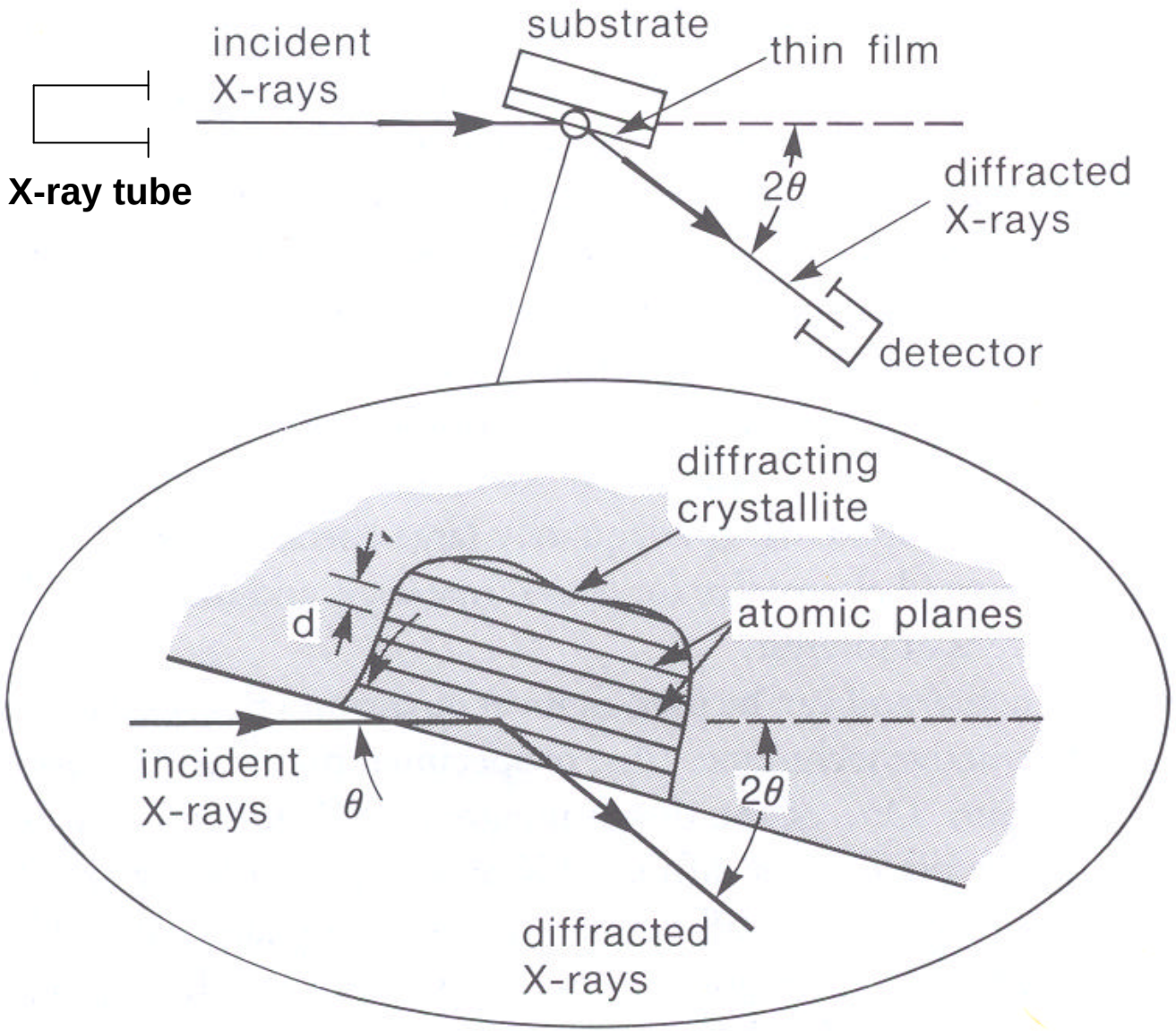
Joint Committee on Powder Diffraction Standards, JCPDS (1969)
Replaced by International Centre for Diffraction Data, ICDF (1978)

A Modern Automated X-ray Diffractometer



Cost: $560K to 1.6M

Basic Features of Typical XRD Experiment



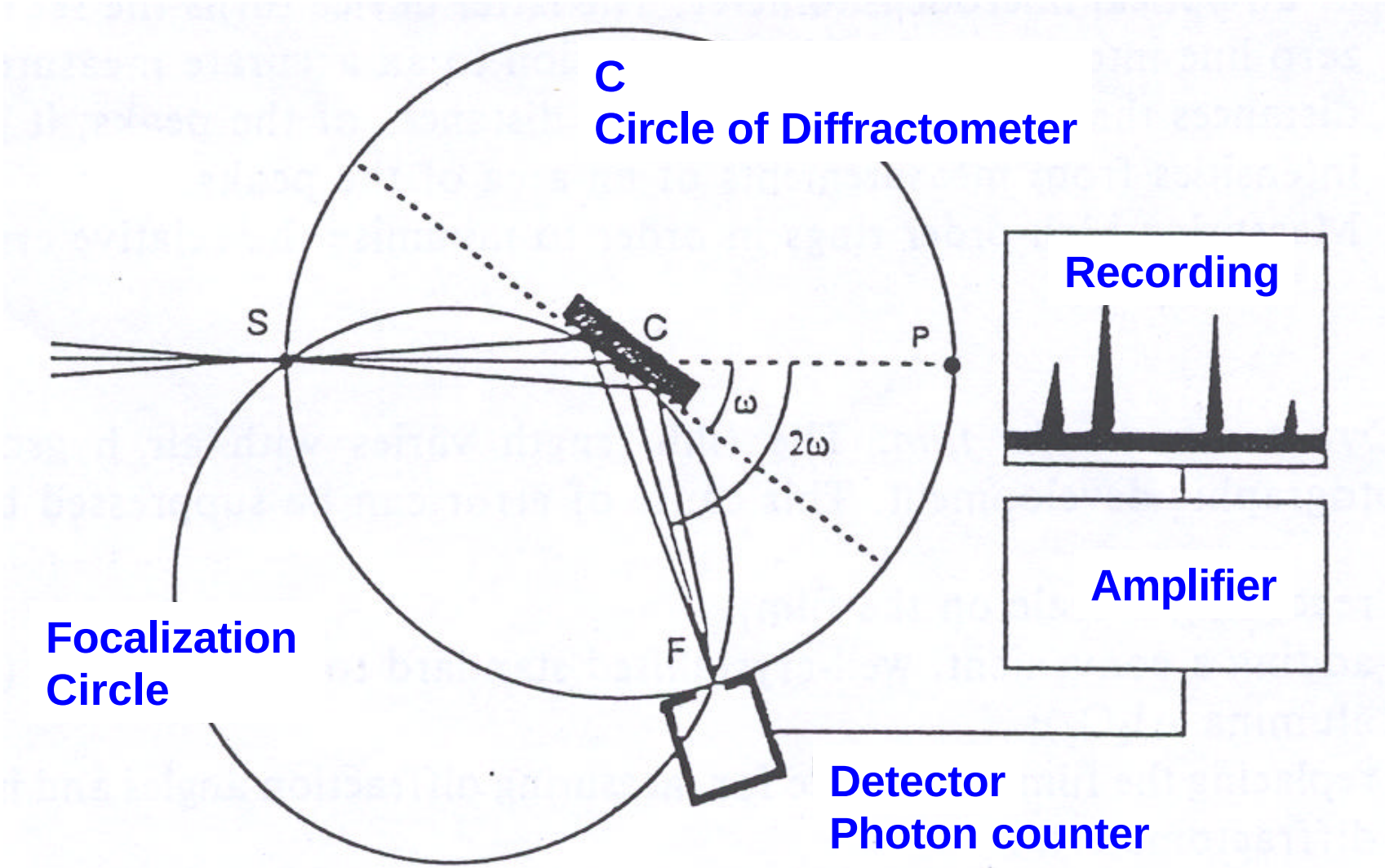
1) Production

2) Diffraction

3) Detection

4) Interpretation

Detection of *Diffracted* X-rays
by a Diffractometer



Bragg - Brentano Focus Geometry, Cullity

Peak Position

d-spacings and lattice parameters

$\lambda = 2d_{hkl}\sin\theta_{hkl}$

Fix λ (Cu kα) = 1.54Å $\quad$ $d_{hkl} = 1.54Å/2\sin\theta_{hkl}$

(Most accurate d-spacings are those calculated from high-angle peaks)

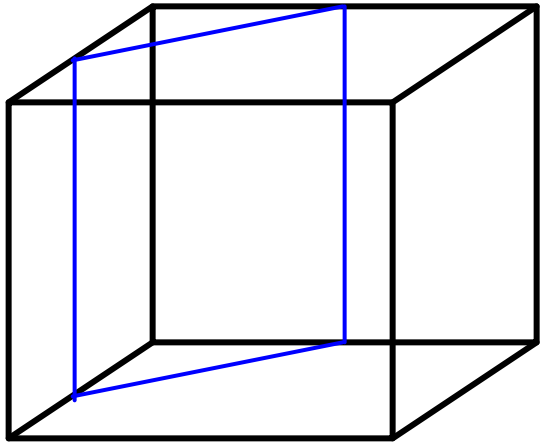
For a simple cubic ($a = b = c = a_0$)

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

→ $a_0 = d_{hkl}/(h^2+k^2+l^2)^{1/2}$

e.g., for NaCl, $2\theta_{220}=46^o$, $\theta_{220}=23^o$,

d_{220} =1.9707Å, a_0=5.5739Å



Bragg's Law and Diffraction:

How waves reveal the atomic structure of crystals

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

Diffraction occurs only when Bragg's Law is satisfied Condition for constructive interference (X-rays 1 & 2) from planes with spacing d

$a_0 = d_{hkl}/(h^2+k^2+l^2)^{1/2}$

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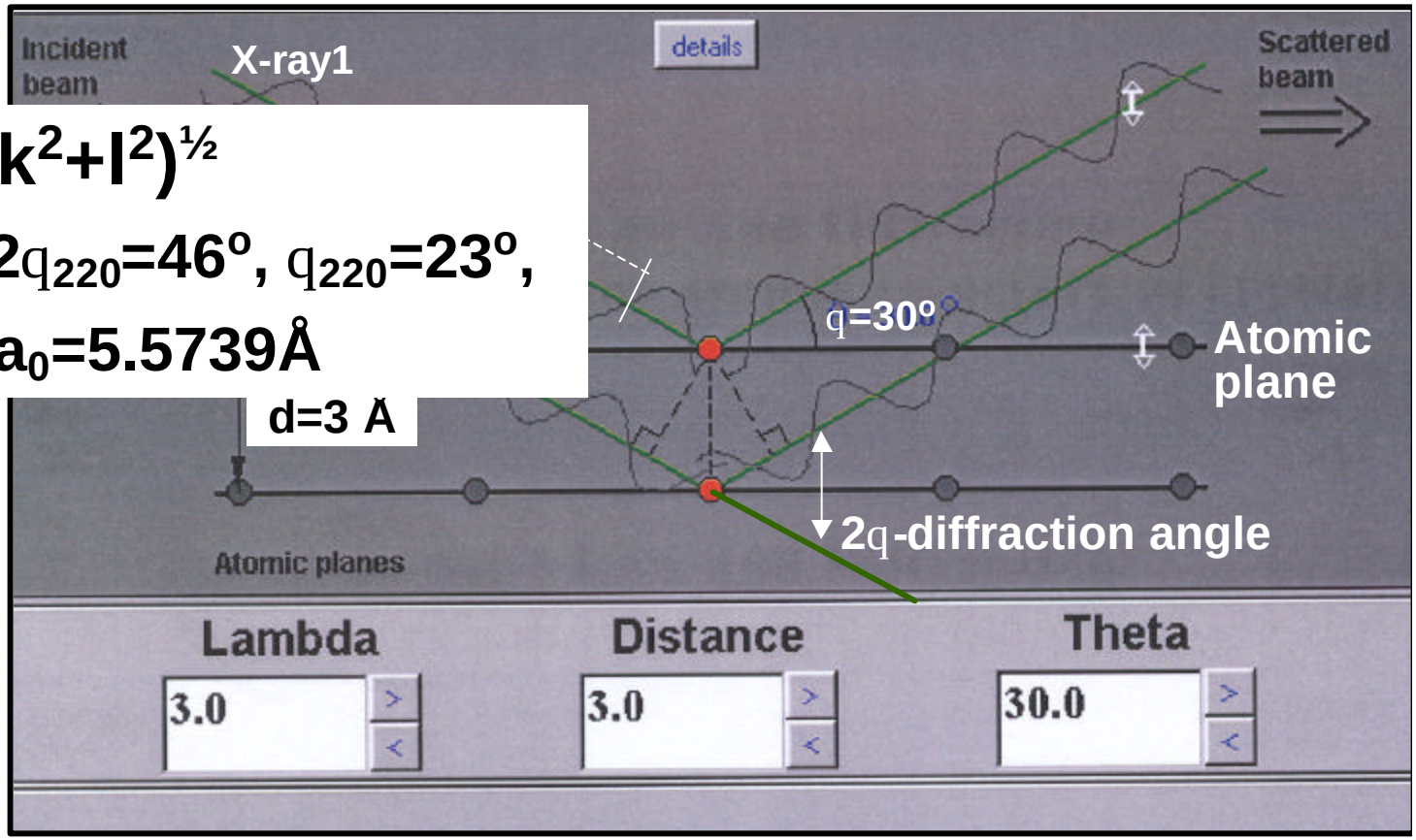
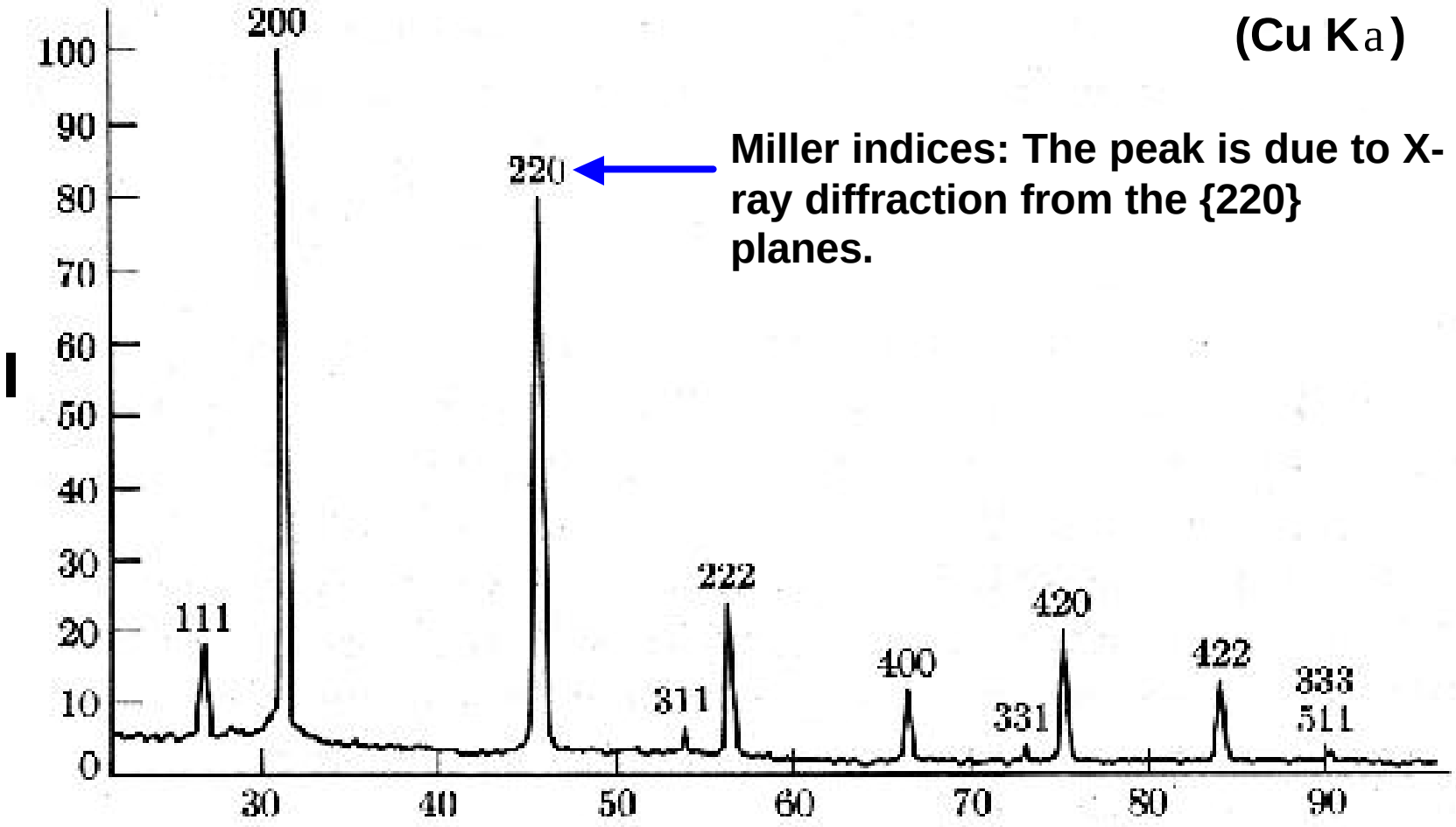


http://www.eserc.stonybrook.edu/ProjectJava/Bragg/

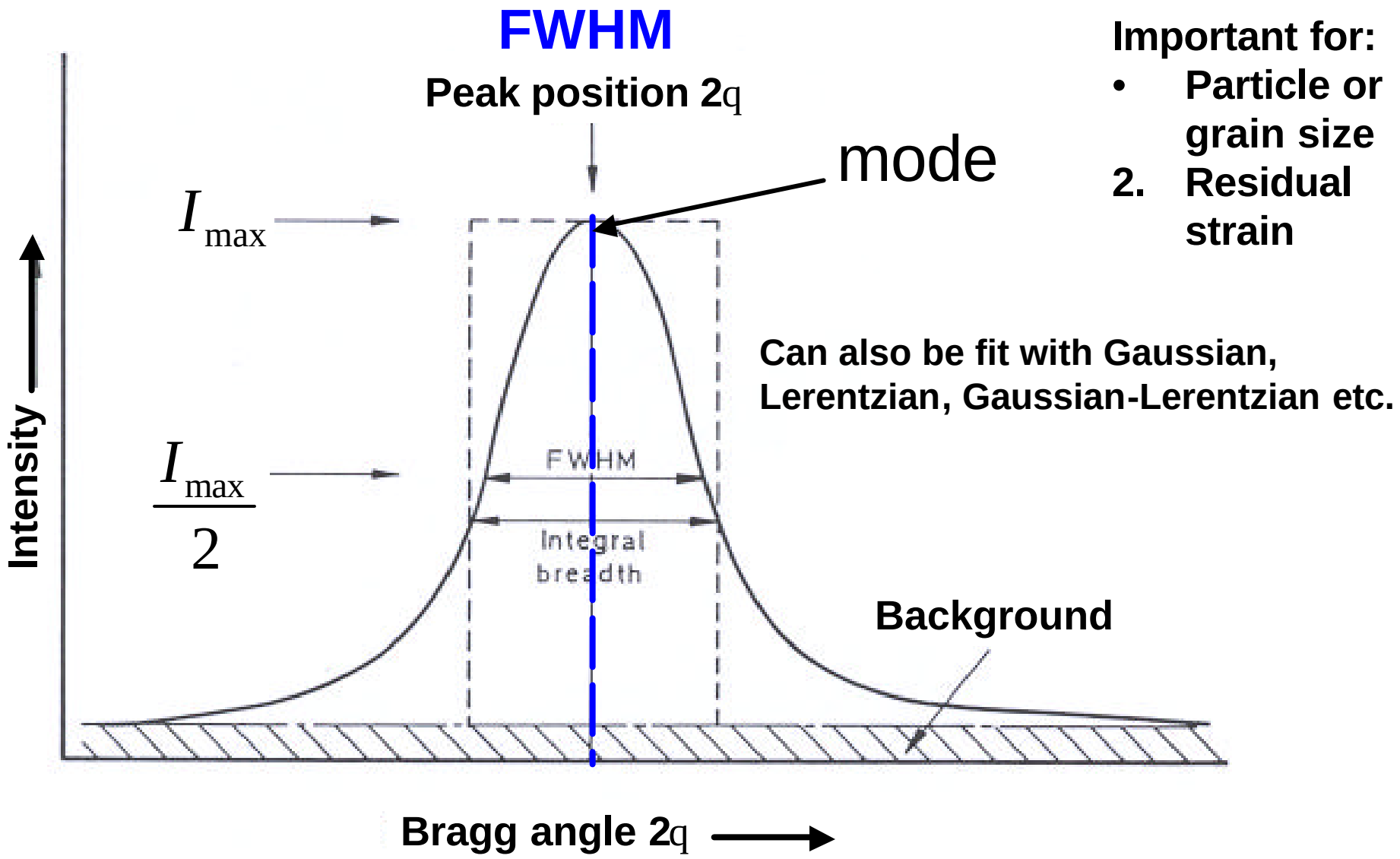
XRD Pattern of NaCl Powder



Significance of Peak Shape in XRD

1. Peak position
2. Peak width
3. Peak intensity

Peak Width-Full Width at Half Maximum



Important for:

- **Particle or grain size**
2. **Residual strain**

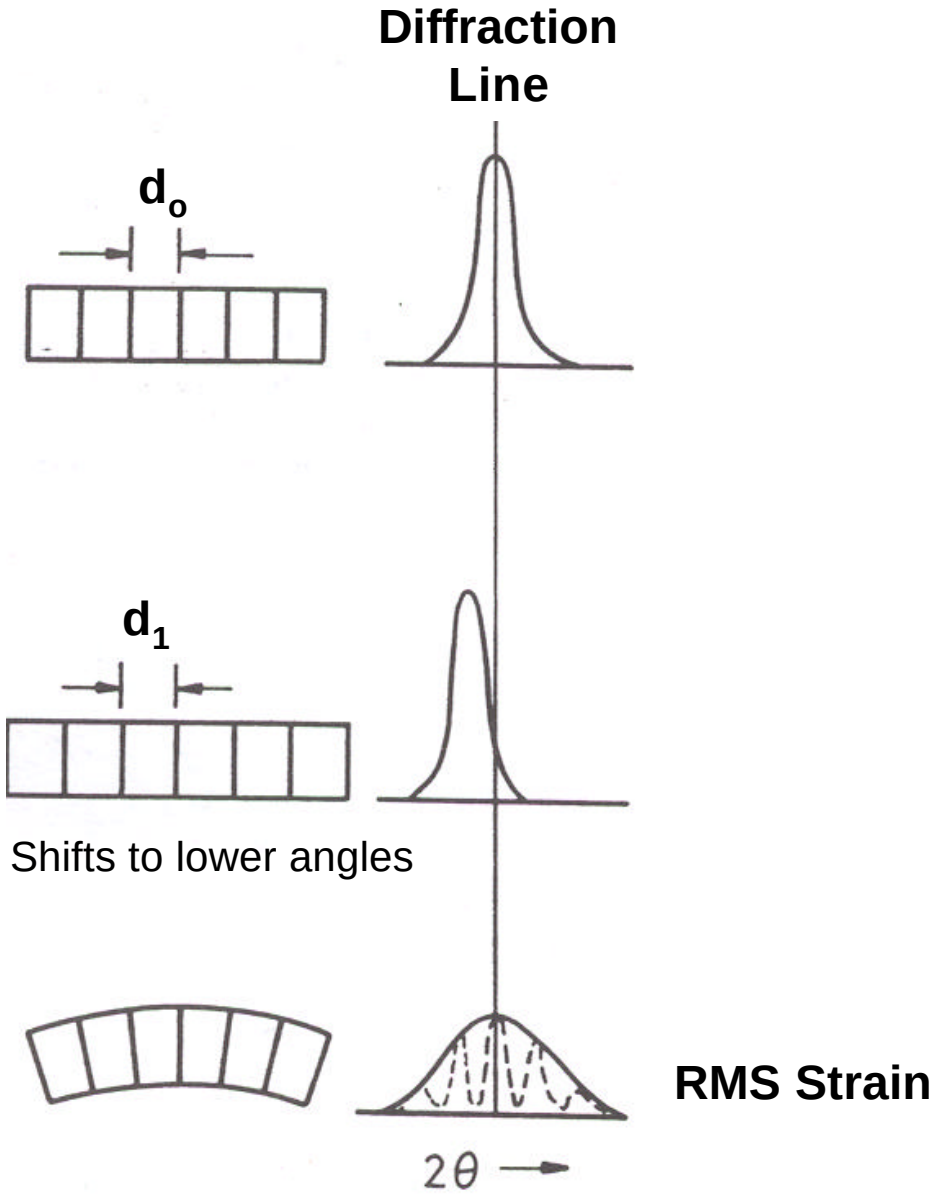
Can also be fit with Gaussian, Lerentzian, Gaussian-Lerentzian etc.

Effect of Lattice Strain on Diffraction Peak Position and Width

No Strain

Uniform Strain
$(d_1-d_o)/d_o$
Peak moves, no shape changes

Non-uniform Strain
d_1 [1] constant
Peak broadens



4.0 Applications of XRD

- **XRD is a nondestructive technique**
- **To identify crystalline phases and orientation**
- **To determine structural properties:**

  Lattice parameters (10^{-4}Å), strain, grain size, expitaxy, phase composition, preferred orientation (Laue) order-disorder transformation, thermal expansion
- **To measure thickness of thin films and multi-layers***
- **To determine atomic arrangement**
- **Detection limits: ~3% in a two phase mixture; can be ~0.1% with synchrotron radiation**

  Spatial resolution: normally none

Phase Identification

<u>One of the most important uses of XRD!!!</u>

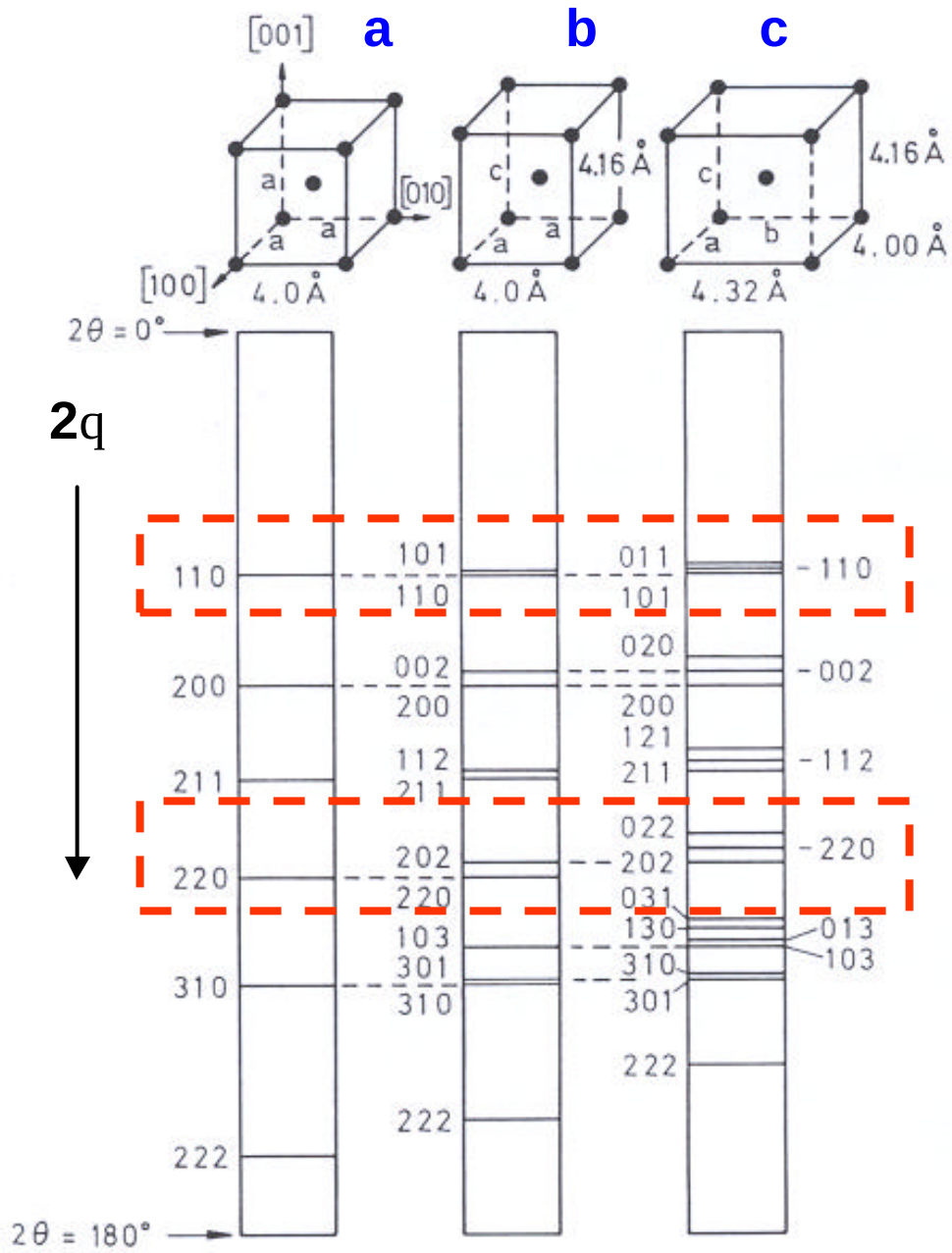
- Obtain XRD pattern
- Measure d-spacings
- Obtain integrated intensities
- Compare data with known standards in the JCPDS file, which are for random orientations (there are more than 50,000 JCPDS cards of inorganic materials).

Mr. Hanawalt

Powder diffraction files: The task of building up a collection of known patterns was initiated by Hanawalt, Rinn, and Fevel at the Dow Chemical Company (1930's). They obtained and classified diffraction data on some 1000 substances. After this point several societies like ASTM (1941-1969) and the JCPS began to take part (1969-1978). In 1978 it was renamed the Int. Center for Diffraction Data (ICDD) with 300 scientists worldwide. In 1995 the powder diffraction file (PDF) contained nearly 62,000 different diffraction patterns with 200 new being added each year. Elements, alloys, inorganic compounds, minerals, organic compounds, organo-metallic compounds.

***Hanawalt*: Hanawalt decided that since more than one substance can have the same or nearly the same d value, each substance should be characterized by it's three strongest lines (d1, d2, d3). The values of d1-d3 are usually sufficient to characterize the pattern of an unknown and enable the corresponding pattern in the file to be located.**

Phase Identification



- Effect of Symmetry on XRD Pattern

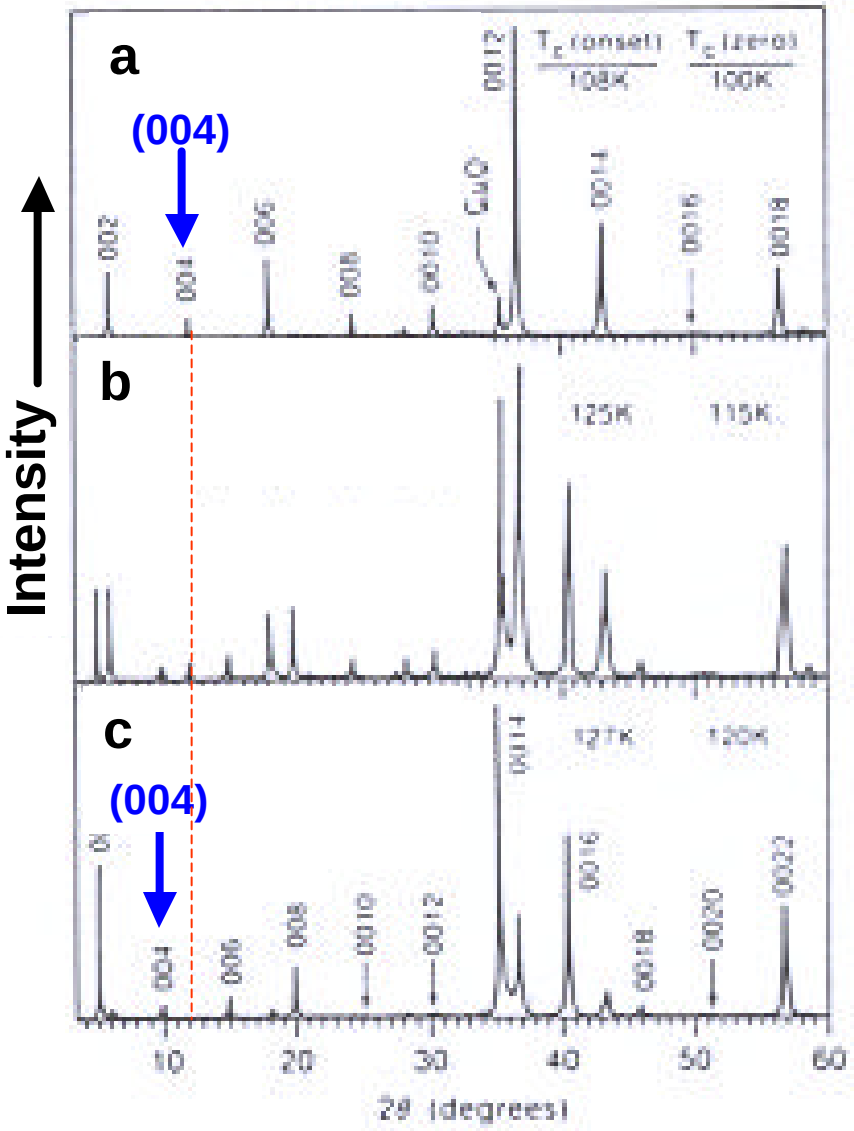
a. **Cubic**
   a=b=c, (a)

b. **Tetragonal**
   a=b≠c (a and c)

c. **Orthorhombic**
   a≠b≠c (a, b and c)

- **Number of reflections**
- **Peak position**
- **Peak splitting**

More Applications of XRD



Diffraction patterns of three Superconducting thin films annealed for different times.

a. $Tl_2CaBa_2Cu_2O_x$ (2122)

b. $Tl_2CaBa_2Cu_2O_x$ (2122) + $Tl_2Ca_2Ba_2Cu_3O_y$ (2223)

b = a + c

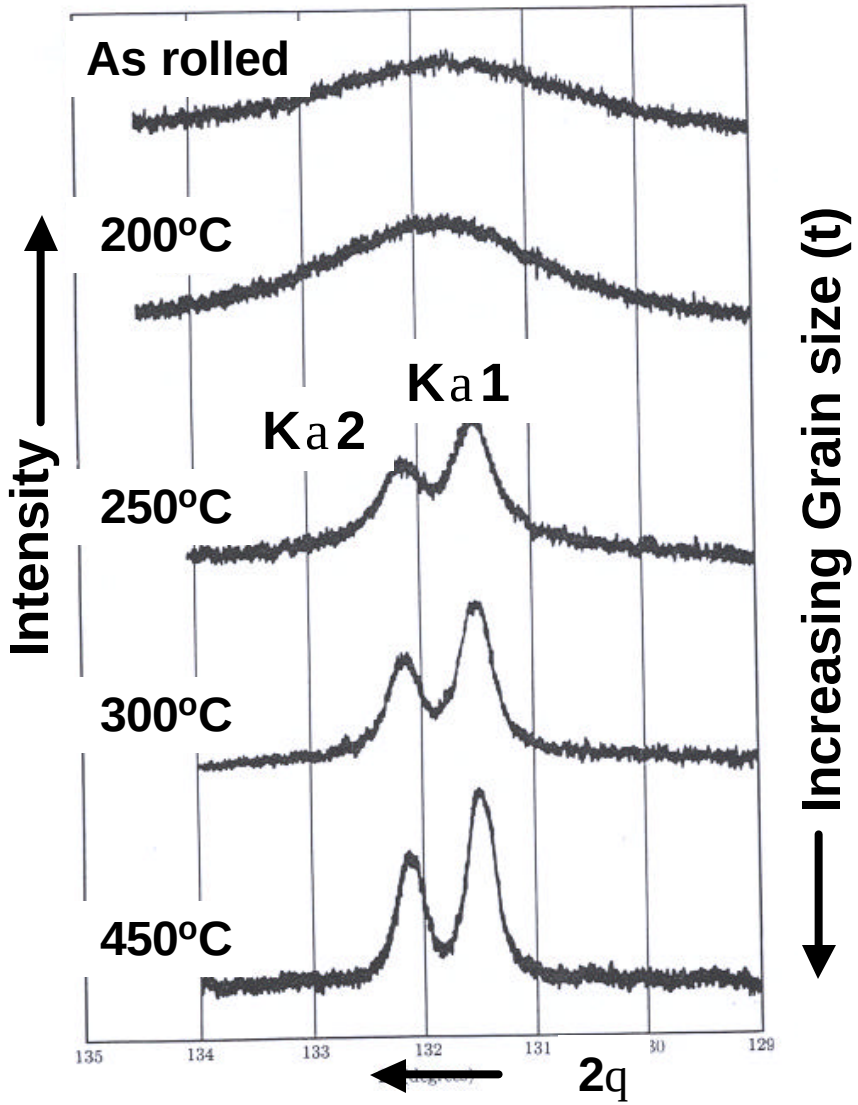
c. $Tl_2Ca_2Ba_2Cu_3O_y$ (2223)

CuO was detected by comparison to standards

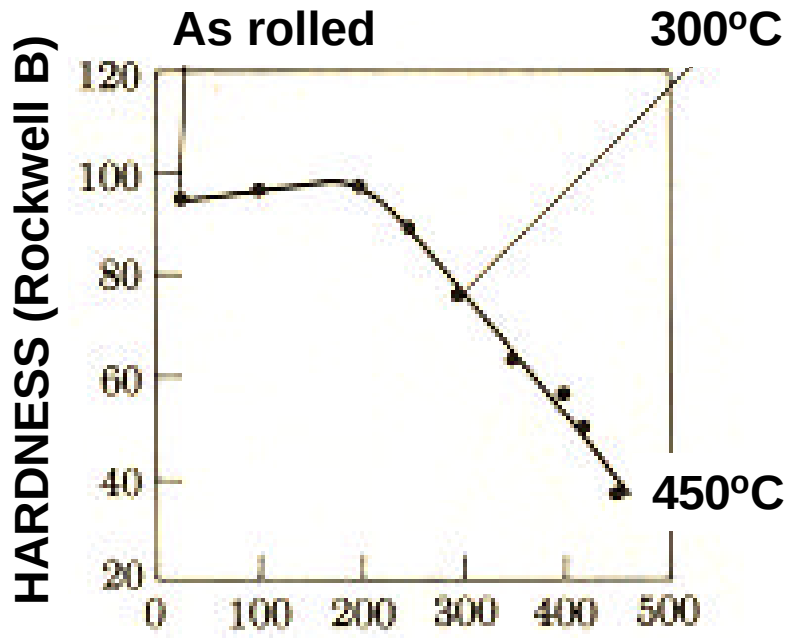
XRD Studies

- **Temperature**
- **Electric Field**
- **Pressure**
- **Deformation**

Effect of Coherent Domain Size



(331) Peak of cold-rolled and Annealed 70Cu-30Zn (brass)

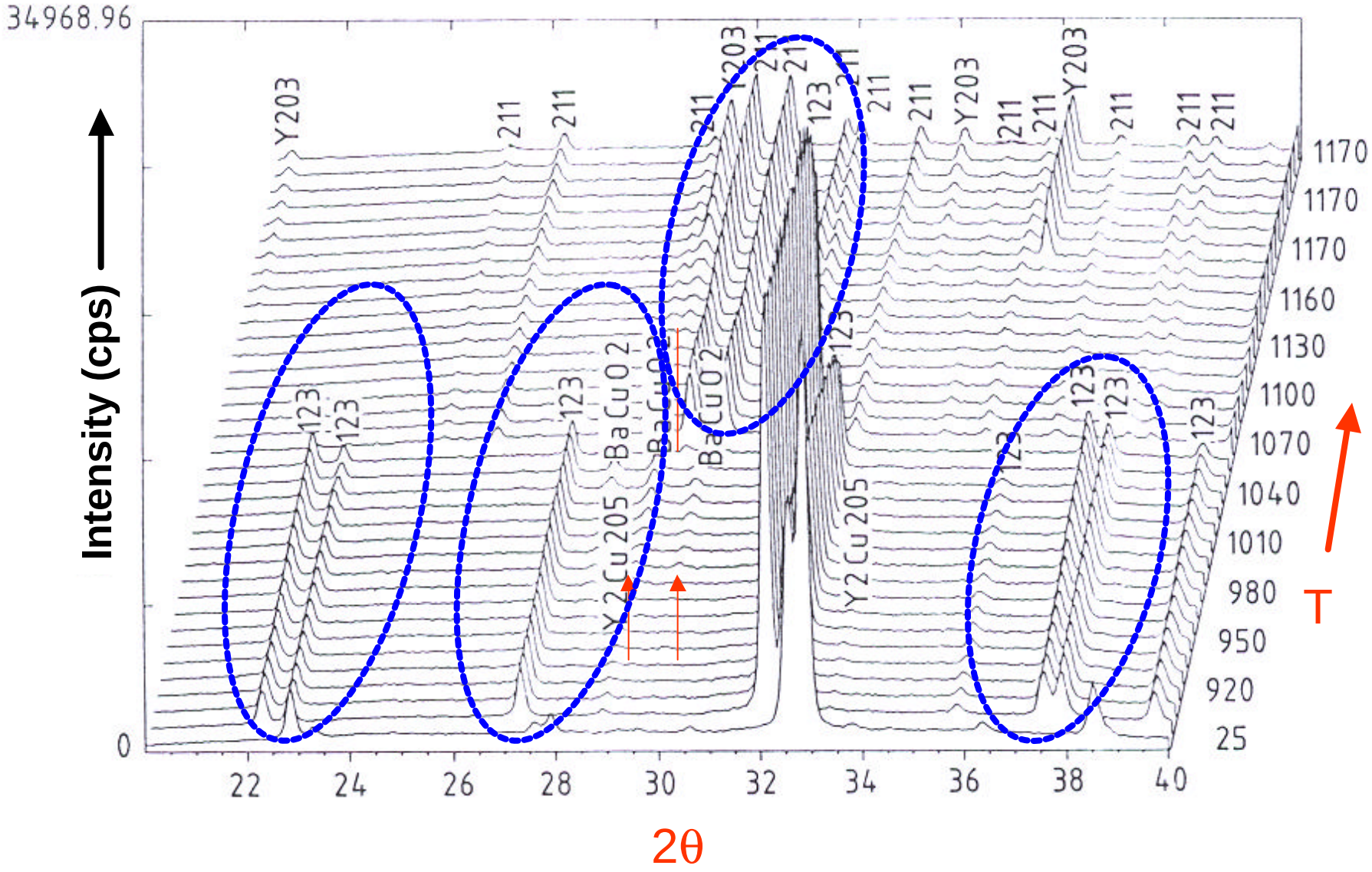


$$B = \frac{0.9 \cdot l}{t \cdot Cosq}$$

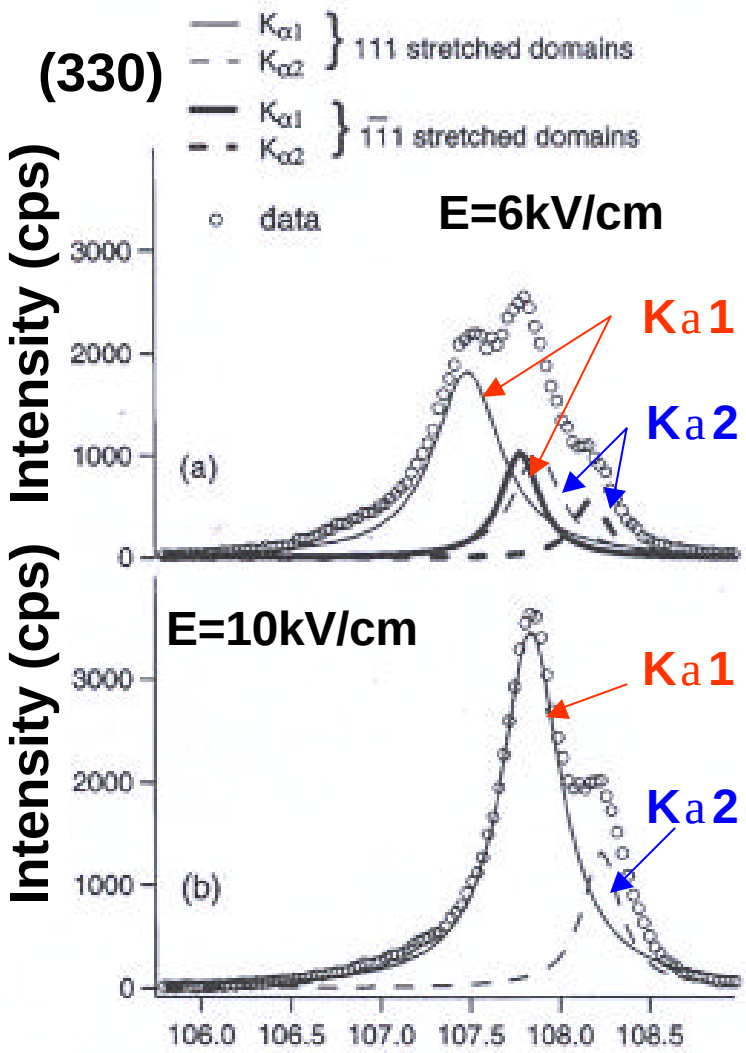
Peak Broadening Scherrer Model

As grain size decreases hardness increases and peaks become broader

High Temperature XRD Patterns of the Decomposition of $YBa_2Cu_3O_{7-d}$



In Situ X-ray Diffraction Study of an Electric Field Induced Phase Transition



Single Crystal *Ferroelectric*

92%Pb($Zn_{1/3}Nb_{2/3}$)O_3 -8%$PbTiO_3$

(330) peak splitting is due to Presence of <111> domains Rhombohedral phase

No (330) peak splitting Tetragonal phase

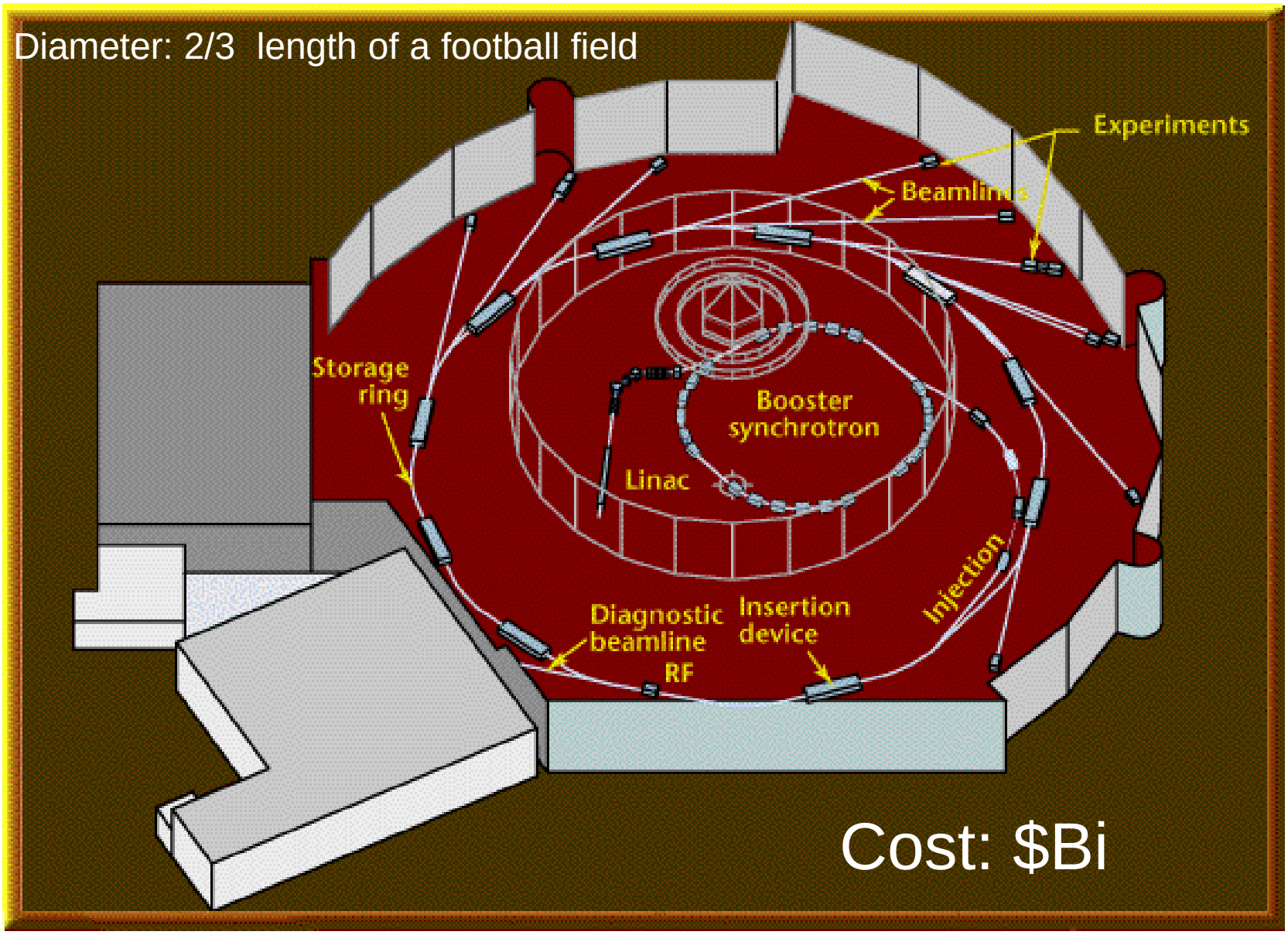
What Is A Synchrotron?

A synchrotron is a particle acceleration device which, through the use of bending magnets, causes a charged particle beam to travel in a circular pattern.

<u>Advantages of using synchrotron radiation:</u>

- **Detecting the presence and quantity of trace elements**
- **Providing images that show the structure of materials**
- **Producing X-rays with 10^8 more brightness than those from normal X-ray tube (tiny area of sample)**
- **Having the right energies to interact with elements in light atoms such as carbon and oxygen**
- **Producing X-rays with wavelengths (tunable) about the size of atom, molecule and chemical bonds**

Synchrotron Light Source



5.0 Instrumental Sources of Error

- **Specimen displacement**
- **Instrument misalignment**
- **Error in zero 2θ position**
- **Peak distortion due to $K\alpha_2$ and $K\beta$ wavelengths**

6.0 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**

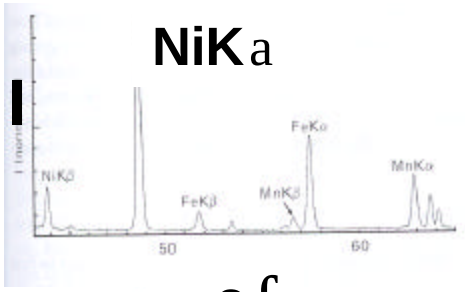
XRF: X-Ray Fluorescence

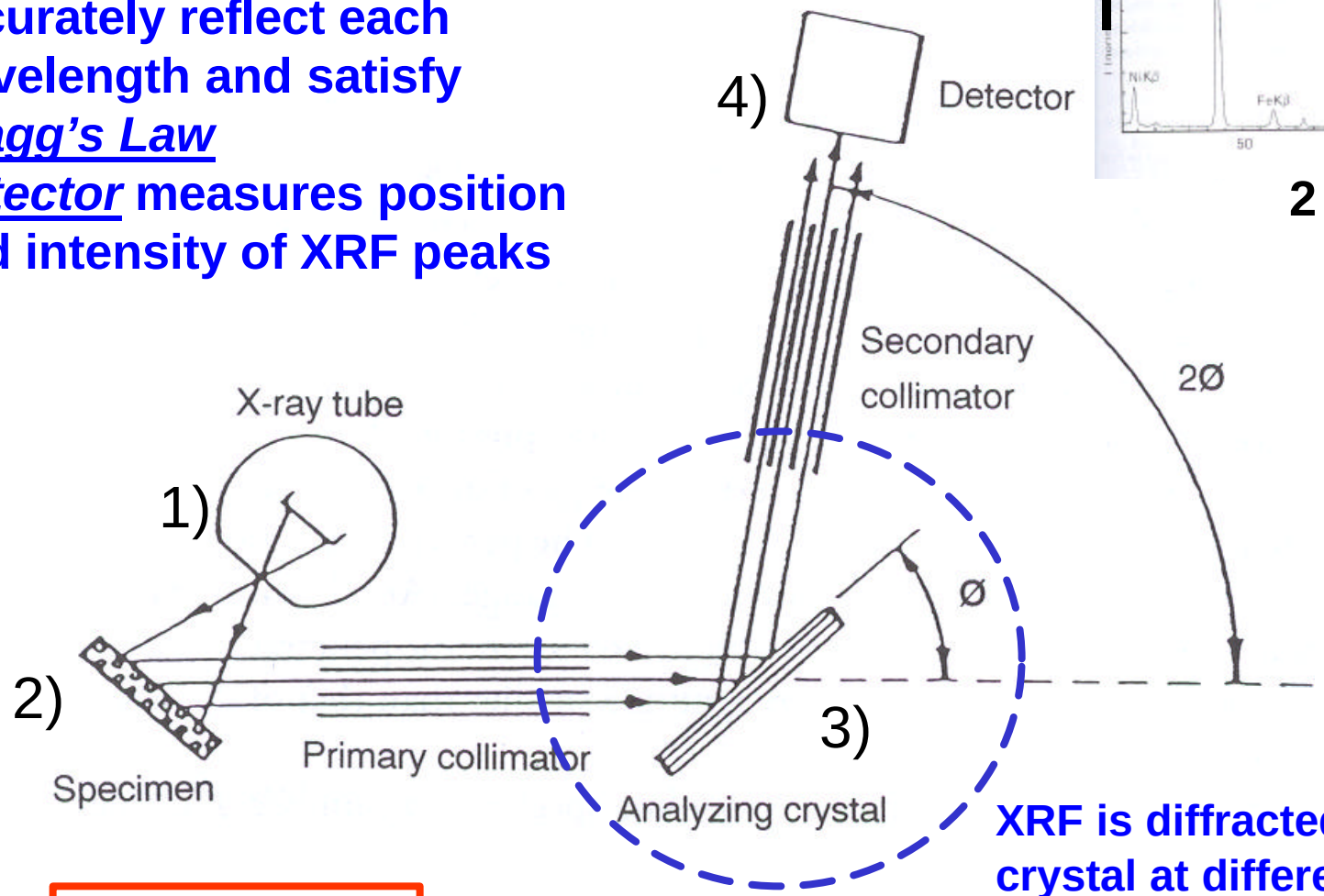
XRF is a ND technique used for chemical analysis of materials. An X-ray source is used to irradiate the specimen and to cause the elements in the specimen to emit (or fluoresce) their characteristic X-rays. A detection system (wavelength dispersive) is used to measure the peaks of the emitted X-rays for qual/quant measurements of the elements and their amounts. The techniques was extended in the 1970's to to analyze thin films. XRF is routinely used for the simultaneous determination of elemental composition and film thickness.

Analyzing Crystals used: LiF (200), (220), graphite (002), W/Si, W/C, V/C, Ni/C

XRF Setup

1) X-ray irradiates specimen
2) ***Specimen emits characteristic X-rays or XRF***
3) Analyzing crystal rotates to accurately reflect each wavelength and satisfy ***Bragg's Law***
4) ***Detector*** measures position and intensity of XRF peaks



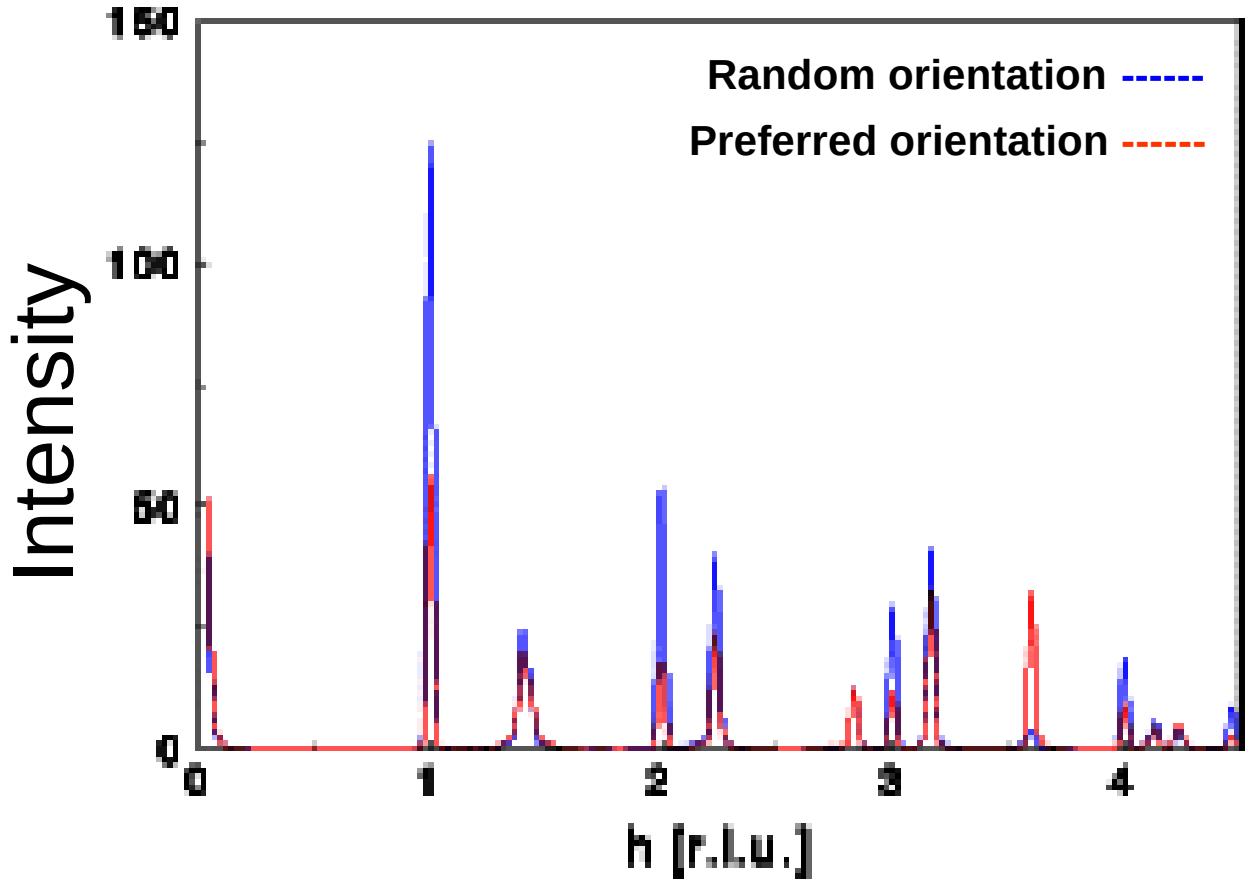


nl=2dsinf - **Bragg's Law**

XRF is diffracted by a crystal at different f to *separate X-ray l* and to identify *elements*

Preferred Orientation

A condition in which the distribution of crystal orientations is non-random, a real problem with powder samples.

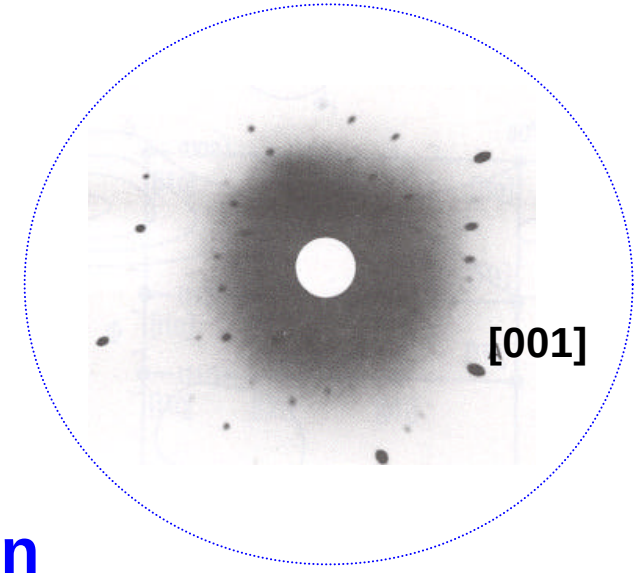


It is noted that due to preferred orientation several blue peaks are completely missing and the intensity of other blue peaks is very misleading. Preferred orientation can substantially alter the appearance of the powder pattern. It is a serious problem in experimental powder diffraction.

3. By Laue Method - *1st Method Ever Used*

Today - To Determine the Orientation of Single Crystals

Back-reflection Laue



pattern

Transmission Laue