Chapter 3: part I: X-Ray Diffraction

- How to identify unknown crystalline materials?
- How to determine crystal structure?

→

- X-ray Diffraction
- Transmission electron diffraction by TEM

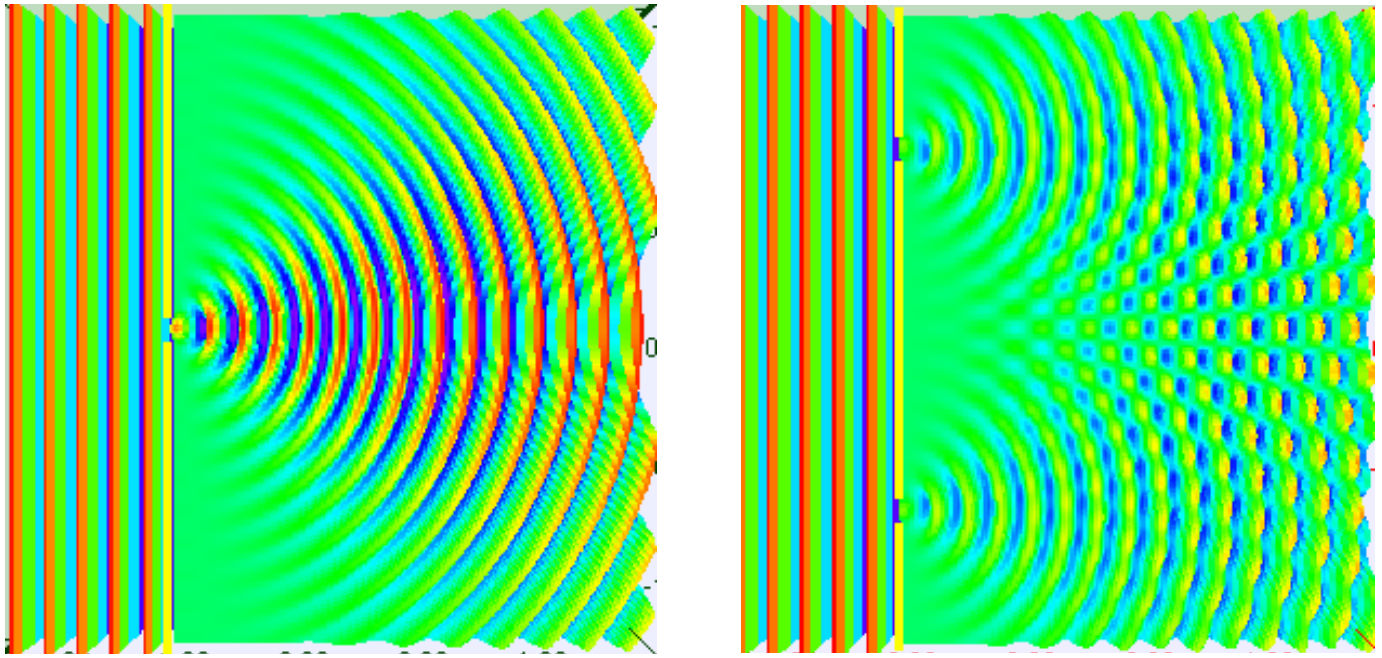
Diffraction is the result of radiation being scattered by a regular array of scattering centers whose spacing is about the same as the wavelength of the radiation.

Reflection vs diffraction

Reflection: scattering at the surface

Diffraction: in-phase scattering

Optical Diffraction

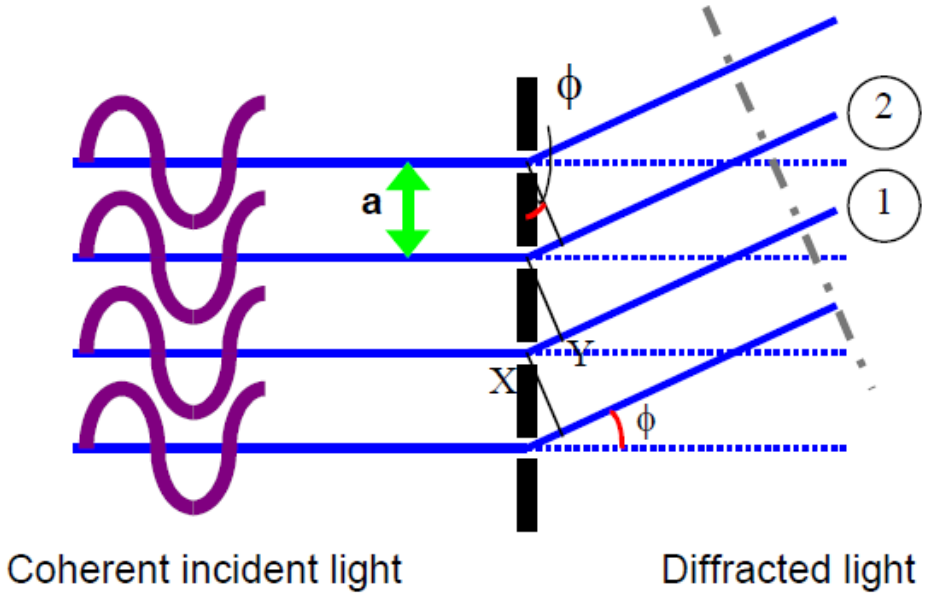


Diffraction - An Optical Grating

Path difference XY between diffracted beams 1 and 2:

$\sin \phi = XY/a$

➔ $XY = a \sin \phi$



For 1 and 2 to be *in phase* and give *constructive interference*, XY = λ, 2 λ, 3 λ, 4 λ …..n λ

So **$a \sin \phi = n\lambda$** where n is the order of diffraction

Diffraction - An Optical Grating

Consequences: maximum value of λ for diffraction

$$\sin \phi = 1 \rightarrow a = \lambda$$

Realistically, $\sin \phi < 1 \rightarrow a > \lambda$

So separation must be same order as, but greater than, wavelength of light.

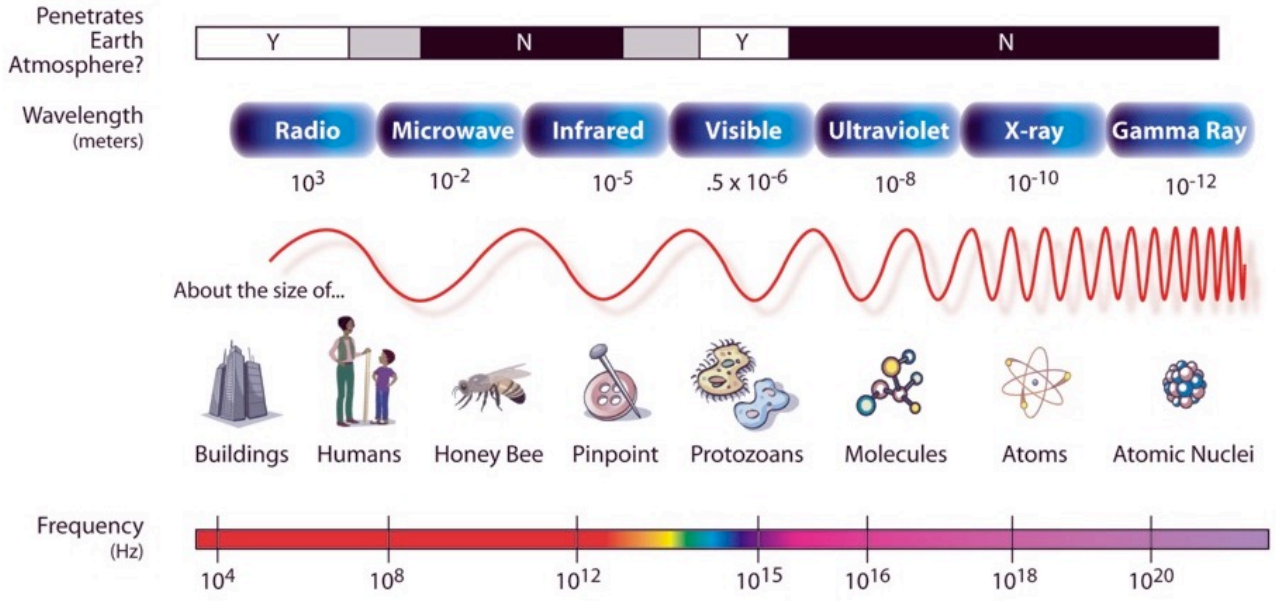
Thus for diffraction from crystals:

Interatomic distances 0.1 - 2 Å

so $\lambda = 0.1 - 2$ Å

X-rays, electrons, neutrons suitable

Electromagnetic Radiation Spectrum: X-Ray



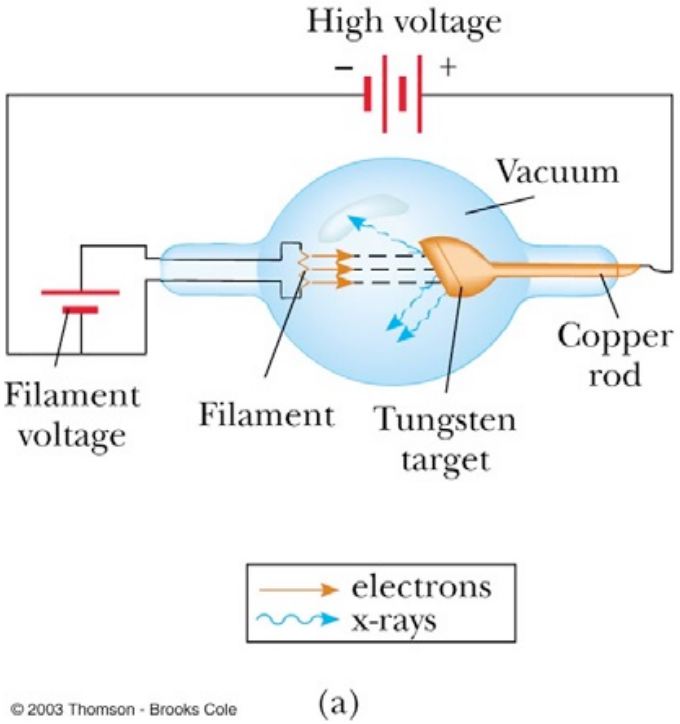
X-RAY

- Electromagnetic radiation with short wavelengths
- Advantages in X-rays for crystal structure analysis: wavelength 0.1~10 Å which is comparable to crystal lattice
- Short wavelength & high energy: x-rays have the ability to penetrate most materials with relatively little absorption

X-Ray Generation

- A current in the filament causes electrons to be emitted
- These freed electrons are accelerated toward a dense metal target
- The target is held at a higher potential than the filament

- X-rays are produced when high-speed electrons are suddenly slowed down
  - Can be caused by the electron striking a metal target



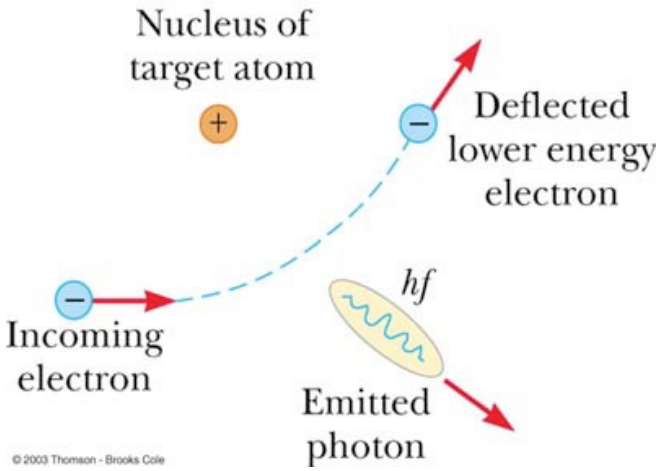
- **Continuous x-ray**
- **Characteristic x-ray**

YouTube: How does an X-ray Tube Work (Radiation Protection)

http://www.youtube.com/watch?v=Bc0eOjWkxpU&feature=related

X-Ray Generation

- An electron passes near a target nucleus
- The electron is deflected from its path by its attraction to the nucleus
  - This produces an acceleration
- It will emit electromagnetic radiation when it is accelerated



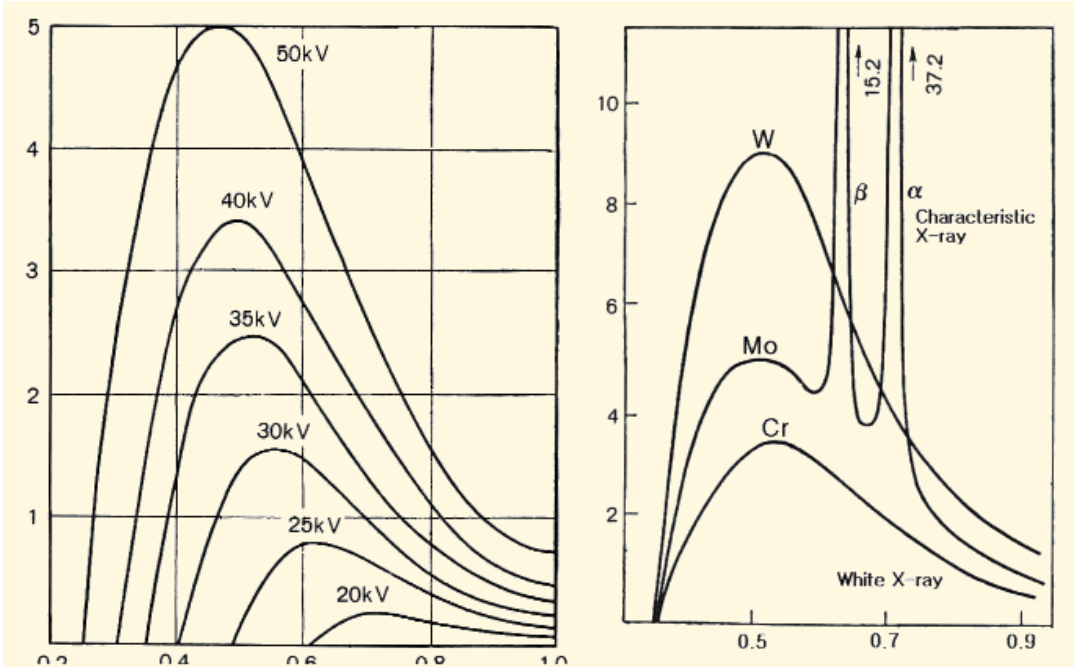
The maximum x-ray energy, and minimum wavelength results when the electron loses all its energy in a single collision, such that

$$E = eV = h\nu_{\max} = h\frac{c}{\lambda_{\min}}$$

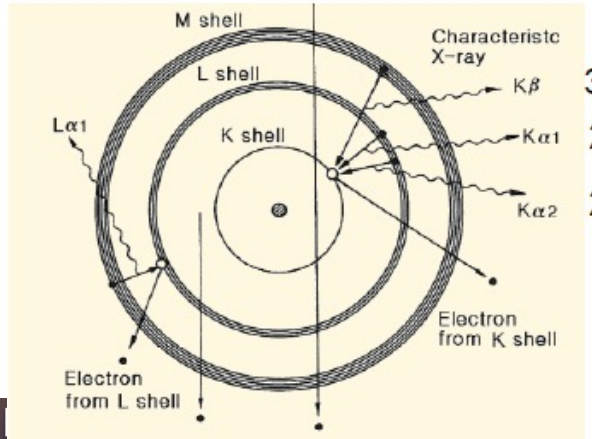
X-Ray Spectrum

- **Continuous x-ray**
  - The maximum x-ray energy, and minimum wavelength results when the electron loses all its energy in a single collision, such that

$$E = eV = h\nu_{max} = h\frac{c}{\lambda_{min}}$$



- **Characteristic x-ray**



$3p \rightarrow 1s$

$2p_{3/2} \rightarrow 1s$

$2p_{1/2} \rightarrow 1s$

X-Ray Absorption and Filter

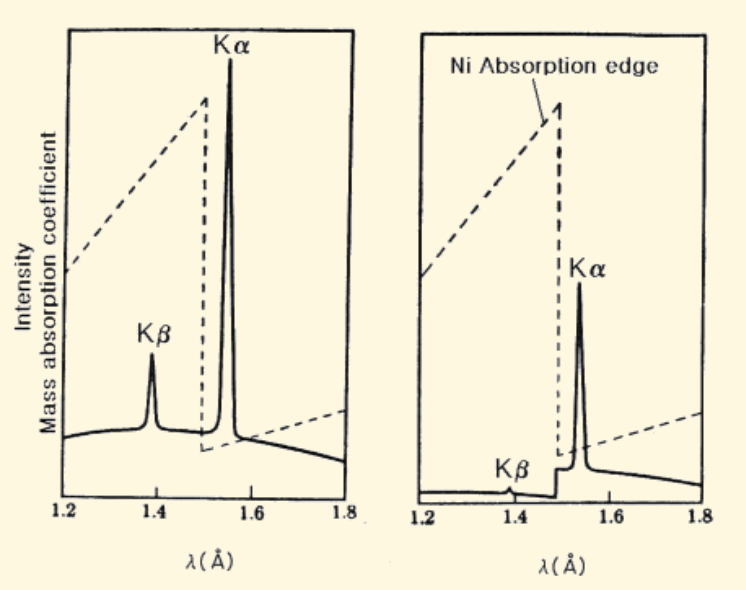
- **X-ray absorption**
  - The intensity of transmitted beam,

$$I_x = I_o e^{-\mu x}$$
$$= I_o e^{-(\mu/\rho)\rho x}$$

μ : linear absorption coefficient

μ/ρ : mass absorption coefficient

- a constant of the material and independent of its physical state
- depending on the wavelength of incident x-ray



The spectra of copper radiation before and after passage through a nickel filter

Mass Absorption Coefficient

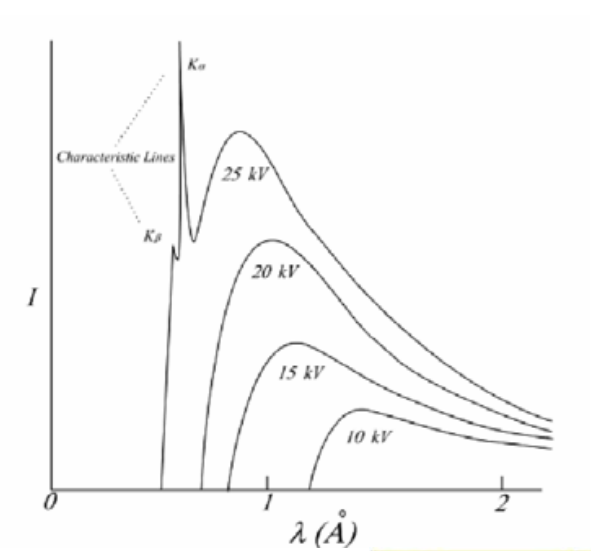
APPENDIX 8
MASS ABSORPTION COEFFICIENTS μ/ρ (cm^2/gm) AND DENSITIES ρ

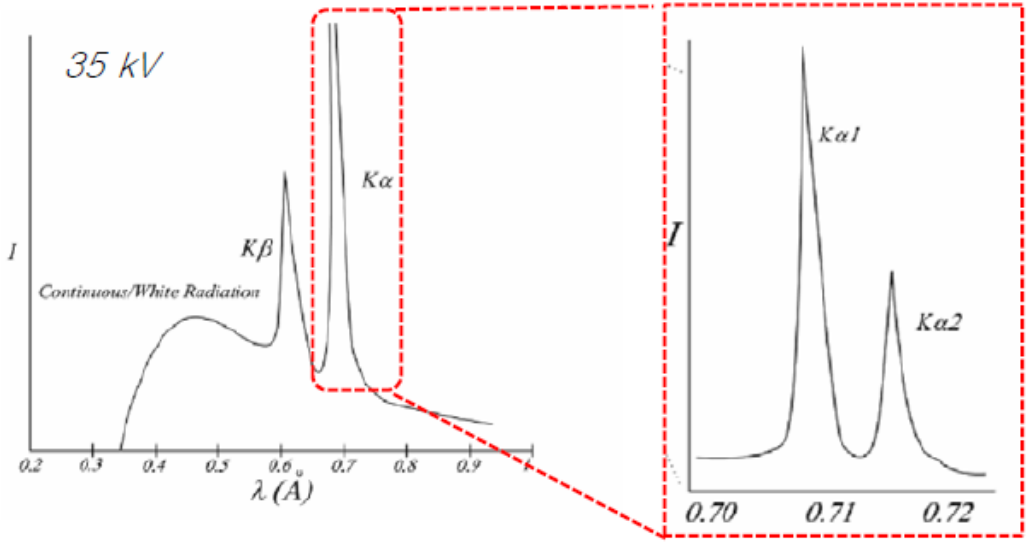
The mass absorption coefficients are extracted from much longer tables on pp. 61–66 of Vol. 4 of the *International Tables for X-Ray Crystallography* [G.11]. Although these coefficients are given to four significant figures, the actual accuracy is much less; the uncertainty ranges from less than 2 percent to more than 15 percent, depending on absorber and wavelength. [G.11] should be consulted for details.

The densities of elements solid at room temperature, except *P*, are x-ray densities, rounded off, from pp. 46–56 of Vol. 3 of [G.11]. Densities of gases are from *Metals Handbook* (Cleveland: American Society for Metals, 1948).

Absorber	Density (gm/cm^3)	Mo		Cu		Co		Cr	
		$K\alpha$ 0.711 Å	$K\beta$ 0.632 Å	$K\alpha$ 1.542 Å	$K\beta$ 1.392 Å	$K\alpha$ 1.790 Å	$K\beta$ 1.621 Å	$K\alpha$ 2.291 Å	$K\beta$ 2.085 Å
1 H	0.08375×10^{-3}	0.3727	0.3699	0.3912	0.3882	0.3966	0.3928	0.4116	0.4046
2 He	0.1664×10^{-3}	0.2019	0.1972	0.2835	0.2623	0.3288	0.2966	0.4648	0.4001
3 Li	0.533	0.1968	0.1866	0.4770	0.3939	0.6590	0.5283	1.243	0.9639
4 Be	1.85	0.2451	0.2216	1.007	0.7742	1.522	1.152	3.183	2.388
5 B	2.47	0.3451	0.2928	2.142	1.590	3.357	2.485	7.232	5.385
6 C	2.27 (graphite)	0.5348	0.4285	4.219	3.093	6.683	4.916	14.46	10.76
7 N	1.165×10^{-3}	0.7898	0.6054	7.142	5.215	11.33	8.330	24.42	18.23
8 O	1.332×10^{-3}	1.147	0.8545	11.03	8.062	17.44	12.86	37.19	27.88
9 F	1.696×10^{-3}	1.584	1.154	15.95	11.66	25.12	18.57	53.14	38.98
10 Ne	0.8387×10^{-3}	2.209	1.597	22.13	16.24	34.69	25.72	72.71	54.91
11 Na	0.966	2.939	2.098	30.30	22.23	47.34	35.18	98.48	74.66
12 Mg	1.74	3.979	2.825	40.88	30.08	63.54	47.38	130.8	99.62
13 Al	2.70	5.043	3.585	50.23	37.14	77.54	58.08	158.0	120.7
14 Si	2.33	6.533	4.624	65.32	48.37	100.4	75.44	202.7	155.6
15 P	1.82 (yellow)	7.870	5.569	77.28	57.44	118.0	89.05	235.5	181.6
16 S	2.09	9.625	6.835	92.53	68.90	141.2	106.6	281.9	217.2
17 Cl	3.214×10^{-3}	11.64	8.261	109.2	81.79	164.7	125.3	321.5	250.2
18 A	1.663×10^{-3}	12.62	8.949	119.5	89.34	180.9	137.3	355.5	275.8
19 K	0.862	16.20	11.51	148.4	111.7	222.0	169.9	426.6	334.2
20 Ca	1.53	19.00	13.56	171.4	129.0	257.4	196.4	499.6	389.3
21 Sc	2.99	21.04	15.00	186.0	140.8	275.5	212.2	520.9	410.7
22 Ti	4.51	23.25	16.65	202.4	153.2	300.5	231.0	571.4	448.0
23 V	6.09	25.24	18.07	222.6	168.0	332.7	254.7	75.06	501.0
24 Cr	7.19	29.25	20.99	252.3	191.1	375.0	288.1	85.71	65.79
25 Mn	7.47	31.86	22.89	272.5	206.7	405.1	311.2	96.06	73.75
26 Fe	7.87	37.74	27.21	304.4	233.6	56.25	345.5	113.1	86.77
27 Co	8.8	41.02	29.51	338.6	258.7	62.86	47.71	124.6	96.06
28 Ni	8.91	47.24	34.18	48.83	282.8	73.75	56.05	145.7	112.5
29 Cu	8.93	49.34	35.77	51.54	38.74	78.11	59.22	155.2	119.5
30 Zn	7.13	55.46	40.26	59.51	45.30	88.71	68.00	171.7	133.5
31 Ga	5.91	56.90	41.69	62.13	46.65	94.15	71.39	186.9	144.0
32 Ge	5.32	60.47	44.26	67.92	51.44	102.0	77.79	199.9	154.5
33 As	5.78	65.97	48.57	75.65	57.01	114.0	86.76	224.0	173.3
34 Se	4.81	68.82	51.20	82.89	62.32	125.1	95.11	246.1	190.4
35 Br	3.12 (liquid)	74.68	55.56	90.29	68.07	135.8	103.5	266.2	206.2

X-Ray Spectrum of Mo

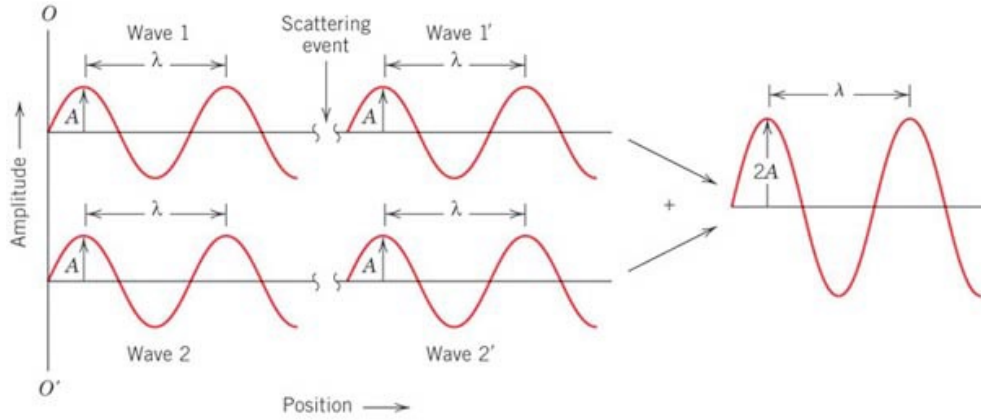




Element	K_{α} (Å)	$K_{\alpha 1}$ (Å)	$K_{\alpha 2}$ (Å)	K_{β} (Å)
Cr	2.29100	2.28970	2.29361	2.08487
Fe	1.93736	1.93604	1.93998	1.75661
Co	1.79026	1.78897	1.79285	1.62079
Cu	1.54184	1.54056	1.54439	1.39222
Mo	0.71073	0.70930	0.71359	0.63229

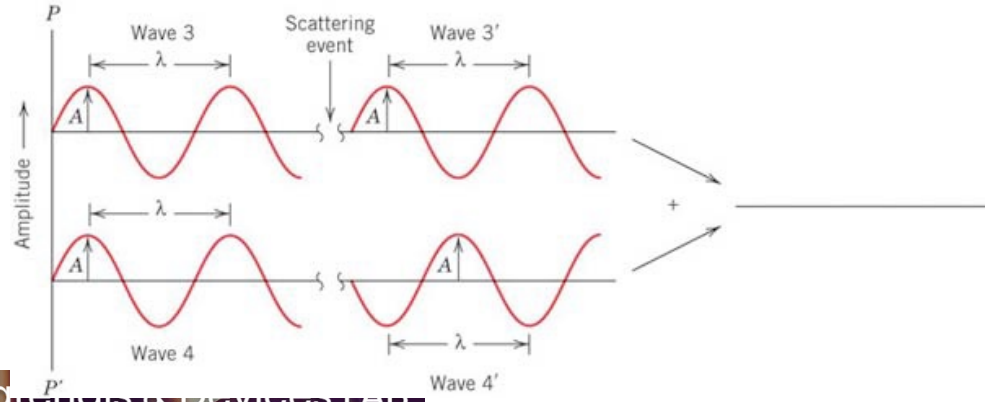
X-Ray Diffraction

Constructive interference



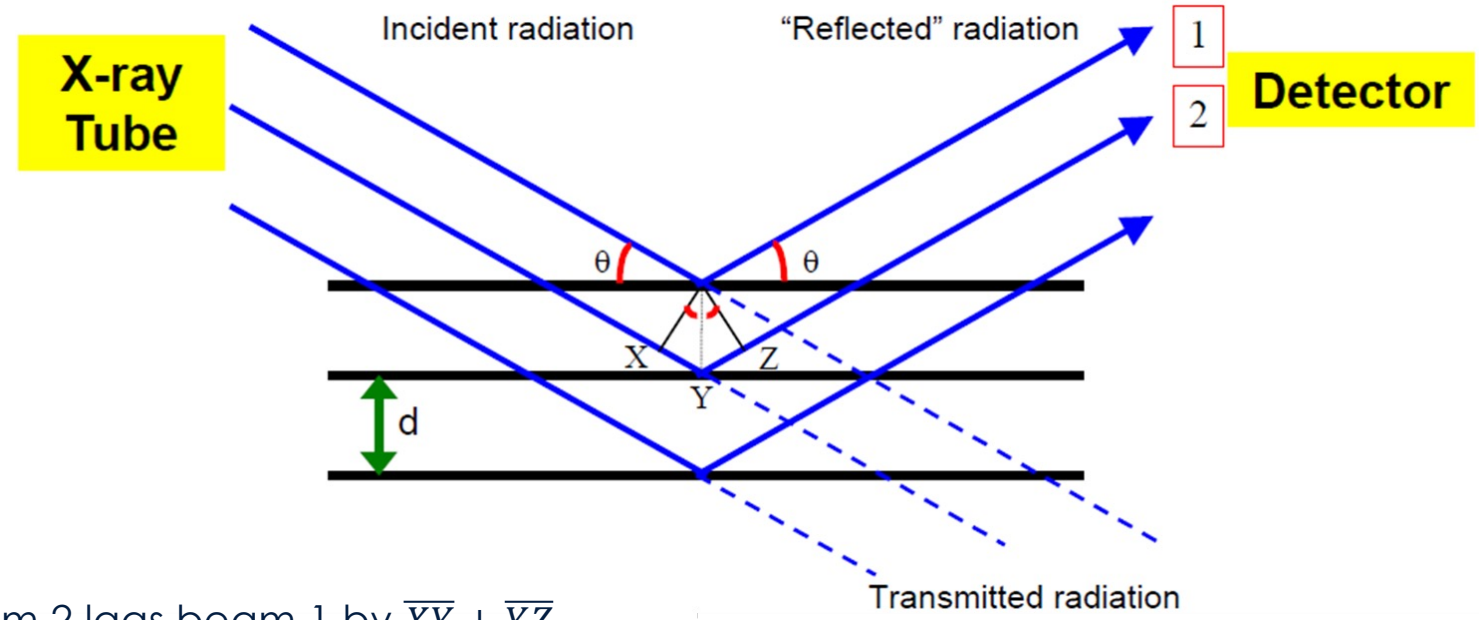
- Same wavelength (λ)
- In phase

Destructive interference



- Same wavelength (λ)
- Out of phase

Diffraction from Crystals



Beam 2 lags beam 1 by $\overline{XY} + \overline{YZ}$

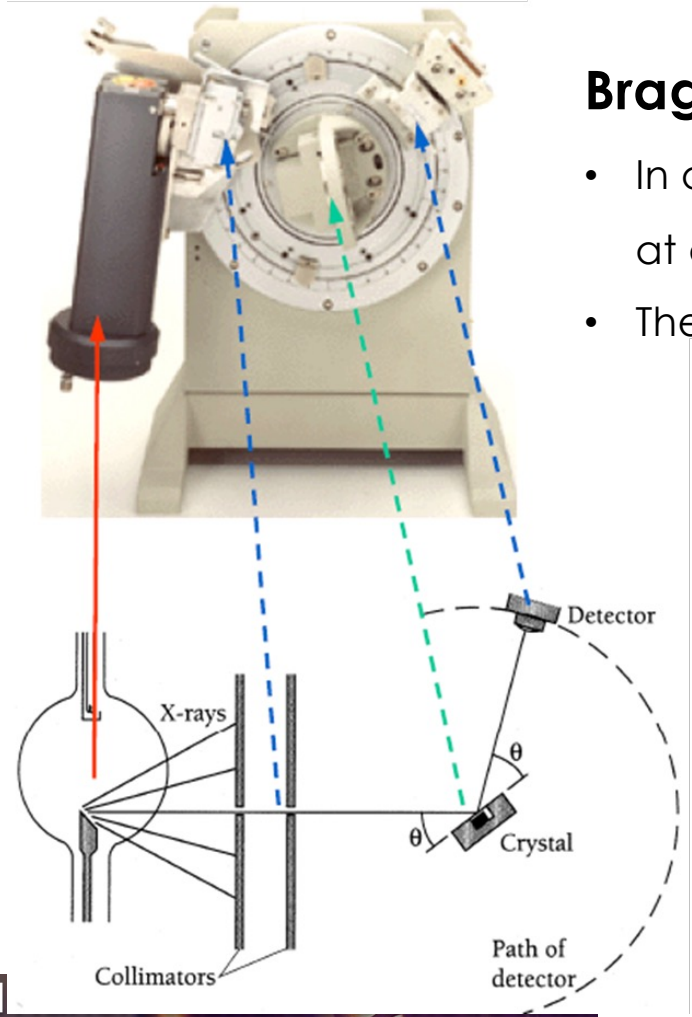
$$n\lambda = \overline{XY} + \overline{YZ}$$

$$n\lambda = d_{hkl} \sin\theta + d_{hkl} \sin\theta = 2 d_{hkl} \sin\theta$$

$$\left(d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \right)$$

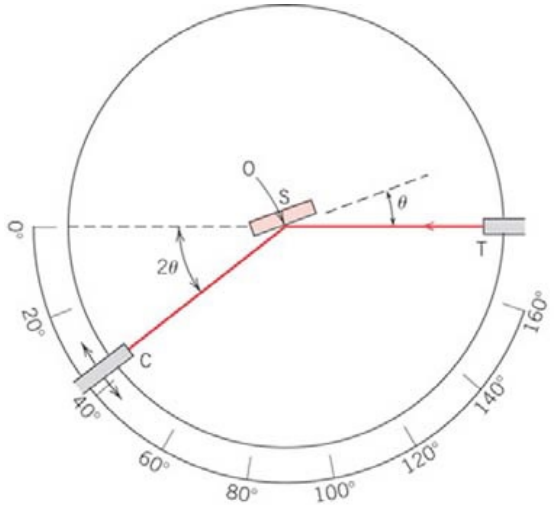
nλ= 2d sin θ **Bragg's Law**

X-Ray Diffraction "Double-Angle Diffractometer"



Bragg-Brentano geometry

- In one type of diffraction experiment a beam of X-rays is **DIRECTED** at a sample, which is then **ROTATED** in a suitable apparatus
- The intensity of the reflected beam is then monitored



YouTube: Grazing Incidence X-Ray Diffraction of InAs NW
http://www.youtube.com/watch?v=qws6Qbuza5E

Essential Parts of the Diffractometer

- X-ray Tube: the source of X Rays
- Incident-beam optics: condition the X-ray beam before it hits the sample
- The goniometer: the platform that holds and moves the sample, optics, detector, and/or tube
- The sample & sample holder
- Receiving-side optics: condition the X-ray beam after it has encountered the sample
- Detector: count the number of X Rays scattered by the sample

Example 1

e.g. X-rays with wavelength 1.54 Å are reflected from planes with d=1.2 Å. Calculate the Bragg angle, θ, for constructive interference.

$\lambda = 1.54 \times 10^{-10}$ m, $d = 1.2 \times 10^{-10}$ m, θ=?

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

$$\theta = \sin^{-1}\left(\frac{n\lambda}{2d}\right)$$

n=1 : θ = 39.9°

n=2 : X (nλ/2d)>1

We normally set n=1 and adjust Miller indices, to give

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

Example 2

Example of equivalence of the two forms of Bragg's law:

Calculate θ for λ=1.54 Å, cubic crystal, **a**=5Å

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

(1 0 0) reflection, d=5 Å
n=1, θ =8.86o
n=2, θ =17.93o
n=3, θ =27.52o
n=4, θ =38.02o
n=5, θ =50.35o
n=6, θ =67.52o
no reflection for n ≥ 7

(2 0 0) reflection, d=2.5 Å
n=1, θ =17.93o
n=2, θ =38.02o
n=3, θ =67.52o
no reflection for n ≥ 4

Use Bragg's law and the d-spacing equation to solve a wide variety of problems

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

or

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

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

Combining Bragg and d-spacing Equation

X-rays with wavelength 1.54 Å are "reflected" from the (1 1 0) planes of a cubic crystal with unit cell **a** = 6 Å.

Calculate the Bragg angle, θ, for all orders of reflection, **n**.

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{1+1+0}{6^2} = 0.056$$

$$d^2 = 18 \quad \Rightarrow \quad d = 4.24 \text{ Å}$$

$$d = 4.24\ \text{Å} \qquad \theta = \sin^{-1}\left(\frac{n\lambda}{2d}\right)$$

n = 1 : $\theta = 10.46^\circ$

n = 2 : $\theta = 21.30^\circ$

n = 3 : $\theta = 33.01^\circ$

n = 4 : $\theta = 46.59^\circ$

n = 5 : $\theta = 65.23^\circ$

Interplanar Spacings in Crystal Systems

Interplanar spacing

The spacing *d* between adjacent (*hkl*) lattice planes is given by:

- Cubic:

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

- Tetragonal:

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

- Hexagonal:

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

- Rhombohedral:

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

- Orthorhombic:

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

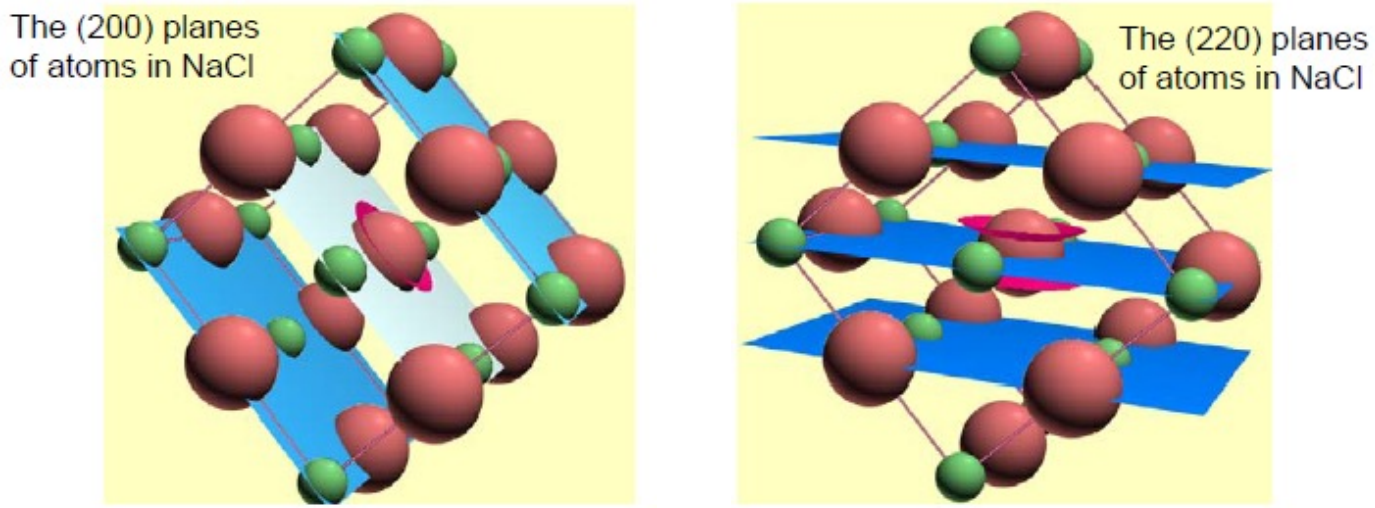
- Monoclinic:

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

- Triclinic:

$$\frac{1}{d^2} = \frac{\frac{h^2}{a^2}\sin^2\alpha + \frac{k^2}{b^2}\sin^2\beta + \frac{l^2}{c^2}\sin^2\gamma}{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

Crystalline materials: periodic arrangements of atoms



- The unit cell is the basic repeating unit that defines a crystal.
- Parallel planes of atoms intersecting the unit cell are used to define directions and distances in the crystal.
  - These crystallographic planes are identified by Miller indices.

The atoms in a crystal are a periodic array of coherent scatterers and thus can diffract light.

- Diffraction occurs when each object in a periodic array scatters radiation coherently, producing concerted constructive interference at specific angles.
- The electrons in an atom coherently scatter light.
  - The electrons interact with the oscillating electric field of the light wave.
- Atoms in a crystal form a periodic array of coherent scatterers.
  - The wavelength of X rays are similar to the distance between atoms.
  - Diffraction from different planes of atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal
- X Rays are also reflected, scattered incoherently, absorbed, refracted, and transmitted when they interact with matter.

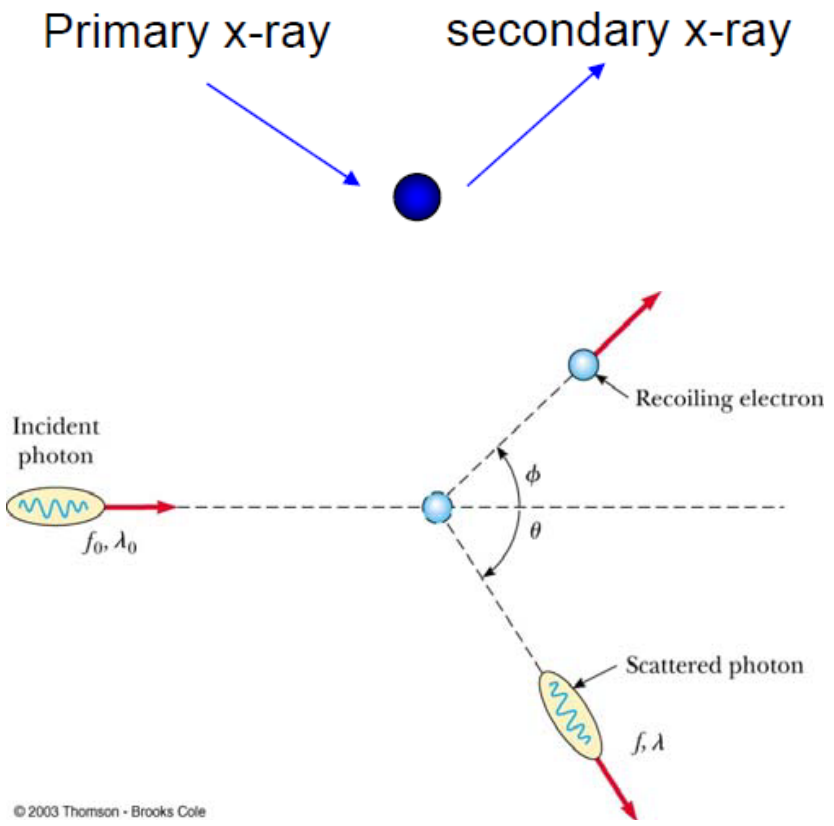
X-Ray Scattering by an Electron

- Thomson scattering
  - Elastic (coherent scattering)
  - $\lambda_{primary} = \lambda_{secondary}$

➔ **x-ray diffraction**

- Compton scattering
  - Inelastic (incoherent scattering)
  - The shift in wavelength
  - $\lambda_{primary} < \lambda_{secondary}$

$$\Delta\lambda = \lambda - \lambda_o = \frac{h}{m_e c}(1 - \cos\theta)$$



X-Ray Scattering by an Atom

- The coherent scattering (Thomson scattering) by atom is due to the electrons contained in that atom, not due to the nucleus
- Atomic scattering factor (f)

$$f = \frac{\text{amplitude of the wave scattered by an atom}}{\text{amplitude of the wave scattered by one electron}}$$

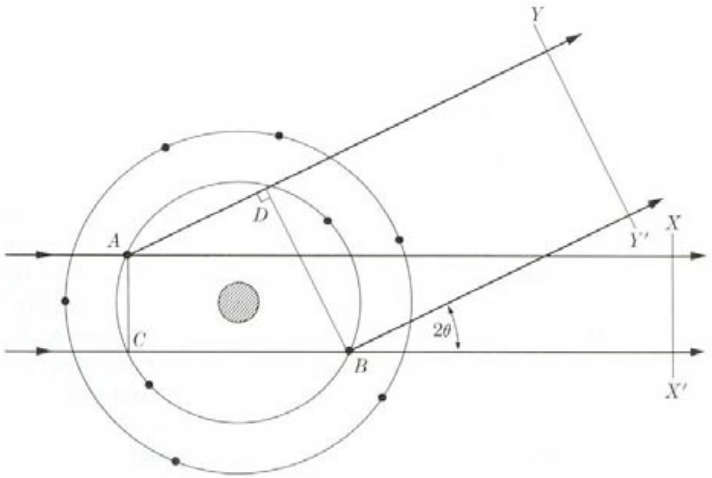
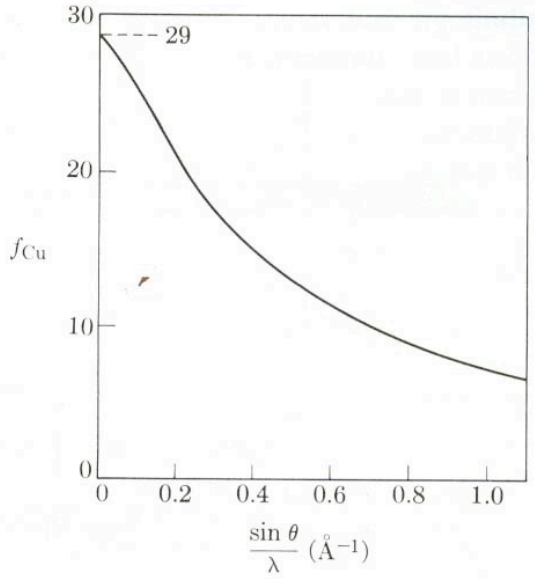


Fig. 4–5 X-ray scattering by an atom.

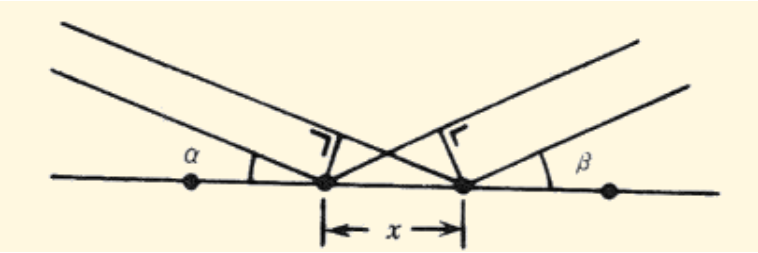
Path difference = CB – AD < λ



As θ → 0,
f → Z

Fig. 4–6 The atomic scattering factor of copper.

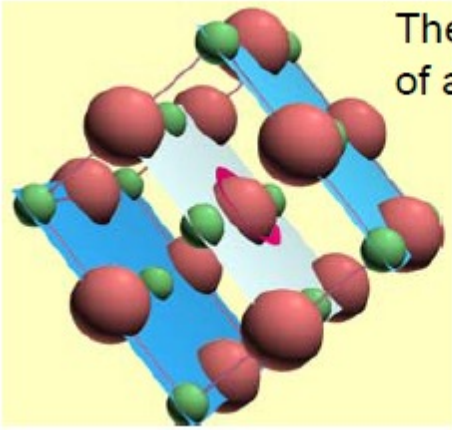
X-Ray Scattering by the Atoms in a Plane

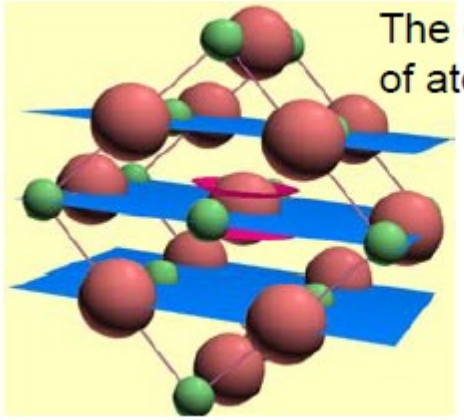


Path difference = $\overline{AD} - \overline{BC}$

$$\overline{AD} - \overline{BC} = \overline{BD}\cos\alpha - \overline{BD}\cos\beta$$
$$= \overline{BD}(\cos\alpha - \cos\beta)$$

If α=β, $\overline{AD} - \overline{BC}$=0
(constructive interference)



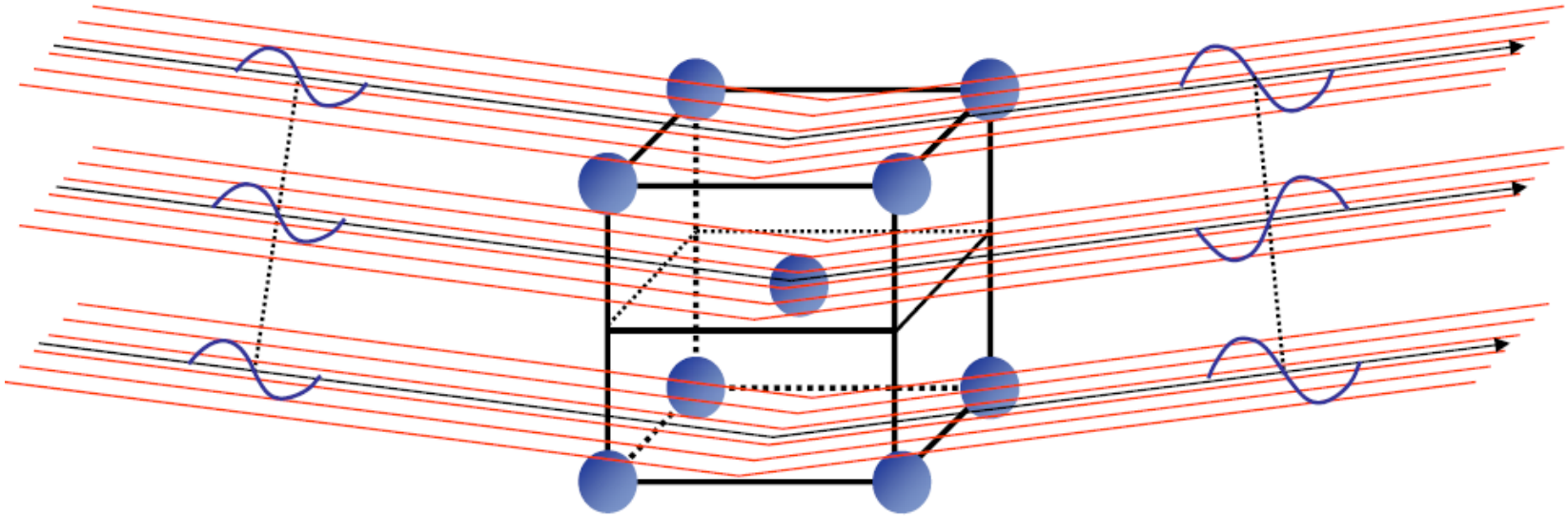


X-Ray Scattering by a Unit Cell: BCC

$h^2 + k^2 + l^2$ must be even for diffraction

{110} {200} {211} {220} {310} {222}

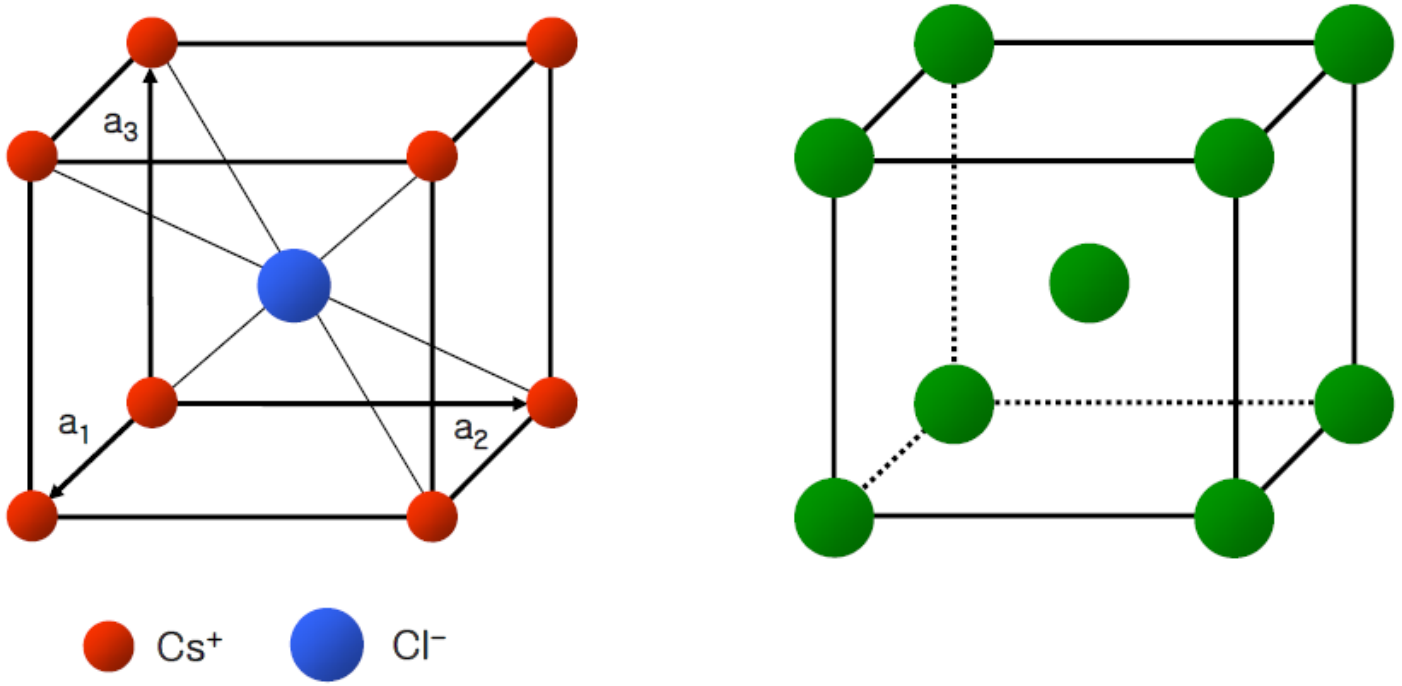
$h^2 + k^2 + l^2$ = 2, 4, 6, 8, 10, 12



Out of phase !! **∴ (100) in BCC does not appear**

X-Ray Scattering by a Unit Cell : CsCl & BCC

difference in CsCl and BCC : (100) peak exists but weak

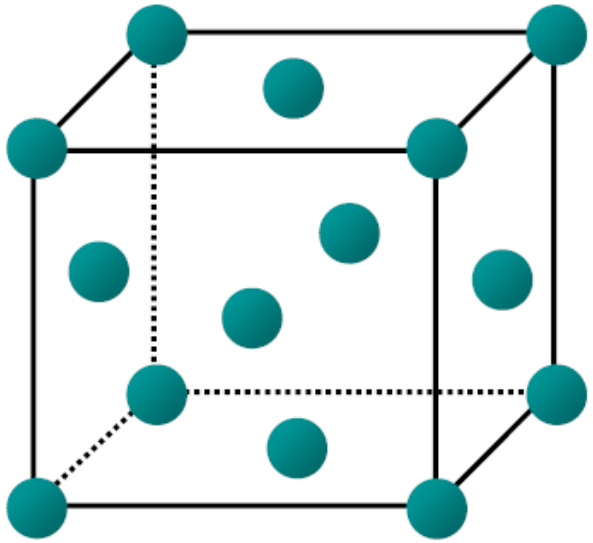


X-Ray Scattering by a Unit Cell : FCC

hkl all even or all odd (unmixed indices)

(111) (200) (221) (311) (222) (400) (331)

$h^2 + k^2 + l^2$ = 3, 4, 8, 11, 12, 16, 19



X-Ray Scattering by a Unit Cell

Bravais lattice	Reflections possibly present	Reflections necessarily absent
Simple	All	None
Based centered	*h* and *k* unmixed	*h* and *k* mixed
Body centered	(*h* + *k* + *l*) even	(*h* + *k* + *l*) odd
Face centered	*h*, *k*, and *l* unmixed	*h*, *k*, and *l* mixed

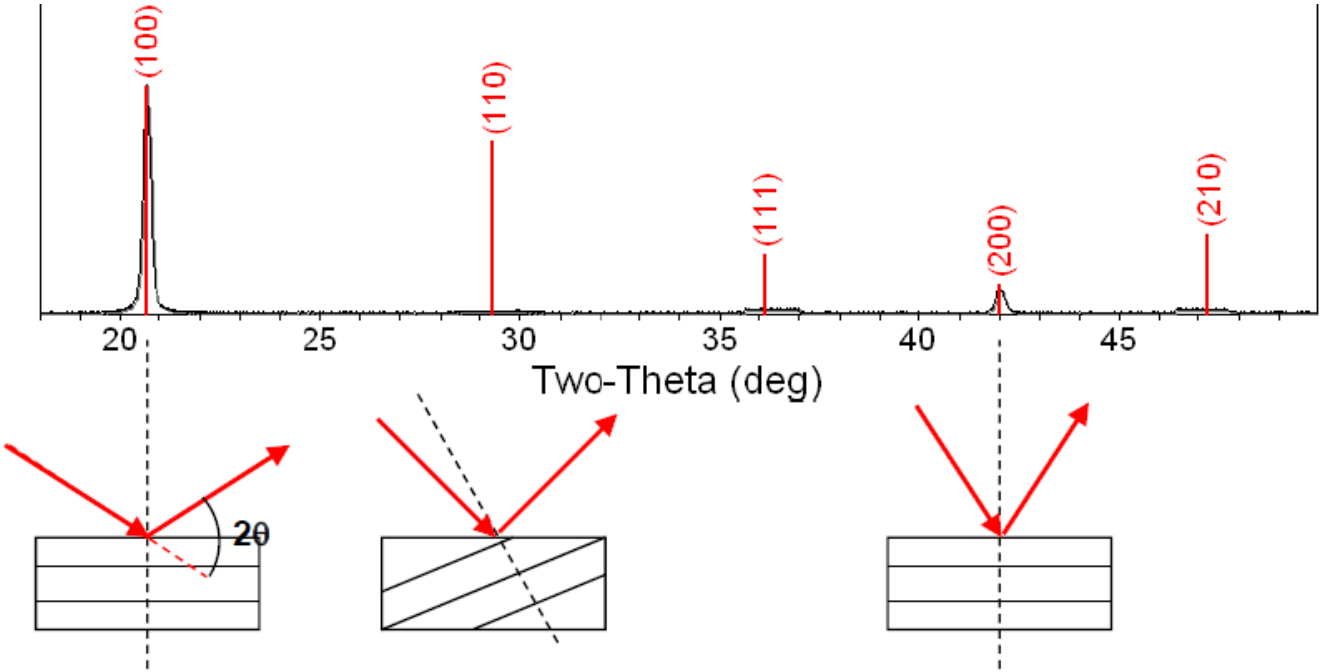
Q2: 다음의 Structure factor (F) 개념을 통해 테이블에 기재된 BCC/FCC의 회절조건을 증명하시오.

$$F_{hkl} = \sum_{1}^{N} f_n \exp\left[2\pi i(hu_n + kv_n + lw_n)\right]$$

Bravais lattice	Reflections possibly present	Reflections necessarily absent
Body centered	$(h + k + l)$ even	$(h + k + l)$ odd
Face centered	h, k, and l unmixed	h, k, and l mixed

XRD in Bragg-Brentano Geometry: Single Crystal

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



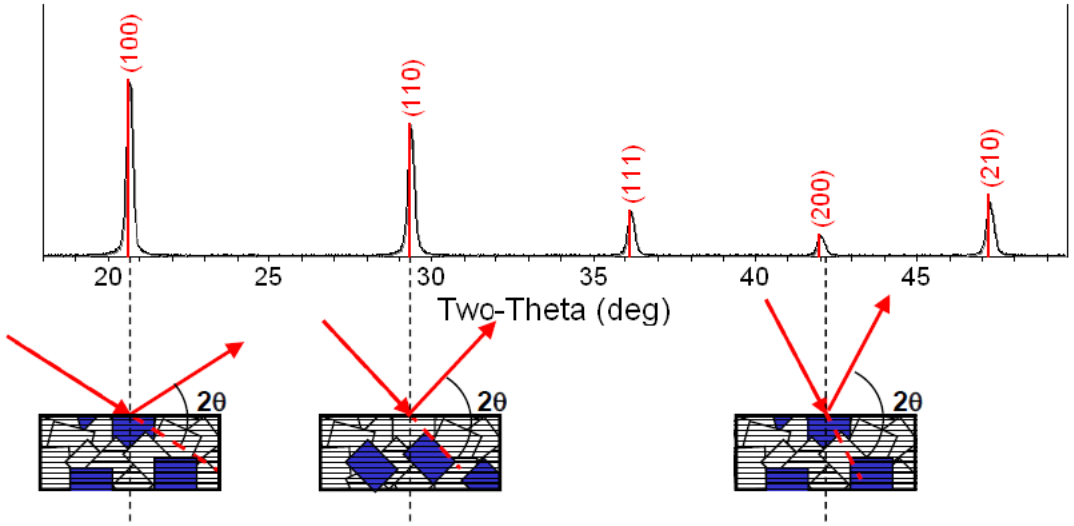
At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.

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.

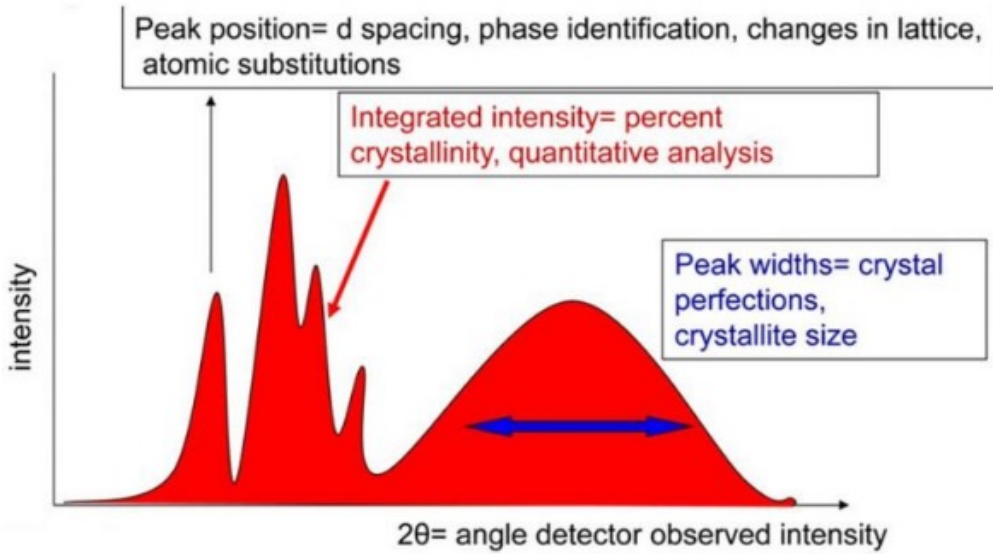
The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d_{200} is ½ d_{100}, they appear at 42 °2θ.

XRD in Bragg-Brentano Geometry: Poly Crystal

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

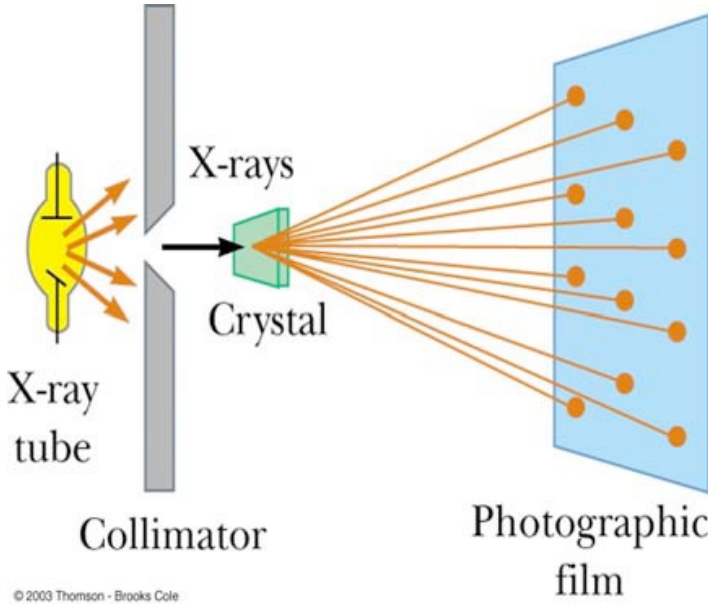


- For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).
- Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that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



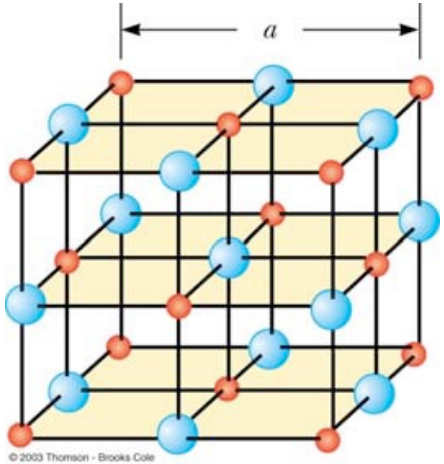
Transmission Laue Method

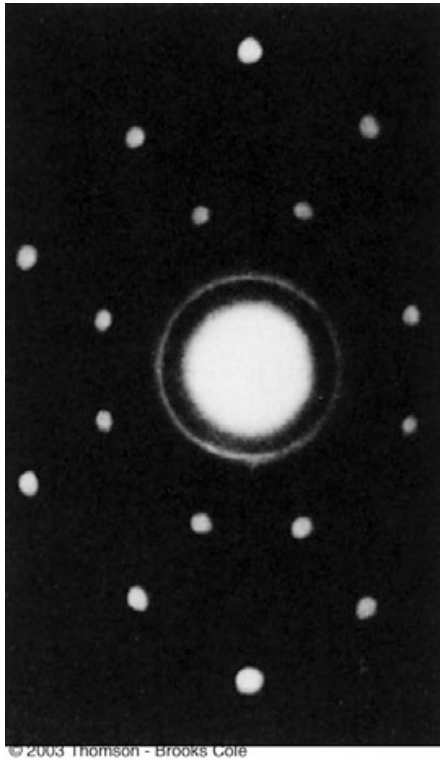
- A continuous beam of X-rays is incident on the crystal
- The diffracted radiation is very intense in certain directions
  - These directions correspond to constructive interference from waves reflected from the layers of the crystal
- The diffraction pattern is detected by photographic film



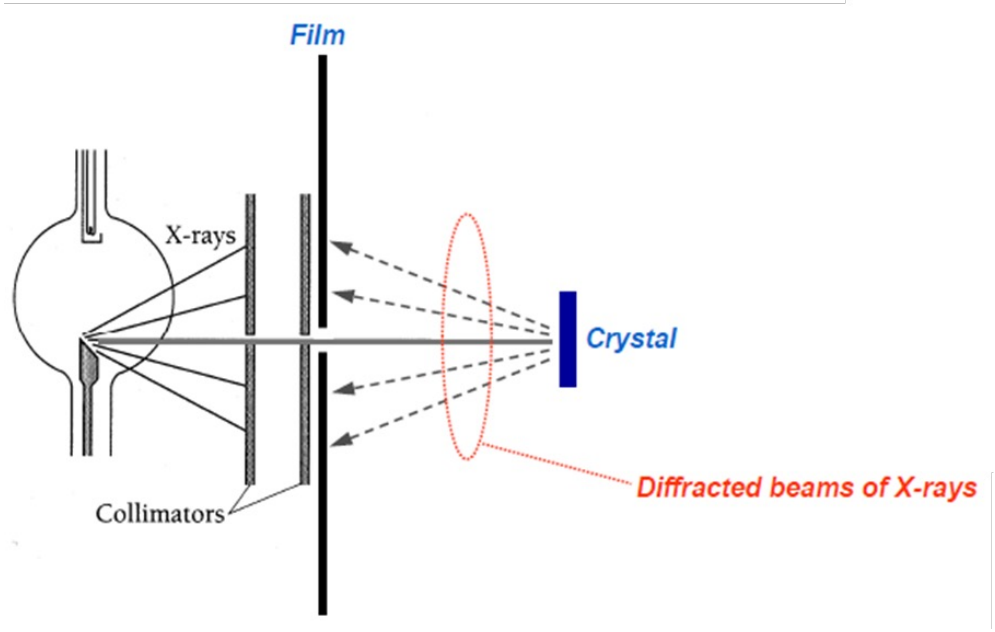
Transmission Laue Method: X-ray Diffraction Pattern

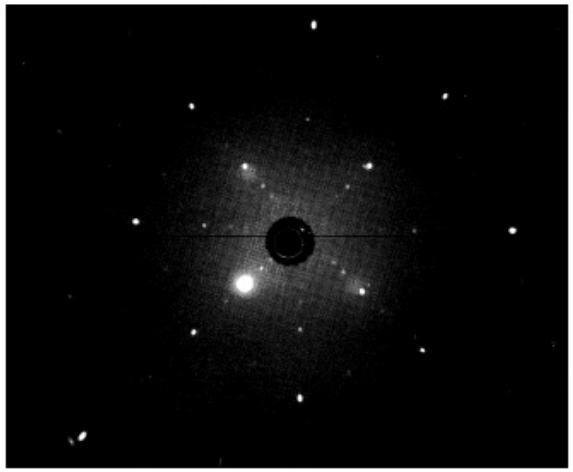
- The array of spots is called a Laue pattern
- The crystal structure is determined by analyzing the positions and intensities of the various spots
- This is for NaCl





Back-reflection Laue Method





Effects Produced by the Passage of X-Rays through Matter

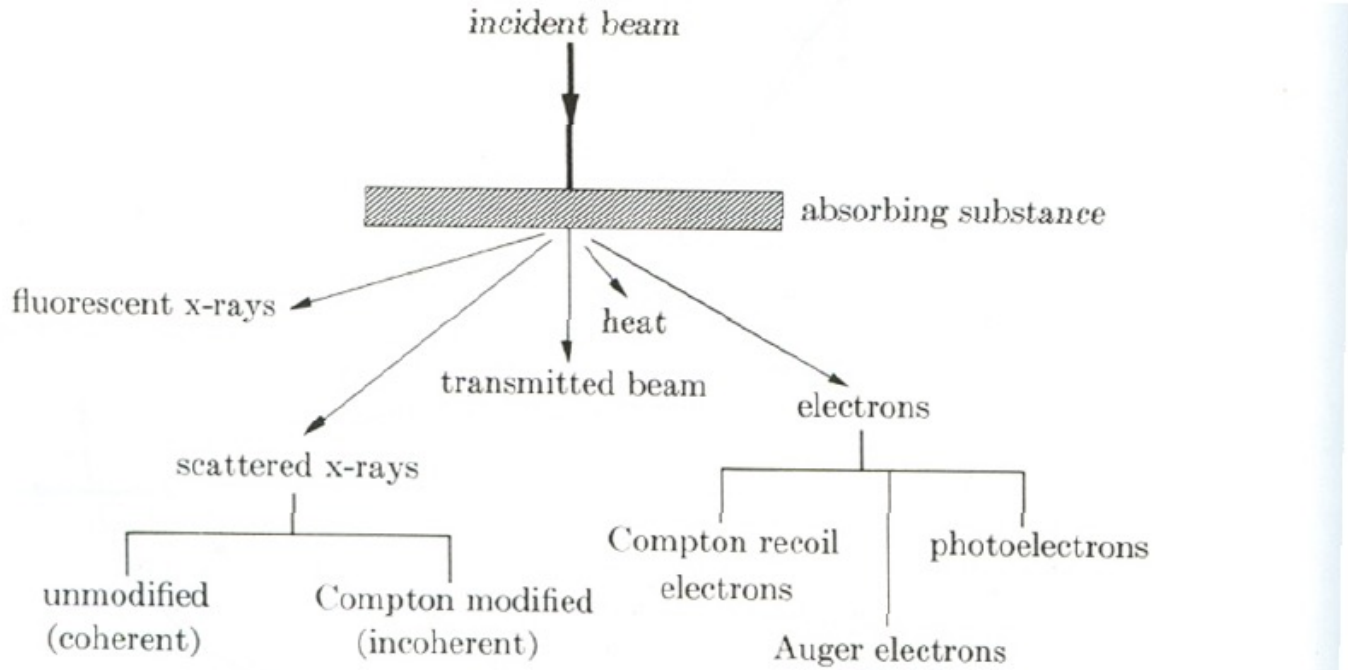
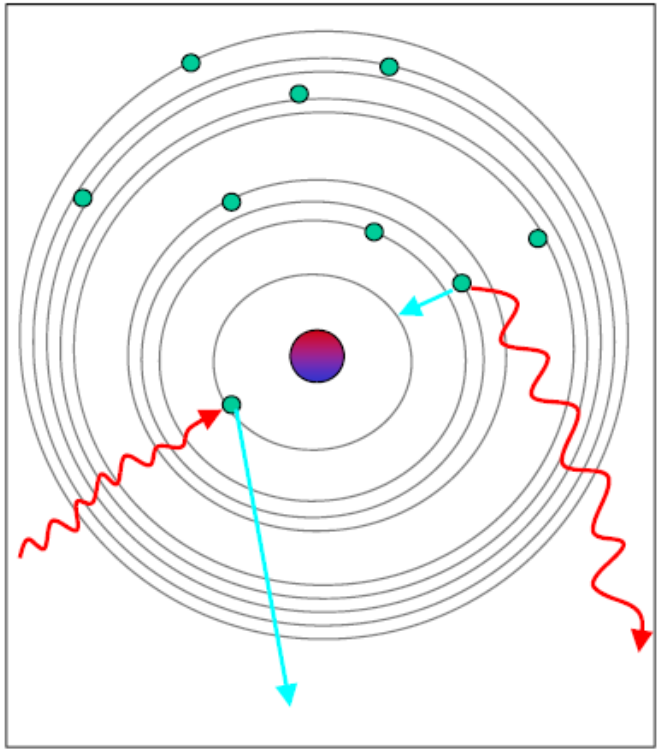


Fig. 4–7 Effects produced by the passage of x-rays through matter, after Henry, Lipson, and Wooster [G.8].

Chap 3 part II: X-Ray Fluorescence (XRF)

Theory



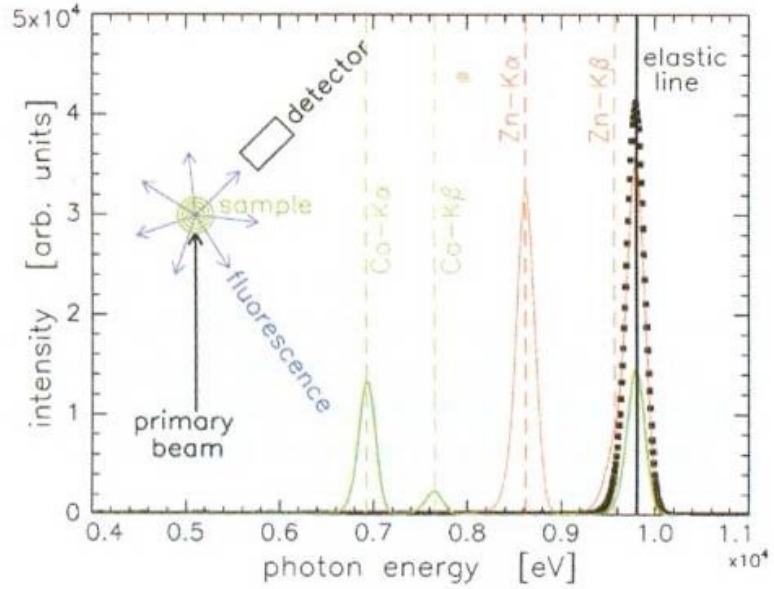
- A source X-ray strikes an inner shell electron. If at high enough energy (above absorption edge of element), it is ejected it from the atom.
- Higher energy electrons cascade to fill vacancy, giving off characteristic fluorescent X-rays.
- For elemental analysis of Be - U.

XRF-Technique

- X-ray Fluorescence (XRF) is an efficient, non-destructive and powerful elemental analysis technique.
- XRF is a fingerprinting method of a sample's elemental components

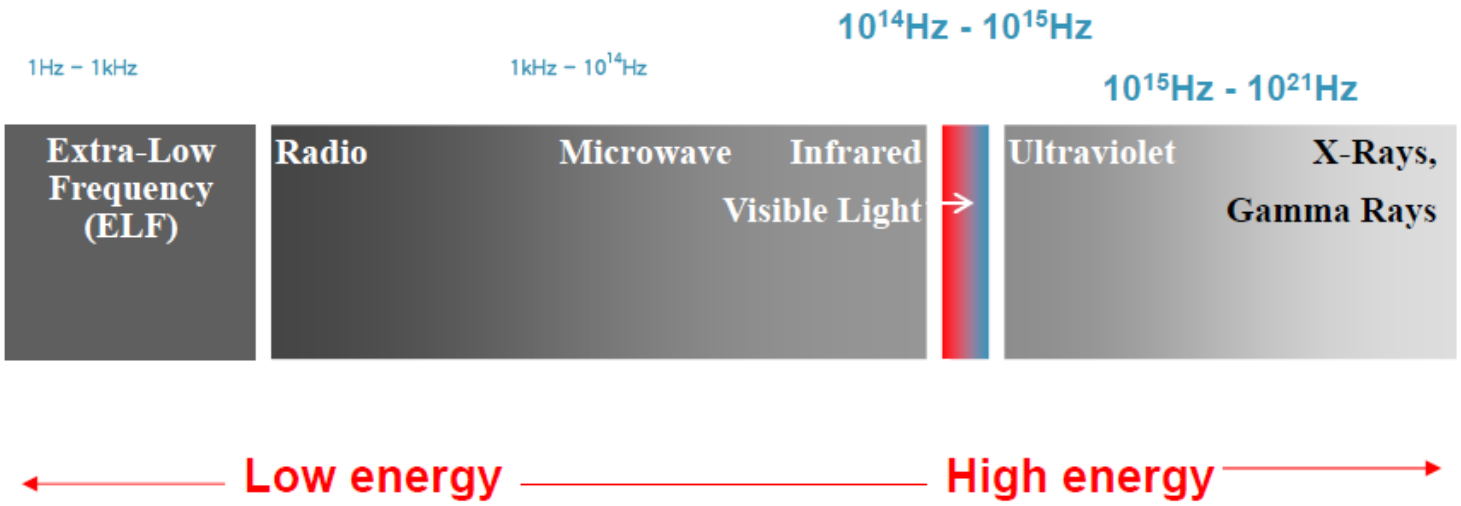
Basic Idea

- A sample is irradiated using an excitation source,
- The X-ray spectrum of the sample, called the fluorescence spectrum is collected,
- The XRF spectrum is constructed using one or both of two methods:
    1) The Energy Dispersive XRF (**EDXRF**),
    2) The Wave Dispersive XRF (**WDXRF**)
- The concentration of an element in the sample is related to the corresponding intensity.



(b) Examples of X-ray fluorescence measurements. The inset shows the experimental setup. The symbols denote data taken with a polymer sample which does not show fluorescence in the displayed energy range. The Zn-Kβ line can be seen as a shoulder close to the elastic line.

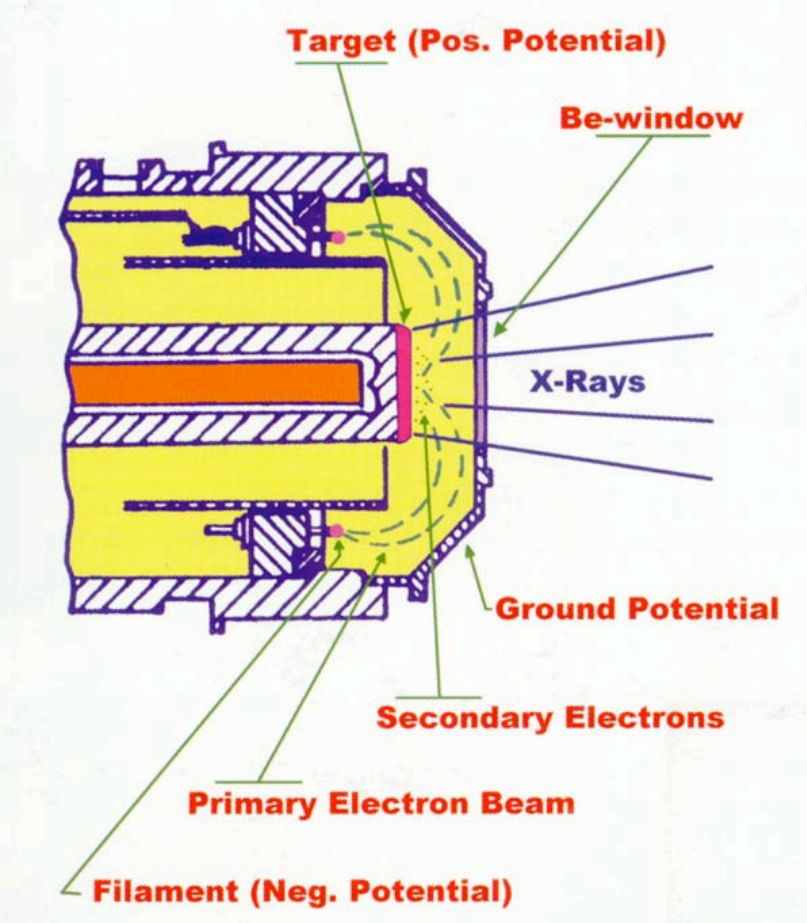
Electromagnetic Radiation



Sources

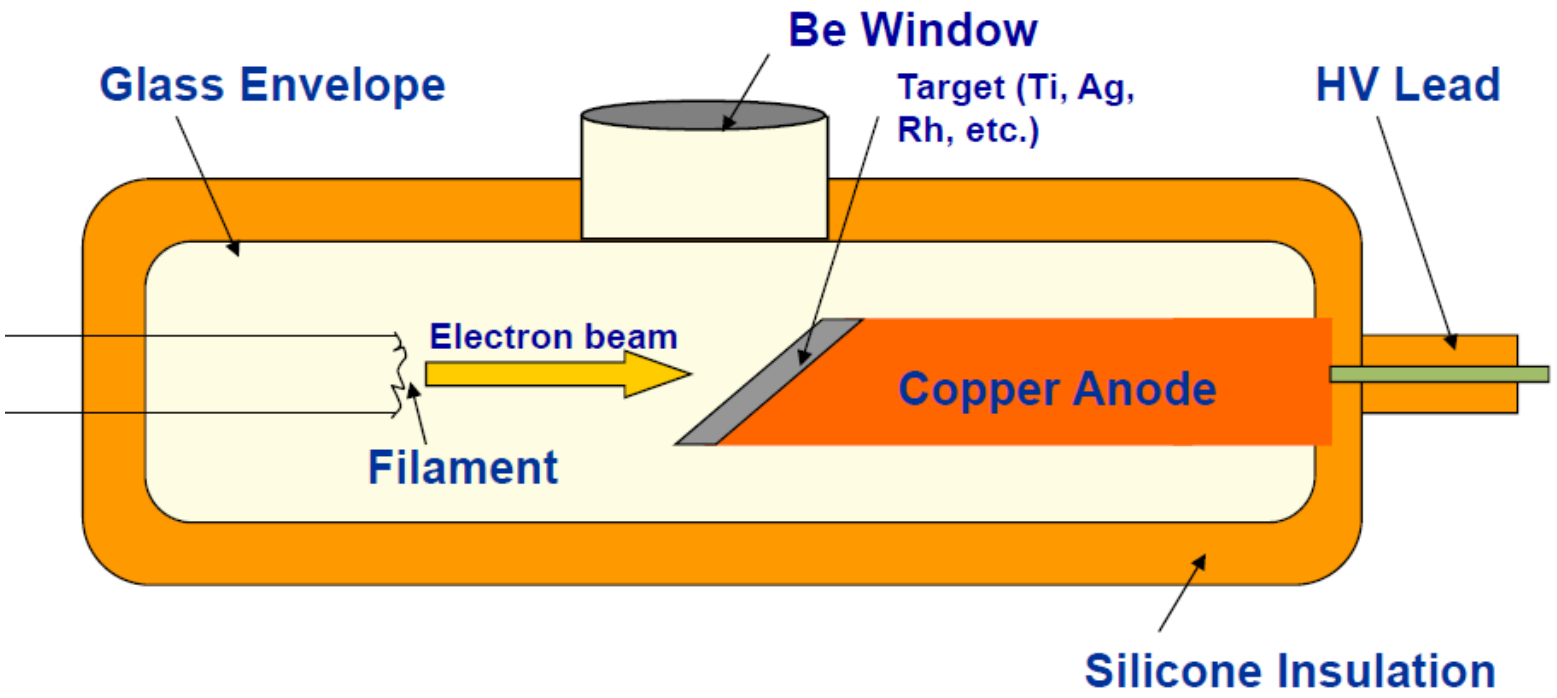
- **End Window X-Ray Tubes**
- **Side Window X-Ray Tubes**
- Radioisotopes
- Other Sources
  1) Scanning Electron Microscopes
  2) Synchrotrons
  3) Positron and other particle beams

End Window X-Ray Tube



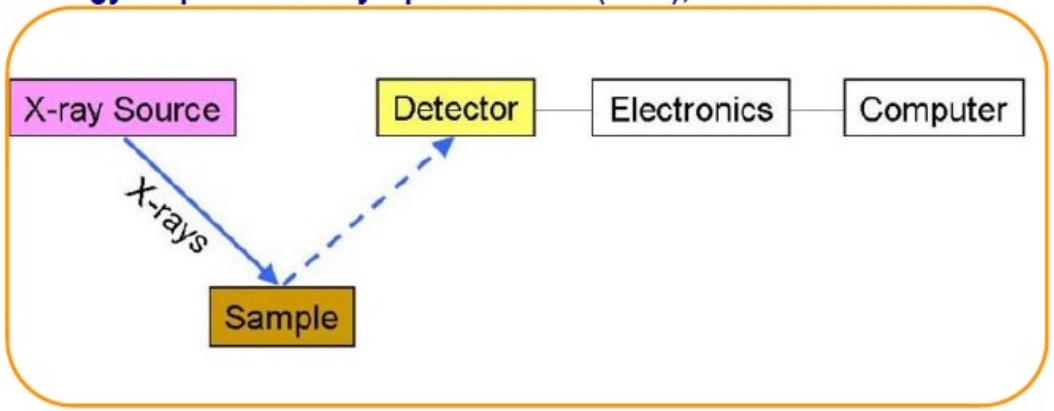
- X-ray Tubes
  1) Voltage determines which elements can be excited.
  2) More power = lower detection limits
  3) Anode selection determines optimal source excitation (application specific).

Side Window X-Ray Tube



Analysis of XRF Spectra

Energy dispersive x-ray Spectrometer (EDS), EDXRF



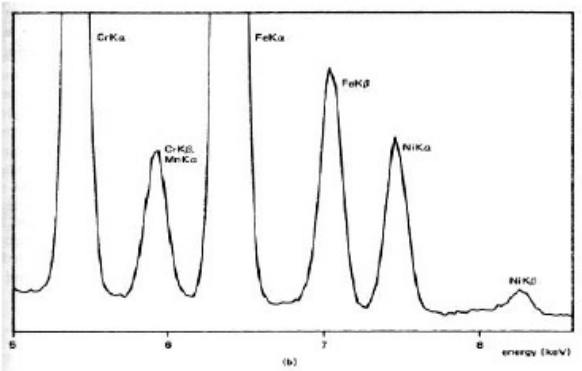
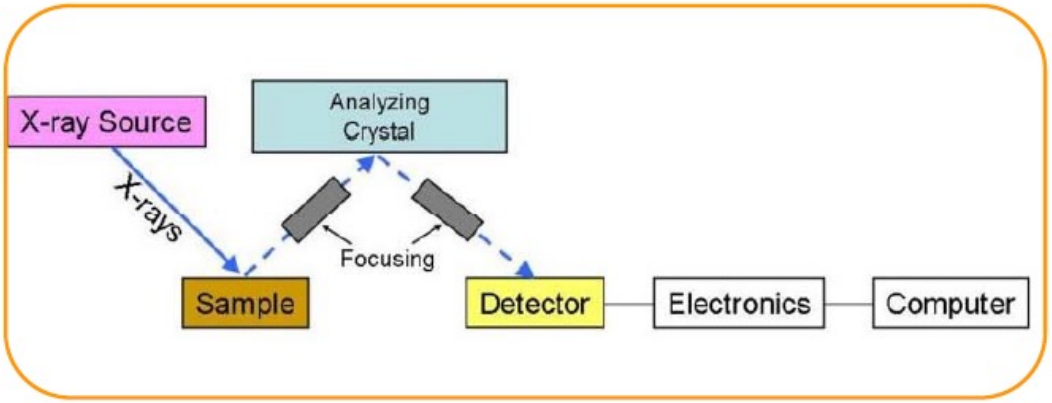
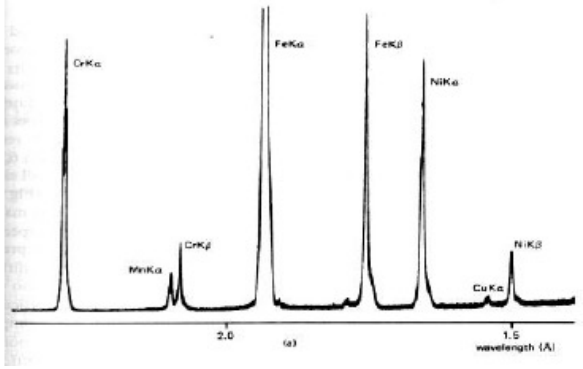


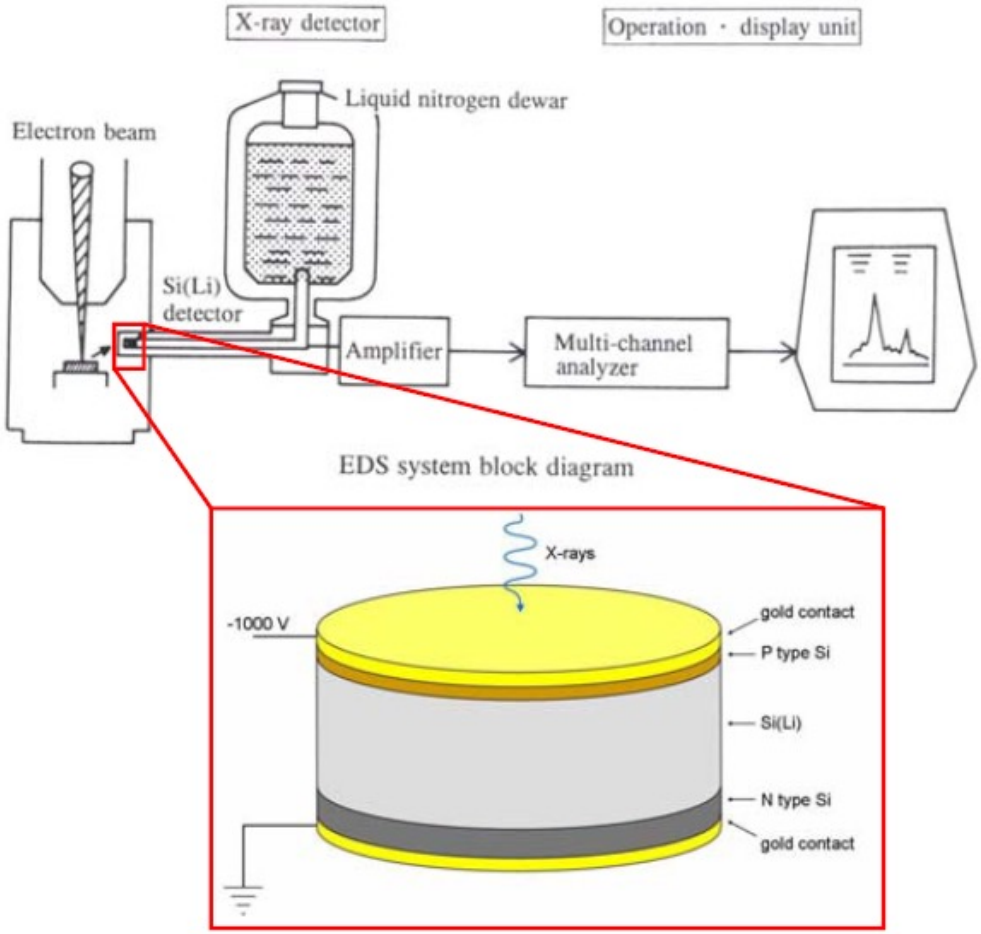
Fig. 6.7 – Comparison of spectra from a steel (1.7 wt % manganese) at 20 kV taken using (a) WDS and (b) EDS; note the manganese Kα peak is not resolved

Wavelength dispersive x-ray Spectrometer (WDS), WDXRF





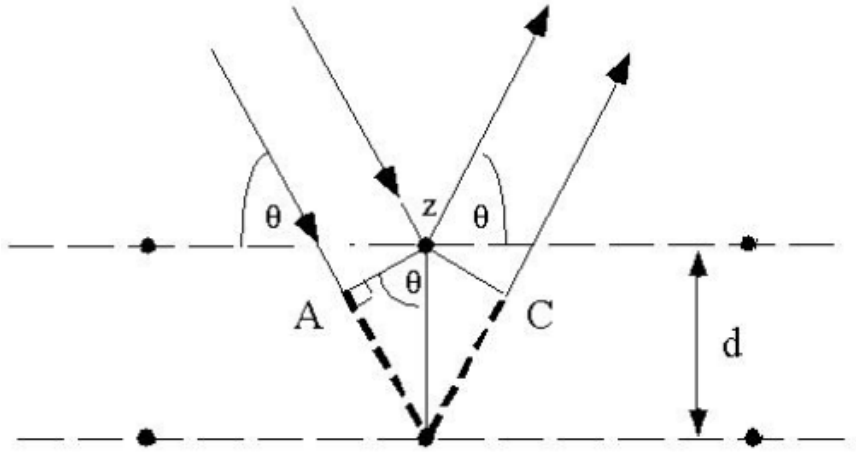
EDS : Energy Dispersive X-Ray Spectroscopy



- Cooled in LN_2 temps, Si crystal converts X-ray photon into charge by ionization.
- Charge is integrated through the FET and is proportional to X-ray energy.

WDXRF: Crystals

The two most common diffraction devices used in WDX instruments are the crystal and multilayer. Both works according to the following formula.

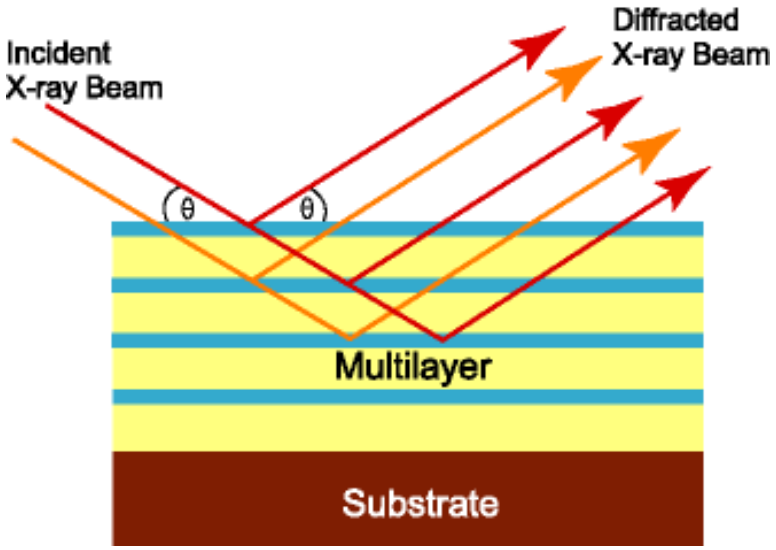


$$n\lambda = 2d \cdot \sin\theta$$

n = integer
d = crystal lattice or multilayer spacing
θ = The incident angle
λ = wavelength

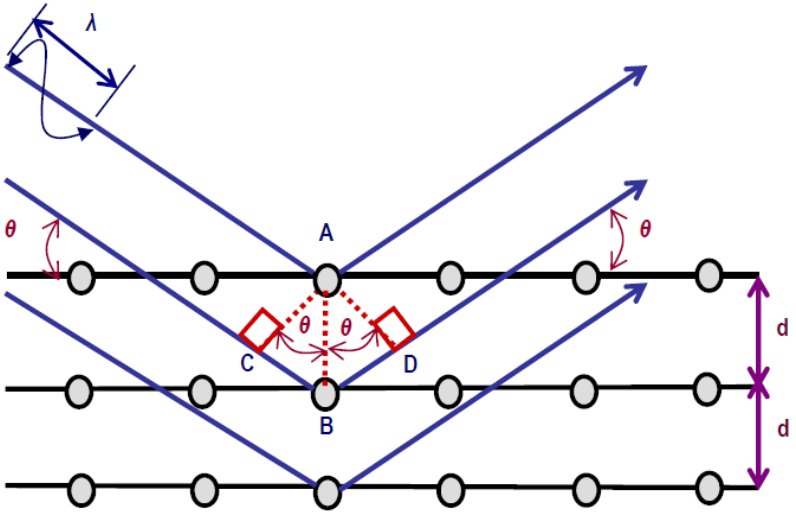
WDXRF: Multilayers

While the crystal spacing is based on the natural atomic spacing at a given orientation the multilayer uses a series of thin film layers of dissimilar elements to do the same thing.



- Modern multilayers are more efficient than crystals and can be optimized for specific elements.
- Often used for low Z elements.

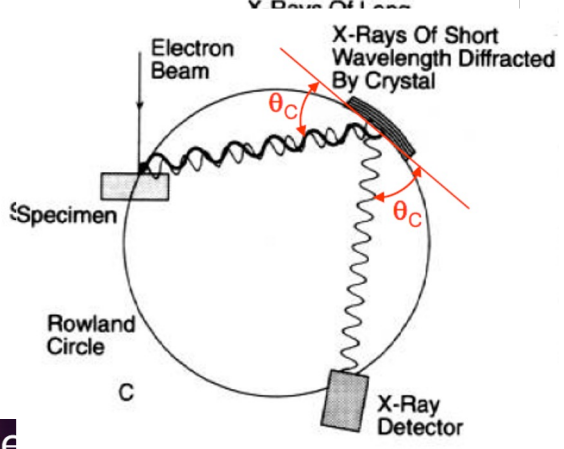
Operation Principle of WDX

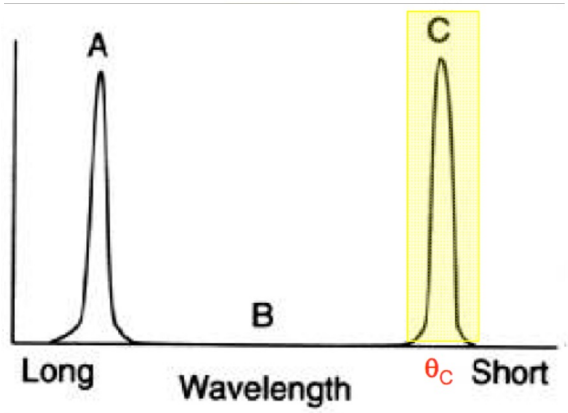


Bragg's Diffraction Law

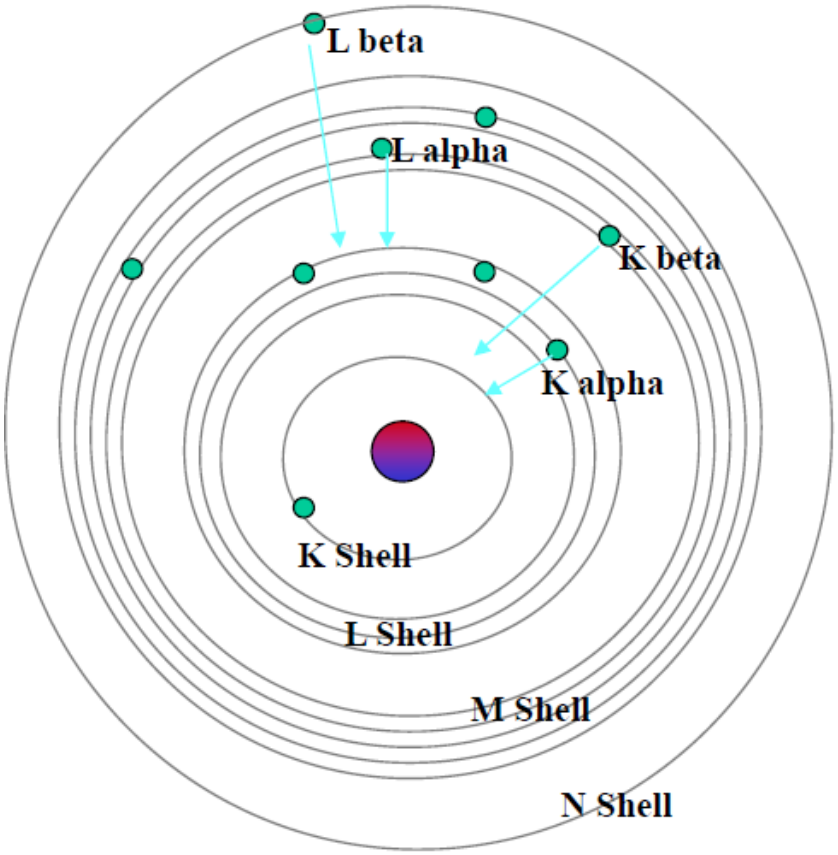
$$n\lambda = 2d\sin\theta$$

n : Diffraction index
Θ: Incident angle
λ: Wavelength:
d : Interspacing distance



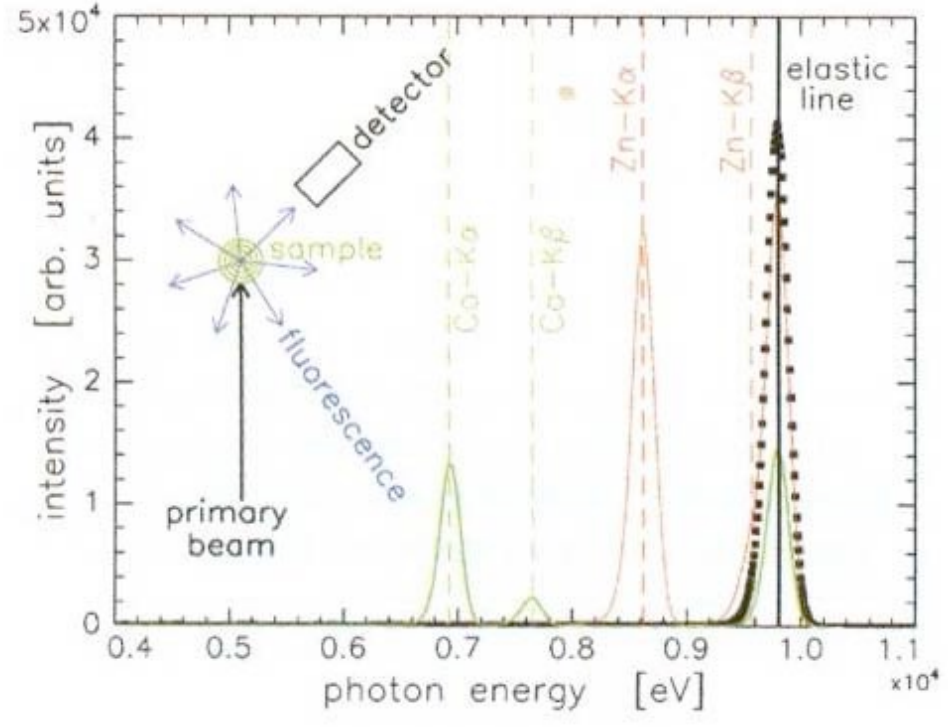


K & L Spectral Peaks



- **K - alpha lines:** L shell e-transition to fill vacancy in K shell. Most frequent transition, hence most intense peak.
- **K - beta lines:** M shell e-transitions to fill vacancy in K shell.
- **L - alpha lines:** M shell e-transition to fill vacancy in L shell.
- **L - beta lines:** N shell e-transition to fill vacancy in L shell.

Recording of Fluorescent Spectrum



Atomic Structure and Characteristic X-Rays

	Name	Values	Defines	Notes
n	*principle*	*positive integers (1, 2, 3…)*	*electron shell (1=K, 2=L, 3=M…)*	*Principle binding energy*
l	*azimuthal*	*integers from 0 to (n-1)*	*electron cloud shape (0=sphere, 1=dumbbell…)*	*Orbital angular momentum. Chemists follow optical spectroscopy conventions using letters rather than numbers: sharp (l = 0),principal, (l = 1), diffuse (l = 2), and fundamental (l = 3)*
m	*magnetic*	*-l to +l (including 0)*	*electron orientation in magnetic field*	*Not significant in absence of an external magnetic field*
s	*spin*	*± ½*	*electron spin direction*	*Clockwise or counterclockwise (up or down)*
j	*inner precession*	*l ± s (s=½, j ≠ 0 - ½)*	*total angular momentum vector*	*Determines which transitions are permitted between electron shells. For s orbitals (l = 0), j can only be +½ (vector sum always positive)*

	K	L_I	L_{II}	L_{III}	M_I	M_{II}	M_{III}	M_{IV}	M_V	N_I	N_{II}	N_{III}	N_{IV}	N_V	N_{VI}	N_{VII}
n	1	2	2	2	3	3	3	3	3	4	4	4	4	4	4	4
l	0	0	1	1	0	1	1	2	2	0	1	1	2	2	3	3
s	+½	+½	-½	+½	+½	-½	+½	-½	+½	+½	-½	+½	-½	+½	-½	+½
j	½	½	½	1½	½	½	1½	1½	2½	½	½	1½	1½	2½	2½	3½

Selection Rule

- The change in *n* must be ≥ 1 ($\Delta n \neq 0$)
- The change in *l* can only be ± 1
- The change in j can only be ± 1 or 0

Sc: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$

	l=0	*l*=1	*l*=2
n=1	1s		
n=2	2s	2p	
n=3	3s	3p	3d
n=4	4s		

	l=0	*l*=1	*l*=2
n=1	1s	NO	
n=2	2s	2p	NO
n=3	3s	3p	3d
n=4	4s	NO	

	l=0	*l*=1	*l*=2
n=1	1s		
n=2	2s	2p	
n=3	3s	3p	3d
n=4	4s		

3d				2p			
l	s	j		*l*	s	j	Δj
2	+½	2½	→	1	+½	1½	1
2	+½	2½	→	1	-½	½	2
2	-½	1½	→	1	+½	1½	0
2	-½	1½	→	1	-½	½	1

2p				1s			
l	s	j		*l*	s	j	Δj
1	+½	1½	→	0	+½	+½	1
1	-½	½	→	0	+½	+½	0

Naming Characteristic X-Rays (Siegbahn Notation)

Karl Manne Georg Siegbahn

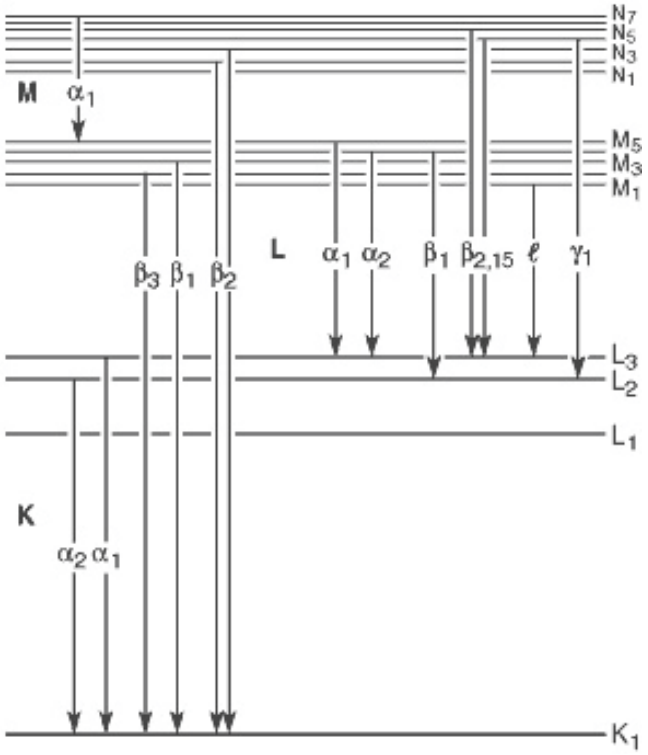


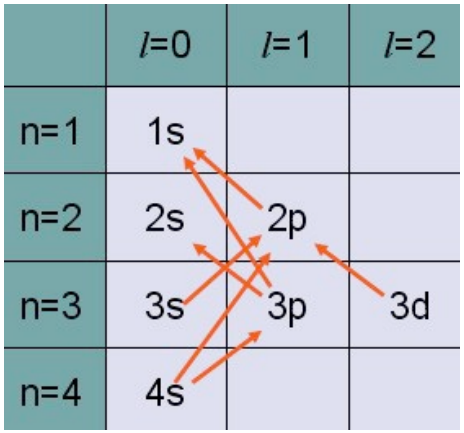
Table 1-1. *Electron binding energies, in electron volts, for the elements in their natural forms.*

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/2}$	N_1 4s	N_2 $4p_{1/2}$	N_3 $4p_{3/2}$
1 H	13.6											
2 He	24.6*											
3 Li	54.7*											
4 Be	111.5*											
5 B	188*											
6 C	284.2*											
7 N	409.9*	37.3*										
8 O	543.1*	41.6*										
9 F	696.7*											
10 Ne	870.2*	48.5*	21.7*	21.6*								
11 Na	1070.8†	63.5†	30.65	30.81								
12 Mg	1303.0†	88.7	49.78	49.50								
13 Al	1559.6	117.8	72.95	72.55								
14 Si	1839	149.7*b	99.82	99.42								
15 P	2145.5	189*	136*	135*								
16 S	2472	230.9	163.6*	162.5*								
17 Cl	2822.4	270*	202*	200*								
18 Ar	3205.9*	326.3*	250.6†	248.4*	29.3*	15.9*	15.7*					
19 K	3608.4*	378.6*	297.3*	294.6*	34.8*	18.3*	18.3*					
20 Ca	4038.5*	438.4†	349.7†	346.2†	44.3 †	25.4†	25.4†					
21 Sc	4492	498.0*	403.6*	398.7*	51.1*	28.3*	28.3*					
22 Ti	4966	560.9†	460.2†	453.8†	58.7†	32.6†	32.6†					
23 V	5465	626.7†	519.8†	512.1†	66.3†	37.2†	37.2†					
24 Cr	5989	696.0†	583.8†	574.1†	74.1†	42.2†	42.2†					
25 Mn	6539	769.1†	649.9†	638.7†	82.3†	47.2†	47.2†					
26 Fe	7112	844.6†	719.9†	706.8†	91.3†	52.7†	52.7†					
27 Co	7709	925.1†	793.2†	778.1†	101.0†	58.9†	59.9†					
28 Ni	8333	1008.6†	870.0†	852.7†	110.8†	68.0†	66.2†					
29 Cu	8979	1096.7†	952.3†	932.7	122.5†	77.3†	75.1†					
30 Zn	9659	1196.2*	1044.9*	1021.8*	139.8*	91.4*	88.6*	10.2*	10.1*			
31 Ga	10367	1299.0*b	1143.2†	1116.4†	159.5†	103.5†	100.0†	18.7†	18.7†			
32 Ge	11103	1414.6*b	1248.1*b	1217.0*b	180.1*	124.9*	120.8*	29.8	29.2			
33 As	11867	1527.0*b	1359.1*b	1323.6*b	204.7*	146.2*	141.2*	41.7*	41.7*			
34 Se	12658	1652.0*b	1474.3*b	1433.9*b	229.6*	166.5*	160.7*	55.5*	54.6*			
35 Br	13474	1782*	1596*	1550*	257*	189*	182*	70*	69*			
36 Kr	14326	1921	1730.9*	1678.4*	292.8*	222.2*	214.4	95.0*	93.8*	27.5*	14.1*	14.1*
37 Rb	15200	2065	1864	1804	326.7*	248.7*	239.1*	113.0*	112*	30.5*	16.3*	15.3 *
38 Sr	16105	2216	2007	1940	358.7†	280.3†	270.0†	136.0†	134.2†	38.9†	21.3	20.1†
39 Y	17038	2373	2156	2080	392.0*b	310.6*	298.8*	157.7†	155.8†	43.8*	24.4*	23.1*
40 Zr	17998	2532	2307	2223	430.3†	343.5†	329.8†	181.1†	178.8†	50.6†	28.5†	27.1†
41 Nb	18986	2698	2465	2371	466.6†	376.1†	360.6†	205.0†	202.3†	56.4†	32.6†	30.8†
42 Mo	20000	2866	2625	2520	506.3†	411.6†	394.0†	231.1†	227.9†	63.2†	37.6†	35.5†
43 Tc	21044	3043	2793	2677	544*	447.6	417.7	257.6	253.9*	69.5*	42.3*	39.9*
44 Ru	22117	3224	2967	2838	586.1*	483.5†	461.4†	284.2†	280.0†	75.0†	46.3†	43.2†
45 Rh	23220	3412	3146	3004	628.1†	521.3†	496.5†	311.9†	307.2†	81.4*b	50.5†	47.3†
46 Pd	24350	3604	3330	3173	671.6†	559.9†	532.3†	340.5†	335.2†	87.1*b	55.7†a	50.9†
47 Ag	25514	3806	3524	3351	719.0†	603.8†	573.0†	374.0†	368.3	97.0†	63.7†	58.3†

j: inner precession (spin-orbit splitting)
j= $l \pm s½$, ($j \neq 0 - ½$)

Selection rule

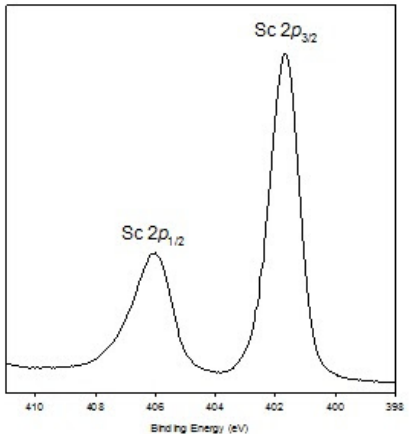
- The change in n must be ≥ 1 ($\Delta n \neq 0$)
- The change in l can only be ± 1
- The change in j can only be ± 1 or 0



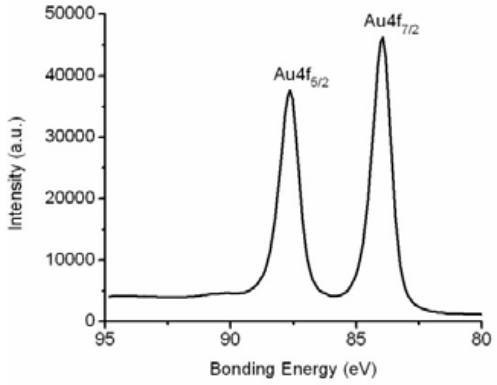
In-Depth Study (Spin Orbit Splitting)

- For p, d and f peaks, two peaks are observed: a doublet with the two possible states having different binding energies.
- The values of spin orbital splitting of a core level of an element in different compounds are nearly the same.
- The peaks will also have specific area ratios based on the degeneracy of each spin state.
- Spin orbital splitting and peak area ratios assist in element identifications.

Spin-orbit splitting in the Sc 2*p* spectrum of Sc_2O_3.



Au 4f spectrum



In-Depth Study (Spin Orbit Splitting)