

Introduction to X-ray Diffractionmeter

by Miguel Santiago,
Scientific Instrumentation Specialist

University of Puerto Rico – Mayagüez Campus

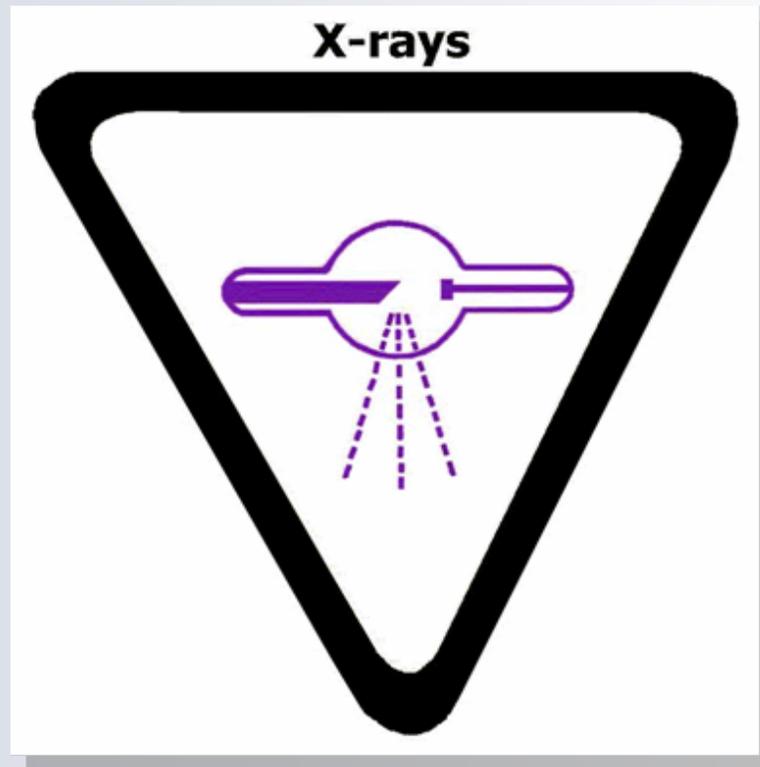
Department of Geology

X-ray / Microanalysis Laboratory



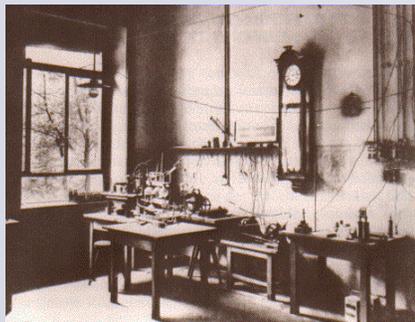
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1. Introduction



1.1 History

- Wilhelm Conrad Röntgen discovered 1895 the X-rays.
- 1901 he was honored by the Noble prize for physics.
In 1995 the German Post edited a stamp, dedicated to him.



Röntgen.



1.2 History

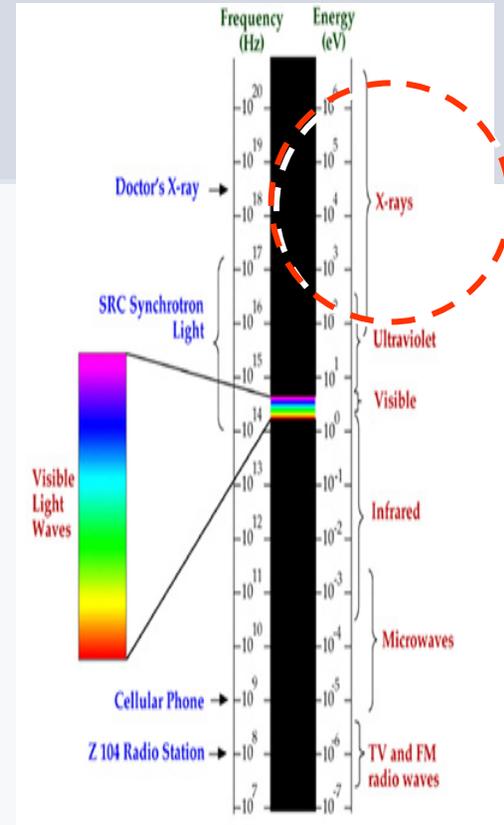
X-RAYS

1895- Roentgen discovers X-rays

X-rays are high-frequency electromagnetic radiation with energy intermediate between far-UV and gamma ray regions. This leads to development in numerous fields, particularly medical.

1911- Barkla recognized characteristic radiation

This scientist recognizes that x-rays emitted from different elements produce x-rays of different energy and wavelength.



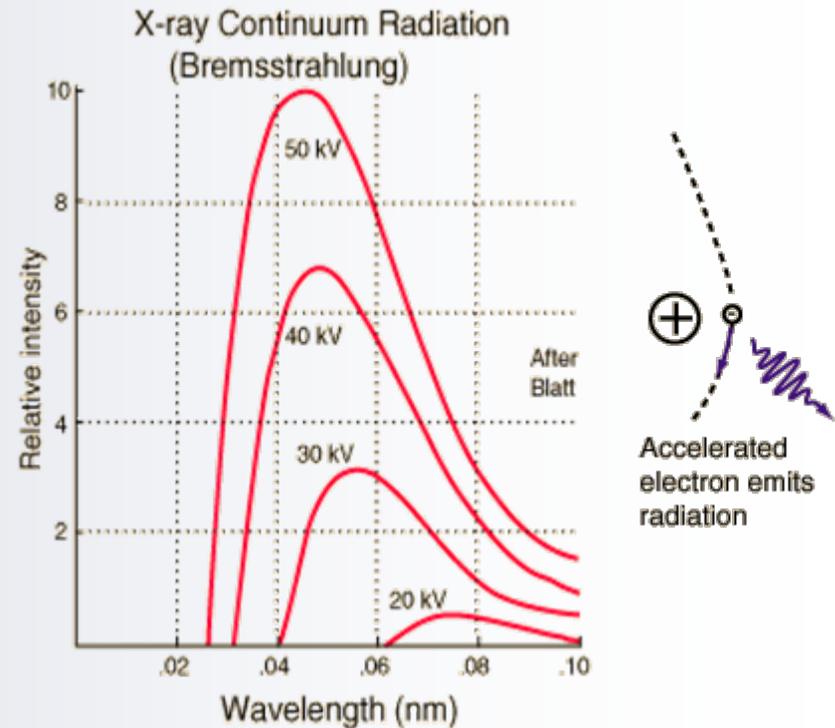
1.2 Characteristics of X-rays

- X-ray was the name given to the highly penetrating rays which emanated when high energy electrons struck a metal target. Within a short time of their discovery, they were being used in medical facilities to image broken bones. We now know that they are high frequency electromagnetic rays which are produced when the electrons are suddenly decelerated - these rays are called [bremstrahlung radiation](#), or "braking radiation".



1.2 Characteristics of X-rays

- "Bremsstrahlung" means "braking radiation" and is retained from the original German to describe the radiation which is emitted when electrons are decelerated or "braked" when they are fired at a metal target.
- Accelerated charges give off electromagnetic radiation, and when the energy of the bombarding electrons is high enough, that radiation is in the [x-ray](#) region of the [electromagnetic spectrum](#).
- It is characterized by a continuous distribution of radiation which becomes more intense and shifts toward higher frequencies when the energy of the bombarding electrons is increased.



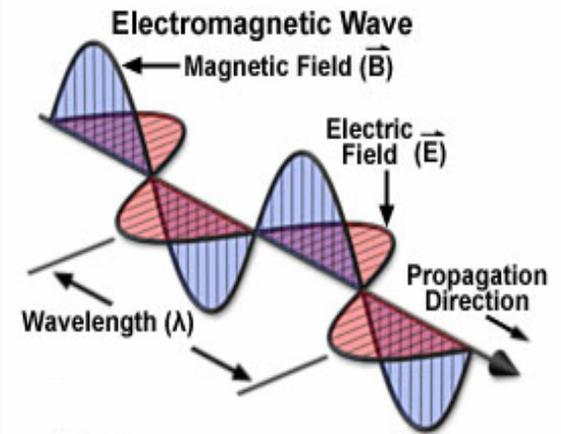
The curves in the are from the 1918 data of Ulrey, who bombarded tungsten targets with electrons of four different energies.

1.2 Characteristics of X-rays

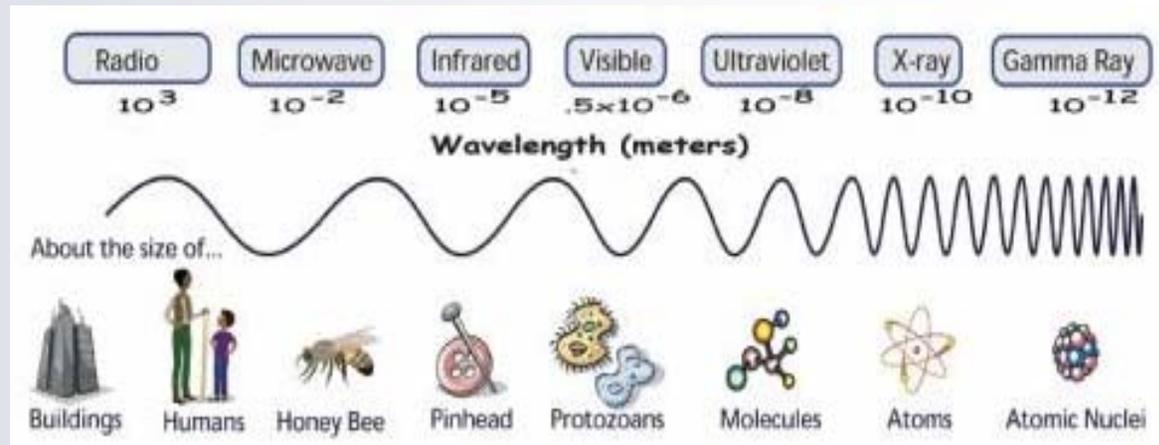
- X-rays are also produced when electrons make transitions between lower atomic energy levels in heavy elements. X-rays produced in this way have definite energies just like other line spectra from atomic electrons. They are called characteristic x-rays since they have energies determined by the atomic energy levels.
- In interactions with matter, x-rays are ionizing radiation and produce physiological effects which are not observed with any exposure of non-ionizing radiation, such as the risk of mutations or cancer in tissue.

1.2 Characteristics of X-rays

- X-rays (like all radiation) can be viewed as waves or particles.
- Transverse electromagnetic wave – **electric field** is important (interacts with electrons), but the **magnetic field** is not important.

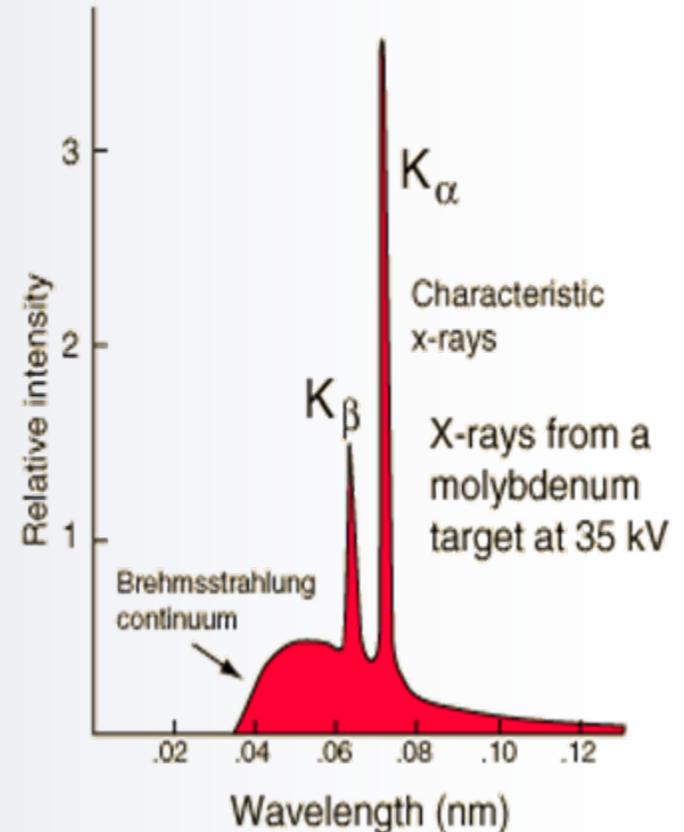


- The wavelength λ is very short (from ~ 0.1 nm to ~ 1.0 nm).



1.2 Characteristics of X-rays

- Characteristic [x-rays](#) are emitted from heavy elements when their electrons make transitions between the lower atomic energy levels. The characteristic x-rays emission which shown as two sharp peaks in the illustration at left occur when vacancies are produced in the $n=1$ or K-shell of the atom and electrons drop down from above to fill the gap.
- The x-rays produced by transitions from the $n=2$ to $n=1$ levels are called K-alpha x-rays, and those for the $n=3 \rightarrow 1$ transition are called K-beta x-rays.
- Transitions to the $n=2$ or L-shell are designated as L x-rays ($n=3 \rightarrow 2$ is L-alpha, $n=4 \rightarrow 2$ is L-beta, etc.). The continuous distribution of x-rays which forms the base for the two sharp peaks at left is called "[bremsstrahlung](#)" radiation.



1.2 Characteristics of X-rays

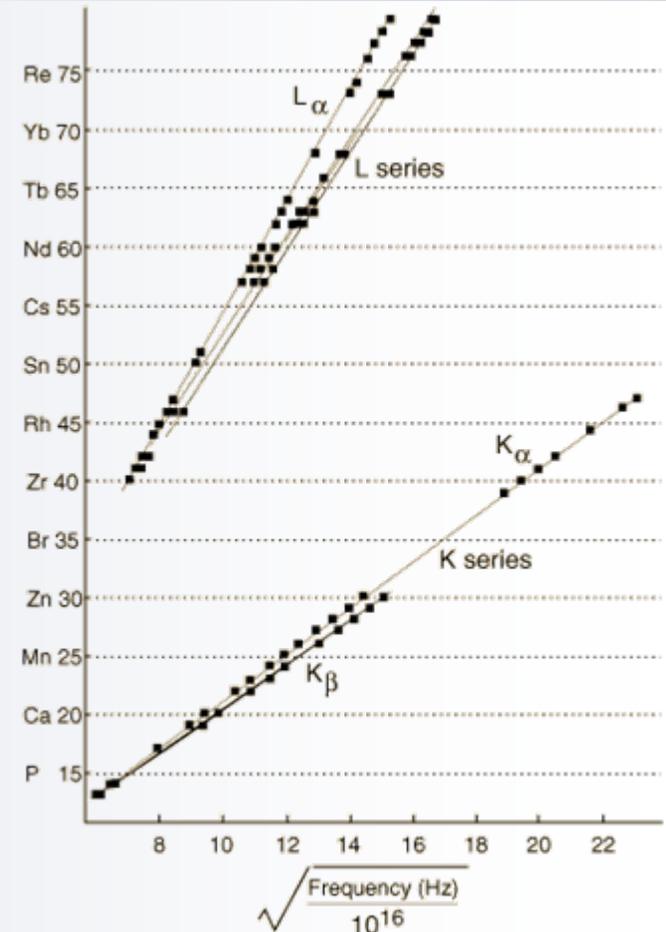
- X-ray production typically involves bombarding a metal target in an [x-ray tube](#) with high speed electrons which have been accelerated by tens to hundreds of kilovolts of potential. The bombarding electrons can eject electrons from the inner shells of the atoms of the metal target. Those vacancies will be quickly filled by electrons dropping down from higher levels, emitting x-rays with sharply defined frequencies associated with the difference between the atomic energy levels of the target atoms.
- The frequencies of the characteristic x-rays can be predicted from the Bohr model . Moseley measured the frequencies of the characteristic x-rays from a large fraction of the elements of the periodic table and produces a plot of them which is now called a "[Moseley plot](#)".
- Characteristic x-rays are used for the investigation of crystal structure by x-ray diffraction. Crystal lattice dimensions may be determined with the use of [Bragg's law](#) in a [Bragg spectrometer](#).

1.2 Characteristics of X-rays

When the square root of the frequencies of the [characteristic x-rays](#) from the elements is plotted against the atomic number, a straight line is obtained. In his early 20's, Moseley measured and plotted the x-ray frequencies for about 40 of the elements of the periodic table. He showed that the K-alpha x-rays followed a straight line when the atomic number Z versus the square root of frequency was plotted. With the insights gained from the Bohr model, we can write his empirical relationship as follows:

$$h\nu_{K\alpha} = 13.6eV (Z-1)^2 \left[\frac{1}{1^2} - \frac{1}{2^2} \right] = \frac{3}{4} 13.6 (Z-1)^2 eV$$

Moseley Plot of Characteristic X-Rays



Adapted from Moseley's original data (H. G. J. Moseley, Philos. Mag. (6) 27:703, 1914)

1.3 Intro. to XRD

- XRD techniques give information about the structure of solids → the arrangement of the atoms that compose the solid.
- XRD → Permits nondestructive structure analyses, although is relatively low in sensitivity.
- **Type of information:**
 - The kinds of materials that compose a solid (Qualitative Analysis)
 - The quantity of materials that compose the solid (Quantitative analysis)

1.3 Intro. to XRD (cont')

- The quantity of materials that are crystallized (Crystallinity)
- The amount of stress present in the solid (residual stress)
- The size of crystallites that compose the solid (crystallite size)
- Average orientation of crystallites that compose the solid (texture)

1.3 Intro. to XRD (cont')

- According to the **type of sample**:
 - The polycrystal method (powder method)
 - The single crystal method
 - The amorphous method
- According to the **way of detecting**:
 - The photographic method using a film
 - The counter method using a photon counter (X-ray diffractometers)

1.3 Intro. to XRD (cont')

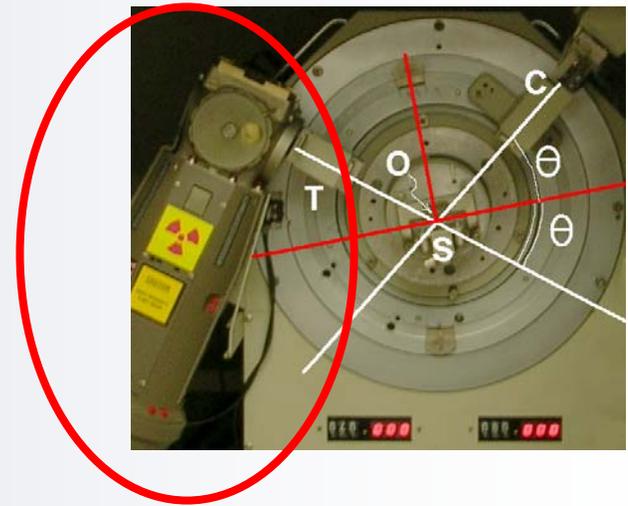
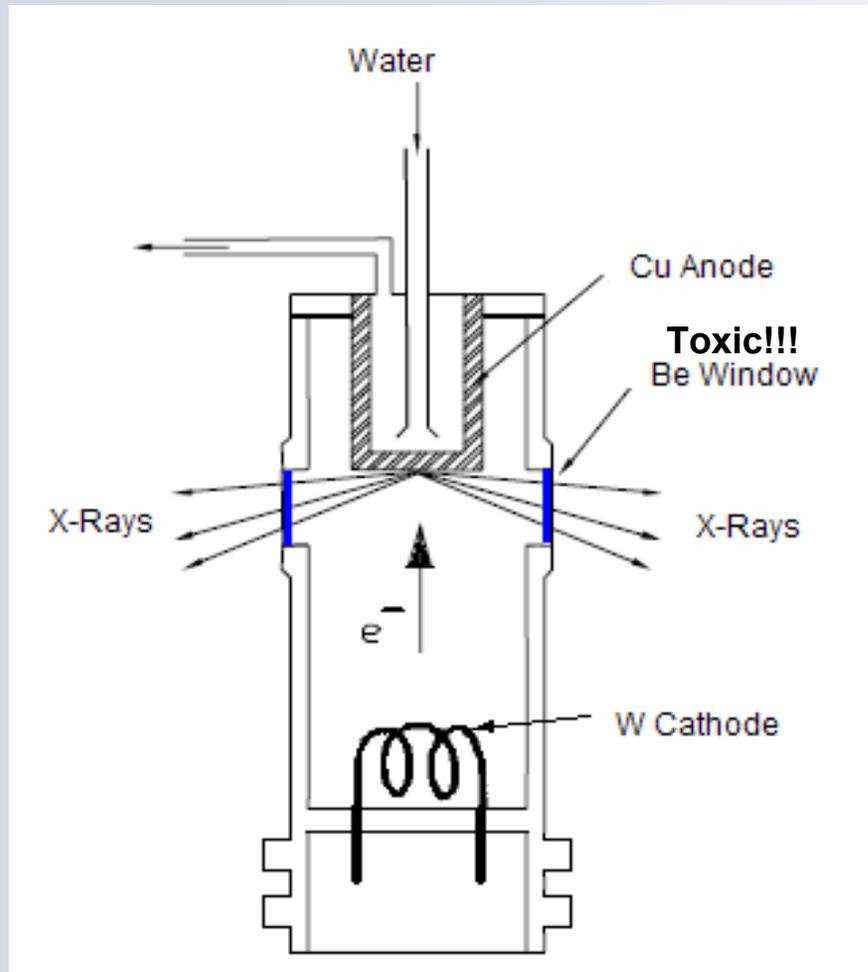
- **In micro-area XRD**, a PSPC (position sensitive proportional counter) is used to simultaneously detect diffracted rays in the shortest time.
- X-ray information is efficiently obtained from micro areas down to 0.01 mm in diameter.
- In thin films XRD techniques, X-ray incidence is made at minimum angle to the sample surface to get as much information as possible on the surface. A monochromator is used to improve the peak-to-background ratio.

2. Generation of X-rays

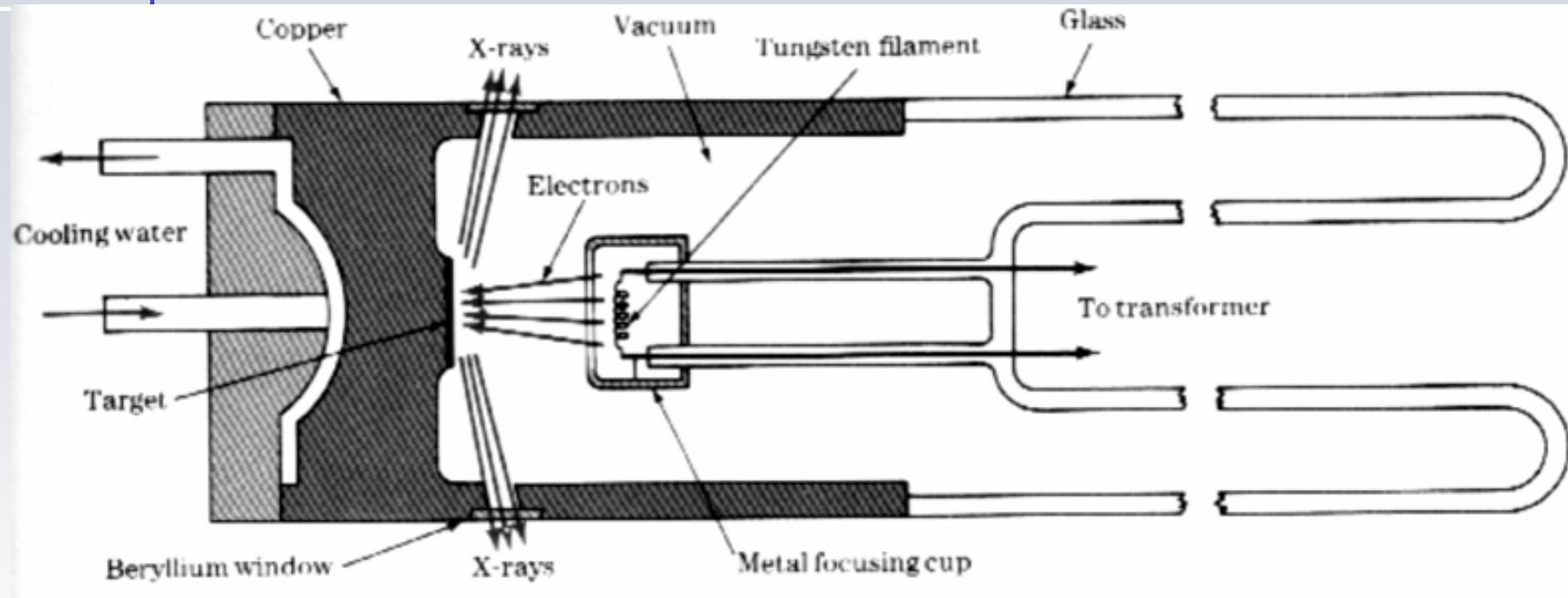
Need:

- A source of a highly energetic electron beam
- A metallic target
- A system that contains and directs the X-rays onto the specimen

2.1 Principles of a X-Ray Tube



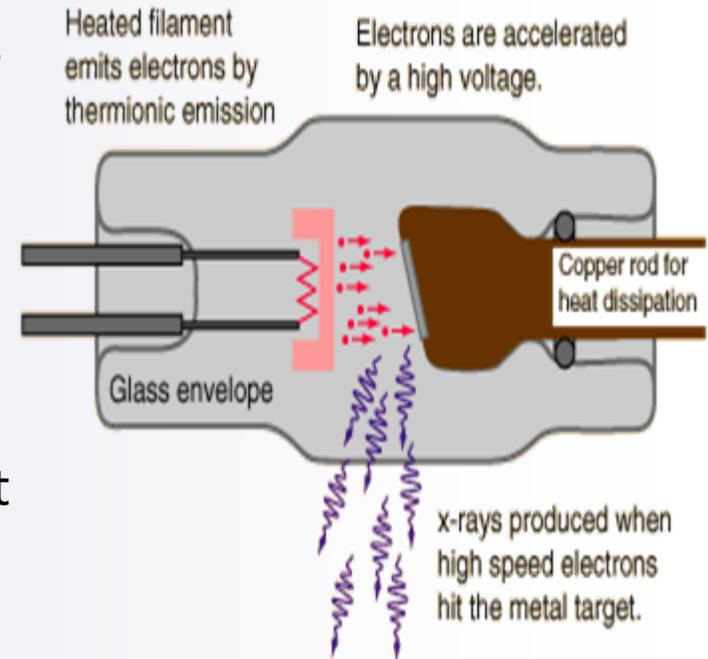
2.1 Principles of a X-Ray Tube



The X-Ray tube

X-ray Tube

- X-rays for medical diagnostic procedures or for research purposes are produced in a standard way: by accelerating electrons with a high voltage and allowing them to collide with a metal target. X-rays are produced when the electrons are suddenly decelerated upon collision with the metal target; these x-rays are commonly called brehmsstrahlung or "braking radiation".
- If the bombarding electrons have sufficient energy, they can knock an electron out of an inner shell of the target metal atoms.
- Then electrons from higher states drop down to fill the vacancy, emitting x-ray photons with precise energies determined by the electron energy levels. These x-rays are called characteristic x-rays.

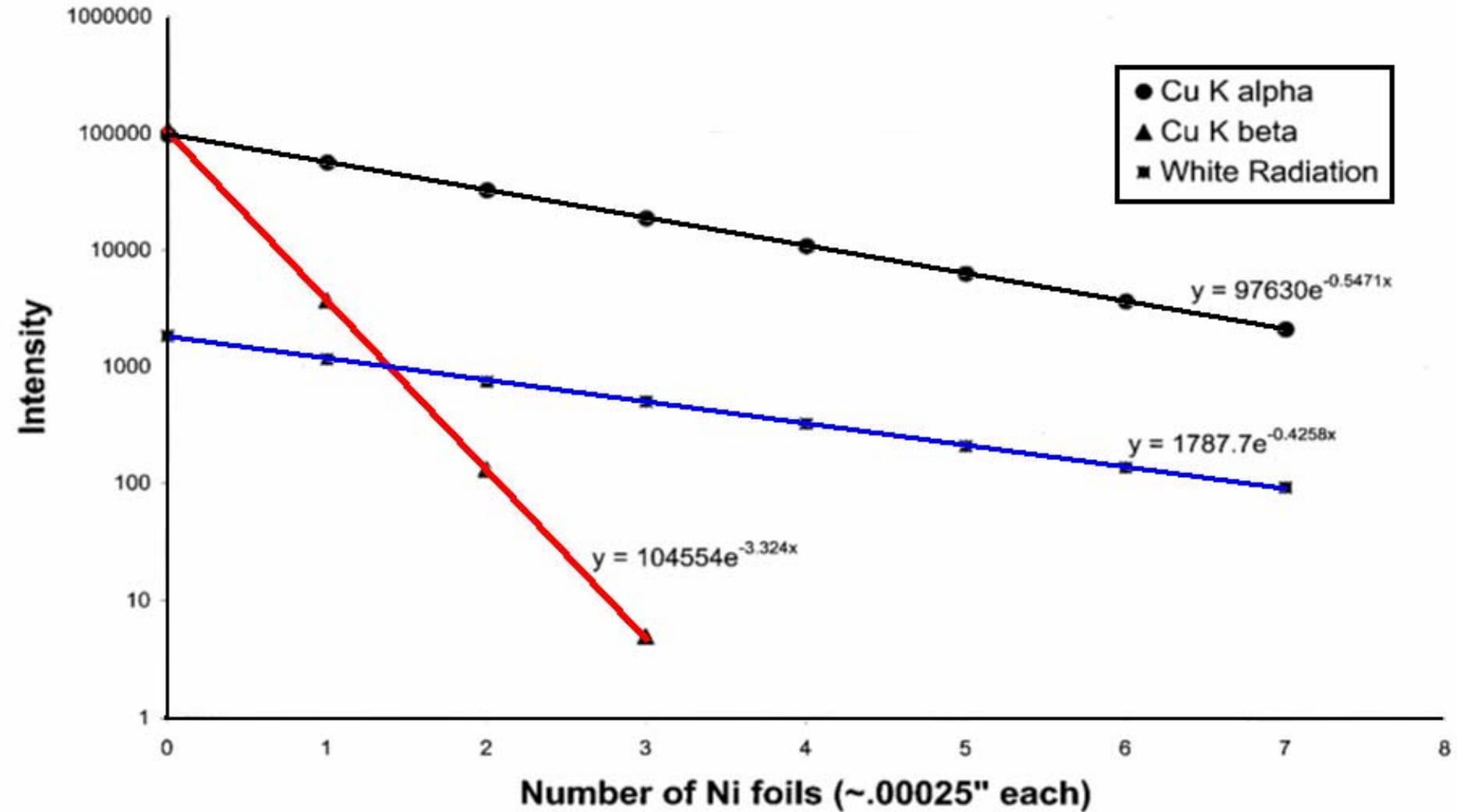


Anode and filter materials and associated constant

	Cr	Fe	Cu	Mo
Z	24	26	29	42
$\alpha_1, \text{Å}$	2.2896	1.9360	1.5405	0.70926
$\alpha_2, \text{Å}$	2.2935	1.9399	1.5443	0.71354
$\bar{\alpha}, \text{Å}$	2.2909	1.9373	1.5418	0.71069
$\beta_1, \text{Å}$	2.0848	1.7565	1.3922	0.63225
$\beta, \text{filt.}$	V, 0.4 mil	Mn, 0.4 mil	Ni, 0.6 mil	Nb, 3 mil
$\alpha, \text{filt.}$	Ti	Cr	Co	Y
Operative conditions:				
Voltage, KV	30 – 40	35 – 45	35 – 45	50 – 55
Ampere, mA	10	10	20	20

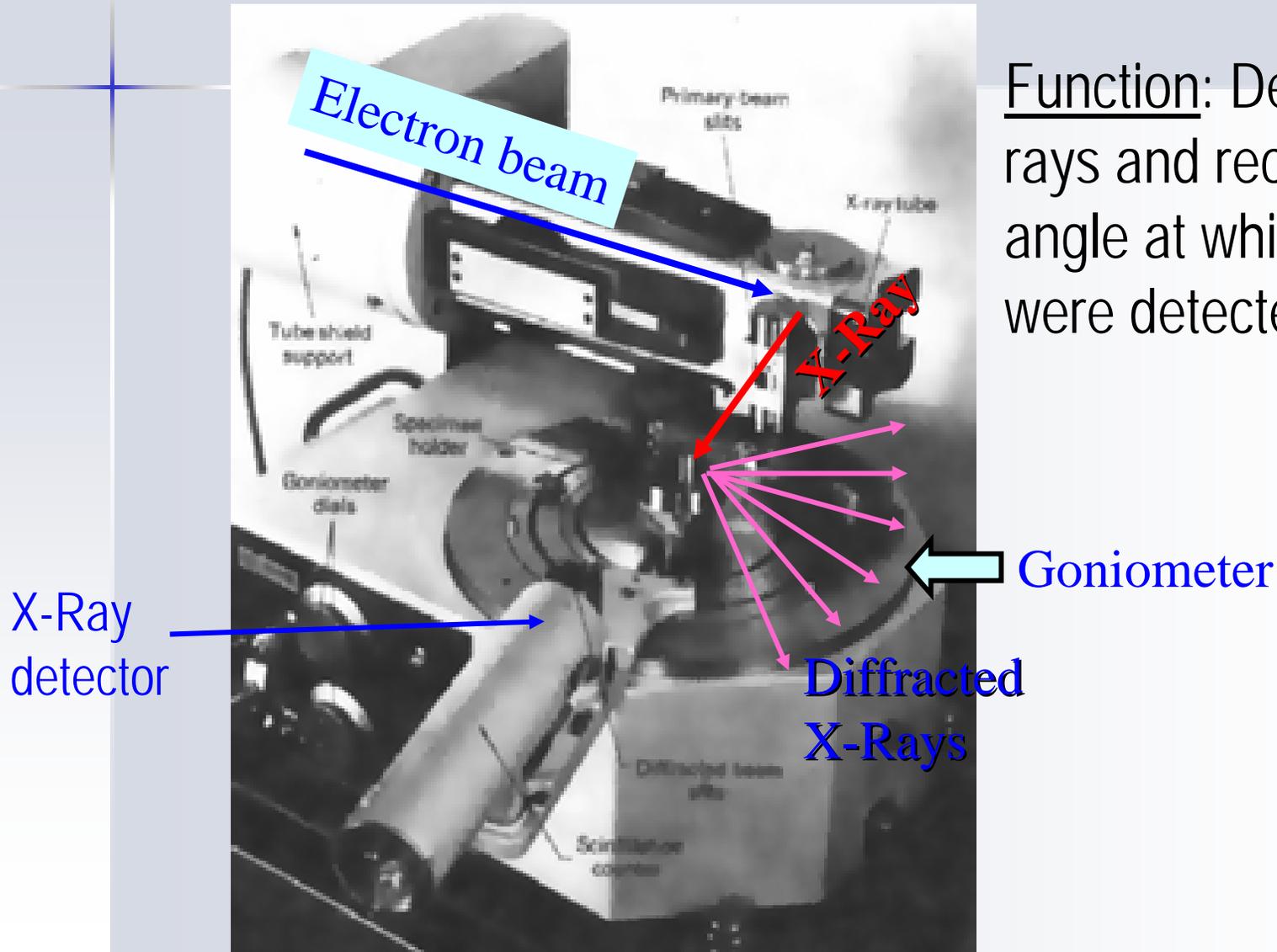
Liang Michael, "Introducción a la Cobertura, Potencial y Aplicaciones del Análisis Por Rayos-X" International Union of Crystallography, pp7, 1981

Effect of Ni Foils on Radiation Intensity



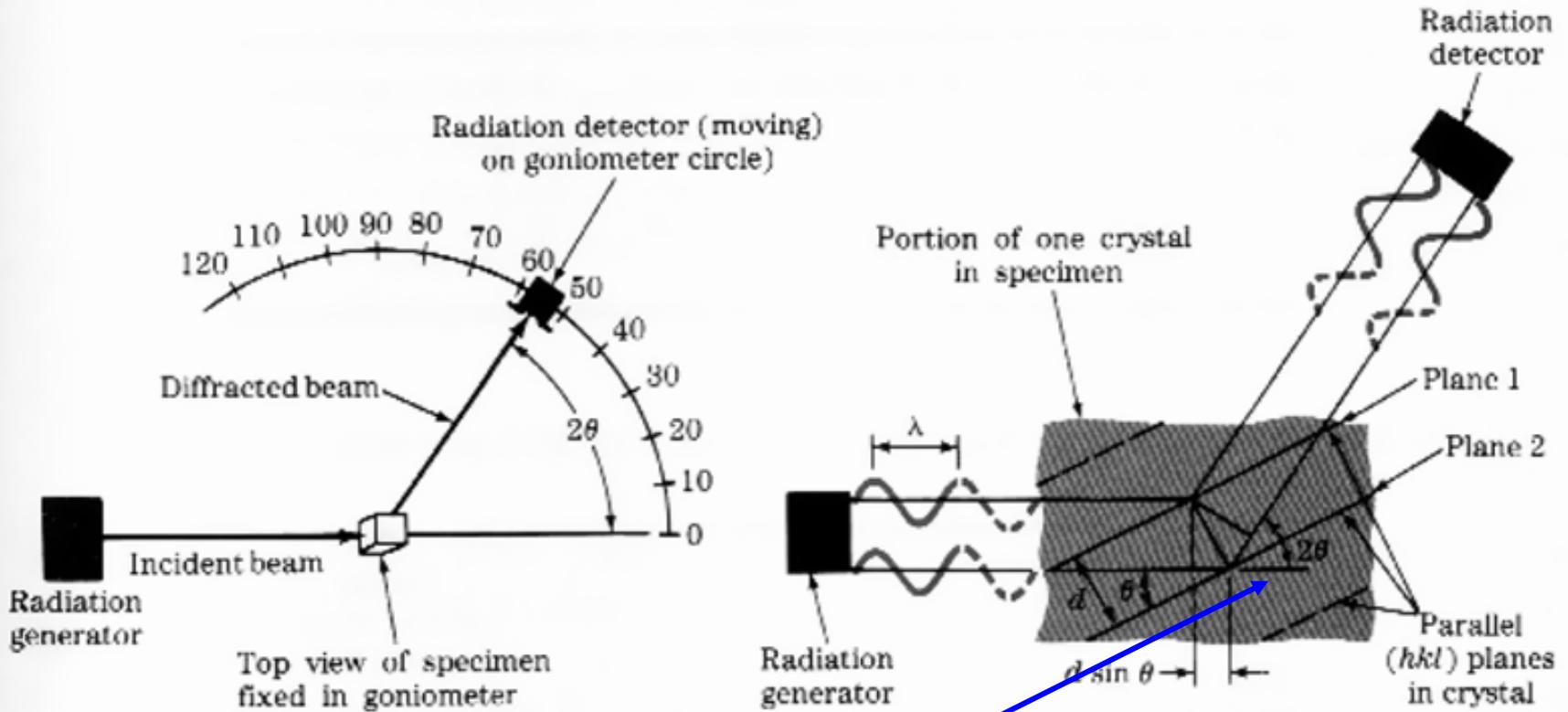
Source: Chang-Beom Eom, PhD; Jon Giencke, Graduate Student
University of Wisconsin, 2006

2.2 The X-Ray Diffractometer



Function: Detects X-rays and records the angle at which they were detected

2.2 X-Ray Diffractometer (cont.)



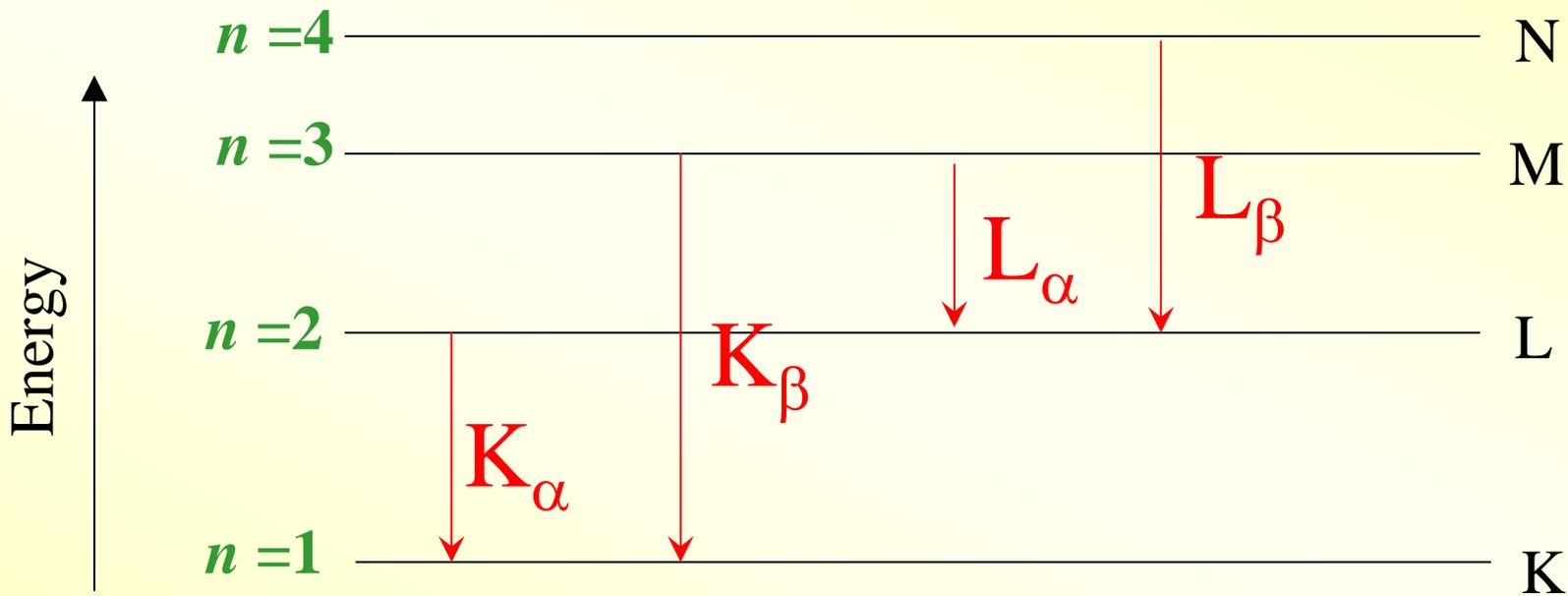
The total diffraction angle is 2θ !!

2.3 Aspects of X-ray tube design and operation

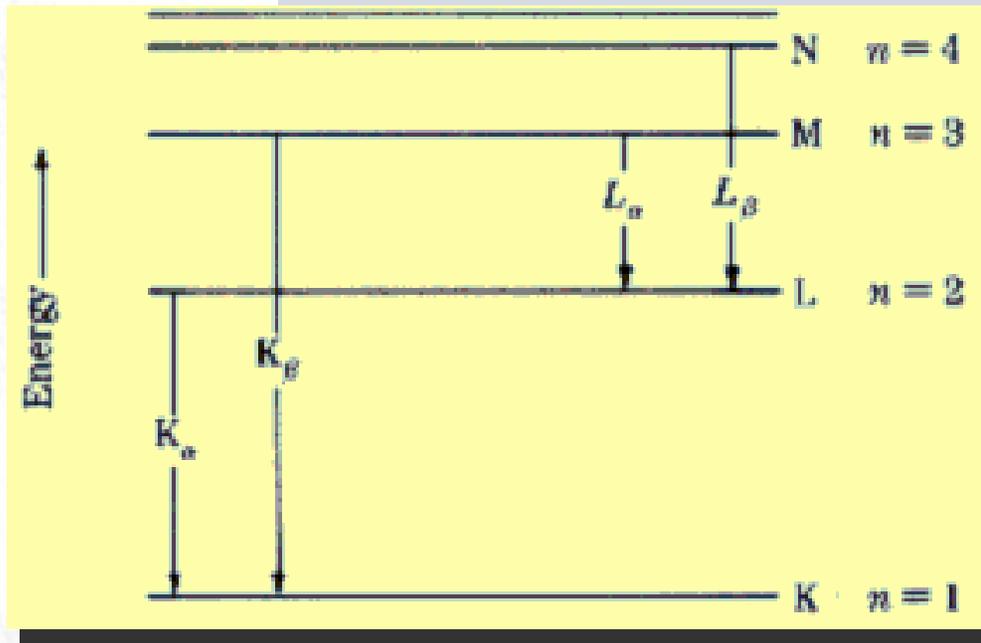
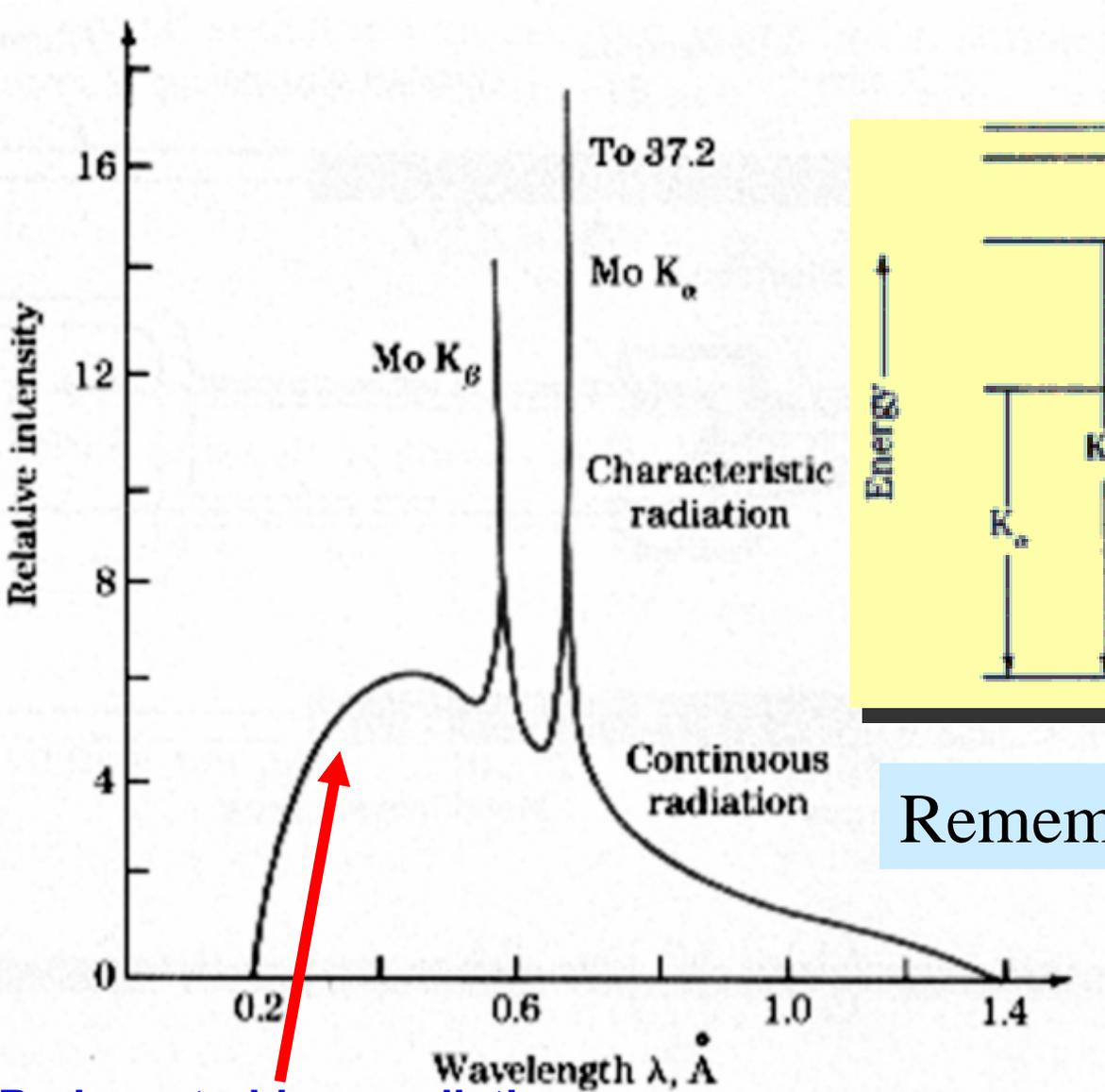
- A new tube is about \$3,000 and should last several thousand hours.
- An important rule of thumb:
 - When turning a tube up, increase the kV first, and then increase the mA.
 - When turning a tube down, decrease the mA first, and then decrease the kV.

2.4 X-Ray Generation (cont.)

How X-Rays are generated or how to knock off electrons from a target



2.5 X-Ray Emission Spectrum

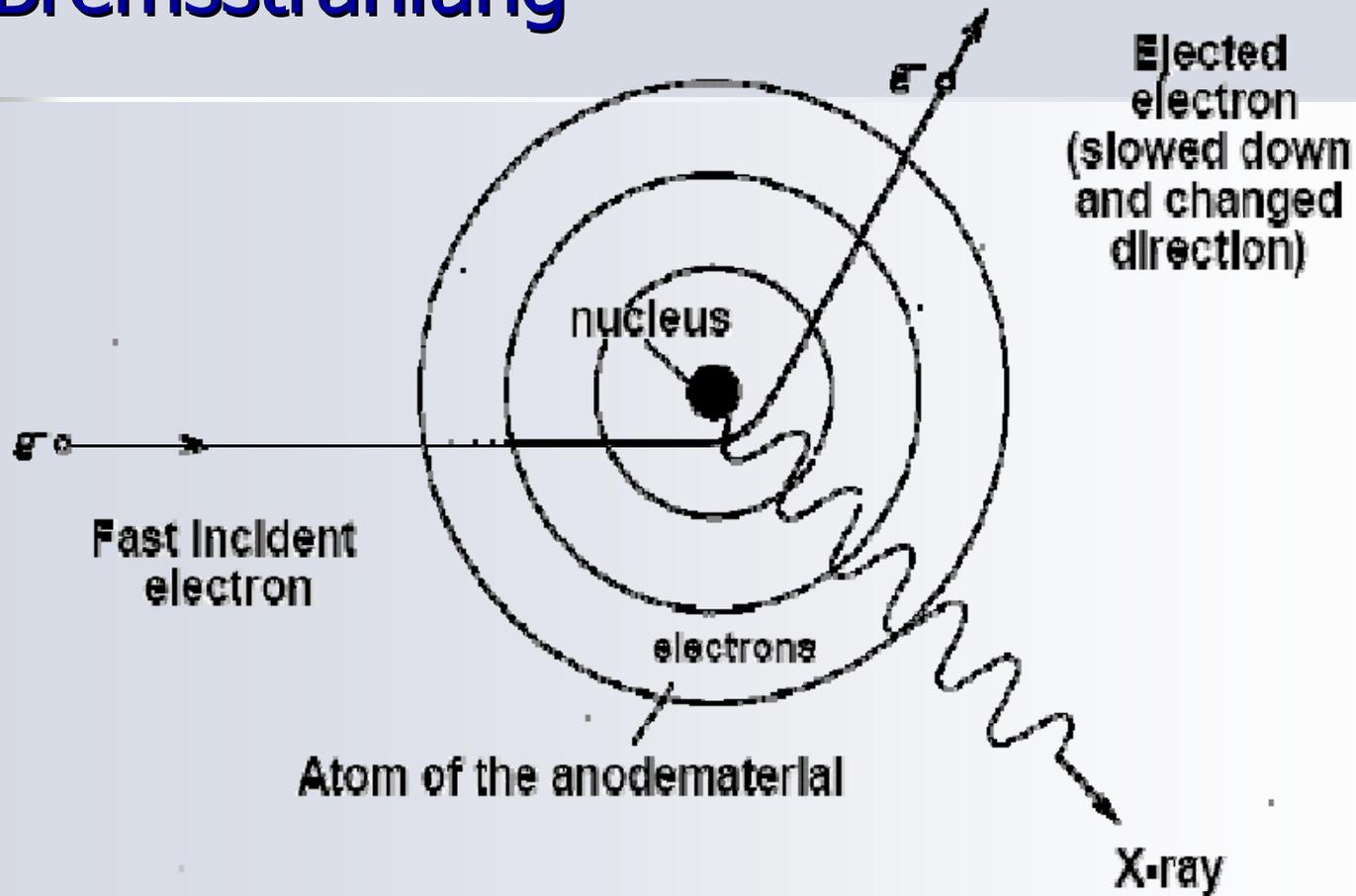


Remember Planck's equation:

$$E \propto \frac{1}{\lambda}$$

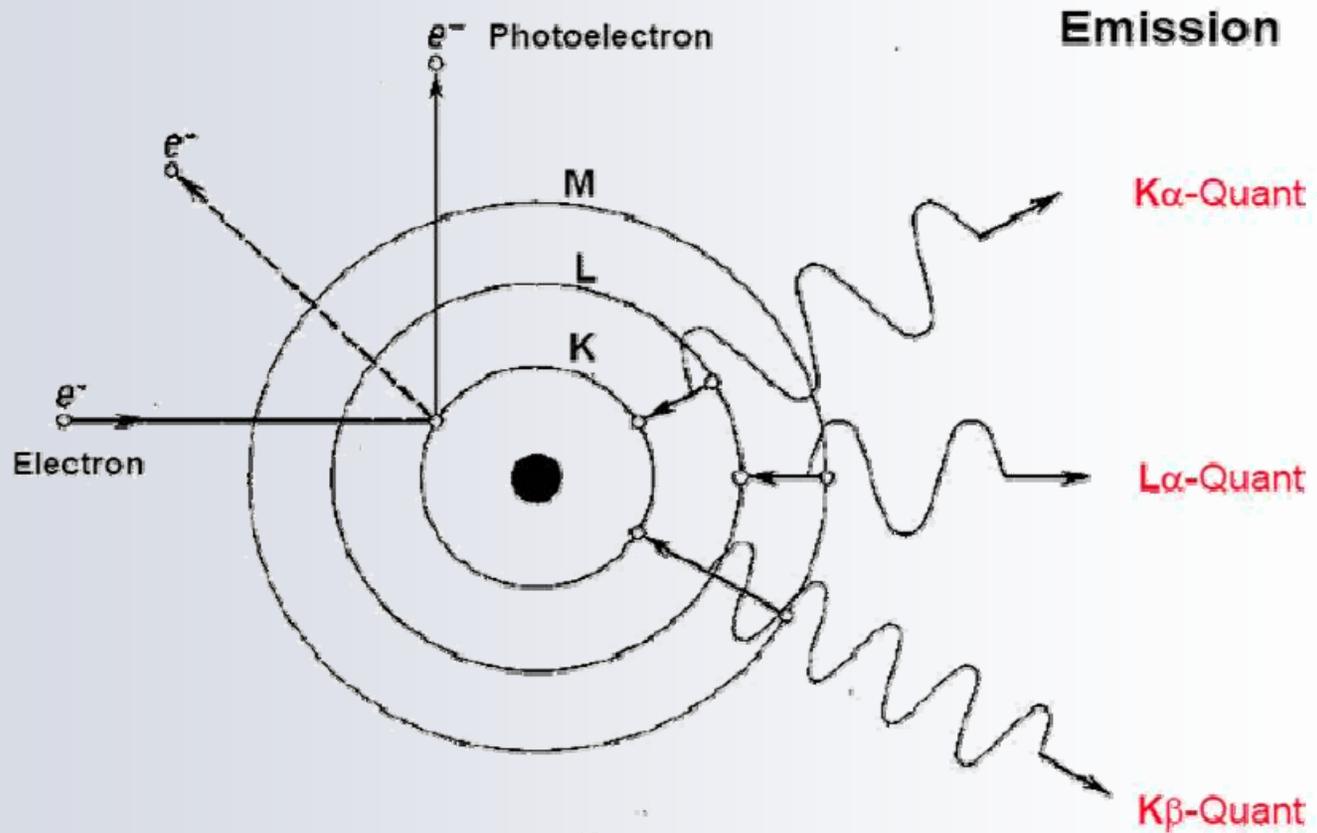
Bremsstrahlung radiation

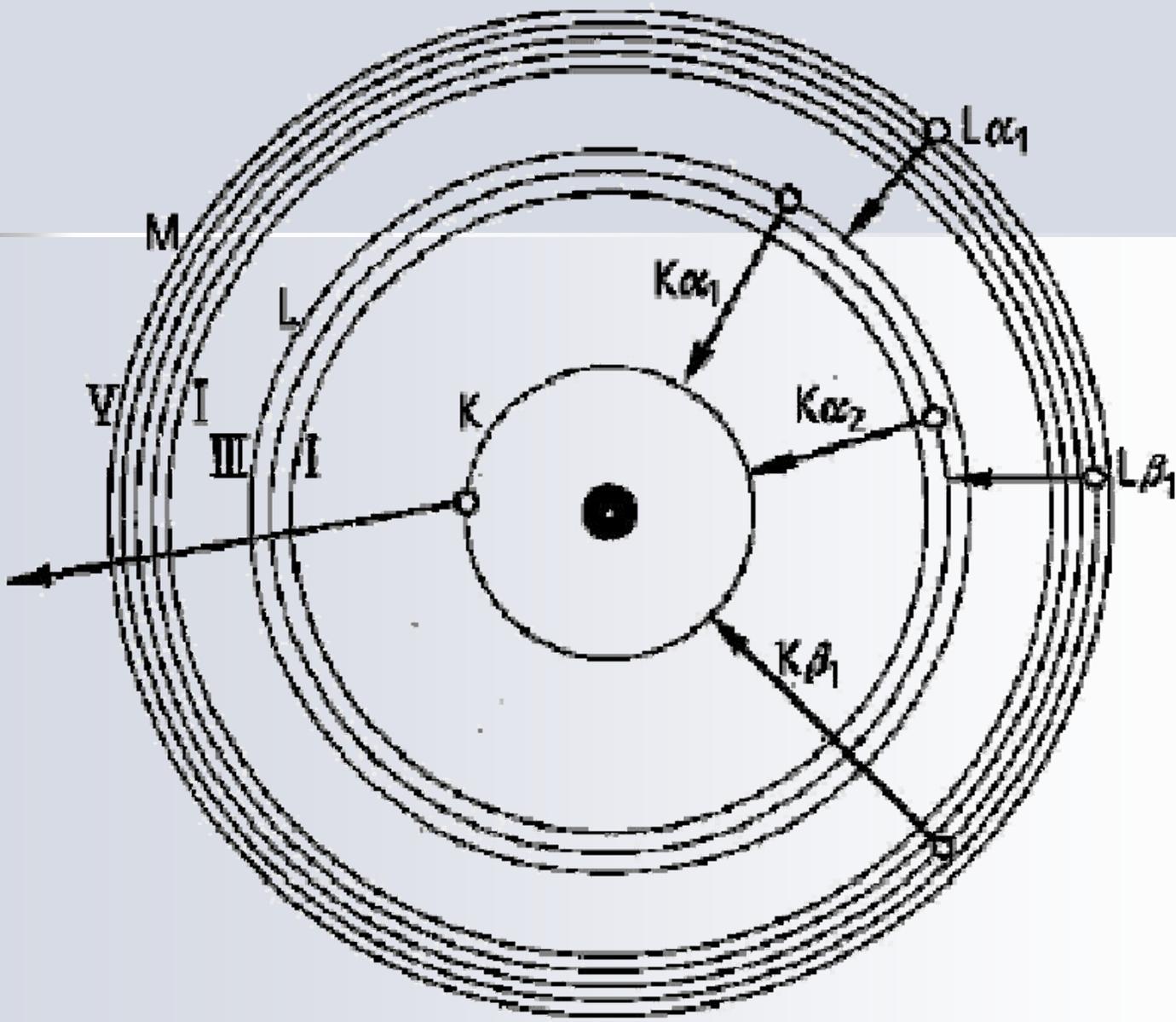
2.6 The Principle of Generation Bremsstrahlung



Bremsstrahlung: a German word meaning "braking radiation" (referring to the deceleration of electrons as the cause of the radiation). Also called general or **white radiation**.

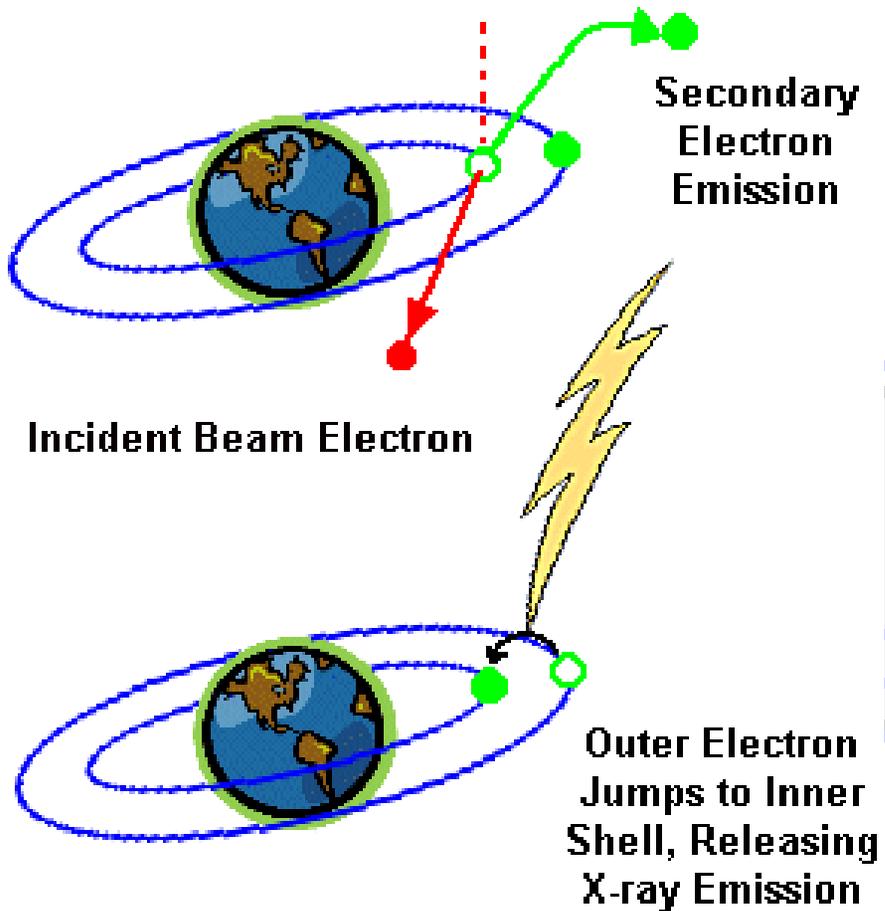
2.7 The Principle of Generation the Characteristic Radiation





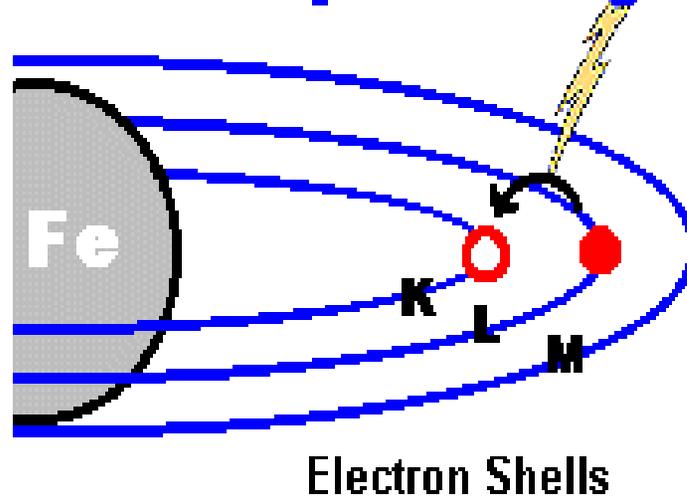
Bohr's model

X-ray Emission



The energy of the characteristic X-ray can be used for specifying a constituent element since the energy at the X-ray peak position is specific to each element.

Fe K Alpha X-rays



For instance, if the innermost shell (the K shell) electron of an iron atom is replaced by an L shell electron, a 6400 eV K- α X-ray is emitted from the sample.

- Atoms and ions are in the order of 0.1 nm in size.
- As seen in the figure, the portion of the electromagnetic spectrum with a wavelength in this range is x-radiation (compared with 100-nm range for the wavelength of the visible light) → X-ray diffraction is capable of characterizing crystalline structure.

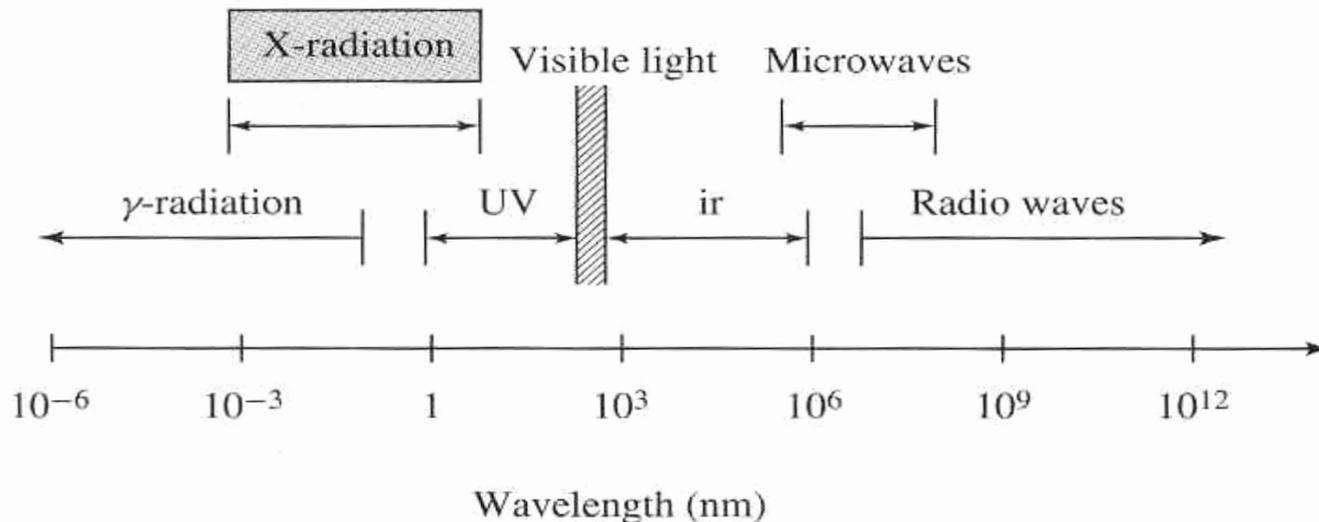
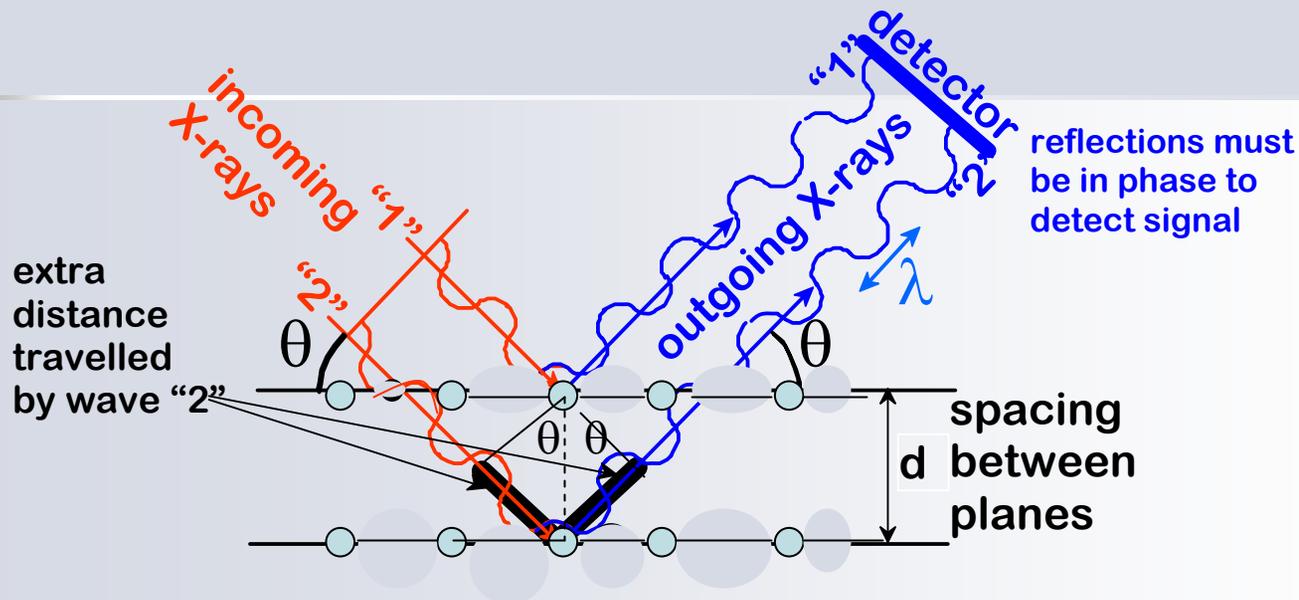


FIGURE 3-35 *Electromagnetic radiation spectrum. X-radiation represents that portion with wavelengths around 0.1 nm.*

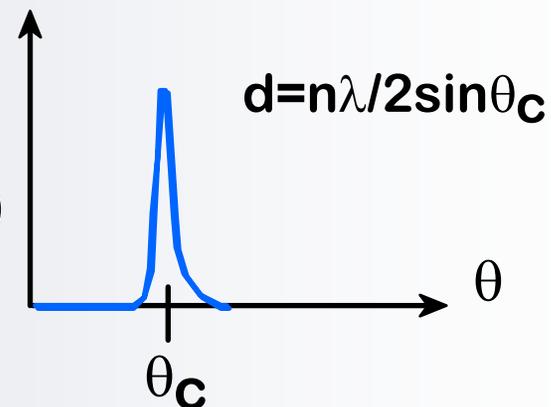
2.8 X-RAYS TO CONFIRM CRYSTAL STRUCTURE

- Incoming X-rays diffract from crystal planes.

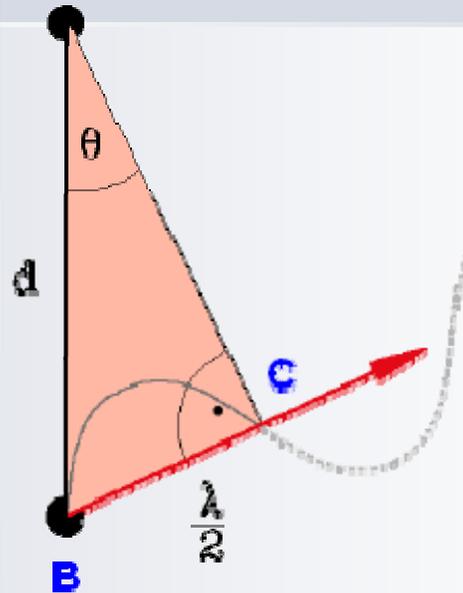
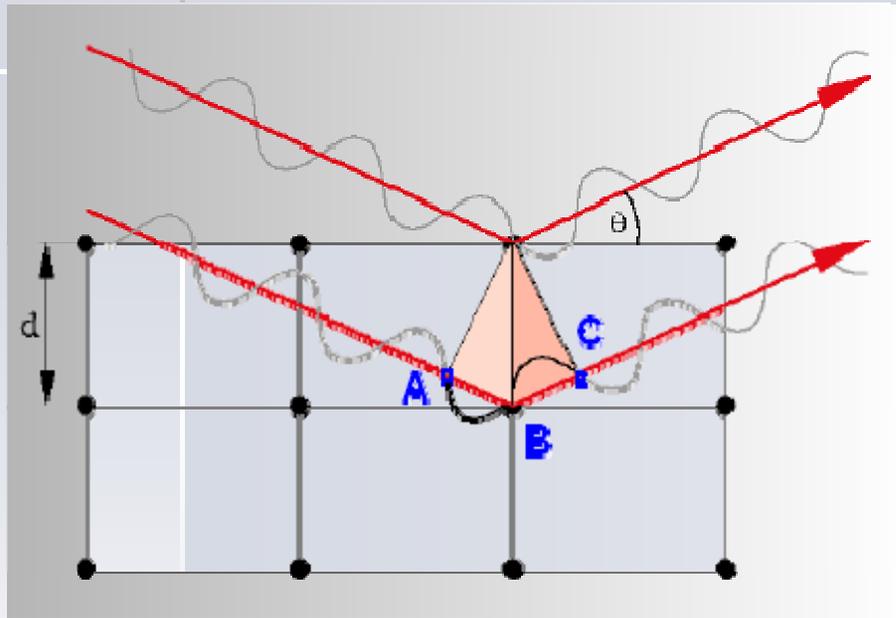


- Measurement of: Critical angles, θ_c , for X-rays provide atomic spacing, d .

x-ray intensity (from detector)



2.9 Derivation of Bragg's Law



$$\begin{aligned} AB &= BC \\ ABC &= 2 BC \\ BC &= d \sin \theta \end{aligned}$$

this path length difference is an integral number of wavelengths

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

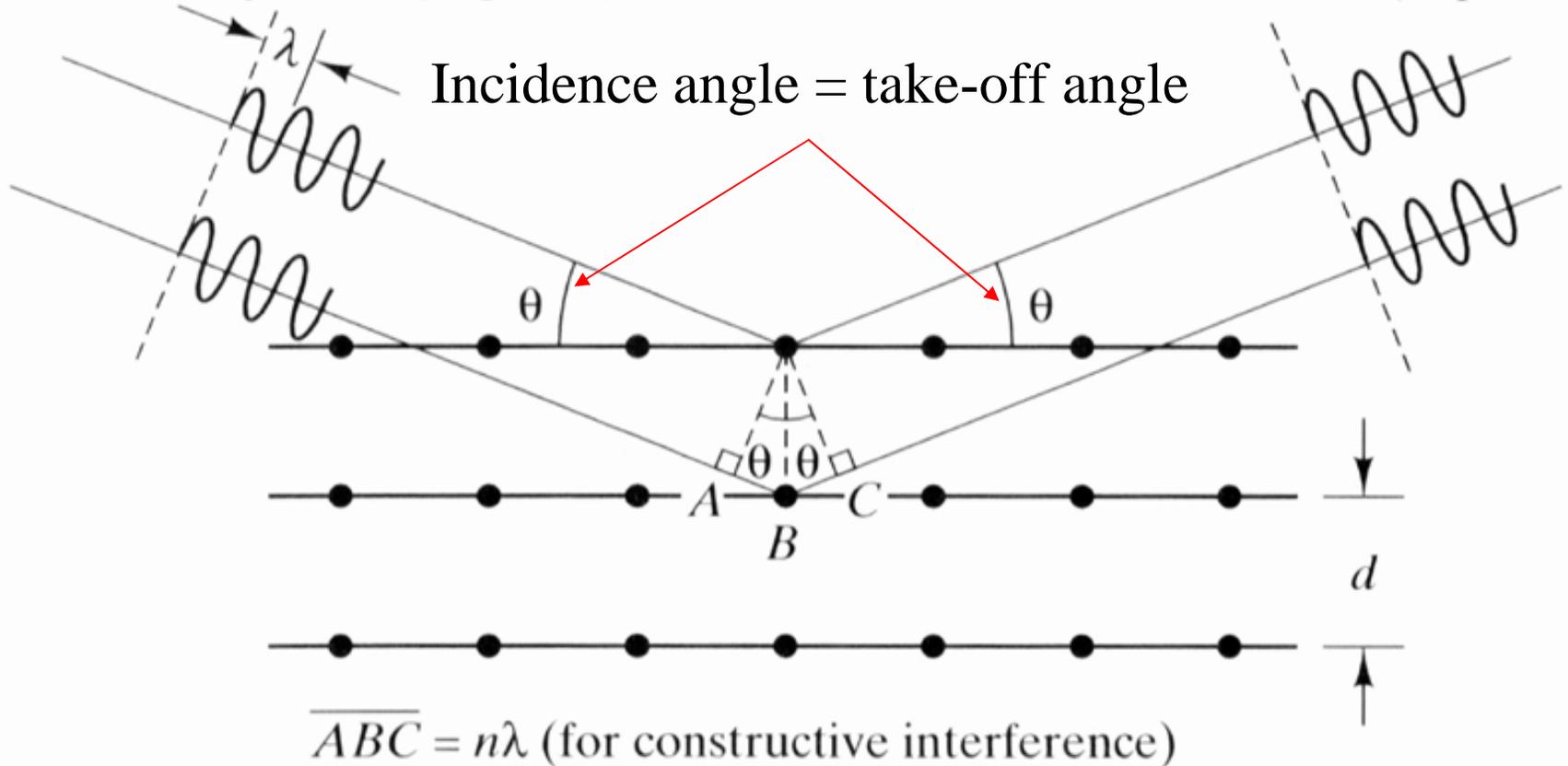
$$n \lambda = 2 d \sin \theta$$

$$d = \frac{n \cdot \lambda}{2 \cdot \sin \theta}$$

2.10 X-Ray Beam Interaction with the Specimen

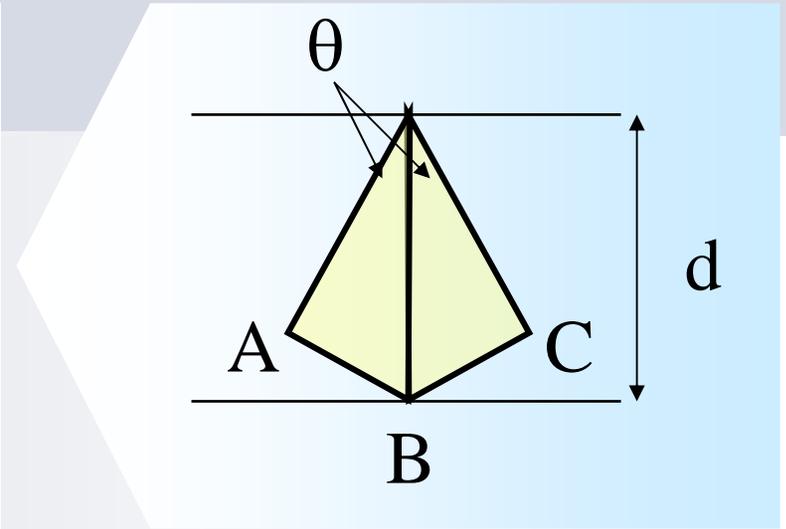
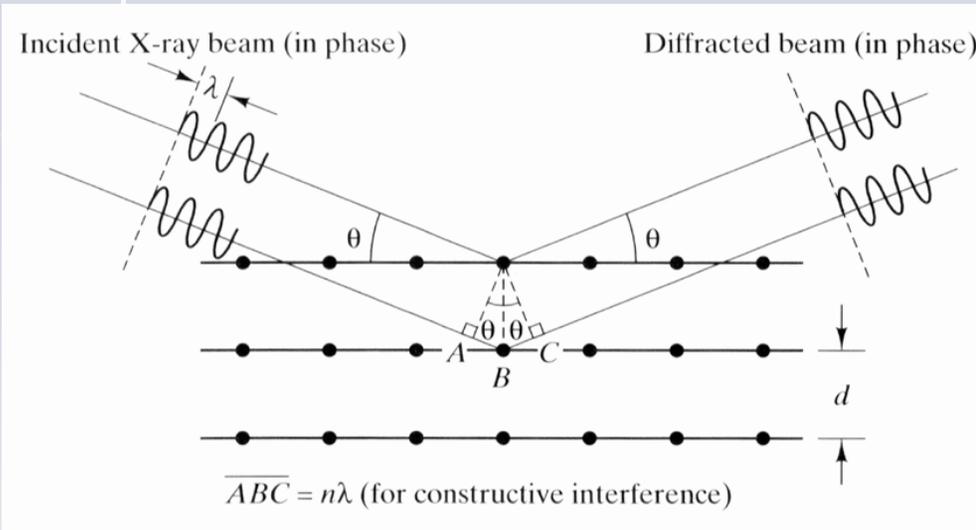
Incident X-ray beam (in phase)

Diffracted beam (in phase)



ABC is the only difference between both X-ray trajectories

2.11 Bragg's Law



In order to get constructive interaction:

$$ABC = n\lambda = 2d \cdot \sin \theta \quad \text{where } n \text{ is an integer}$$

and d is the interplanar distance:

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

Indexing of Cubic Patterns

◆ Non-cubic structures -- much more complex!

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:
$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

Rhombohedral:
$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)}{a^2 (1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}$$

Monoclinic:
$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$$

2.12 Other Conditions for Diffraction

- Bragg's law is a necessary but not sufficient condition for diffraction.
- It defines the diffraction condition for primitive unit cells, that is, those Bravais lattices with lattice points only at unit cell corners, such as SC and simple tetragonal.
- Crystal structures with non primitive unit cells have atoms at additional lattice sites located along a unit cell edge, within a unit cell face or in the interior of the unit cell.
- The extra scattering centers can cause out-of-phase scattering to occur at certain Bragg angles → some of the diffraction lines predicted by Bragg's law does not occur.

3. Factors that Affect the Diffracted Intensity

- Structure Factor
- Polarization Factor
- Lorentz Factor
- Multiplicity Factor
- Temperature Factor
- Absorption Factor

3.1 Structure Factor

- The structure factor for a particular hkl reflection is given by:

$$F_{hkl} = \sum_j f_j e^{2\pi i(hu_j + kv_j + lw_j)}$$

- The intensity of a Bragg reflection is proportional to the square of the structure factor:

$$I \propto F_{hkl} F_{hkl}^* = |F_{hkl}|^2$$

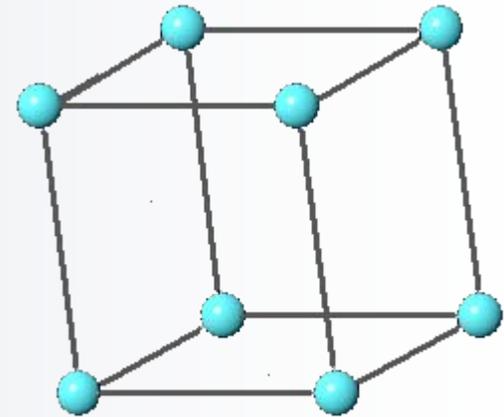
3.1-1 Primitive Cubic Cell

$$F_{hkl} = f_j e^{2\pi i(h \cdot 0 + k \cdot 0 + l \cdot 0)} = 1$$

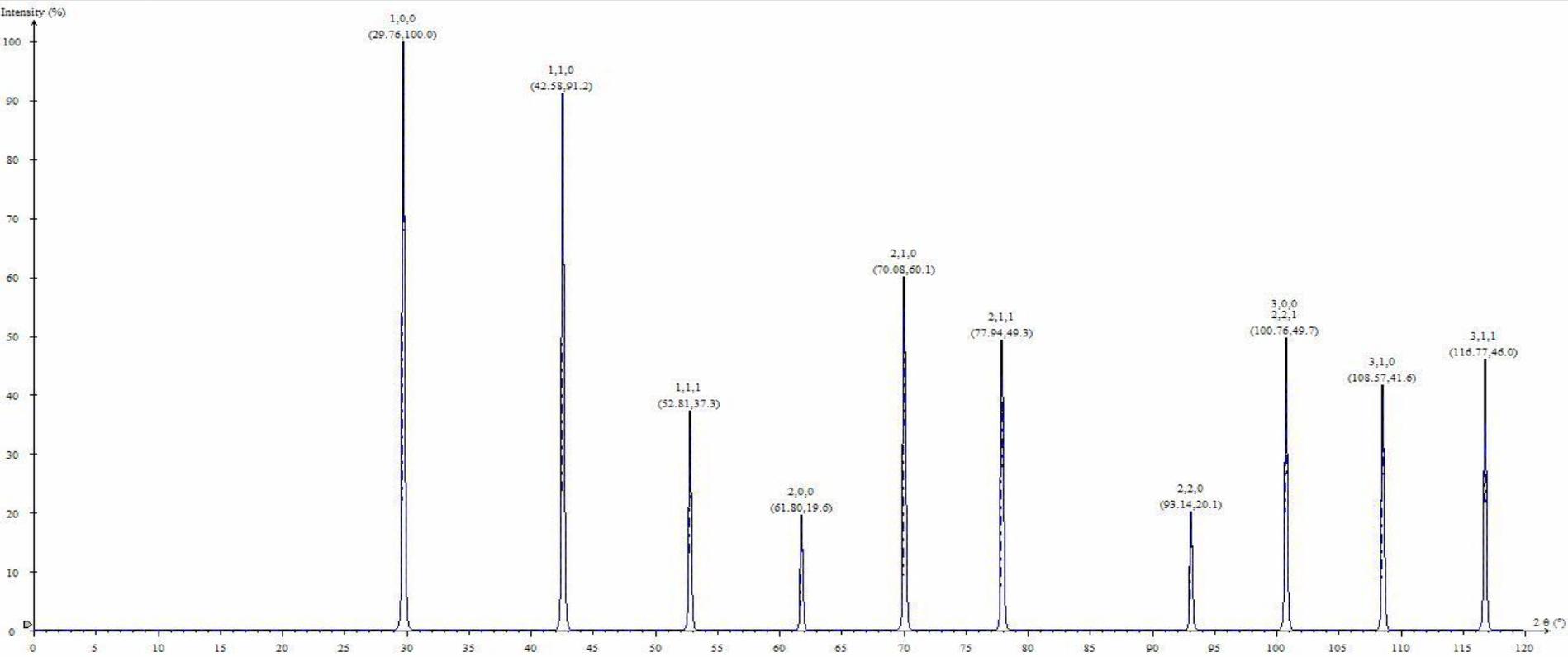
$$F_{hkl} = f_j$$

$$I = |F_{hkl}|^2$$

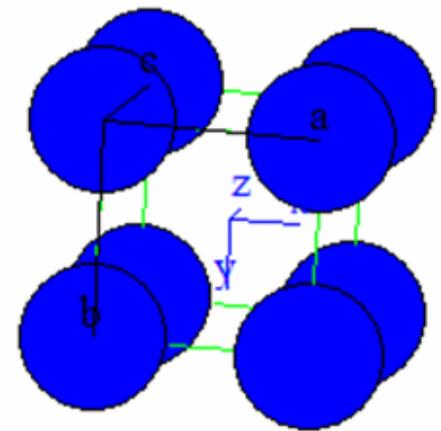
$$I = |F_{hkl}|^2 = f_j^2$$



1 atom:
(0,0,0)



Diffraction pattern of a Primitive Cubic Cell



3.1-2 Body Centered Cubic Cell

$$F_{hkl} = f_j \left[e^{2\pi i(h \cdot 0 + k \cdot 0 + l \cdot 0)} + e^{2\pi i(h \cdot \frac{1}{2} + k \cdot \frac{1}{2} + l \cdot \frac{1}{2})} \right]$$

$$F_{hkl} = f_j \left[1 + e^{\pi i(h+k+l)} \right]$$

$$e^{2\pi i} = 1$$

$$e^{\pi i} = -1$$

$$h + k + l = \text{even number}$$

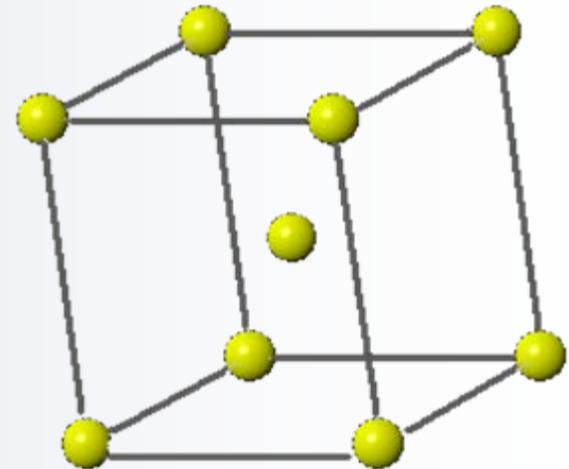
$$F_{hkl} = 2f_j$$

$$I = |F_{hkl}|^2 = 4f_j^2$$

$$h + k + l = \text{odd number}$$

$$F_{hkl} = 0$$

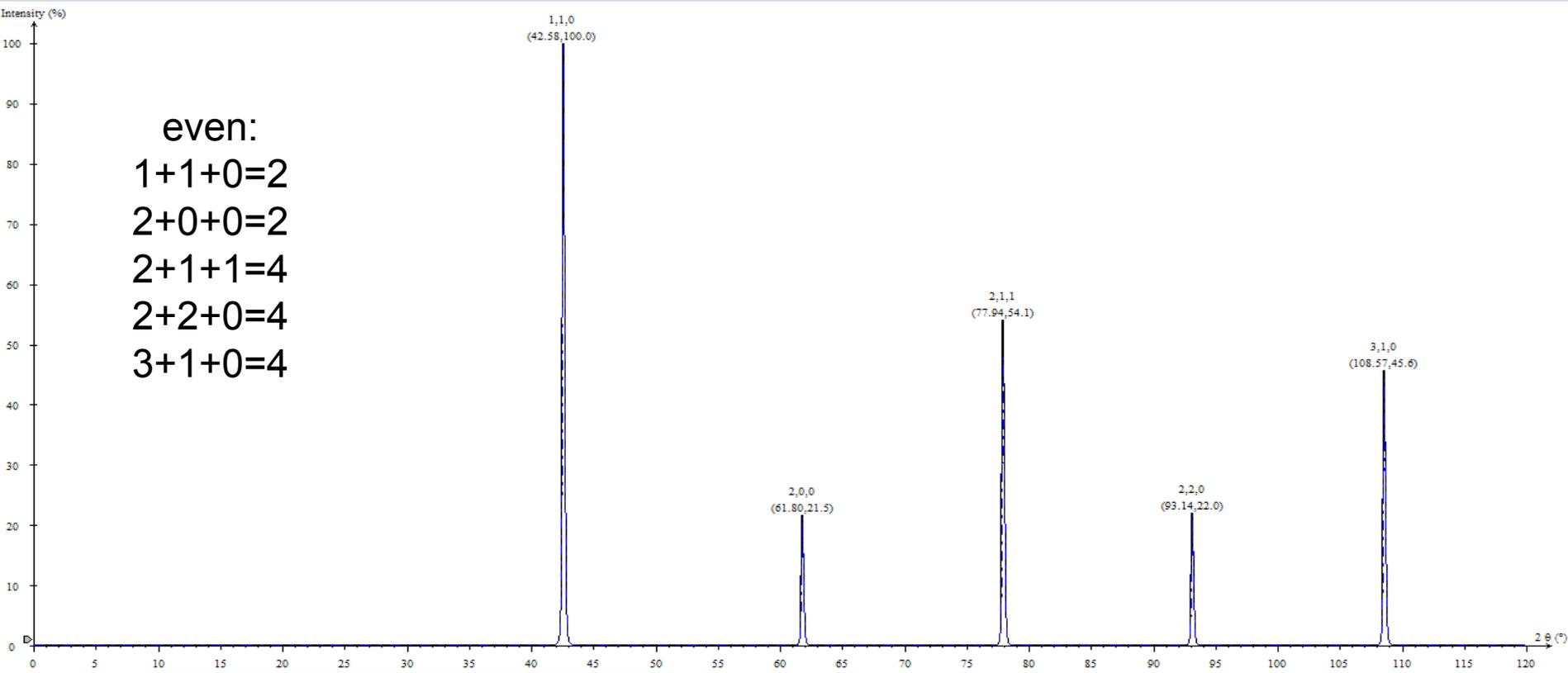
$$I = |F_{hkl}|^2 = 0$$



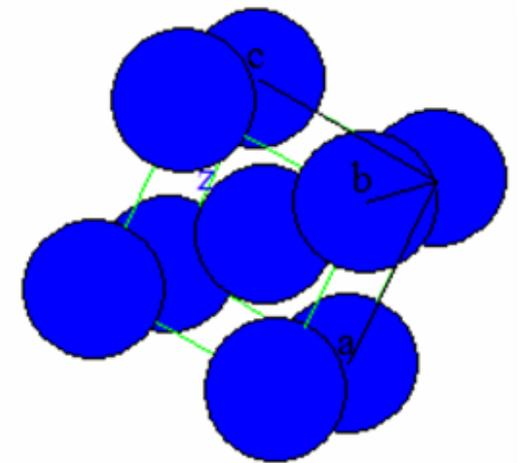
2 atoms:

(0,0,0)

(1/2,1/2,1/2)



Diffraction pattern of a
Body Centered Cubic
Cell



3.1-3 Face Centered Cubic Cell

$$F_{hkl} = f_j \left[e^{2\pi i(h \cdot 0 + k \cdot 0 + l \cdot 0)} + e^{2\pi i\left(h \cdot \frac{1}{2} + k \cdot \frac{1}{2} + l \cdot 0\right)} + e^{2\pi i\left(h \cdot \frac{1}{2} + k \cdot 0 + l \cdot \frac{1}{2}\right)} + e^{2\pi i\left(h \cdot 0 + k \cdot \frac{1}{2} + l \cdot \frac{1}{2}\right)} \right]$$

$$F_{hkl} = f_j (1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)})$$

$$\text{mixed} \quad 1 \quad -1 \quad -1 \quad 1 \quad = 0$$

$$\text{unmixed} \quad 1 \quad 1 \quad 1 \quad 1 \quad = 4$$

3.1-4 Face Centered Cubic Cell

$h, k, l = \textit{unmixed}$

all even

all odd

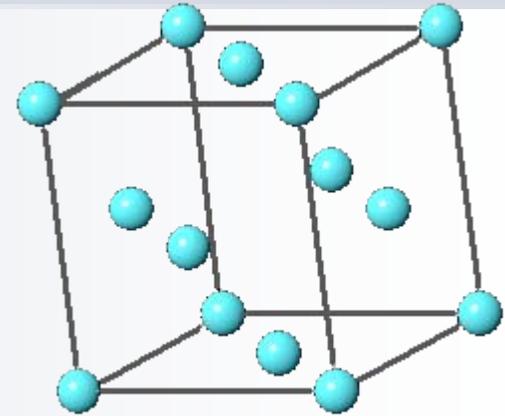
$$F_{hkl} = 4f_j$$

$$I = 16f_j^2$$

$h, k, l = \textit{mixed}$

$$F_{hkl} = 0$$

$$I = 0$$



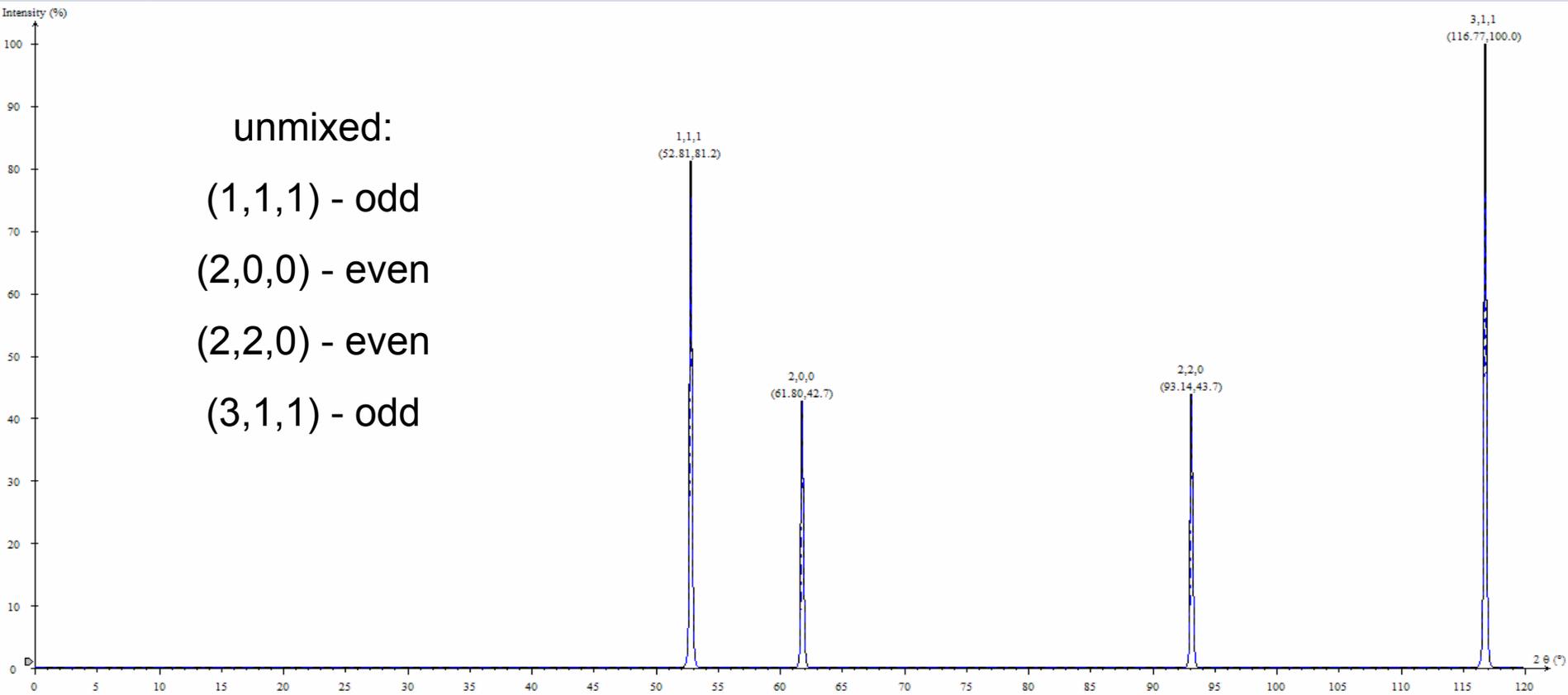
4 atoms:

(0,0,0)

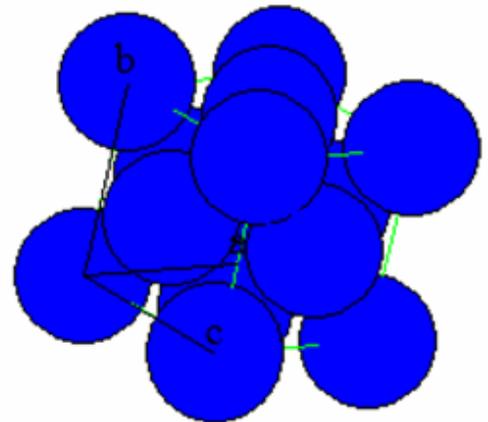
(1/2, 1/2, 0)

(1/2, 0, 1/2)

(0, 1/2, 1/2)



Diffraction of a Face
Centered Cubic Cell



Example: CsCl

$$F_{hkl} = \left[f_{\text{Cs}^+} e^{2\pi i(h \cdot 0 + k \cdot 0 + l \cdot 0)} + f_{\text{Cl}^-} e^{2\pi i\left(h \cdot \frac{1}{2} + k \cdot \frac{1}{2} + l \cdot \frac{1}{2}\right)} \right]$$

$$F_{hkl} = \left[f_{\text{Cs}^+} + f_{\text{Cl}^-} e^{\pi i(h+k+l)} \right]$$

$$h + k + l = \text{even}$$

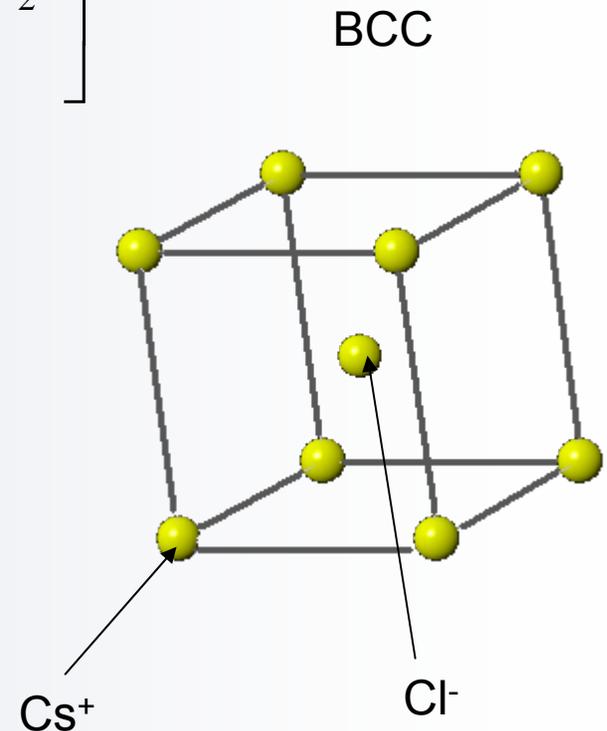
$$F_{hkl} = f_{\text{Cs}^+} + f_{\text{Cl}^-}$$

$$I = \left(f_{\text{Cs}^+} + f_{\text{Cl}^-} \right)^2$$

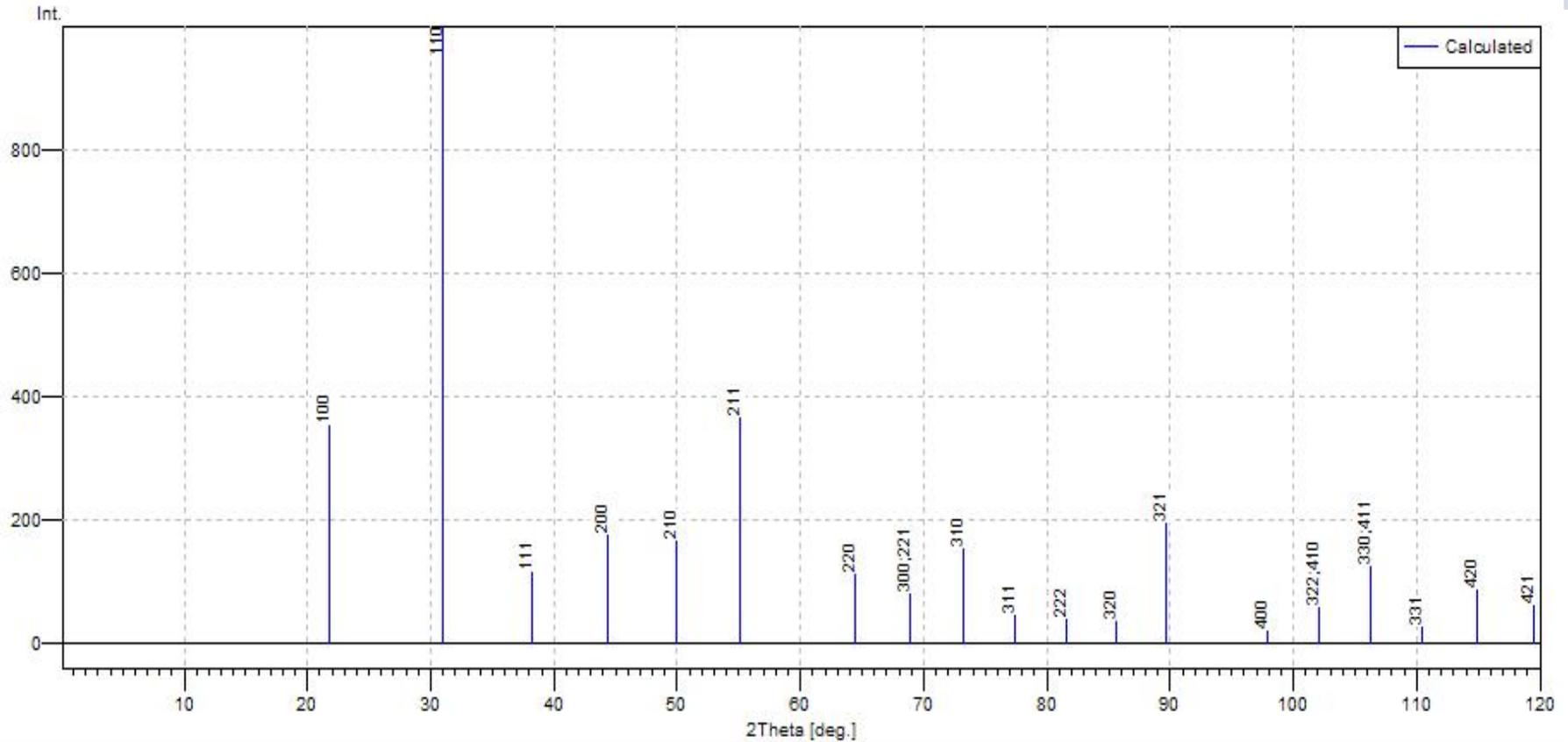
$$h + k + l = \text{odd}$$

$$F_{hkl} = f_{\text{Cs}^+} - f_{\text{Cl}^-}$$

$$I = \left(f_{\text{Cs}^+} - f_{\text{Cl}^-} \right)^2$$



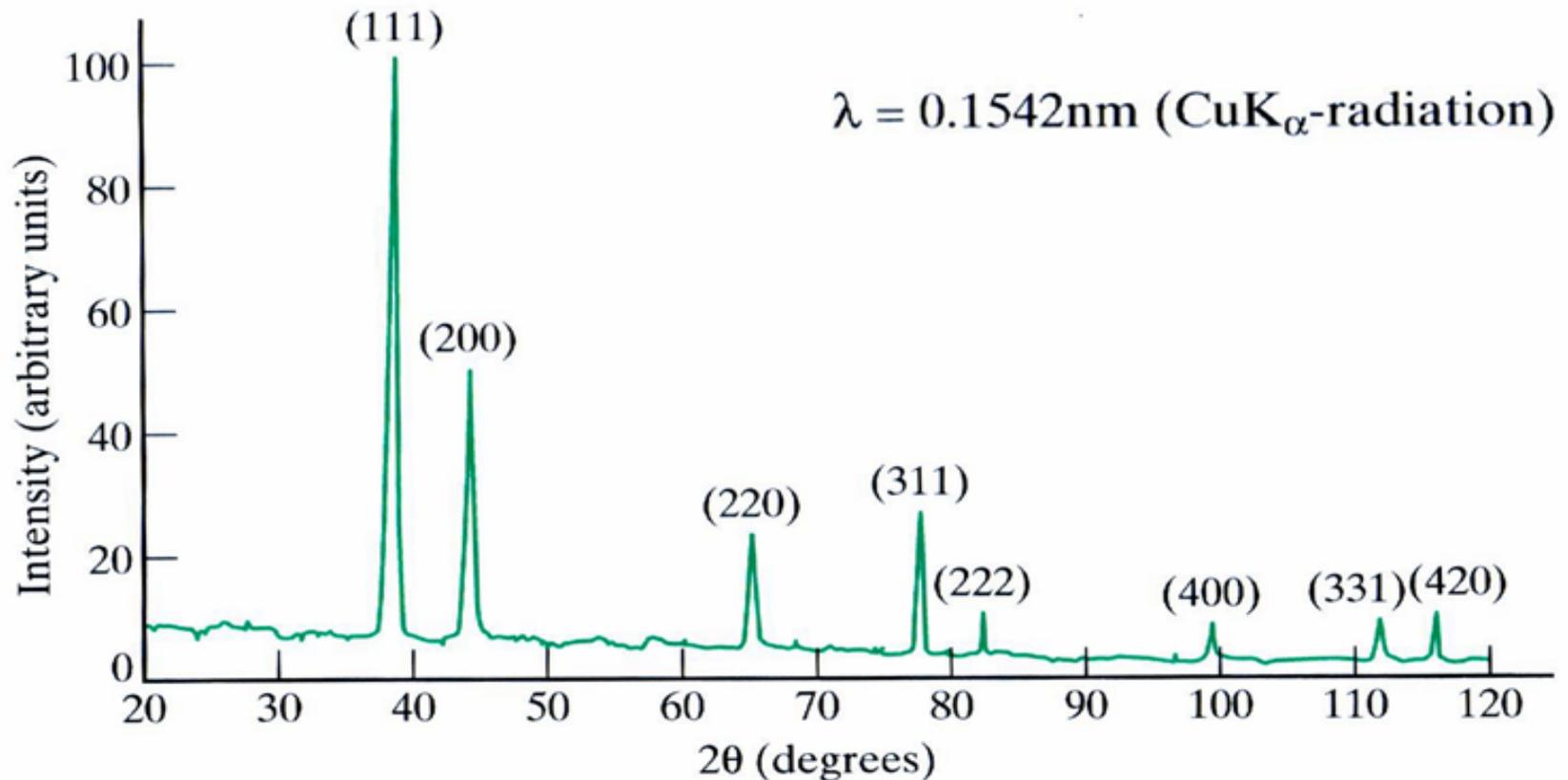
CsCl Diffractogram



REFLECTION RULES OF X-RAY DIFFRACTION FOR THE COMMON METAL STRUCTURES

Crystal structure	Diffraction does not occur when:	Diffraction occurs when:
Body-centered cubic (bcc)	$h + k + l = \text{odd number}$	$h + k + l = \text{even number}$
Face-centered cubic (fcc)	h, k, l mixed (i.e., both even and odd numbers)	h, k, l unmixed (i.e., are all even numbers or all odd numbers)
Hexagonal close packed (hcp)	$(h + 2k) = 3n, l$ odd (n is an integer)	All other cases

4. The X-Ray Diffraction Spectrum



X-Ray diffraction pattern generated by a pure Al sample, under Cu-K α radiation

4.1 Qualitative Analysis in XRD

- The diffraction pattern of an unknown sample is measured and is compared with already known standards (JCPDS cards) to identify it.

4.2 Power Diffraction File (PDF) Database

- ◆ Supplements to the ASTM file were published in 1945 and 1950, enlarging the database to 4000 compounds
- ◆ 1969 -- the Joint Committee on Powder Diffraction Standards (JCPDS) was formed as a non-profit corporation to oversee the database
- ◆ By 1971 the Powder Diffraction File (PDF) contained 21 sets of data with about 21,500 entries
- ◆ 1978 -- name change to the International Centre for Diffraction Data (ICDD)
- ◆ 1996 -- 46 sets, 75,011 diffraction patterns
- ◆ 2000 -- we have over 85,000 patterns
- ◆ Closely coupled with NIST (NBS) to check accuracy

- ◆ Release 2002 Highlights
 - 148,379 total phases
 - 90,011 experimental patterns
 - 54,378 patterns calculated from entries in the ICSD

4.3 Special Features in PDF Cards

- ◆ Special symbols give extra information
 - * well-characterized chemistry, quantitative measure of intensity, high-quality d -spacing data (3 to 4 significant digits, no serious systematic errors)
 - i reasonable range and even spread of intensity, “sensible” completeness of the pattern, good d -spacing data (3 significant digits)
 - o low precision data, possible multi-phase mixture, possible poor chemical characterization
 - C powder pattern calculated from structural parameters

Power Diffraction File (PDF) Database

1		2			3		4				
5 - 6 2 8		d	2.82	1.99	1.63	3.26	NaCl ★				
		I_0	100	55	15	13	Sodium Chloride (Halite)				
5		Rad. CuK α_1 , λ 1.5405 Filter Ni Dia. Cut-off I_0 Diffractometer ITeor. Ref. Swanson and Fayat, NBS Circular 539, Vol. 2, 41 (1953)				d, Å	I_0	hkl	d, Å	I_0	hkl
6		Sys. Cubic S.G. Fm $\bar{3}m$ (225) a_0 3.56402 b_0 c_0 α β γ Z 4 D_6 2.164 Ref. Ibid.				3.258	13	111			
7		na $n = \beta$ 1.542 n_γ Sign 2V D mp Color Colorless Ref. Ibid.				2.821	100	200			
8		An ACS reagent grade sample recrystallized twice from hydrochloric acid. X-ray pattern at 26°C. Merck Index, 8th Ed., p. 956.				1.994	55	220			
						1.701	2	311			
						1.628	15	222			
						1.410	6	400			
						1.294	1	331			
						1.261	11	420			
						1.1515	7	422			
						1.0855	1	511			
						0.9969	2	440			
						.9533	1	531			
						.9401	3	600			
						.8917	4	620			
						.8691	1	533			
						.8503	3	622			
						.8141	2	444			

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

4.4 The Hanawalt Method

- ◆ Hanawalt decided to use the d -values of the three strongest lines in the powder pattern (d_1, d_2, d_3) along with their intensities to search the PDF database
- ◆ Cards are grouped in ranges of d_1 spacings (e.g. 2.29Å to 2.25Å) in order of decreasing d_2 spacing
- ◆ The three most intense lines are permuted:

$d(A), d(B), d(C)$
 $d(B), d(C), d(A)$
 $d(C), d(A), d(B)$

Hanawalt Grouping Scheme

d (Å)	Hanawalt Groups
999.99–10.00	One group
9.99–8.00	One group
7.99–6.00	Grouped in steps of 1.00 Å
5.99–5.00	Grouped in steps of 0.50 Å
4.99–4.60	One group
4.59–4.30	One group
4.29–3.90	Grouped in steps of 0.20 Å
3.89–3.60	Grouped in steps of 0.15 Å
3.59–3.40	Grouped in steps of 0.10 Å
3.39–3.32	One group
3.31–3.25	One group
3.24–1.80	Grouped in steps of 0.05 Å
1.79–1.40	Grouped in steps of 0.10 Å
1.39–1.00	Grouped in steps of 0.20 Å

4.4 The Hanawalt Method (cont')

- ◆ Locate proper d_1 group in the numerical search manual.
- ◆ Read down the second column of d values to find the closest match to d_2 . Allow the variation for d by $\pm 0.01 \text{ \AA}$.
- ◆ After the closest match has been found for d_1 , d_2 , and d_3 , compare their relative intensities with the tabulated values.
- ◆ When good agreement has been found for the lines listed in the search manual, locate the proper PDF card and compare the d and I/I_1 values of all the observed lines with those tabulated. When full agreement is obtained, identification is complete.

4.4 The Hanawalt Method (cont')

Pattern of the unknown

$d(\text{\AA})$	MI_1	$d(\text{\AA})$	MI_1
3.25	10	1.00	20
2.82	100	0.95	5
2.18	5	0.94	20
1.99	60	0.89	20
1.71	5	0.86	5
1.63	30	0.85	20
1.42	20	0.82	10
1.25	30	0.79	10
1.15	30	0.78	20
1.09	5		

$$d_1 = 2.82 \text{ \AA}$$

$$d_2 = 1.99 \text{ \AA}$$

$$d_3 = 1.63 \text{ \AA}$$

4.4 The Hanawalt Method (cont')

Portion of the ICDD Hanawalt search manual

QM	Strongest reflections								Chemical PSC formula	Mineral name; common name	PDF #	d/c
*	2.82 ₁	1.99 ₂	3.99 ₂	1.63 ₂	1.41 ₁	1.26 ₁	1.07 ₁	1.78 ₁	cP5 Ca _{0.6} Sr _{0.4} NbO ₃	47-35	7.05	
	2.82 ₁	1.99 ₂	3.26 ₃	1.63 ₂	1.41 ₁	1.26 ₁	1.15 ₁	1.73 ₁	cF8 PdO	46-1211		
*	2.82 ₁	1.99 ₂	2.30 ₆	1.41 ₄	1.63 ₂	0.89 ₁	1.20 ₁	1.15 ₁	cP5 KMgF ₃	18-1033	0.90	
*	2.82 ₁	1.99 ₂	1.63 ₂	3.26 ₁	1.26 ₁	1.15 ₁	0.94 ₁	0.89 ₁	cF8 NaCl	5-628		
C	2.82 ₁	1.99 ₂	1.99 ₃	1.26 ₃	1.63 ₂	1.15 ₂	0.94 ₁	1.41 ₁	cP2 BePd	18-428		

$$d_1 = 2.82 \text{ \AA}$$

$$d_2 = 1.99 \text{ \AA}$$

$$d_3 = 1.63 \text{ \AA}$$

4.4 The Hanawalt Method (cont')

d Å	I/I ₁	hkl	d Å	I/I ₁	hkl
3.258	13	111	Not observed		
2.821	100	200			
1.994	55	220			
1.701	2	311			
1.628	15	222			
1.410	6	400			
1.294	1	331			
1.261	11	420			
1.1515	7	422			
1.0855	1	511			
0.9969	2	440			
.9533	1	531			
.9401	3	600			
.8917	4	620			
.8601	1	533			
.8503	3	622			
.8141	2	444			

220 of Cu K α

d(Å)	I/I ₁
3.25	10
2.82	100
2.18	5
1.99	60
1.71	5
1.63	30
1.42	20
1.25	30
1.15	30
1.09	5
1.00	20
0.95	5
0.94	20
0.89	20
0.86	5
0.85	20
0.82	10
0.79	10
0.78	20

Measured intensities are higher

Observed but not listed

4.5 Computer Search of the PDF

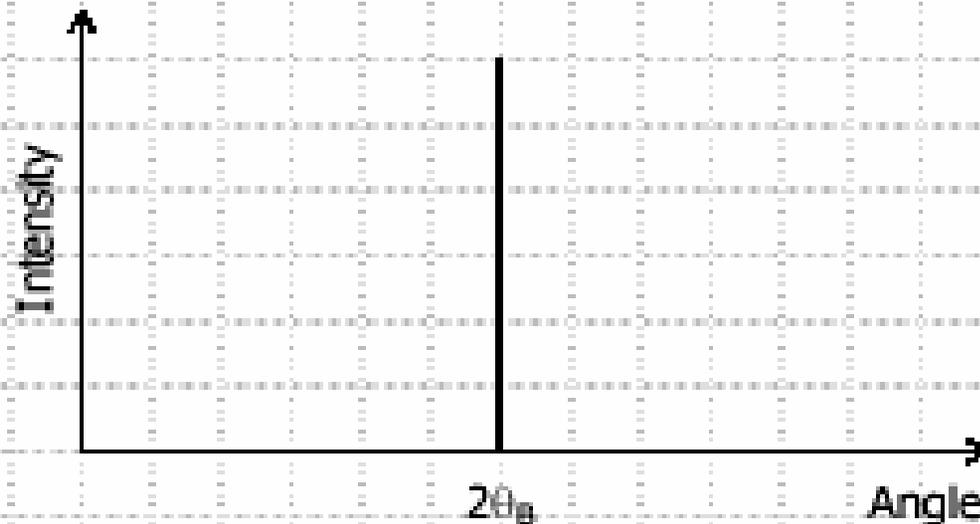
- ◆ Computerization has dramatically improved the efficiency of searching the JCPDS database
- ◆ Cards are no longer printed – data are on CD-ROM
- ◆ Numerous third-party vendors have software for searching the PDF database
- ◆ Computerized “cards” can contain much more crystallographic information
- ◆ Evolution of the database is continuing...

4.6 XRD: Crystallite Size

- The peak width in in XRD pattern is related to the size of crystallites that compose the material

4.6 Crystallite Size

- ◆ As the crystallites in a powder get smaller the diffraction peaks in a powder pattern get wider.
- ◆ Consider diffraction from a crystal of thickness t and how the diffracted intensity varies as we move away from the exact Bragg angle
 - If thickness was infinite we would only see diffraction at the Bragg angle



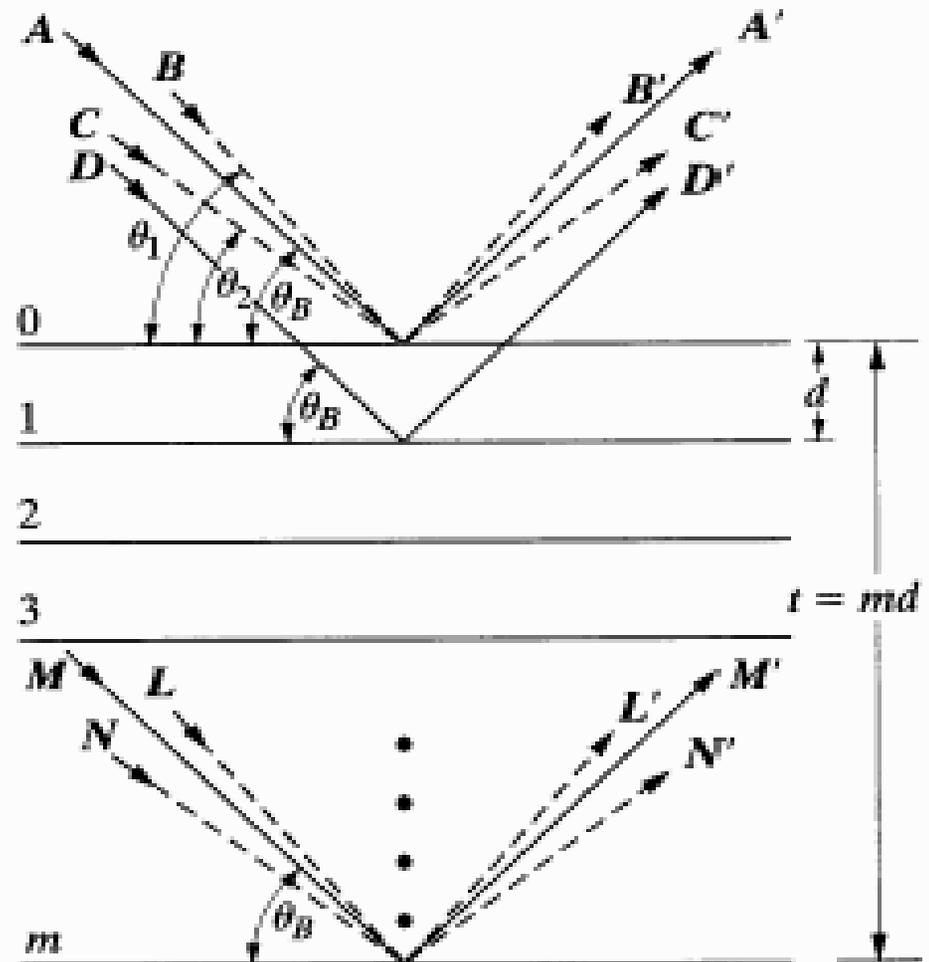
4.6 Crystallite Size

Suppose the crystal of thickness t has $(m + 1)$ planes in the diffraction direction.

Let say θ is variable with value θ_B that exactly satisfies Bragg's Law:

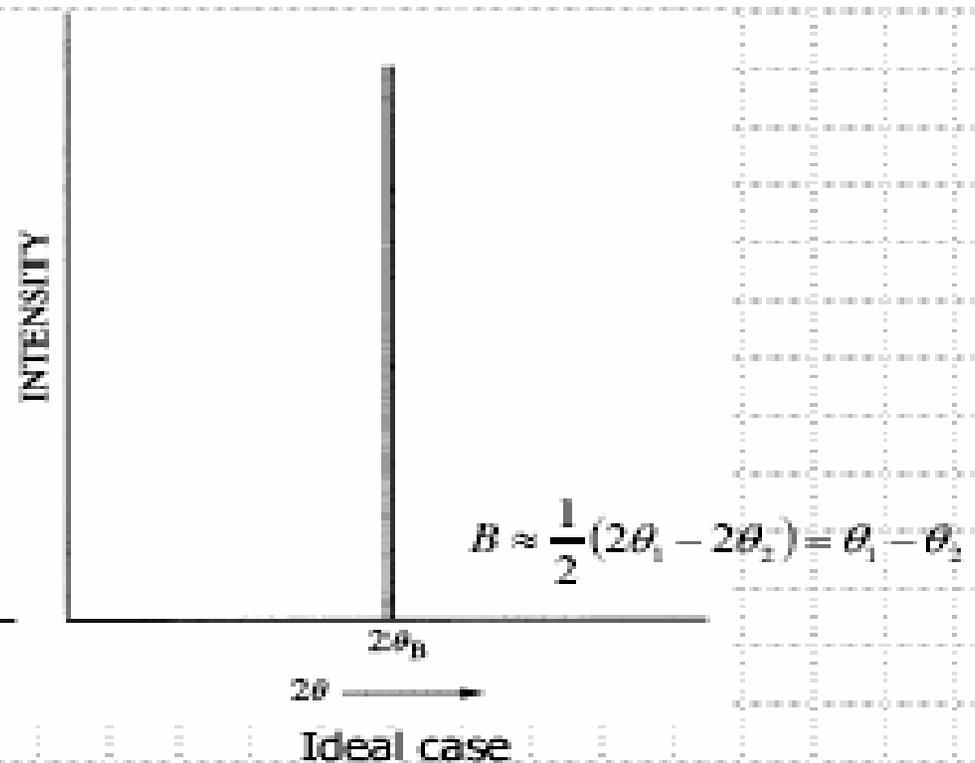
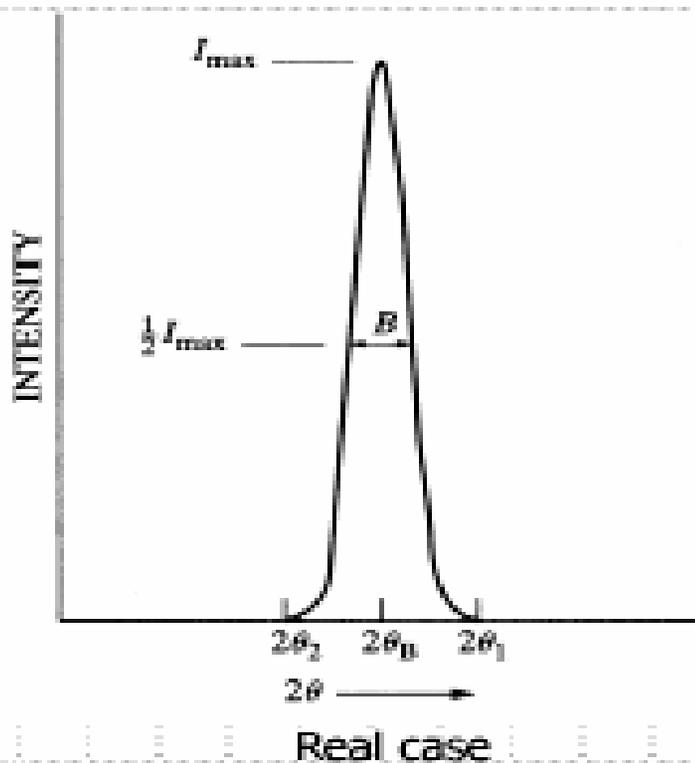
$$\lambda = 2d \sin \theta_B$$

- ◆ Rays **A, D, ..., M** makes angle θ_B
- ◆ Rays **B, ..., L** makes angle θ_1
- ◆ Rays **C, ..., N** makes angle θ_2



4.6 Crystallite Size

- For angle θ_B diffracted intensity is maximum
- For θ_1 and θ_2 – intensity is 0.
- For angles $\theta_1 > \theta > \theta_2$ – intensity is nonzero.



4.7 Derivation of Scherrer's Equation

- Bragg's law is given by,

$$n \lambda = 2 d \sin \theta \dots\dots\dots (1)$$

- Multiply both sides by an integer m such that md=t, the thickness of the crystal. This leads to, n=1:

$$\begin{aligned} m \lambda &= 2 m d \sin \theta \\ m \lambda &= 2 t \sin \theta \dots\dots\dots (2) \end{aligned}$$

- Eqn. (2) can also be interpreted as the mth order reflection from a set of planes with a interplanar distance t. Differentiate both sides of eqn. (2) remembering m λ is a constant. This gives,

$$0 = 2 \Delta t \sin \theta + 2 t \cos \theta \Delta \theta \dots (3)$$

- Remembering that as Δθ can be positive or negative (we are only interested in absolute values) leads to,

$$t = \frac{\Delta t \cdot \sin(\theta)}{\cos(\theta) \Delta \theta} \dots\dots\dots (4)$$

- Since the smallest increment in t is d, using Δt=d, and substituting λ/2 for d sinθ (from Bragg's law) we get,

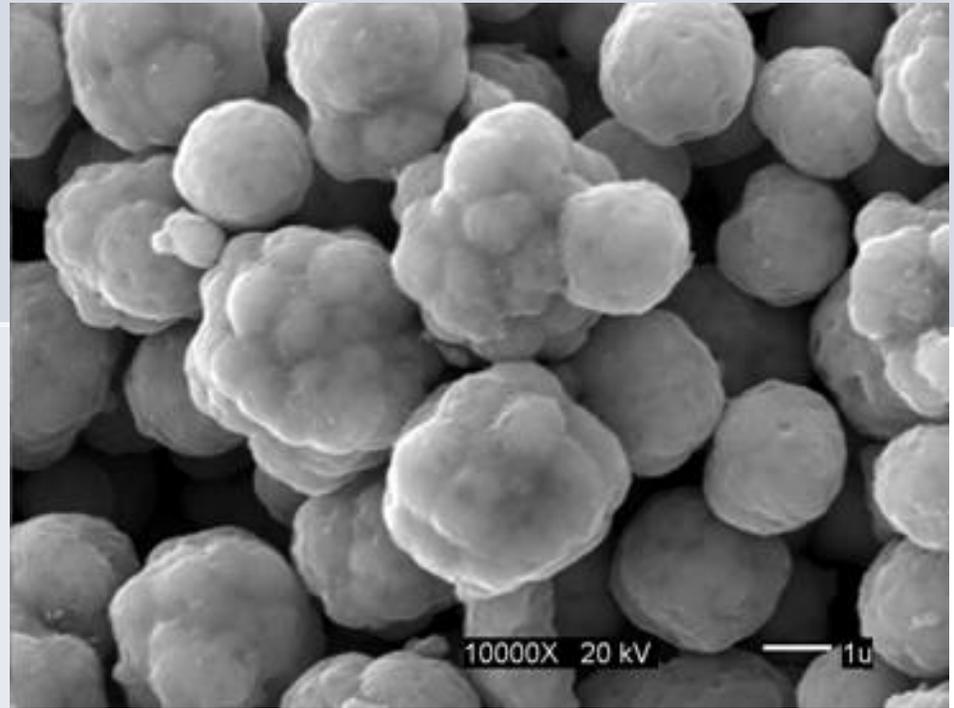
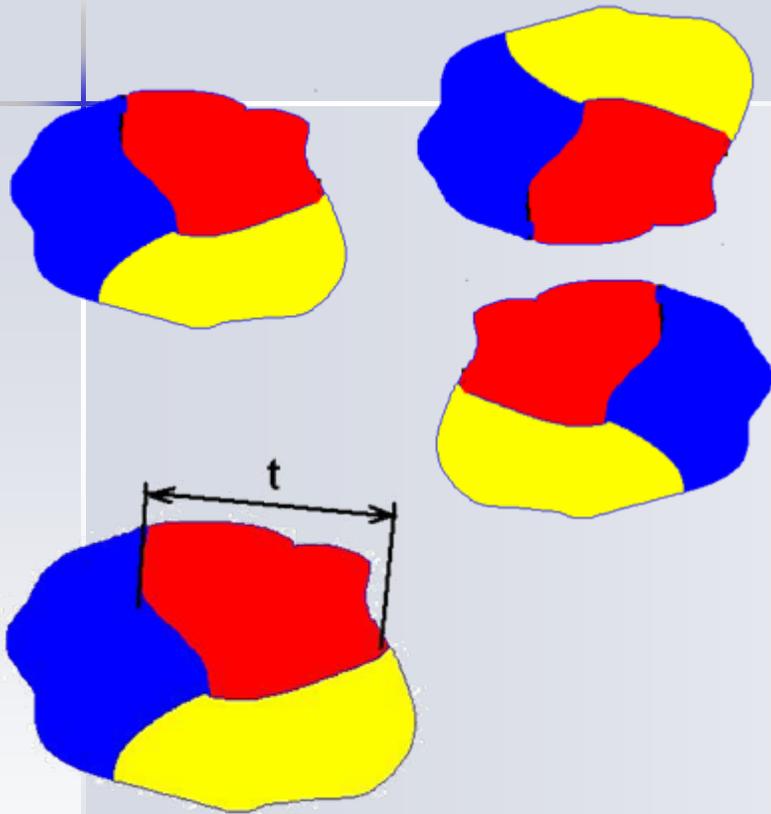
$$t = \frac{\lambda}{2 \cos(\theta) \Delta \theta} \dots\dots\dots (5)$$

- Substituting B for 2 Δθ, the angular width, we get,

$$t = \frac{\lambda}{B \cos(\theta)} \dots\dots\dots (6)$$

- which is essentially Scherrer's equation.
- A more sophisticated analysis of the problem only adds a prefactor of 0.9 to the right hand side of eqn. (6) and leads to the correct Scherrer's equation.

$$t = \frac{0.9 \cdot \lambda}{B \cos(\theta)}$$



ϵ - Cobalt particles gold plated
 (High Coercivity Materials Group 2006)

$$t = \frac{0.9 \cdot \lambda}{B \cos(\theta)}$$

The Scherrer's Equation

$$2t \sin \theta_1 = (m+1)\lambda,$$

$$2t \sin \theta_2 = (m-1)\lambda.$$

Subtracting:

$$t(\sin \theta_1 - \sin \theta_2) = \lambda,$$

$$2t \cos\left(\frac{\theta_1 + \theta_2}{2}\right) \sin\left(\frac{\theta_1 - \theta_2}{2}\right) = \lambda.$$

θ_1 and θ_2 are close to θ_B , so:

$$\theta_1 + \theta_2 \approx 2\theta_B,$$

$$\sin\left(\frac{\theta_1 - \theta_2}{2}\right) \approx \left(\frac{\theta_1 - \theta_2}{2}\right).$$

Thus:

$$2t \left(\frac{\theta_1 - \theta_2}{2}\right) \cos \theta_B = \lambda,$$

$$t = \frac{\lambda}{B \cos \theta_B}$$

The Scherrer's Equation

◆ More exact treatment (see *Warren*) gives:

$$t = \frac{0.9\lambda}{B \cos \theta_B}$$

← Scherrer's formula

Suppose $\lambda = 1.54 \text{ \AA}$, $d = 1.0 \text{ \AA}$, and $\theta = 49^\circ$:

for crystal size of 1 mm, $B = 10^{-5} \text{ deg.}$

for crystal size of 500 \AA , $B = 0.2 \text{ deg.}$

4.8 Peak Broadening

- If crystal size $< 0.2 \mu\text{m}$, then peak broadening occurs
- At $< 50\text{nm}$, becomes significant.
- Why?

Bragg's law gives the condition for constructive interference.

- At slightly higher θ than the Bragg angle, each plane gives a "lag" in the diffracted beam.
- For many planes, these end up cancelling out and thus the net diffraction is zero.
- Peak broadness also depend on the presence of lattice imperfections and non uniform distortion of the crystallite.

4.8 Peak Broadening

We can calculate the average size of the crystals from the broadening:

$$t = \frac{0.9\lambda}{B \cos \theta_B} \quad \text{Scherrer formula}$$

t is the thickness of the crystal, λ the wavelength, θ_B the Bragg angle.

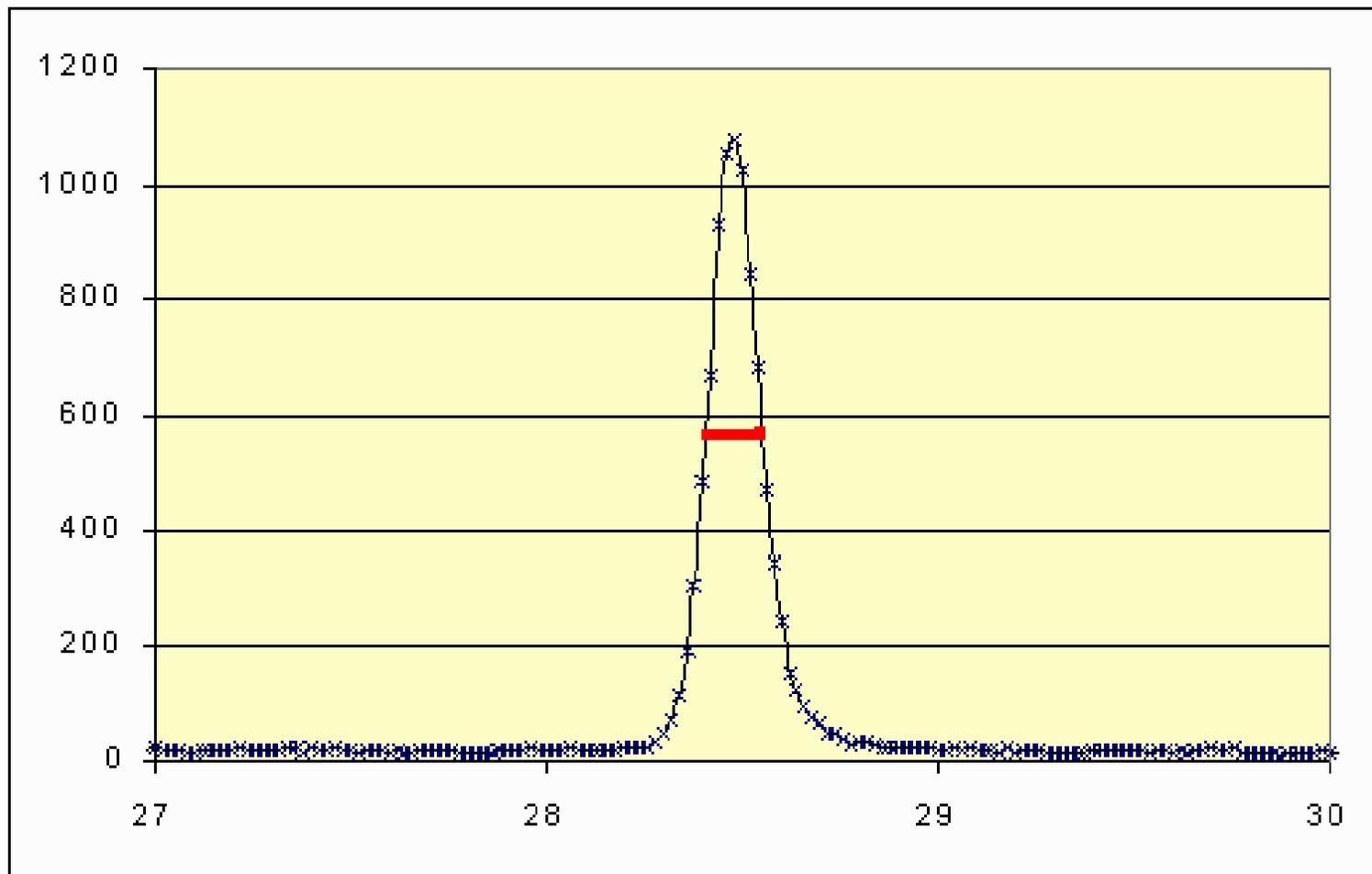
B is the line broadening, by reference to a standard, so that

$$B^2 = B_M^2 - B_S^2$$

where B_S is the *halfwidth* of the standard material *in radians*. (A normal halfwidth is around 0.1°)

4.8 Peak Broadening

Halfwidth: “Full width at half-maximum” - FWHM



4.8 Peak Broadening

Example:

Peak at $28.2^\circ 2\theta$ with FWHM of $0.36^\circ 2\theta$

Standard material has FWHM of $0.16^\circ 2\theta$

$$\lambda = \text{CuK}\alpha = 1.540\text{\AA}$$

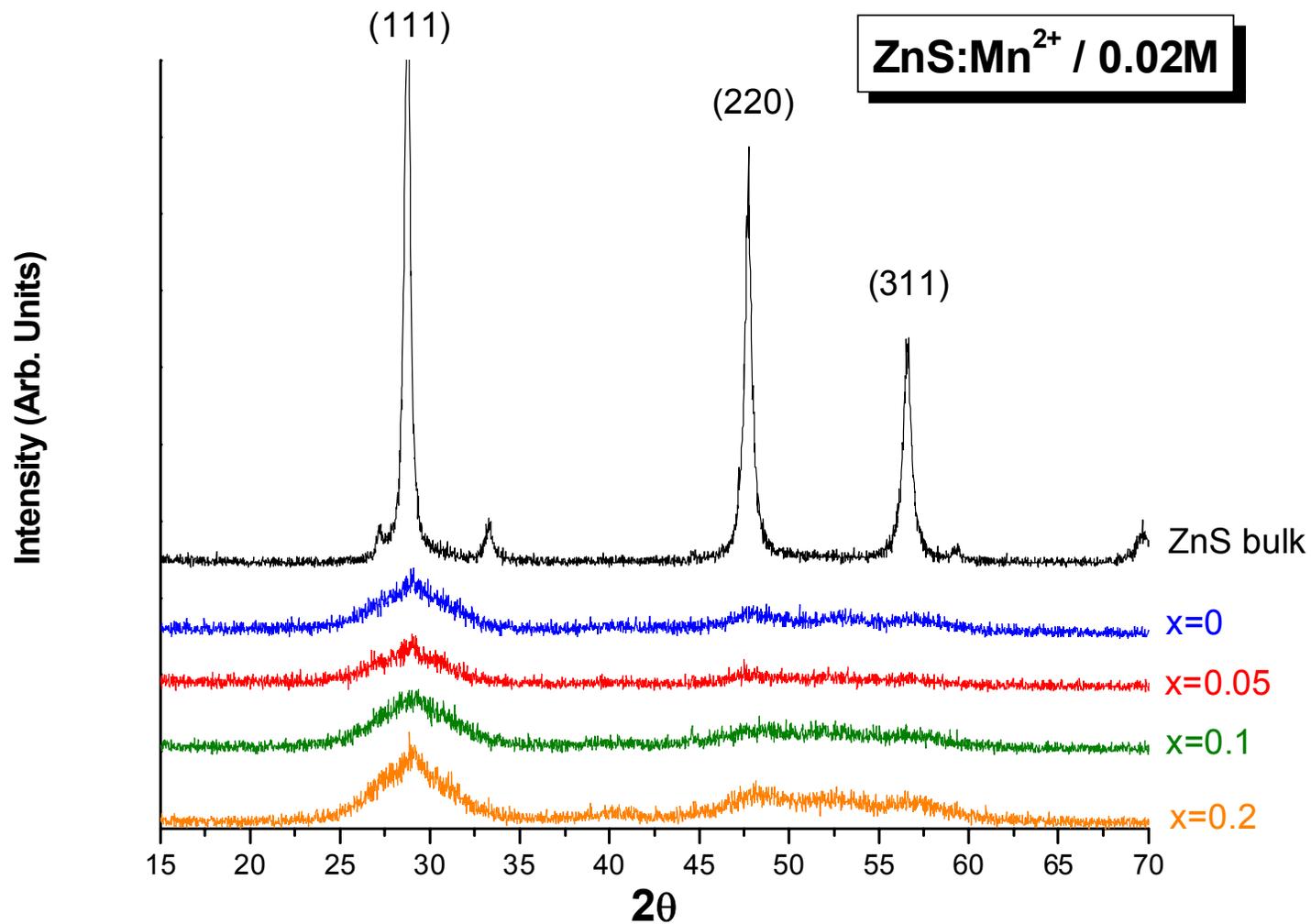
$$0.36^\circ = 0.36 \times \pi/180 = 0.0063 \text{ rad}$$

$$0.16^\circ = 0.16 \times \pi/180 = 0.0028 \text{ rad}$$

$$B = 0.0056 \text{ rad}$$

$$t = 255 \text{\AA} = 0.0255 \mu\text{m}$$

Nanocrystalline Mn-doped ZnS



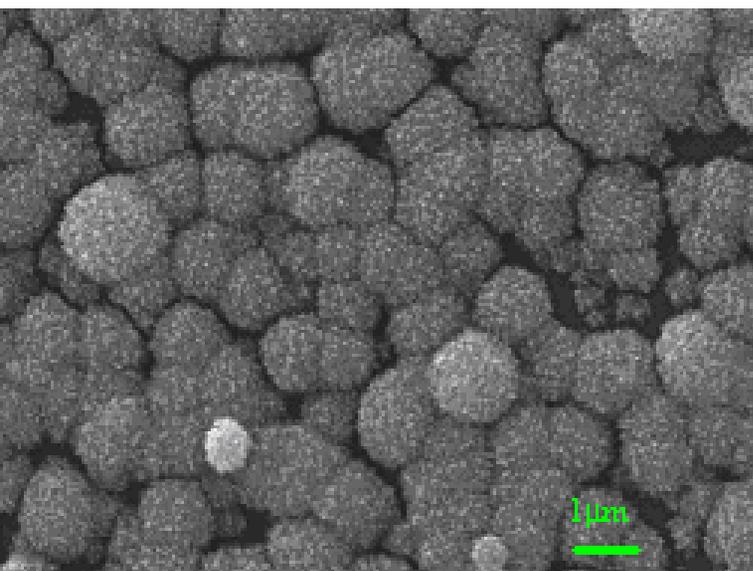
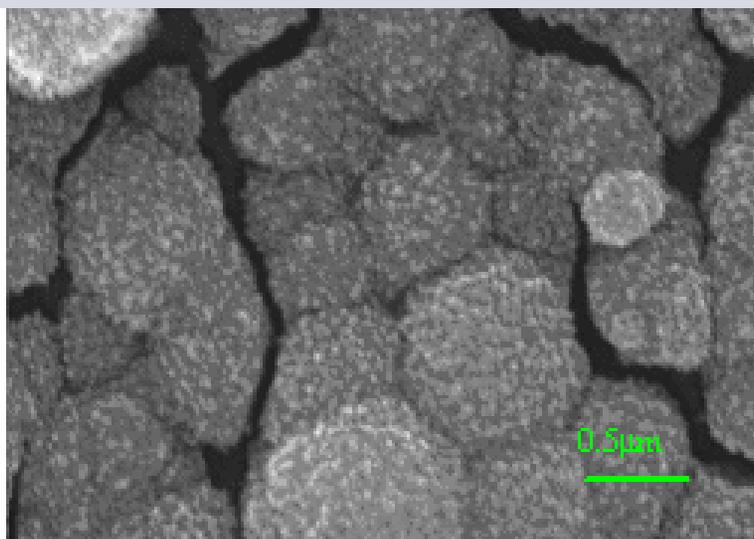
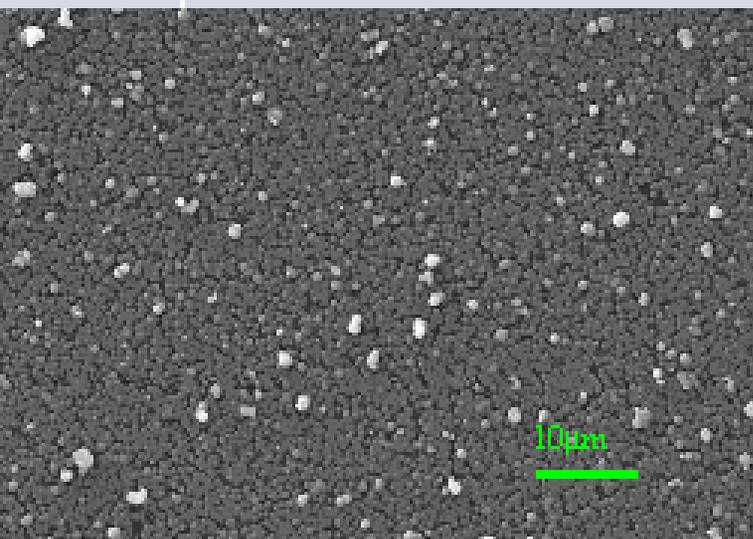


Fig. 2 SEM micrographs (a & b) at different magnifications corresponding to the films deposited from a bath solution with a total concentration of metal ions (Zn + Mn) 0.02 M and a Mn mole fraction, $x = 0.1$. Very tiny primary particles are observed inside each micronsize particle. Fig. (C) is for $[M] = 0.03M$ showing some cracks.

Corrections for Instrumental Broadening

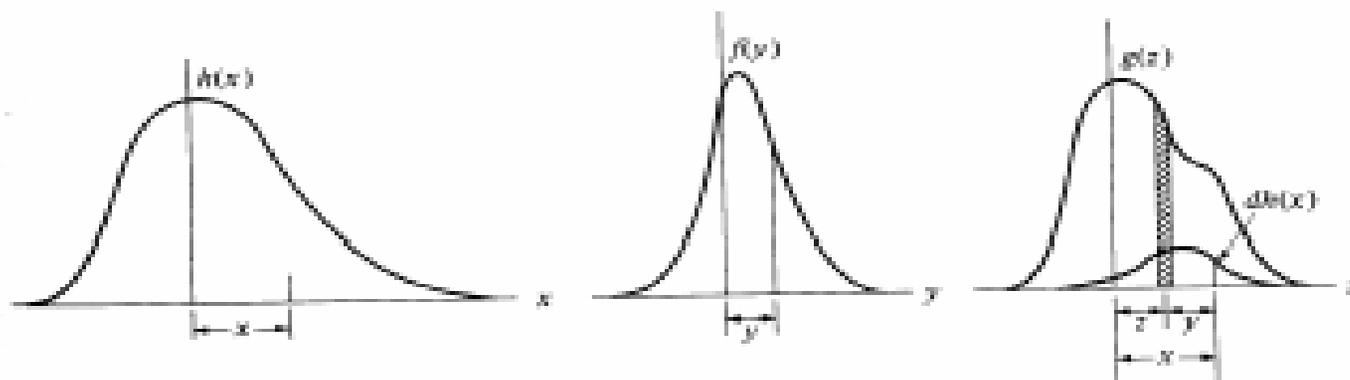
- ◆ There is a link between peak width and crystallite size, but other sources of peak broadening have to be considered when analyzing diffraction data
 - Instrumental broadening:
 - + slit widths
 - + sample size
 - + penetration in the sample
 - + imperfect focusing
 - + unresolved α_1 and α_2 peaks
 - + or wavelengths widths where α_1 and α_2 peaks are resolved
 - Microstrain can also lead to peak broadening

Generally:

$$B_{true}^2 = B_{measured}^2 - B_{instrument}^2$$

Corrections for Instrumental Broadening

- ◆ To correct for instrumental broadening:
 - measure the sample
 - measure the standard with particles large enough to eliminate particle-size broadening



$h(x)$ – broadening from the sample (desired + instrumental broadening)
 $f(y)$ – no instrumental broadening (desired)
 $g(z)$ – instrumental broadening from the standard

4.9 XRD: Residual Stress

- When force is applied on a solid matter with its elastic limit, it is deformed → 'd' will change → XRD peak will be shifted

Strain

Two types of stresses:

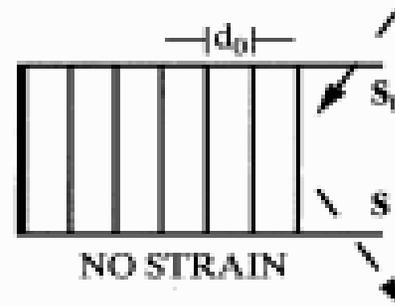
- microstresses – vary from one grain to another on a microscopic scale.
- macrostresses – stress is uniform over large distances.

Usually:

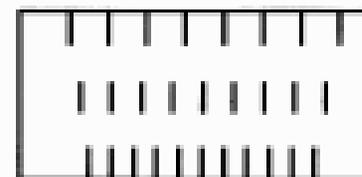
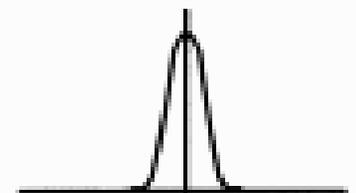
- macrostrain is uniform – produces peak shift
- microstrain is nonuniform – produces peak broadening

$$b = \Delta 2\theta = -2 \frac{\Delta d}{d} \tan \theta$$

CRYSTAL LATTICE



DIFFRACTION LINE



2θ

Williamson-Hall's analysis:

It can be used to estimate crystallite size and average lattice strain

A method of interpreting particle size broadening and strain broadening. $\beta \cos \theta$ vs $\sin \theta$ should be plotted

$$\beta \cos \theta = 4e (\sin \theta) + \lambda/\varepsilon$$

β = integral width in radians (crystallite size + non uniform distortion)

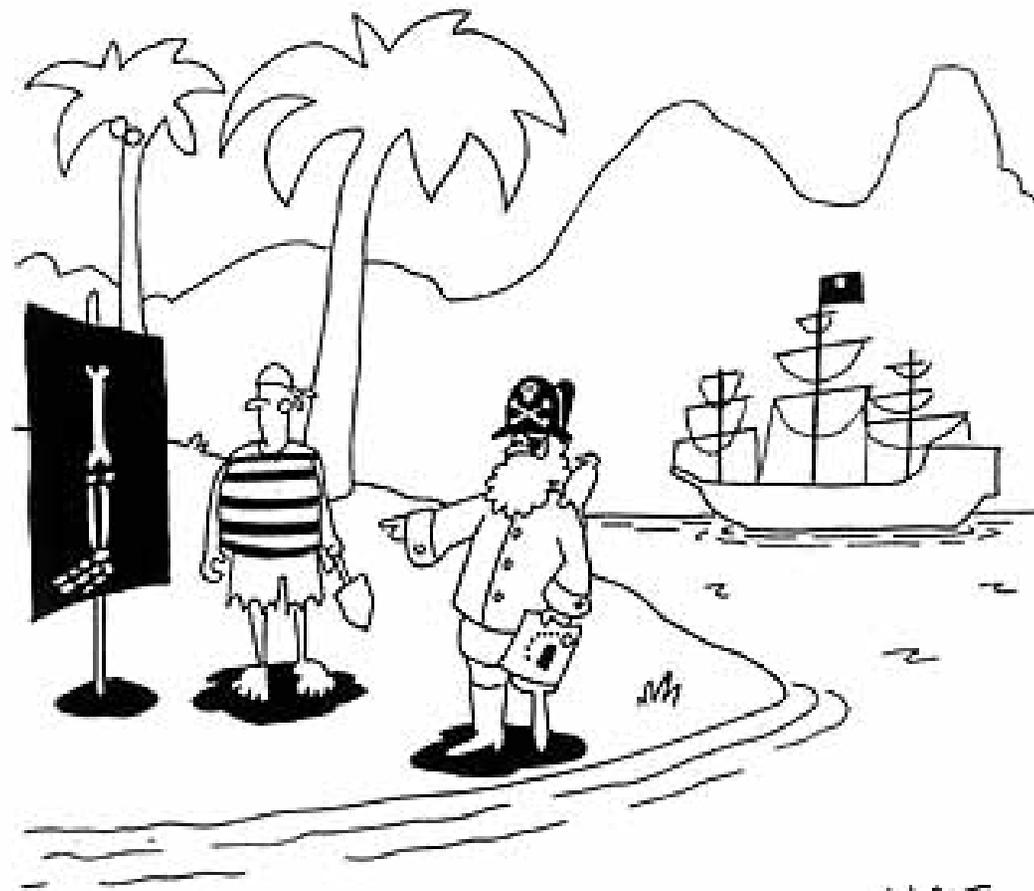
θ = Bragg's' angle of diffracted rays

ε = crystallite size

e = mean lattice strain

Reference

- O. Perales, PhD. Introduction To Characterization of Nanomaterials: XRD and Electron Microscopy Techniques; Power Point Presentation, 1st Semester Introduction to Material Characterization 2006-07 UPRM
- Siemens D5000: X Ray Diffraktometer – Operating Manual
- Web site: Hyper Physics



.NAF.

"This is it! According to the map an X-ray marks the spot."