LECTURE NOTES ON

MM-15-022 : MATERIALS CHARACTERIZATION

6th Semester, MME

MM-15-022

MATERIALS CHARACTERIZATION

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MM-15-022 : MATERIALS CHARACTERIZATION

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MATERIALS CHARACTERIZATION

REFERENCES

❑ Fundamentals of light microscopy and electronic imaging

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❑ Electron Microscopy and Microanalysis

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❑ Elements of X-Ray Diffraction

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❑ Transmission Electron Microscopy
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❑ Introduction to Thermal Analysis Techniques and Applications

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❑ Materials Characterization

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Introduction

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Introduction

❑ Committee on Characterization of Materials, Materials Advisory Board, National Research Council developed the definition of Material Characterization: “ Characterization describes those features of composition and structure (including defects) of a material that are significant for a particular preparation, study of properties, or use, and suffice for reproduction of the material ”.

❑ Materials Characterization has 2 main aspects:

- Accurately measuring the physical and chemical properties of materials
- Accurately measuring (determining) the structure of a material
  - (Atomic level structure & Microscopic level structures)

❑ Mechanical, electrical and magnetic properties of a material are strongly dependent on its structural characteristics. Therefore, material characterization is very important part of any structure-property correlation exercise.

Fundamentals of crystallography

- ❑ Crystallography gives a concise representation of a large assemblage of species by describing and characterizing the structure of crystals.
- ❑ It gives the 'first view' towards understanding of the properties of the crystal.

CRYSTAL

A 3D translationally periodic arrangement of atoms in a space is called a crystal.

LATTICE

A 3D translationally periodic arrangement of points in a space is called a crystal.

MOTIF/BASIS

An atom or a group of atoms associated with each lattice point .

Crystal = lattice + motif

Lattice ➢ the underlying periodicity of the crystal

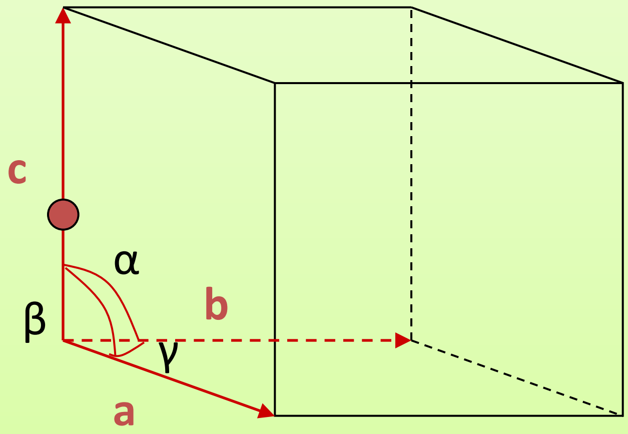
Basis ➢ Entity associated with each lattice points

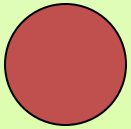
SPACE LATTICE

A 3D network of imaginary lines connecting the atoms.

UNIT CELL

- Smallest unit having the full symmetry of the crystal is called the unit cell.
- The simplest portion of a lattice that can be repeated by translation to cover the entire 1-D, 2-D, or 3-D space.
- The specific unit cell for each metal is defined by its parameters, which are the edges of the unit cell a, b, c and the angles α (between b and c), β (between a and c) and γ (between a and b).
- There are 14 possible types of space lattices (Bravais lattice), and they fall into 7 crystal systems.





Replaces repeating element
(atoms, molecule, base etc.)

14 Bravais Lattices divided into 7 Crystal Systems

A Symmetry based concept

'Translation' based concept

	Crystal System	Lattice Parameters	Bravais Lattices			
			P	I	F	C
1	Cubic	$(a = b = c,\ \alpha = \beta = \gamma = 90°)$	✓	✓	✓	
2	Tetragonal	$(a = b \neq c,\ \alpha = \beta = \gamma = 90°)$	✓	✓		
3	Orthorhombic	$(a \neq b \neq c,\ \alpha = \beta = \gamma = 90°)$	✓	✓	✓	✓
4	Hexagonal	$(a = b \neq c,\ \alpha = \beta = 90°,\ \gamma = 120°)$	✓			
5	Trigonal	$(a = b = c,\ \alpha = \beta = \gamma \neq 90°)$	✓			
6	Monoclinic	$(a \neq b \neq c,\ \alpha = \gamma = 90° \neq \beta)$	✓			✓
7	Triclinic	$(a \neq b \neq c,\ \alpha \neq \beta \neq \gamma)$	✓			

Basis of definition of crystals is 'symmetry' and hence the classification of crystals is also based on symmetry

P	Primitive
I	Body Centred
F	Face Centred
C	A/B/C- Centred

Symmetries of the 7 crystal systems

If an object is brought into self coincidence after some operation it is said to possess symmetry with respect to that operation

Symmetry

Translational symmetry.

Rotational Symmetry

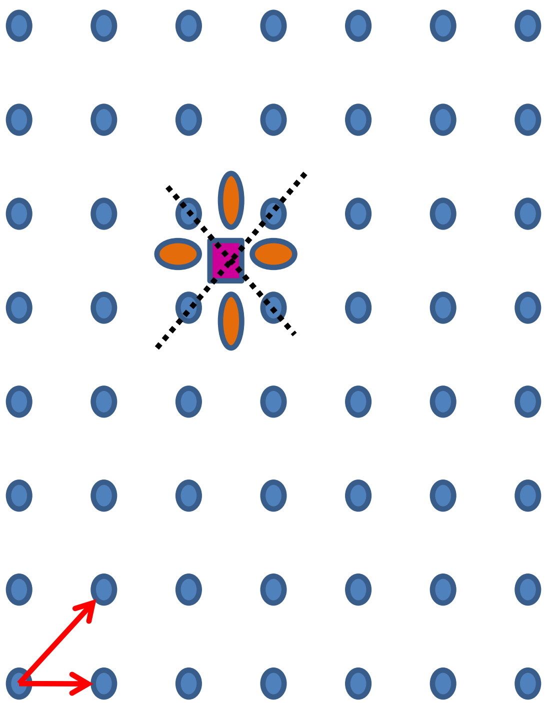
	Characteristic symmetry
Cubic	Four 3-fold rotation axes *(two will generate the other two)*
Hexagonal	One 6-fold rotation axis (or roto-inversion axis)
Tetragonal	(Only) One 4-fold rotation axis (or roto-inversion axis)
Trigonal	(Only) One 3-fold rotation axis (or roto-inversion axis)
Orthorhombic	(Only) Three ⊥ 2-fold rotation axes (or roto-inversion axis)
Monoclinic	(Only) One 2-fold rotation axis (or roto-inversion axis)
Triclinic	None

Lattices have….!

Translational Symmetry

Rotational Symmetry

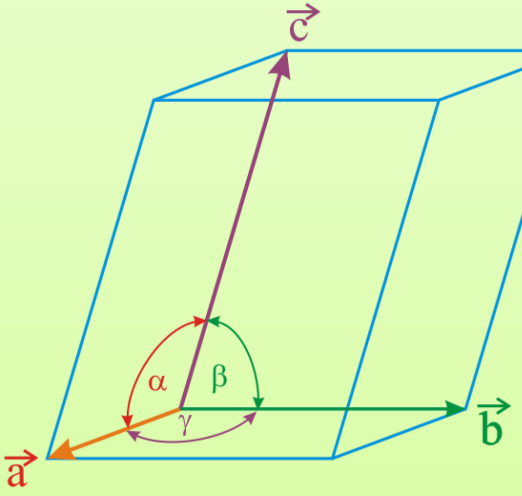
Reflection Symmetry



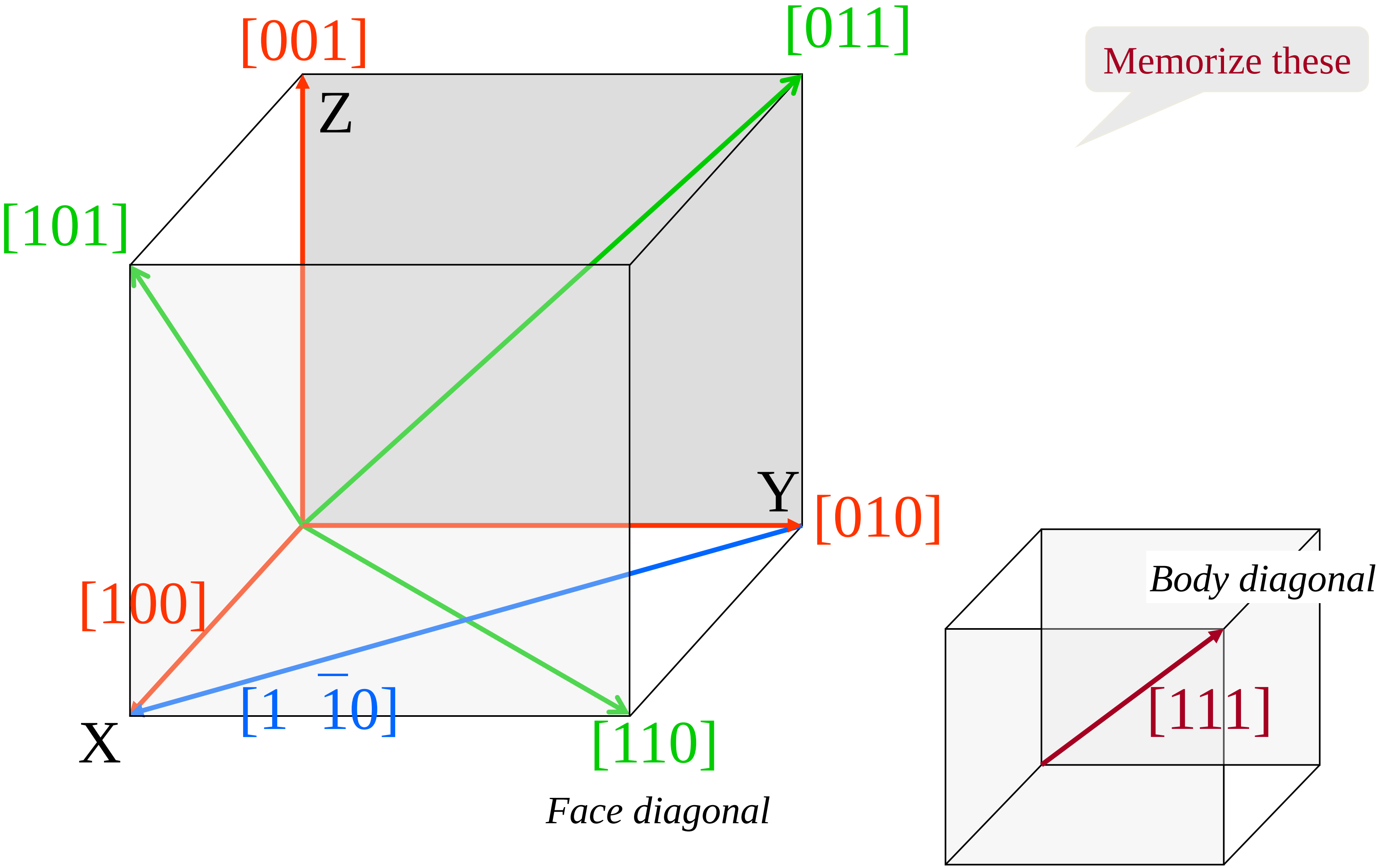
Crystallographic Directions

- A crystallographic direction is defined as a line between 2 points, or a vector.
- The following steps are utilized in the determination of the 3 directional indices:
  - A vector of convenient length is positioned such that it passes through the origin of the coordinate system.
  - Any vector may be translated throughout the crystal lattice without alteration, if parallelism in maintained.
  - The length of the vector projection on each of the 3 axes is determined; these are measured in terms of the unit cell dimensions a, b, and c.
  - These 3 numbers are multiplied or divided by a common factor to reduce them to the smallest integer values.
  - The 3 indices (not separated by commas) are enclosed in square brackets: [uvw] where u, v, and w integers correspond to the reduced projection along the x, y, and z axes, respectively.
- A vector **r** passing from the origin to a lattice point can be written as:

  $\mathbf{r} = r_1\,\mathbf{a} + r_2\,\mathbf{b} + r_3\,\mathbf{c}$ Where, **a**, **b**, **c** → basic vectors
- *Note their length is not 1 unit! (like for the basis vectors of a coordinate axis).*

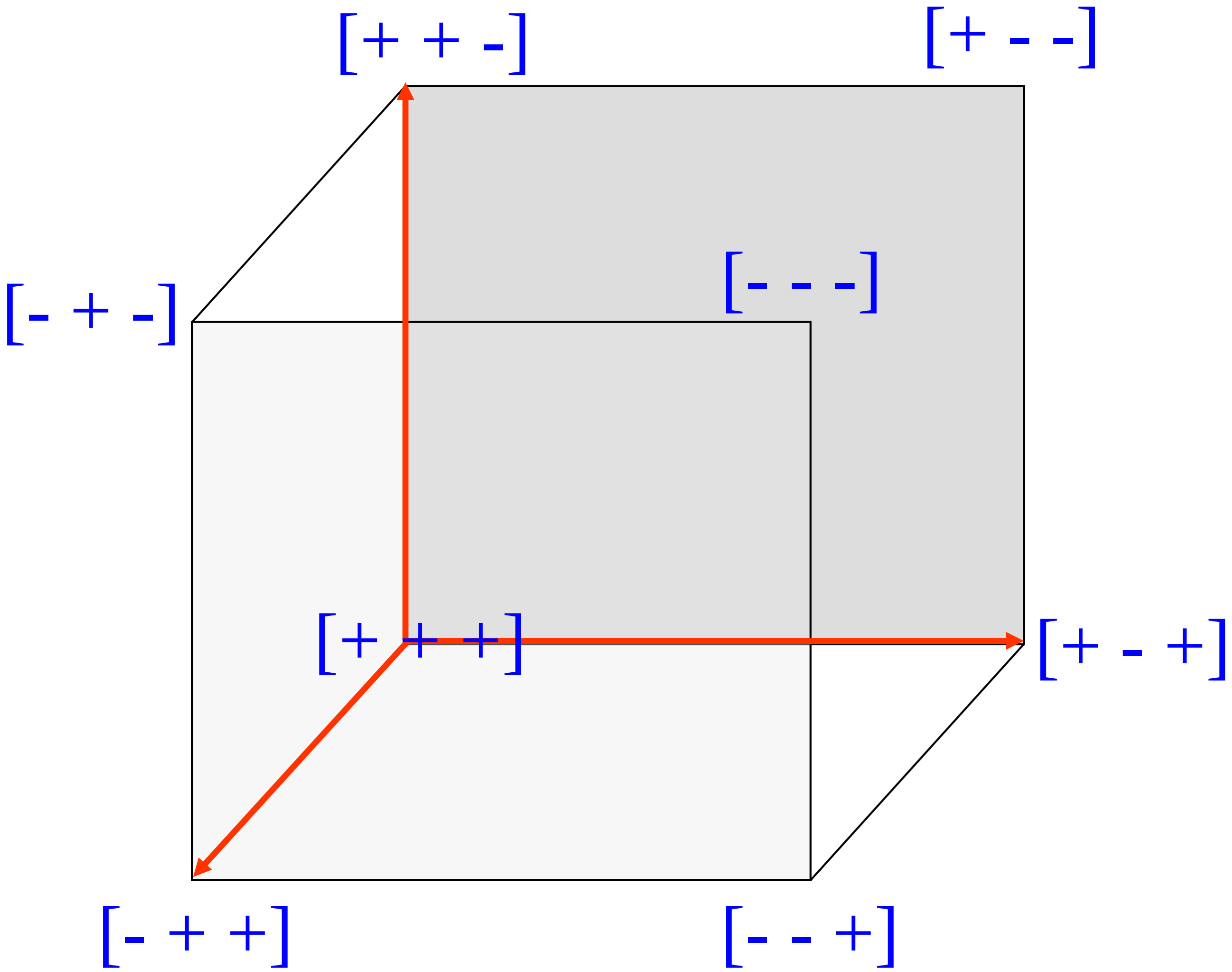


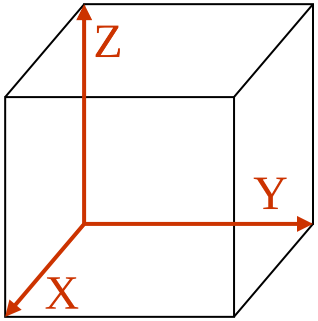
Important directions in 3D represented by Miller Indices (cubic lattice)



Memorize these

Possible coordinates in 3D





If you have confusion while selecting origin in negative indices refer this figure

Family of directions

- ❑ A set of directions related by symmetry operations of the lattice or the crystal is called a family of directions
- ❑ A family of directions is represented (Miller Index notation) as: <u v w>

Index	Members in family for **cubic lattice**	Number
<100>	$[100],[\bar{1}00],[010],[0\bar{1}0],[001],[00\bar{1}]$	3 x 2 = 6
<110>	$[110],[\bar{1}10],[1\bar{1}0],[\bar{1}\bar{1}0],[101],[\bar{1}01],[10\bar{1}],[\bar{1}0\bar{1}],[011],[0\bar{1}1],[01\bar{1}],[0\bar{1}\bar{1}]$	6 x 2 = 12
<111>	$[111],[\bar{1}11],[1\bar{1}1],[11\bar{1}],[\bar{1}\bar{1}1],[\bar{1}1\bar{1}],[1\bar{1}\bar{1}],[\bar{1}\bar{1}\bar{1}]$	4 x 2 = 8

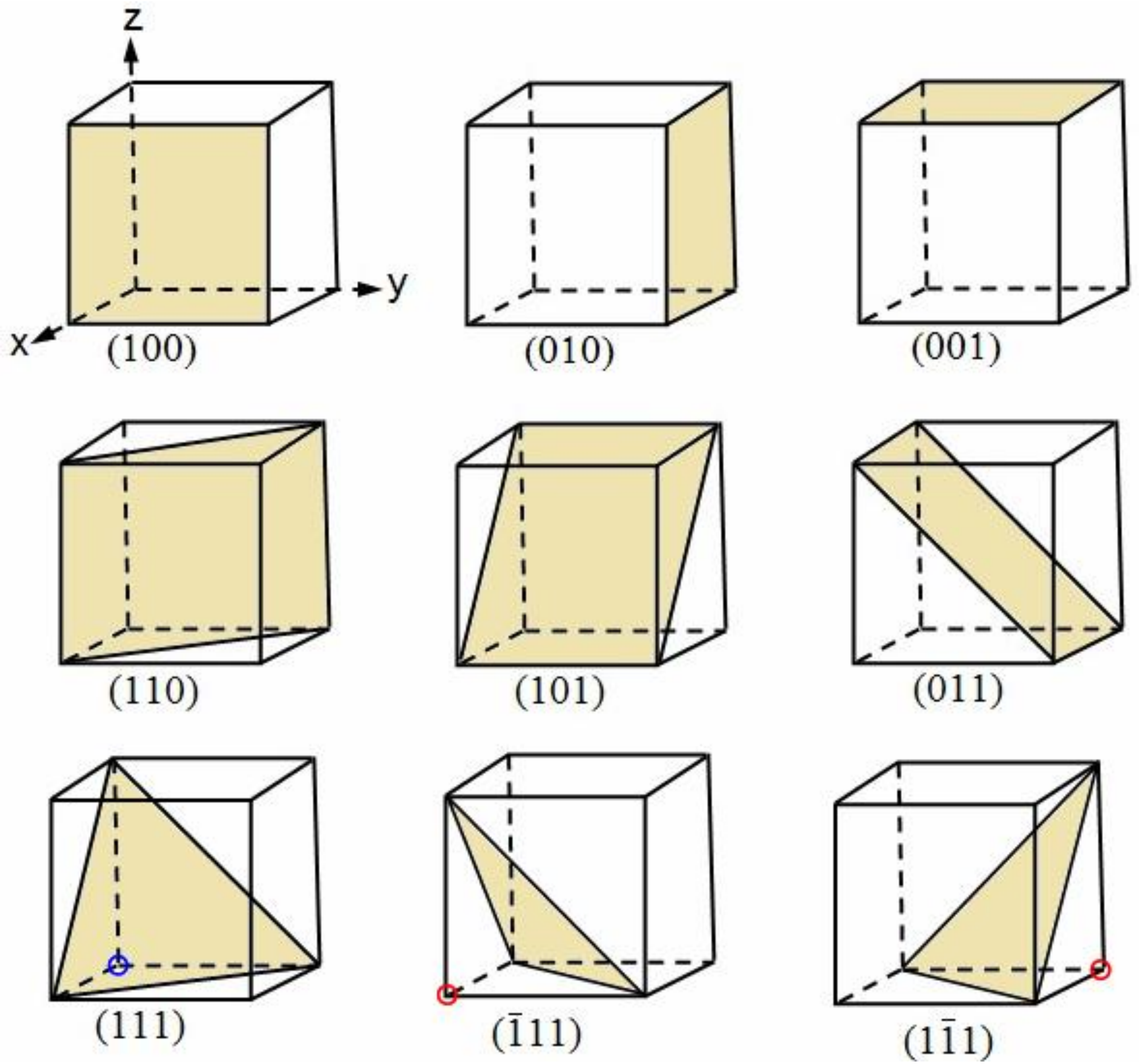
the 'negatives' (opposite direction)

Symbol	Alternate symbol		
[ ]		→	Particular direction
< >	[[ ]]	→	Family of directions

Crystallographic Planes

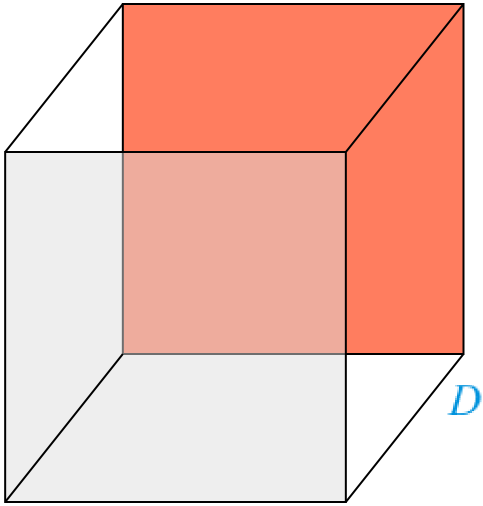
- A crystallographic in all but the hexagonal crystal system are specified by 3 Miller indices: (hkl). Any 2 planes parallel to each other are equivalent & have identical indices.
- The procedure used in determination of the h, k, and l Miller index numbers is as follows:
  - If the plane passes through the selected origin, either another parallel plane must be constructed within the unit cell by an appropriate translation, or a new origin must be established at the corner of another unit cell.
  - At this point, the crystallographic plane either intersects or parallels each of the 3 axes; the length of the planar intercept for each axis is determined in terms of the lattice constants a, b, and c.
  - The reciprocals of these numbers are taken. A plane that parallels an axis may be considered to have an infinite intercept, &, therefore, a zero index.
  - If necessary, these 3 numbers are changed to the set of smallest integers by multiplication or division by a common factor.
  - Finally, the integer indices (not separated by commas) are enclosed in parentheses: (hkl).

Important Planes in 3D represented by Miller Indices (cubic lattice)

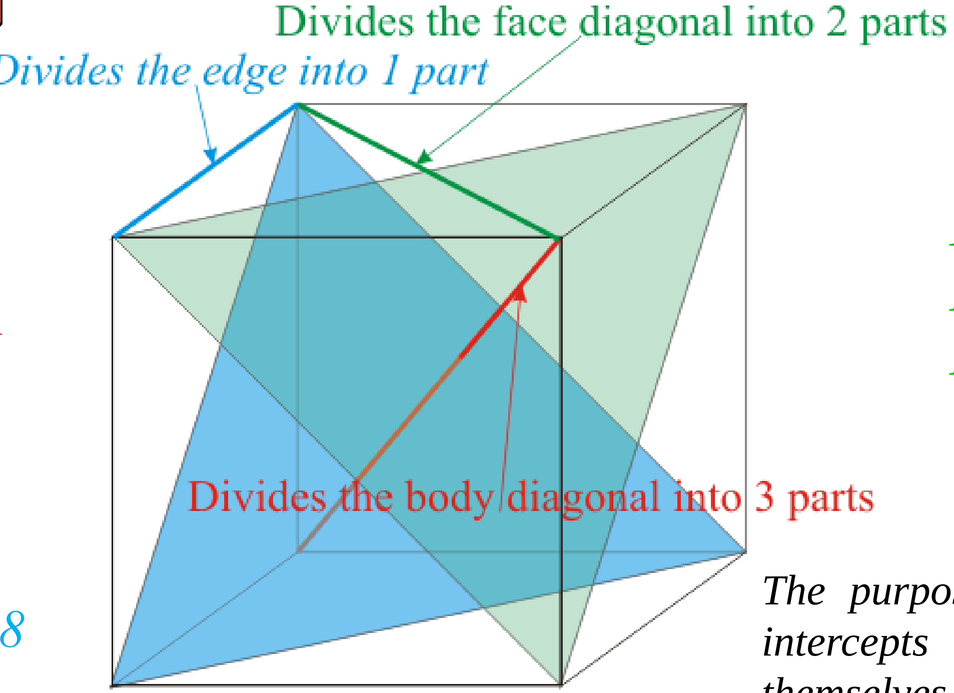


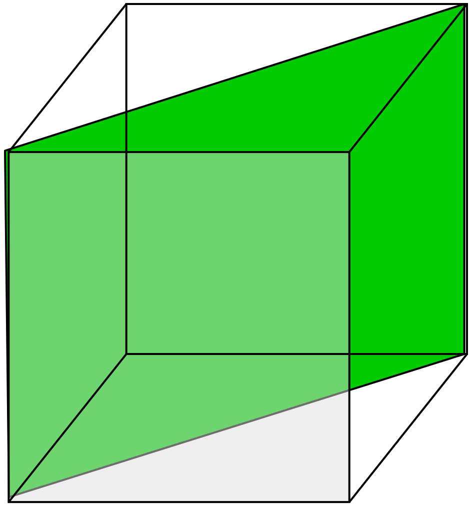
- A set of planes related by symmetry operations of the lattice or the crystal is called a family of planes
- All the points which one should keep in mind while dealing with directions to get the members of a family, should also be kept in mind when dealing with planes

Family of planes



Intercepts → 1 ∞ ∞
Plane → (100)
Family → {100} → 6





Intercepts → 1 1 ∞
Plane → (110)
Family → {110} → 6

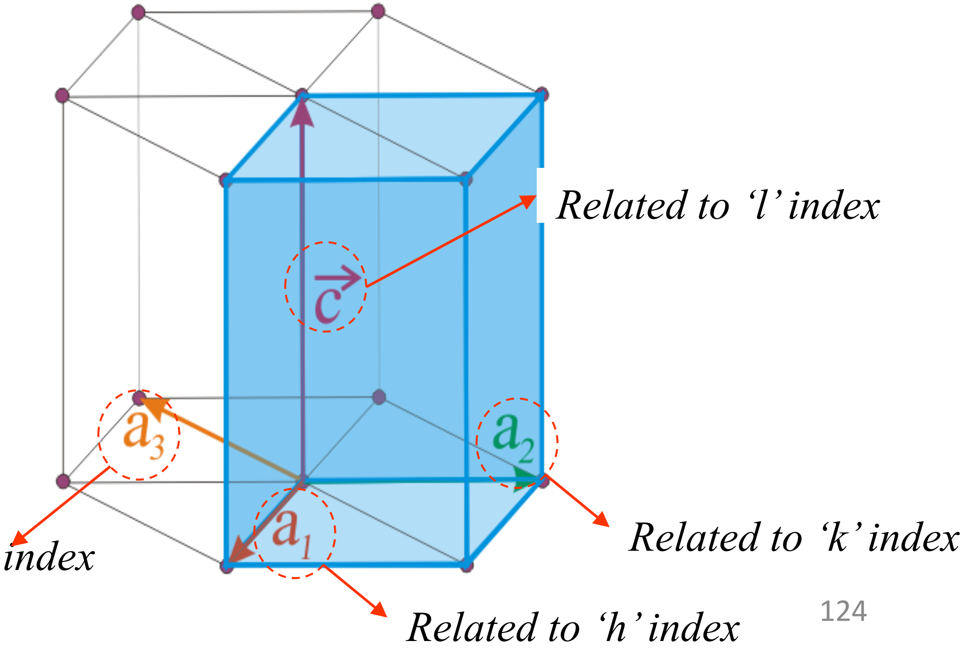
Intercepts → 1 1 1
Plane → (111)
Family → {111} → 8
(Octahedral plane)

The purpose of using reciprocal of intercepts and not intercepts themselves in Miller indices becomes clear → the ∞ are removed

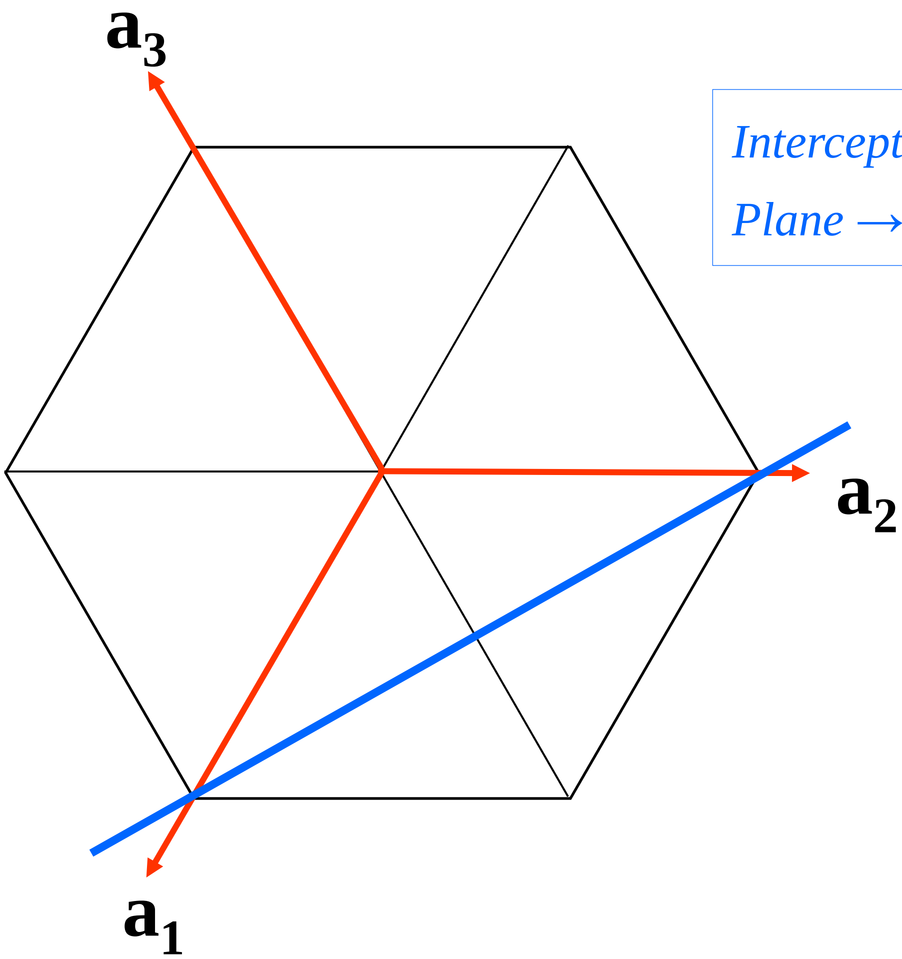
Hexagonal crystals → Miller-Bravais Indices : PLANES

- ❑ Directions and planes in hexagonal lattices and crystals are designated by the 4-index Miller-Bravais notation
- ❑ In the four index notation:
  - ➢ the first three indices are a symmetrically related set on the basal plane
  - ➢ the third index is a redundant one (which can be derived from the first two) and is introduced to make sure that members of a family of directions or planes have a set of numbers which are identical
  - ➢ the fourth index represents the 'c' axis (⊥ to the basal plane)

- ❑ Hence the first three indices in a hexagonal lattice can be permuted to get the different members of a family; while, the fourth index is kept separate.



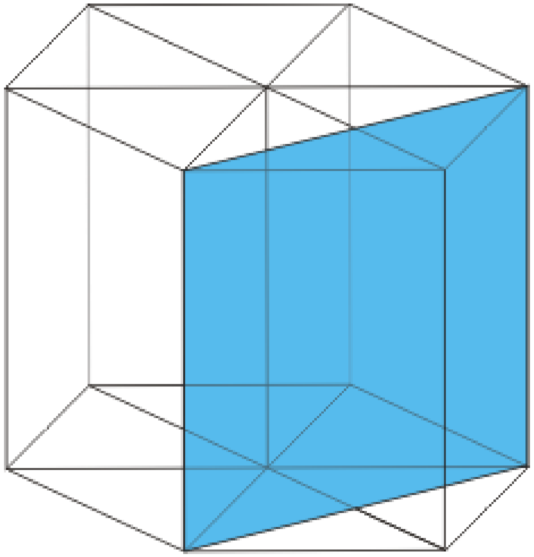
Hexagonal crystals → Miller-Bravais Indices : PLANES



Intercepts → *1 1 - ½ ∞*

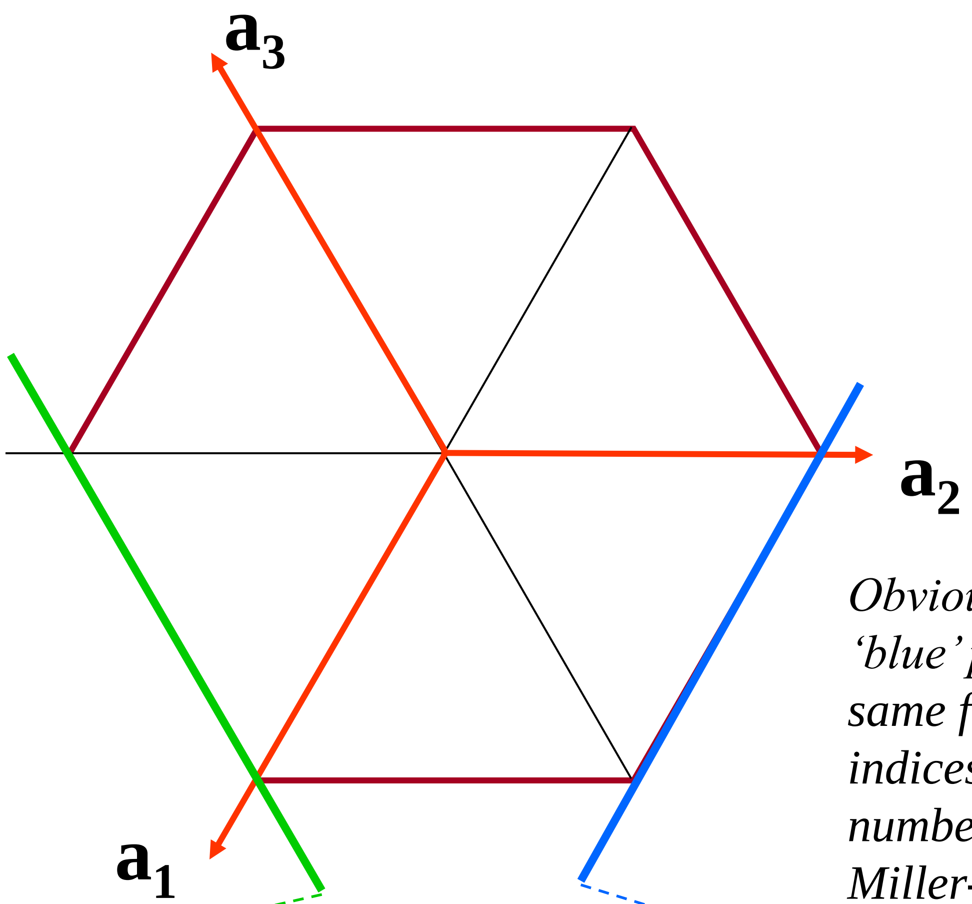
Plane → *$(1\ 1\ \bar{2}\ 0)$*

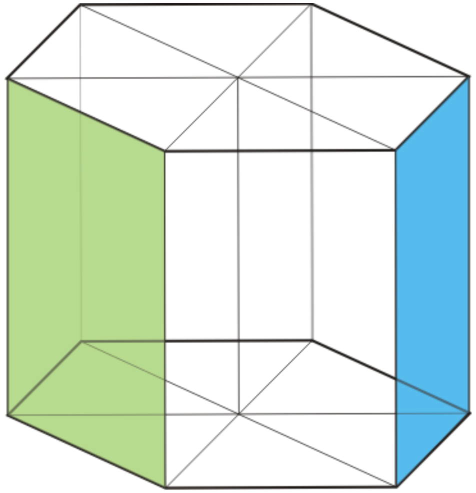
(h k i l)
i = –(h + k)



In general three indices point is denoted as miller indices i.e., (h k l). But hexagonal crystals we are using 4 indices point is denoted by miller-bravais indices i.e., (h k i l)The use of the 4 index notation is to bring out the equivalence between crystallographically equivalent planes and directions.

Hexagonal crystals → Miller-Bravais Indices : PLANES





Obviously the 'green' and 'blue' planes belong to the same family and first three indices have the same set of numbers (as brought out by the Miller-Bravais system)

Intercepts → 1 -1 ∞ ∞

Miller → $(1\ \bar{1}\ 0)$

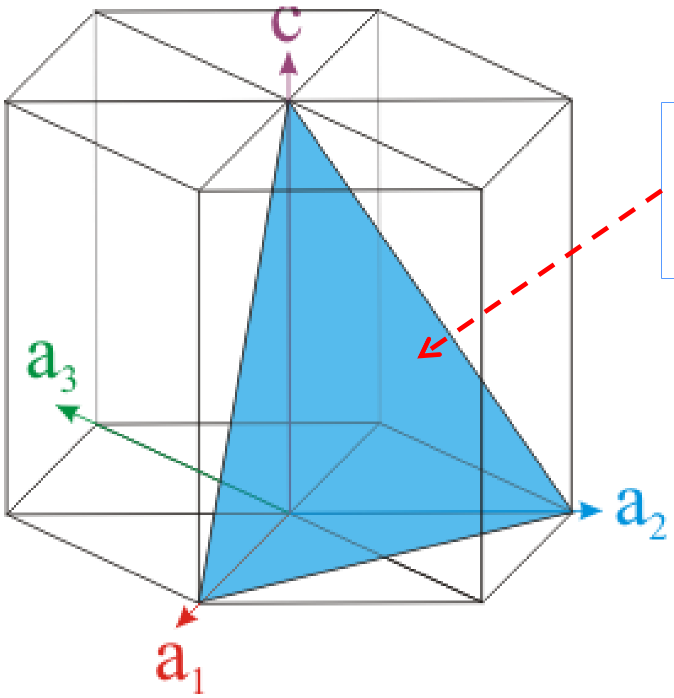
Miller-Bravais → $(1\ \bar{1}\ 0\ 0)$

Intercepts → ∞ 1 -1 ∞

Miller → $(0\ 1\ 0)$

Miller-Bravais → $(0\ 1\ \bar{1}\ 0)$

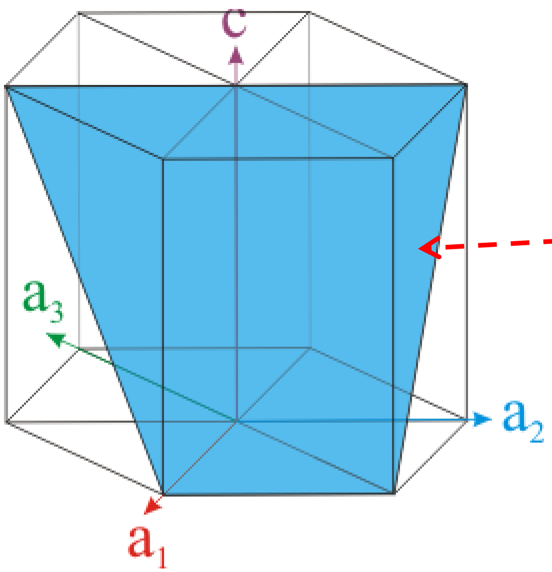
Hexagonal crystals → Miller-Bravais Indices : PLANES



Intercepts → 1 1 - ½ 1

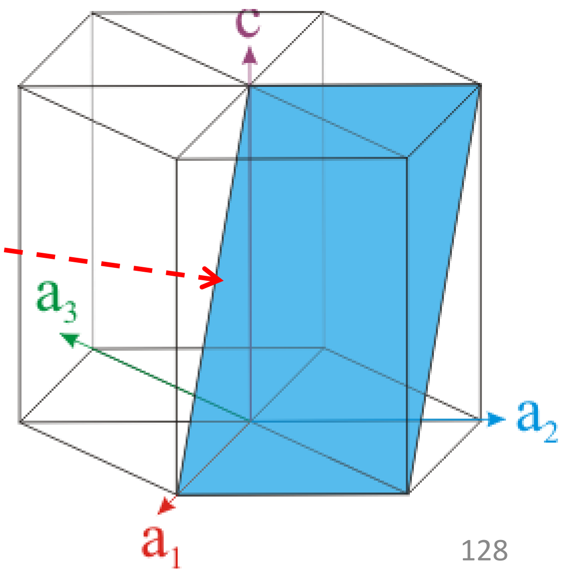
Plane → $(1\ 1\ \bar{2}\ 1)$

Both planes contain same intercepts. The common thing in these planes is **a_2** axis is infinite



Intercepts → $1\ \infty\ -1\ 1$

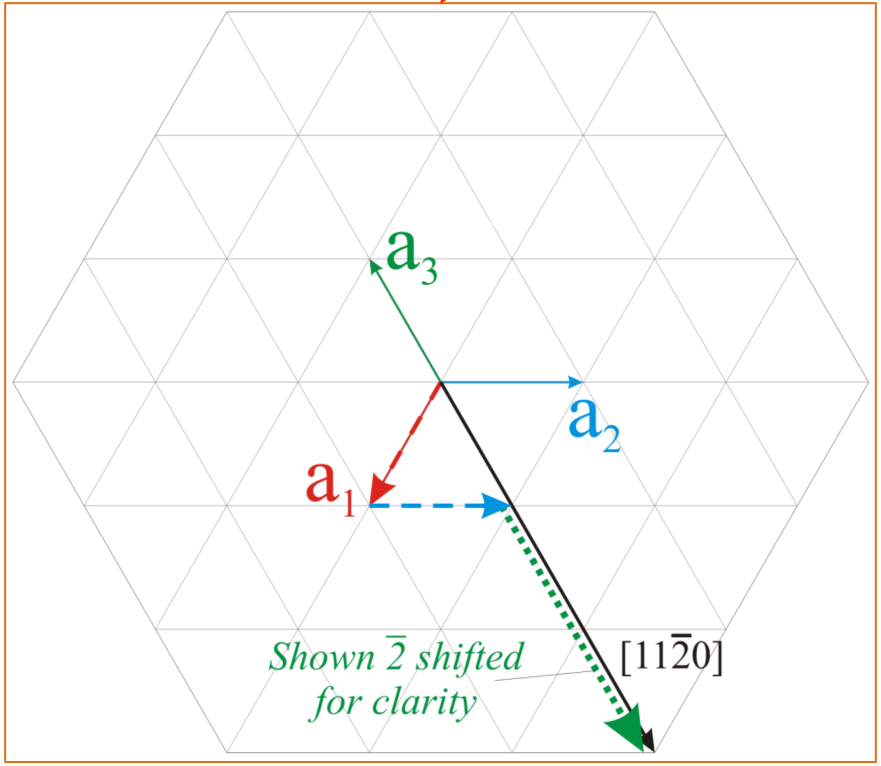
Plane → $(1\ 0\ \bar{1}\ 1)$



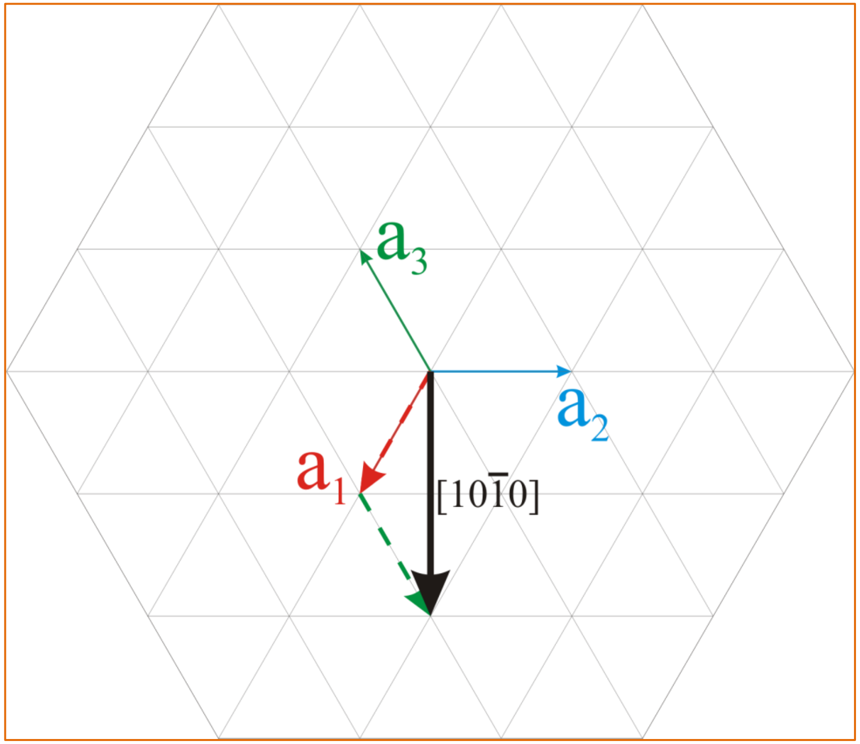
Hexagonal crystals → Miller-Bravais Indices : DIRECTIONS

Drawing the $[11\bar{2}0]$ *direction*

- Trace a path along the basis vectors as required by the direction. In the current example move 1unit along a_1, 1unit along a_2 and –2 units along a_3.
- Directions are projected onto the basis vectors to determine the components and hence the Miller-Bravais indices can be determined as in the table.



Drawing the $[10\bar{1}0]$ direction



Points about planes and directions

- Unknown direction → [uvw]
- Unknown plane → (hkl)
- Double digit indices should be separated by commas → (12,22,3)
- In cubic lattices/crystals [hkl] ⊥ (hkl)

Interplanar spacing (d_{hkl}) in cubic lattice (& crystals)

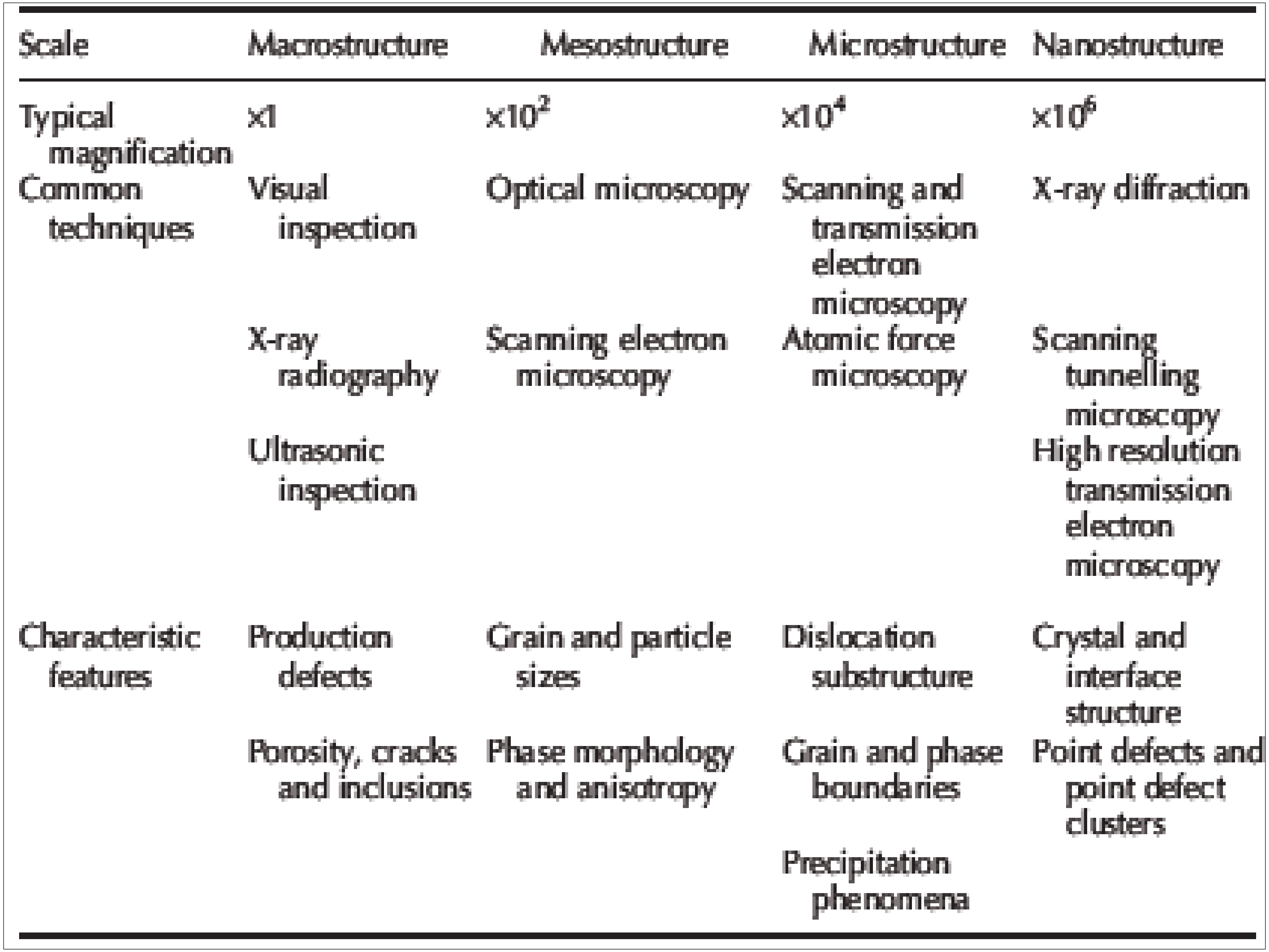
$$d_{hkl}^{\text{cubic lattice}} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

	Symbol		Alternate symbols		
Direction	[ ]	[uvw]		→	Particular direction
	< >	<uvw>	[[ ]]	→	Family of directions
Plane	( )	(hkl)		→	Particular plane
	{ }	{hkl}	(( ))	→	Family of planes

Crystalline and Noncrystalline Materials

- **Isotropic Materials:** If the properties of the material are independent of the direction in which they are measured, the material is categorized as isotropic.
- **Anisotropy Materials:** If the properties of the material are dependent of the direction in which they are measured, the material is categorized as anisotropic. Examples of these properties include: Periodicity of atoms in a crystal structure, Density of a material of crystalline solids, Carrier velocity, Phonon velocity etc.
- **Allotropy:** Elements that can exhibit more than one crystal structure are allotropic.
- **Polymorphism:** Compounds that behave in the same manner as allotropic materials are referred to as polymorphism.
- **Single Crystal:** A continuous periodic crystal structure only interrupted by the boundaries of the solid
- **Amorphous:** Although short range periodicity may be present, long range periodicity is absent. Hence, amorphous material is not crystalline.
- **Polycrystalline:** A material composed of from two to many single crystal grains.

Levels of characterization



Scale	Macrostructure	Mesostructure	Microstructure	Nanostructure
Typical magnification	×1	$\times 10^2$	$\times 10^4$	$\times 10^6$
Common techniques	Visual inspection	Optical microscopy	Scanning and transmission electron microscopy	X-ray diffraction
	X-ray radiography	Scanning electron microscopy	Atomic force microscopy	Scanning tunnelling microscopy
	Ultrasonic inspection			High resolution transmission electron microscopy
Characteristic features	Production defects	Grain and particle sizes	Dislocation substructure	Crystal and interface structure
	Porosity, cracks and inclusions	Phase morphology and anisotropy	Grain and phase boundaries	Point defects and point defect clusters
			Precipitation phenomena	

Optical Microscopy

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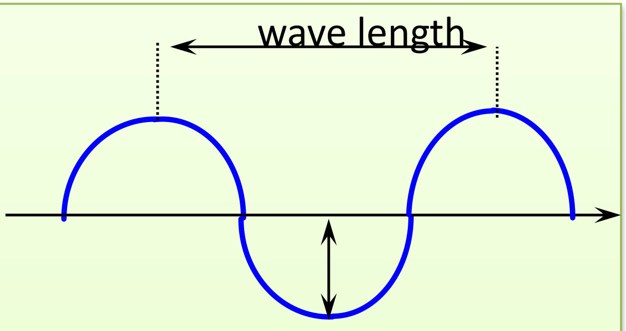
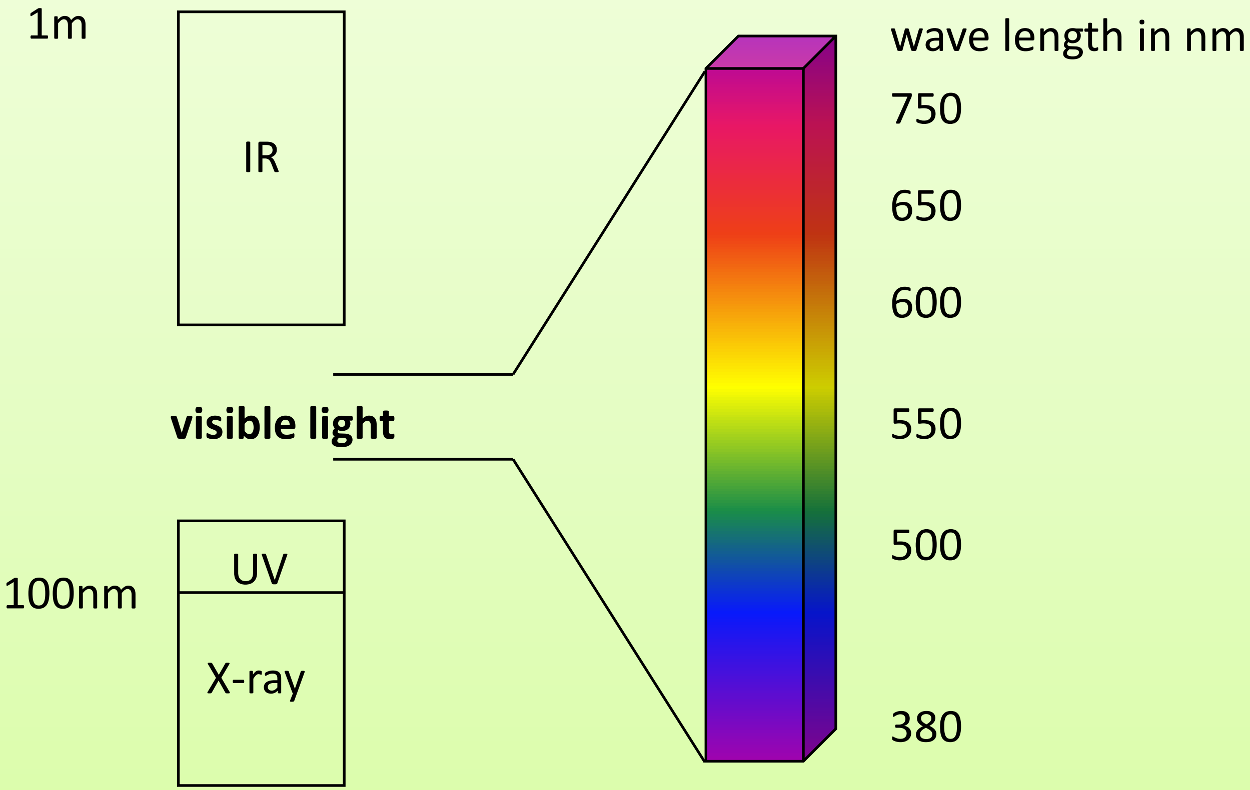
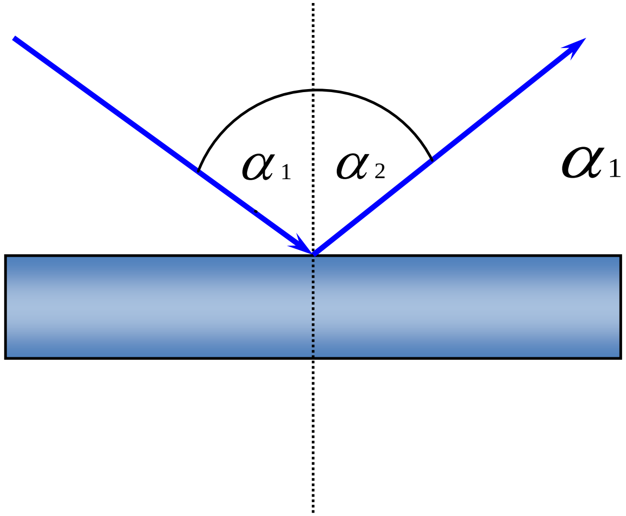
Theories of Light

- light is a stream of invisible particles or corpuscles
- light is an electromagnetic wave



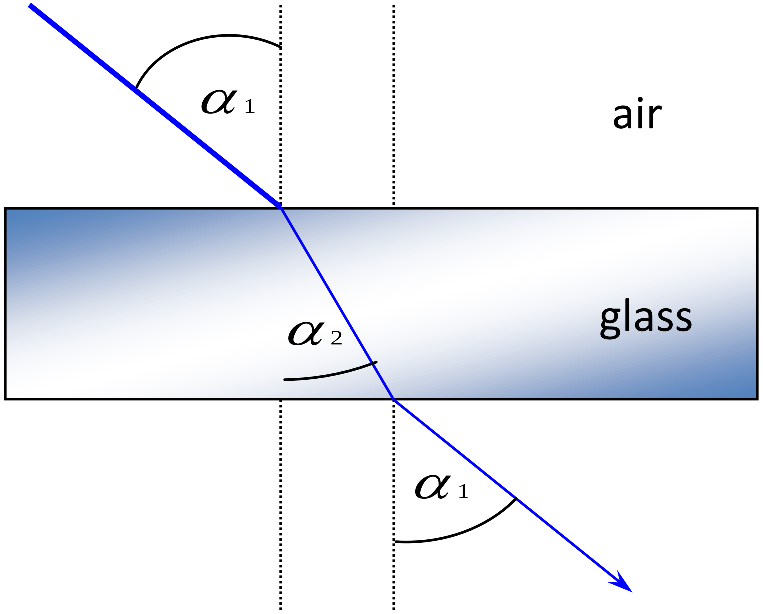


Reflection of light



$$\alpha_1 = \alpha_2$$

Refraction of light



$$\text{Index of refraction of the substance} = \frac{\text{speed of light in air}}{\text{speed of light in the substance}}$$

$$C_0 = f \times \lambda$$

speed of light in vacuum
3 x 10^10 cm/sec.

Frequency

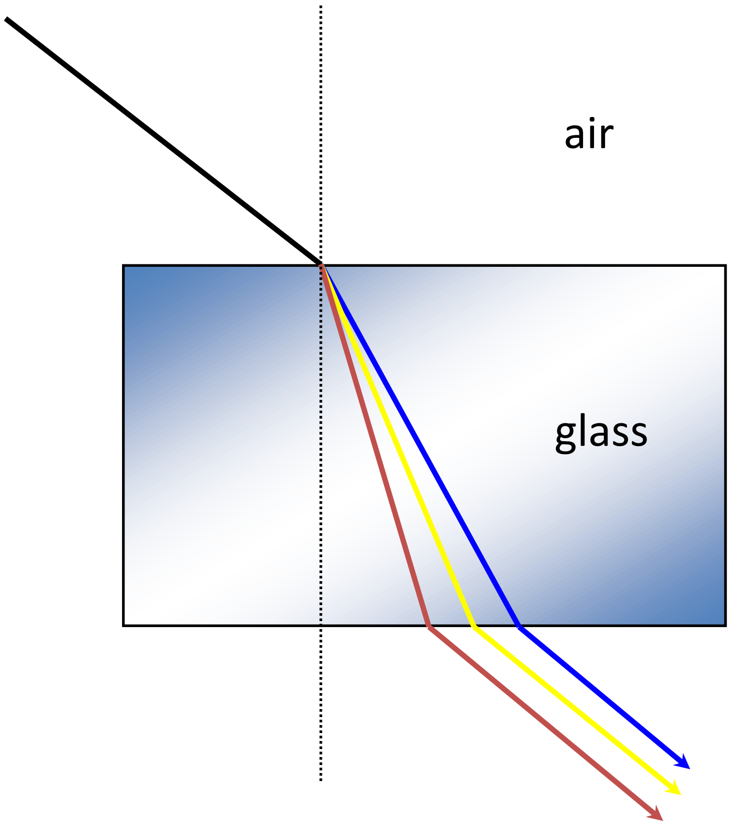
wave length

$$n_s = \frac{c_0}{c_s}$$

$$\frac{n_2}{n_1} = \frac{\sin \alpha_1}{\sin \alpha_2}$$

n (air) = 1,0 n (water) = 1,33 n(glass)=1,5

Dispersion of light



Diffraction of light

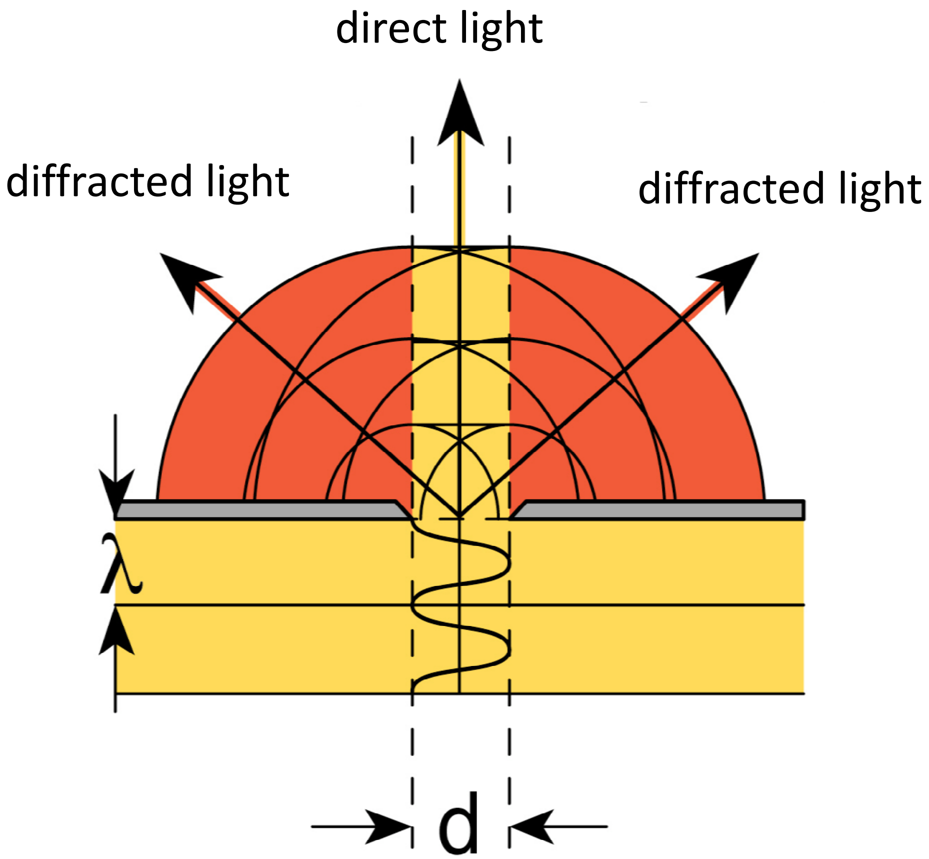


Image Formation by a Converging lens

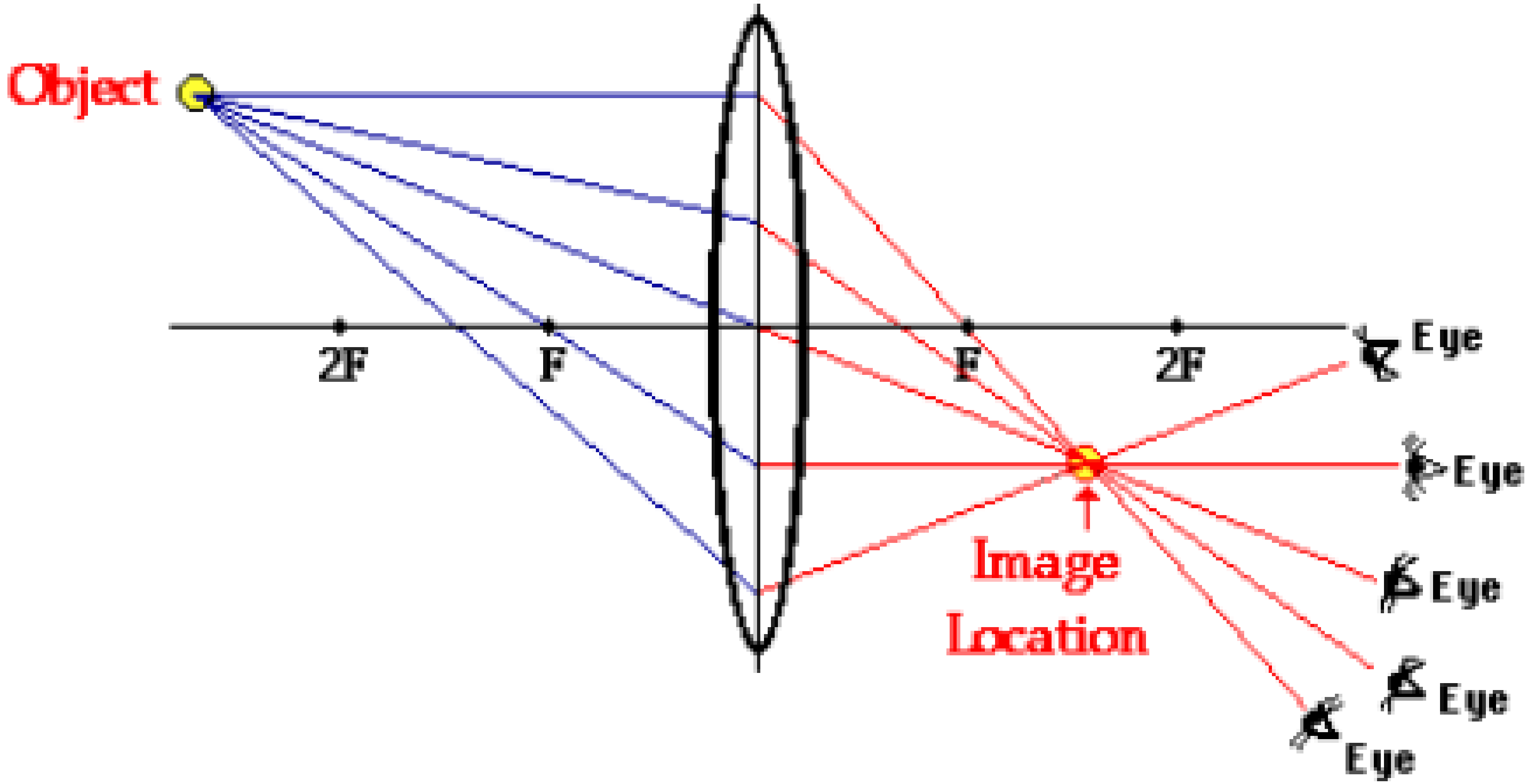
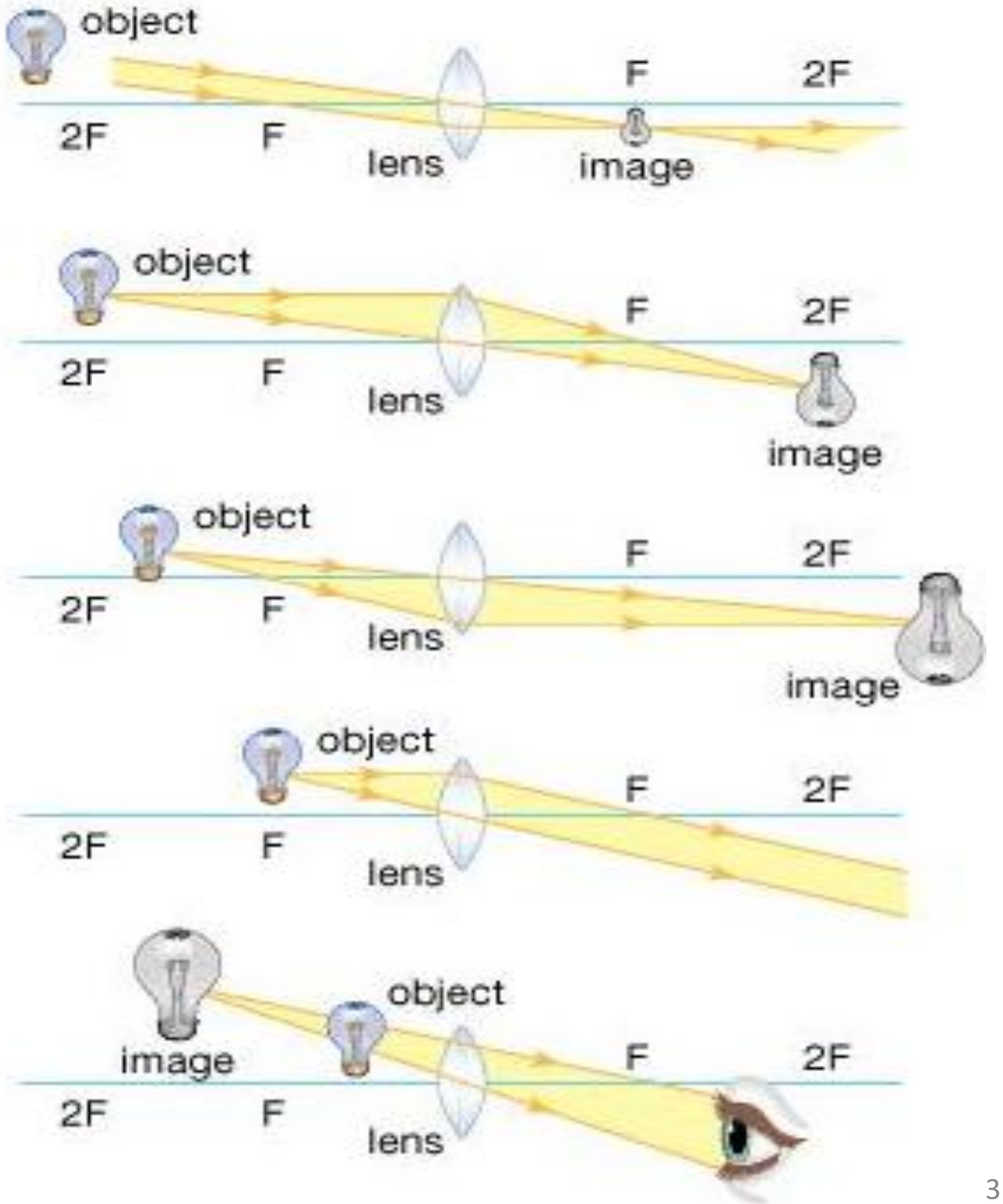


Image Formation by a Converging lens



distant object
real, inverted,
smaller than object, at F

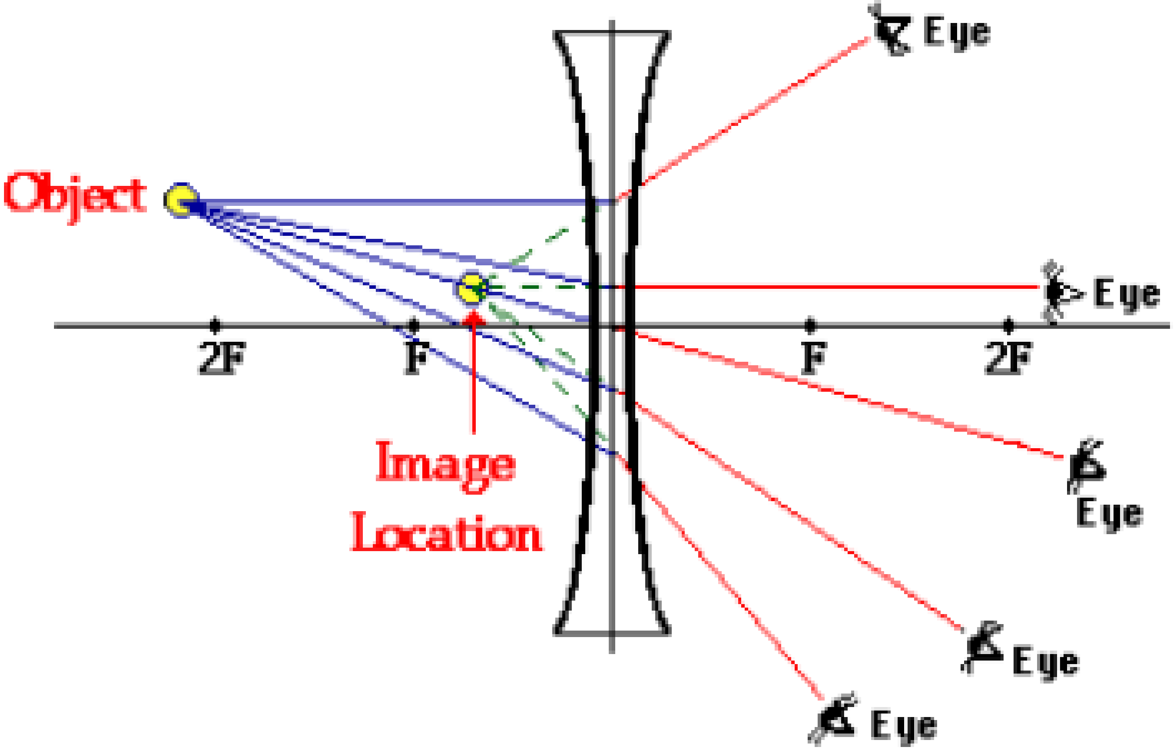
object at 2F
real, inverted,
same size as object, at 2F

object between 2F and F
real, inverted,
larger than object, beyond 2F

object at F
no image,
refracted rays are parallel

object between F and lens
virtual, upright,
larger than object,
behind object on the same
side of the lens

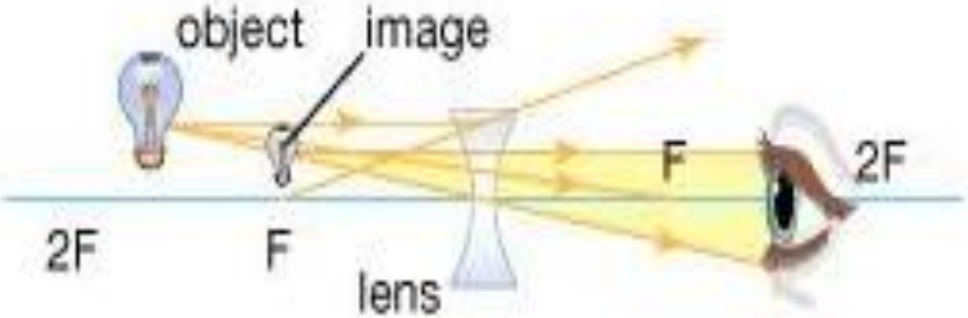
Image Formation by a Diverging lens



characteristics of image regardless of object position

virtual, upright,

smaller than object, between object and the lens



Methods of image formation

- Three basic ways by which image can be formed:
    - Projection image- formation of a shadows when an object is placed in front of a point source of illumination.
    - Optical image- formed by conventional lens systems.
    - Scanning image- each point of the picture is presented serially (e.g.- television picture).

Magnification

Magnification: Image size/Object size

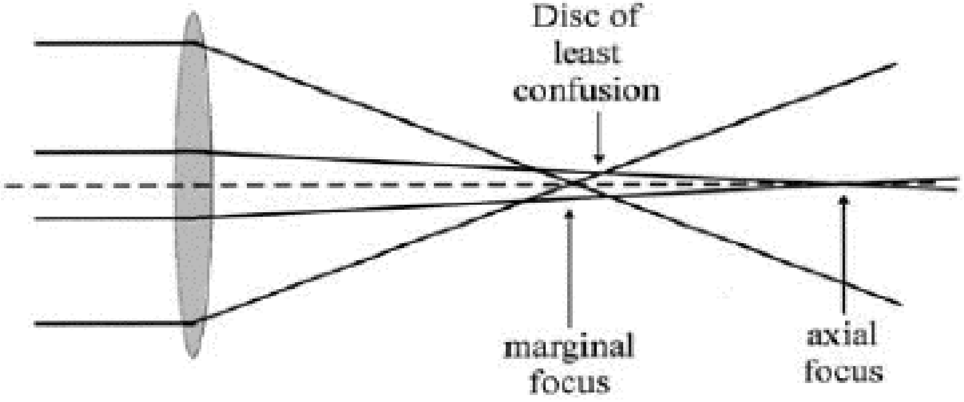
Resolution

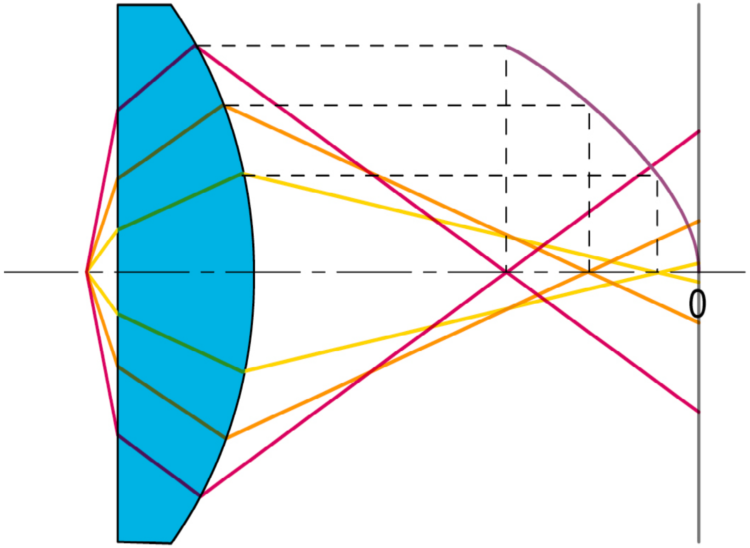
- The fineness of detail that can be distinguished in an image.
- The smallest distance between two points that we can resolve with our eyes is about 0.1- 0.2 mm → Resolution/Resolving power of human eye
- Any instrument that can show us pictures revealing detail finer than 0.1 mm could be described as a microscope
- Shorter wavelength ⇒ greater resolution

Aberrations of a lens

- It has been assumed that all the components in the microscope are perfect and will focus the light from any point on the object into similar unique point in the image.
- This is difficult to achieve due to lens aberrations.
- The effect of aberration is to distort the image in each point of the object in a particular way, leading to an overall loss of quality and resolution of image.
- The most important ones to consider are:
  - Spherical aberration
  - Chromatic aberration
  - Astigmatism

Spherical aberration





- The portion of the lens furthest from the optic axis brings rays to a focus nearer the lens than does the central portion of the lens.
- Optical ray path length from object point to focused image point should always be same.
- Disc of minimum confusion results instead of point focus.

Remedy of Spherical Aberration:

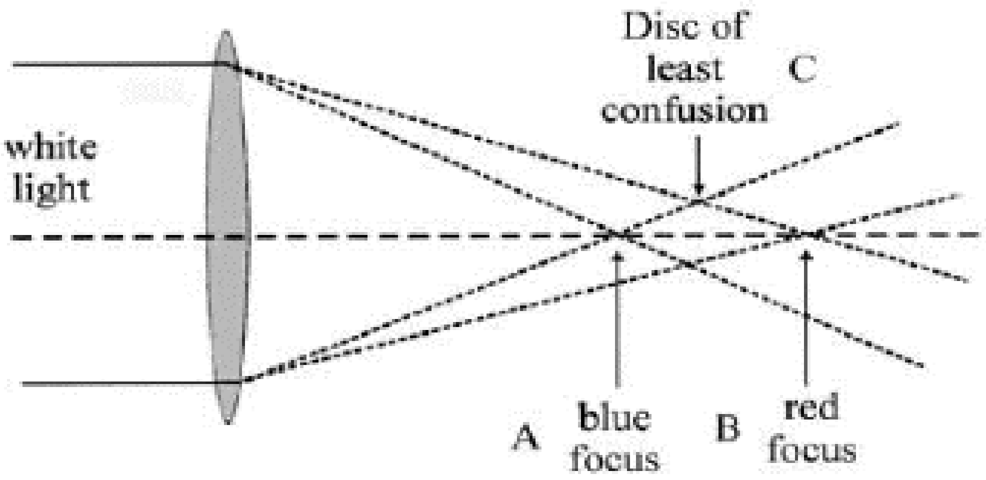
- ❑ Can be reduced by a proper choice of radii of curvature of the lens surfaces (if only central portion of the lens is used)
- ❑ Inserting a diaphragm in the beam so as to expose only the central portion of the lens
- ❑ Disc of minimum confusion has diameter given by:

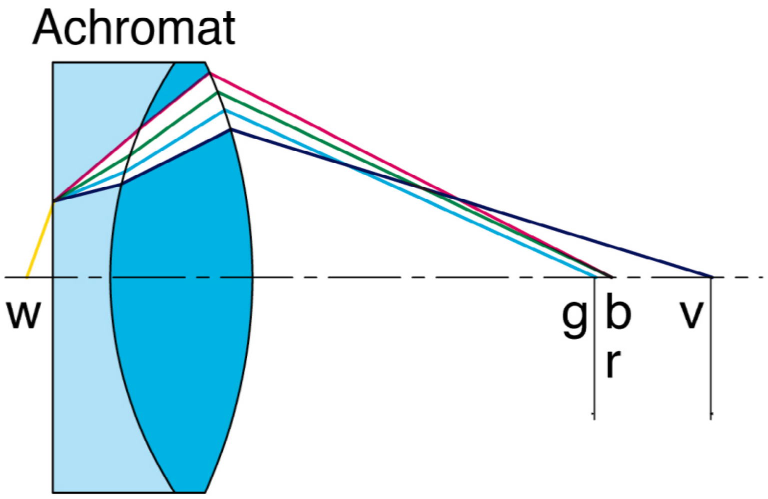
$$d = C_s \alpha^3$$

C_s = spherical aberration constant, α = Size of aperture}

- ✓ Reducing α gives a large reduction in d
- ✓ for optimal resolution we need *large* α!
- ✓ best compromise is with $\alpha = 10^{-3}$ radians (= f/500)
- ✓ In order to make the disc as small as possible, in other words to make the image of each point as small as possible, the aperture must be as large as is feasible

Chromatic aberration

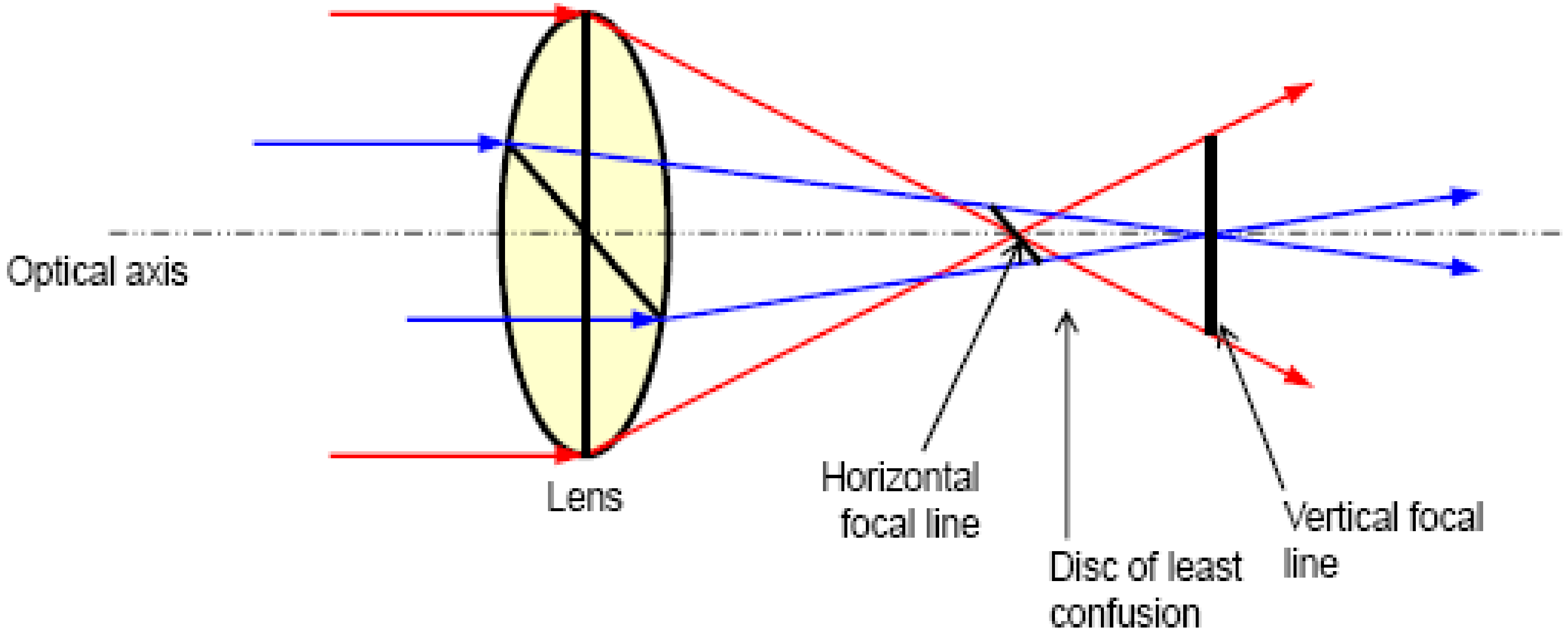




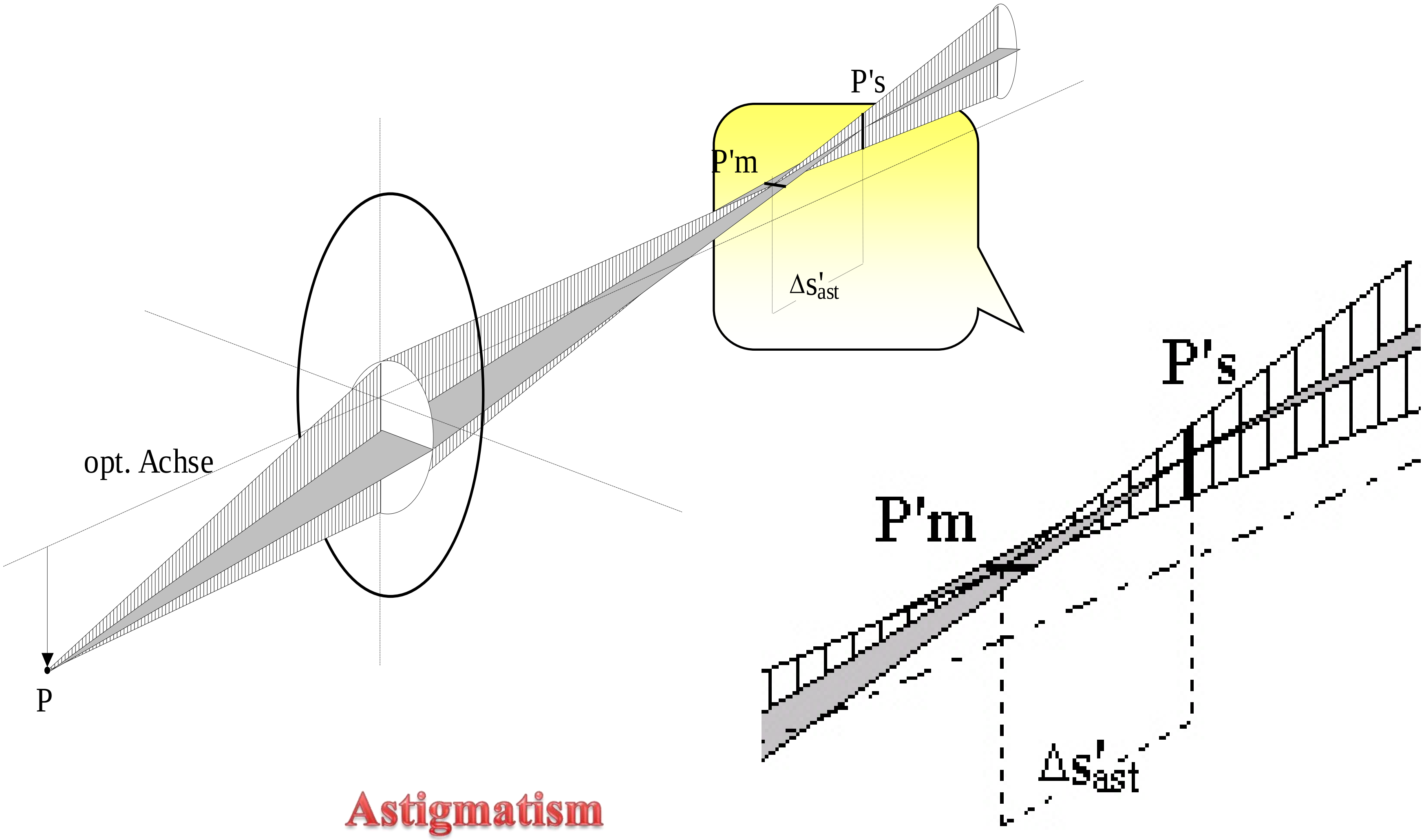
Remedy of Spherical Aberration:

- Chromatic aberration can be improved either by combining lenses of different shapes and refractive indices or by eliminating the variation in wavelength from the light source by using filter.
- Can be brought under control by proper combinations of glass types used in the convergent and divergent lens elements

Astigmatism



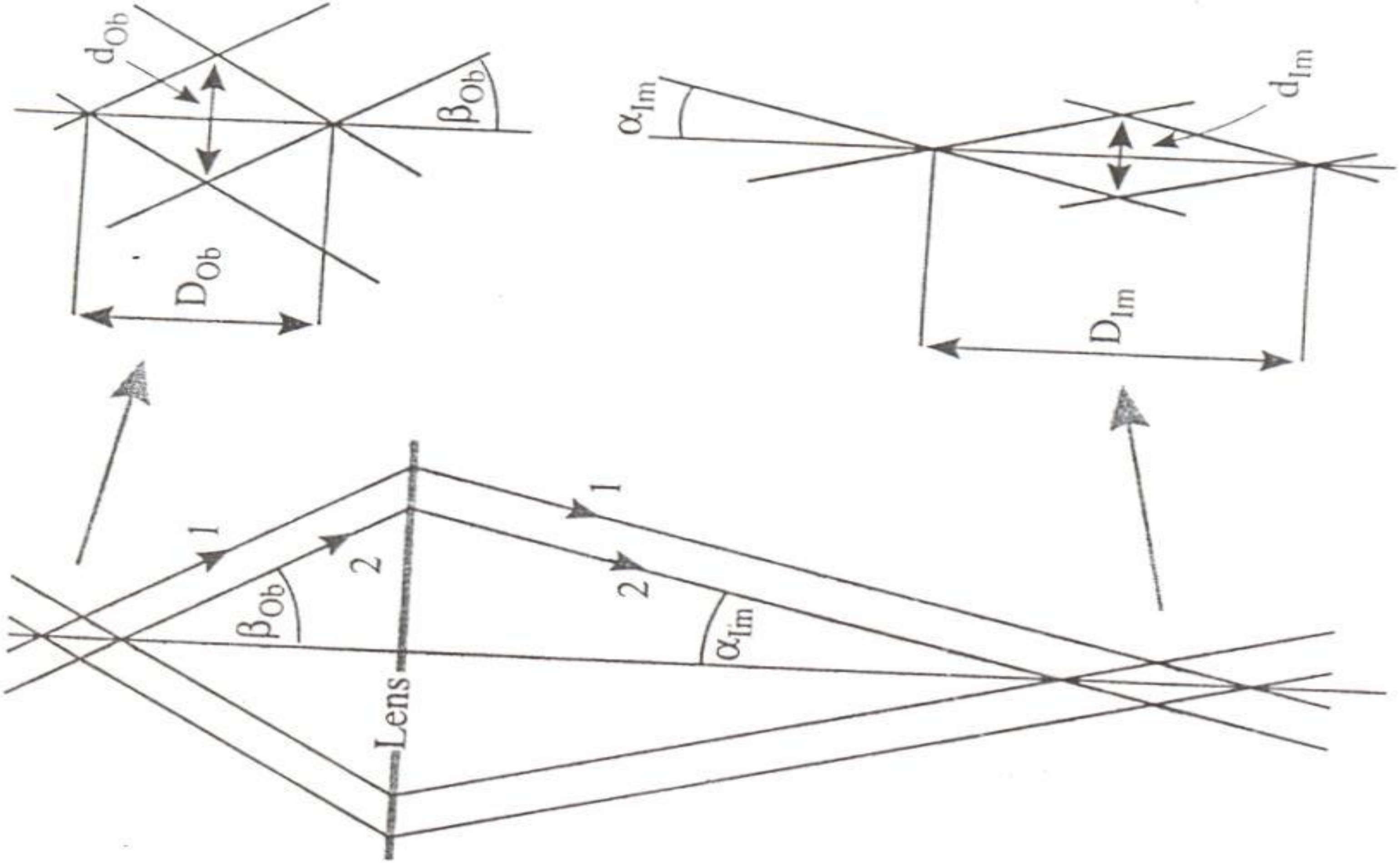
- Caused by light rays passing through vertical diameters of a lens that are not focused on the same image plane as rays passing through horizontal diameters
- The lens aberration in which horizontal and vertical lines parallel to the optical axis are focused at different points (distances) along the optical axis
- The image is clearest somewhere between these two points



Astigmatism

Depth of field and Depth of focus

- Depth of field is the distance along the axis on both sides of the object plane within which the object can be moved without detectable loss of sharpness in the image.
- Depth of focus is the distance along the axis on both sides of the image plane within which the image appears sharp.



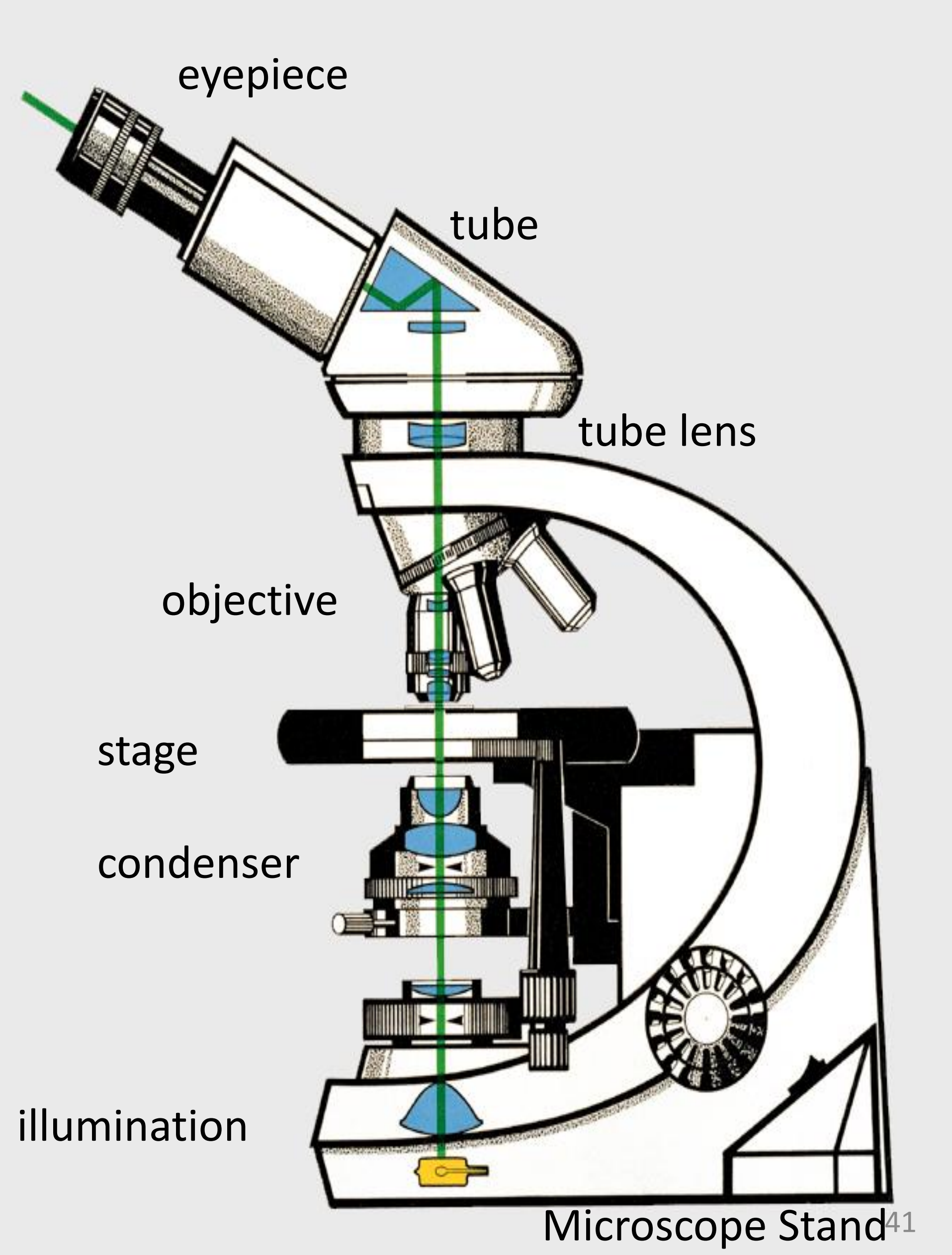
Microscope components

Microscope stand

- ❑ Carrier of all changeable components
- ❑ High mechanical stability
- ❑ High thermal stability
- ❑ Precise focusdrive

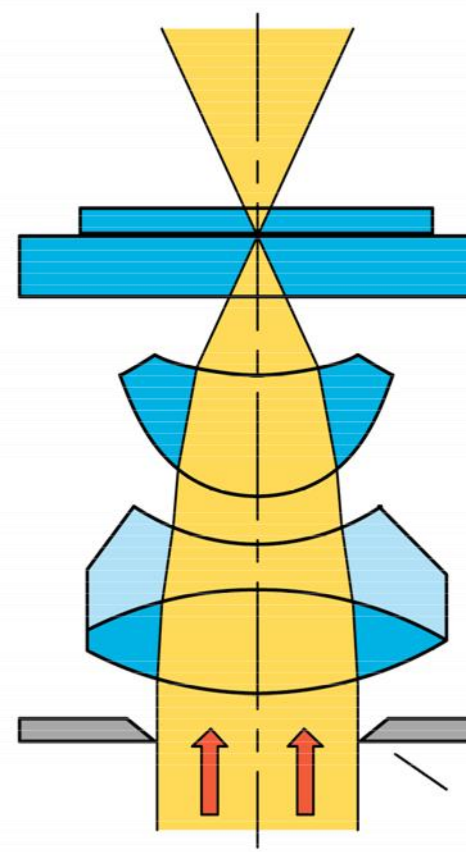
Lampe house

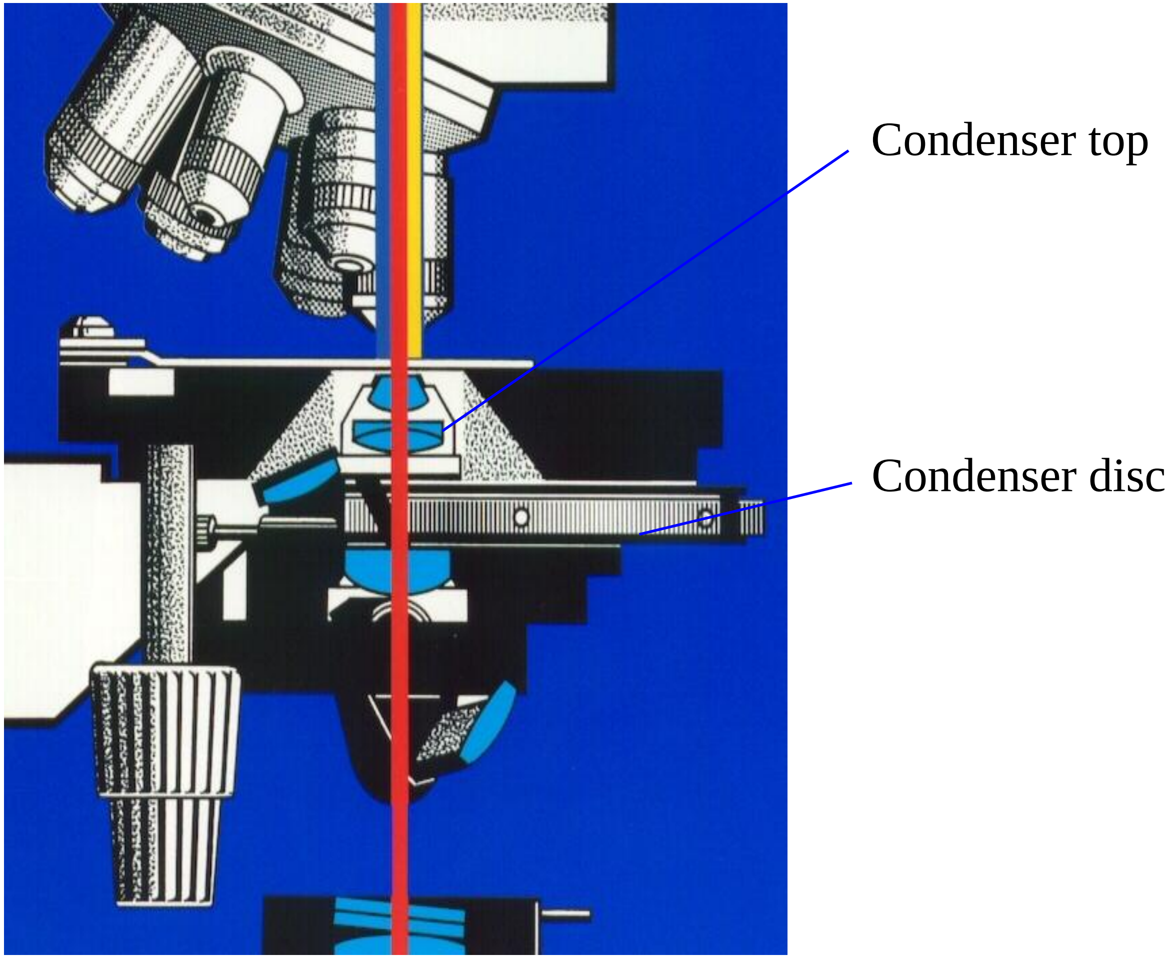
- ❑ Integrated illumination for transmitted light
- ❑ separate lampehouses for incident- and transmitted light.
- ❑ special lampehouses for fluorescence



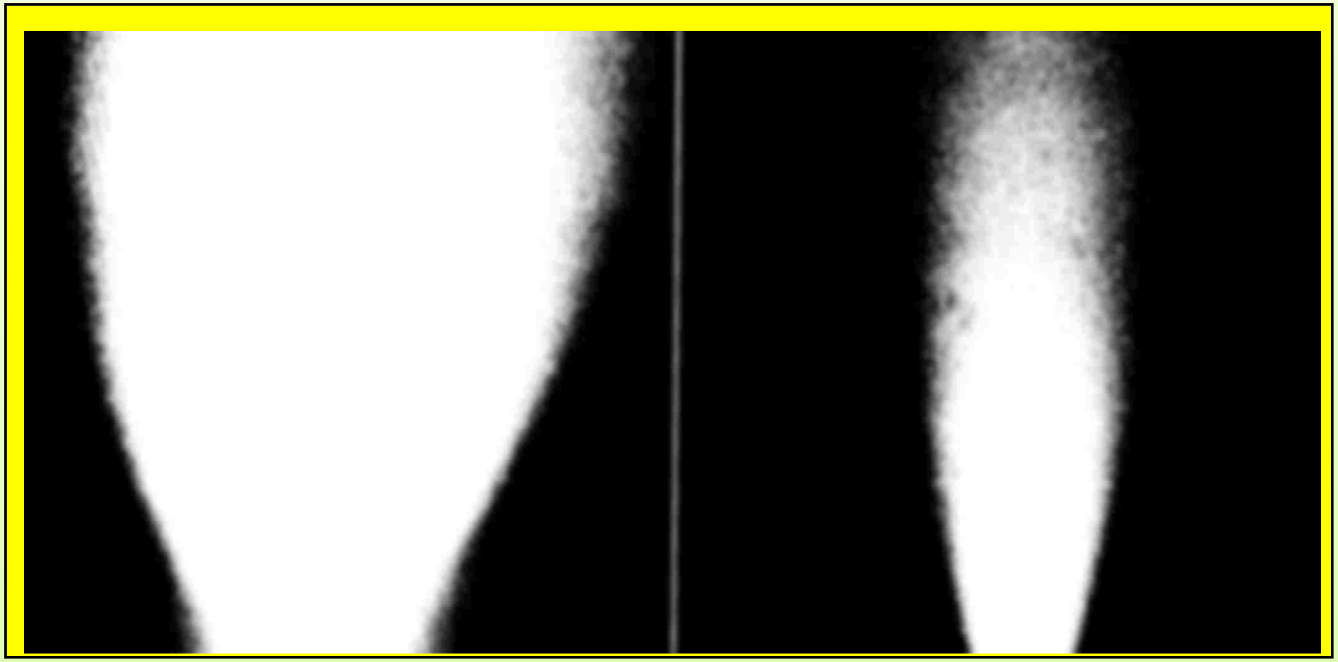
Condenser

- ❑ Collect illumination light rays and converge them to a focus
- ❑ Contains the aperture diaphragm for homogeneous illumination
- ❑ Increases resolution, enhances contrast, reduces glare





- ☐ Diaphragm reduces the internal glare
- ☐ Illumination, when aperture diaphragm is



Open

Close

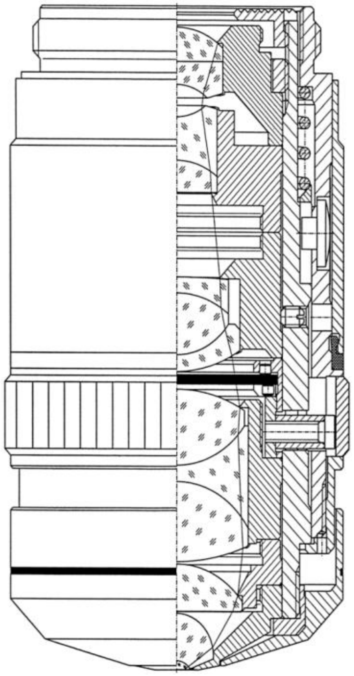
Specimen stages

- ❑ Object guide
- ❑ x/y - stage
- ❑ Scanning stage
- ❑ Pol rotary stage
- ❑ Heated stage

Objective

- ❑ Tubus length 160mm
- ❑ different objective classes
- ❑ Magnification (1,6x - 100x)
- ❑ 4x -red, 10x-yellow, 40x blue, 100x grey
- ❑ Different apertures

Objective lens



Cross section of a typical objective

Objective

magnification

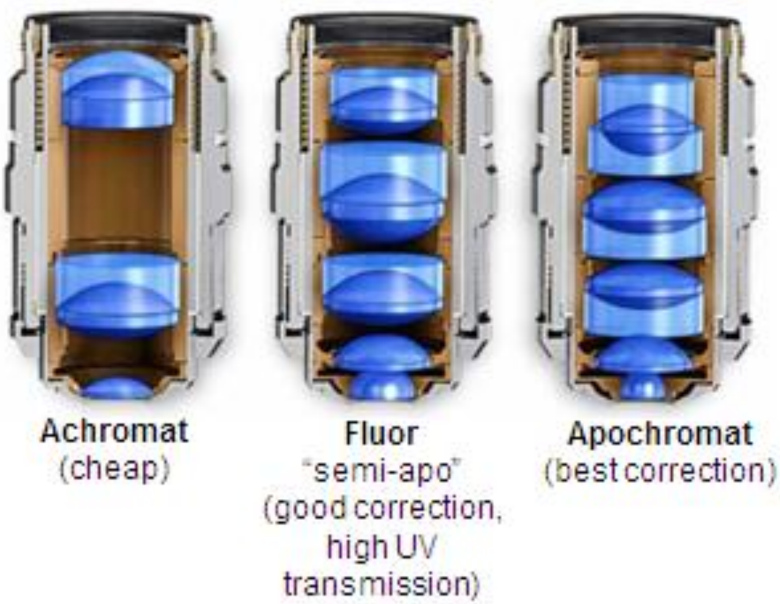
objective type

coverglass specification

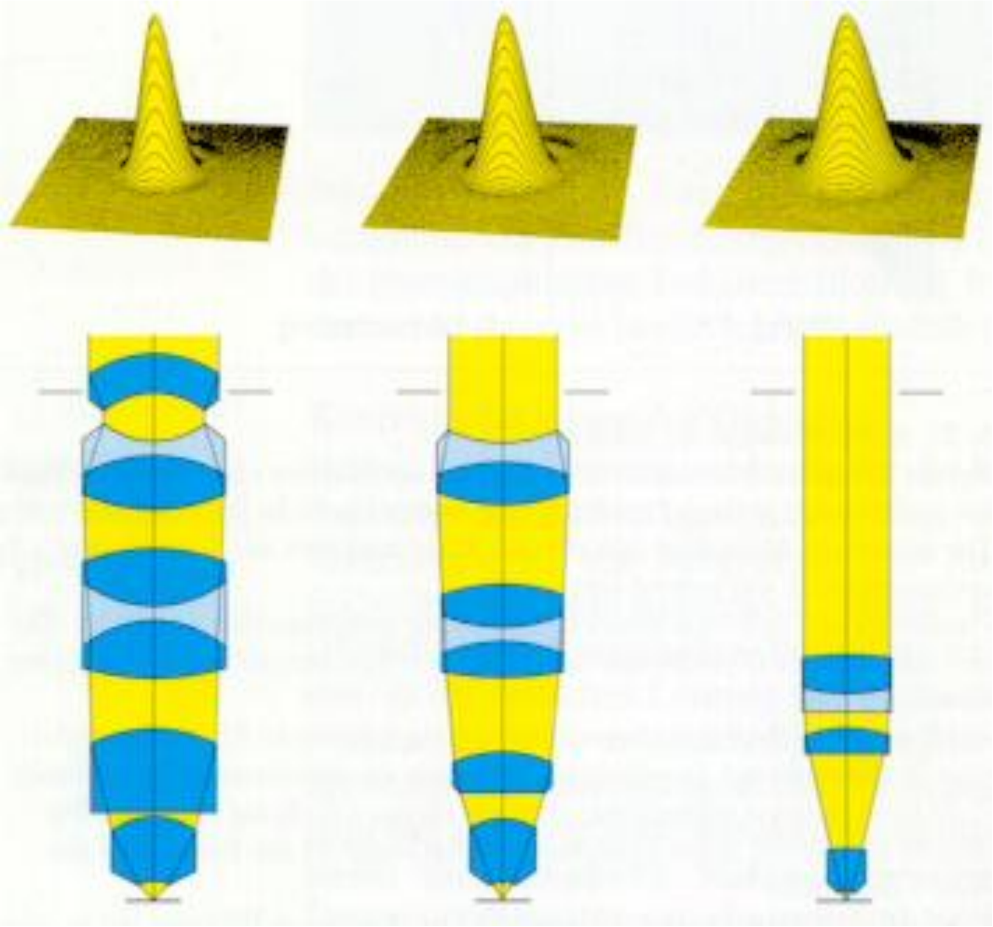
Numerical aperture

Correction classes of objectives

Objectiv class	*Field of view*	*Chromatic correction*
C PLAN	20mm	Achromat
N PLAN	22mm	Achromat
PL FLUOTAR	>25mm	Semi Apochromat
PLAN APO	>25mm	Apochromat
PL APO (CS)	>25mm	Apochromat, smaller tollerances for confocal applications
APO U-V-I	20mm	Apochromat UV, visual light, IR-Transmission



Objective Working and Parfocal Distance



PL APO
20x/0.60

PL FLUOTAR
20x/0.50

N PLAN
20x/0.40

Tube

- monocular tube
- binocular tube
- binocular Phototube
- Ergonomy tube
- Special tubes

L Plan 10x/20 L Plan 15x/20

IMAGE FORMATION IN A SIMPLE MICROSCOPE

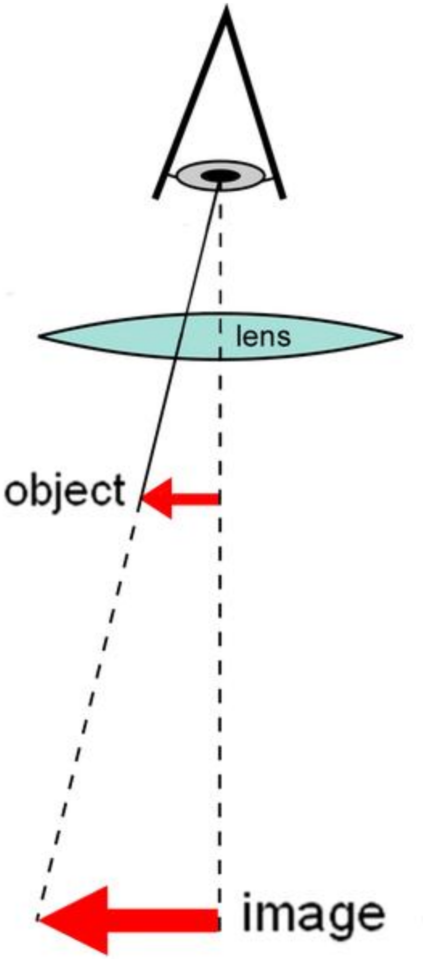


IMAGE FORMATION IN A COMPOUND MICROSCOPE

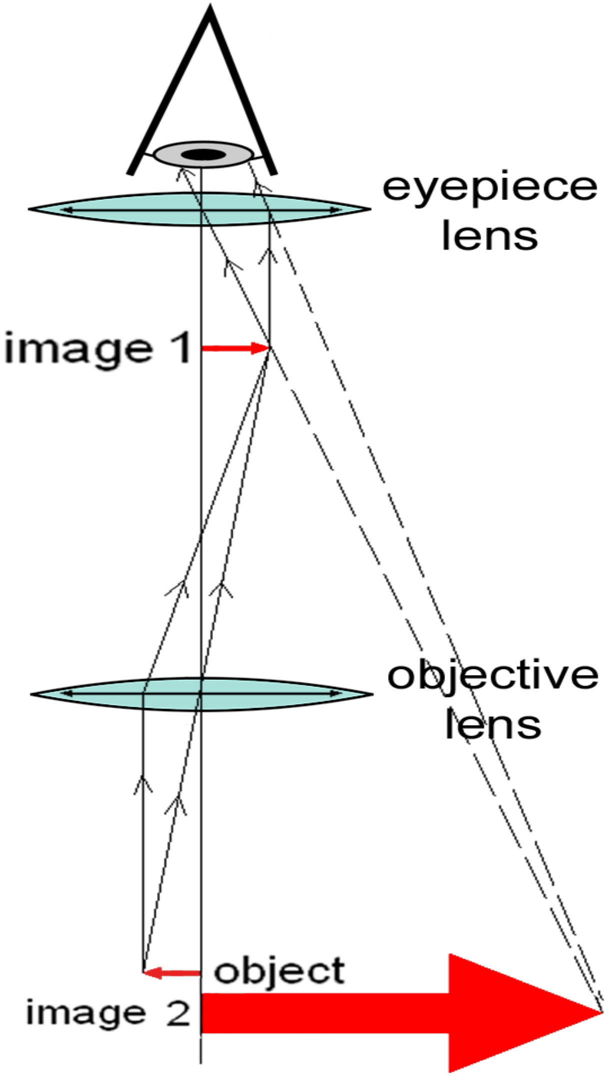


Image Formation in Transmission Light Microscope
(For thin and Translucent samples)

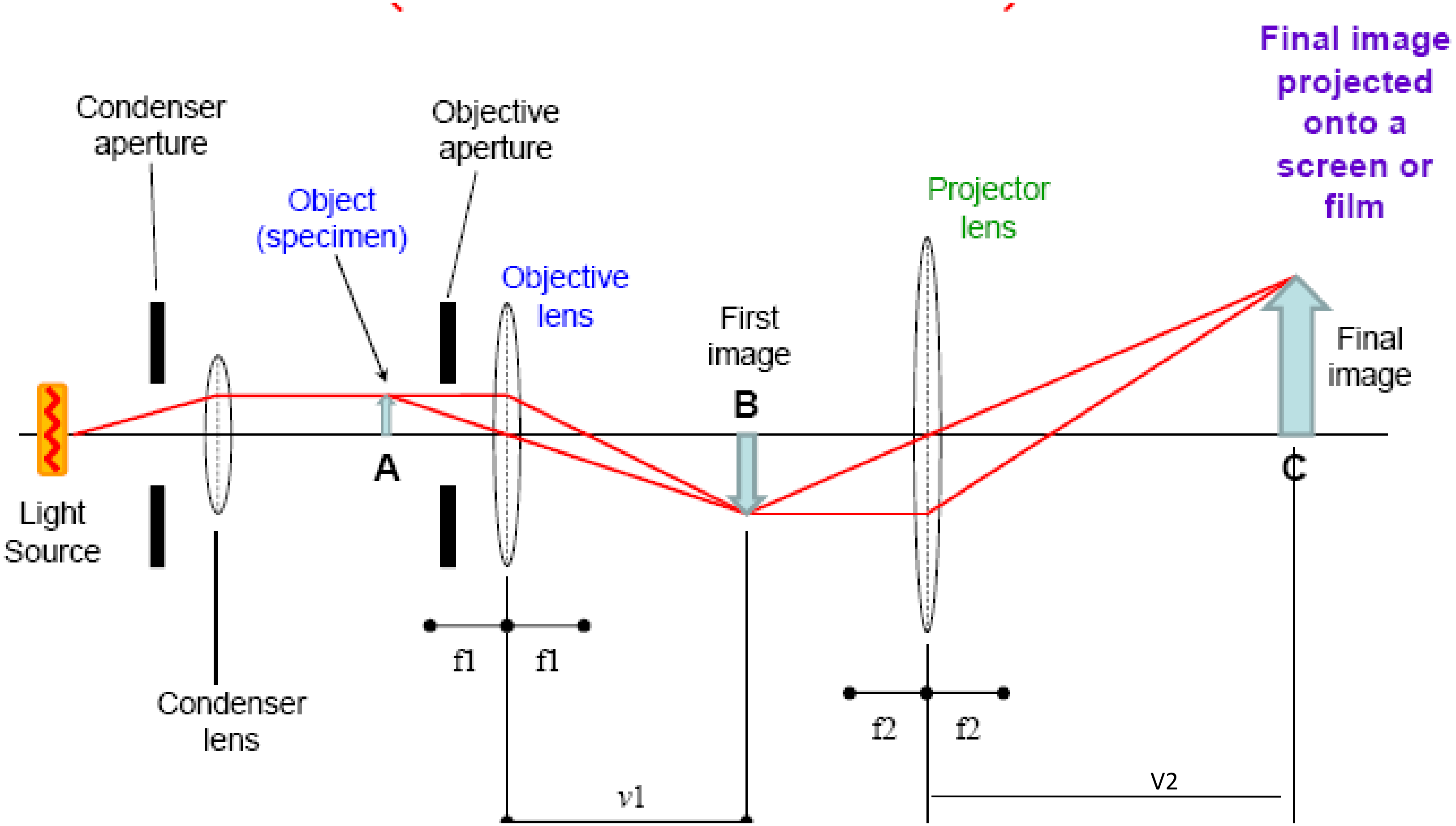
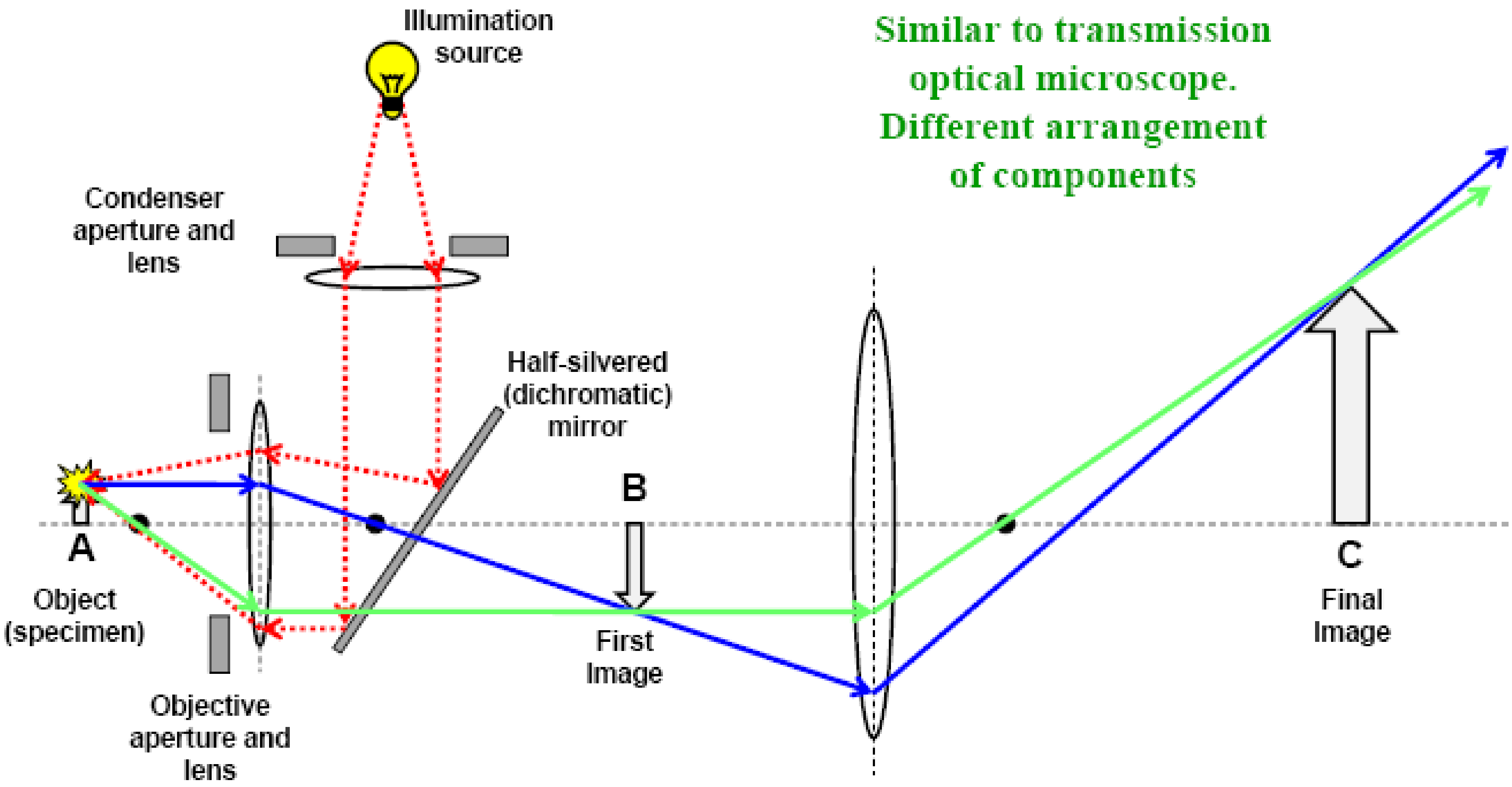
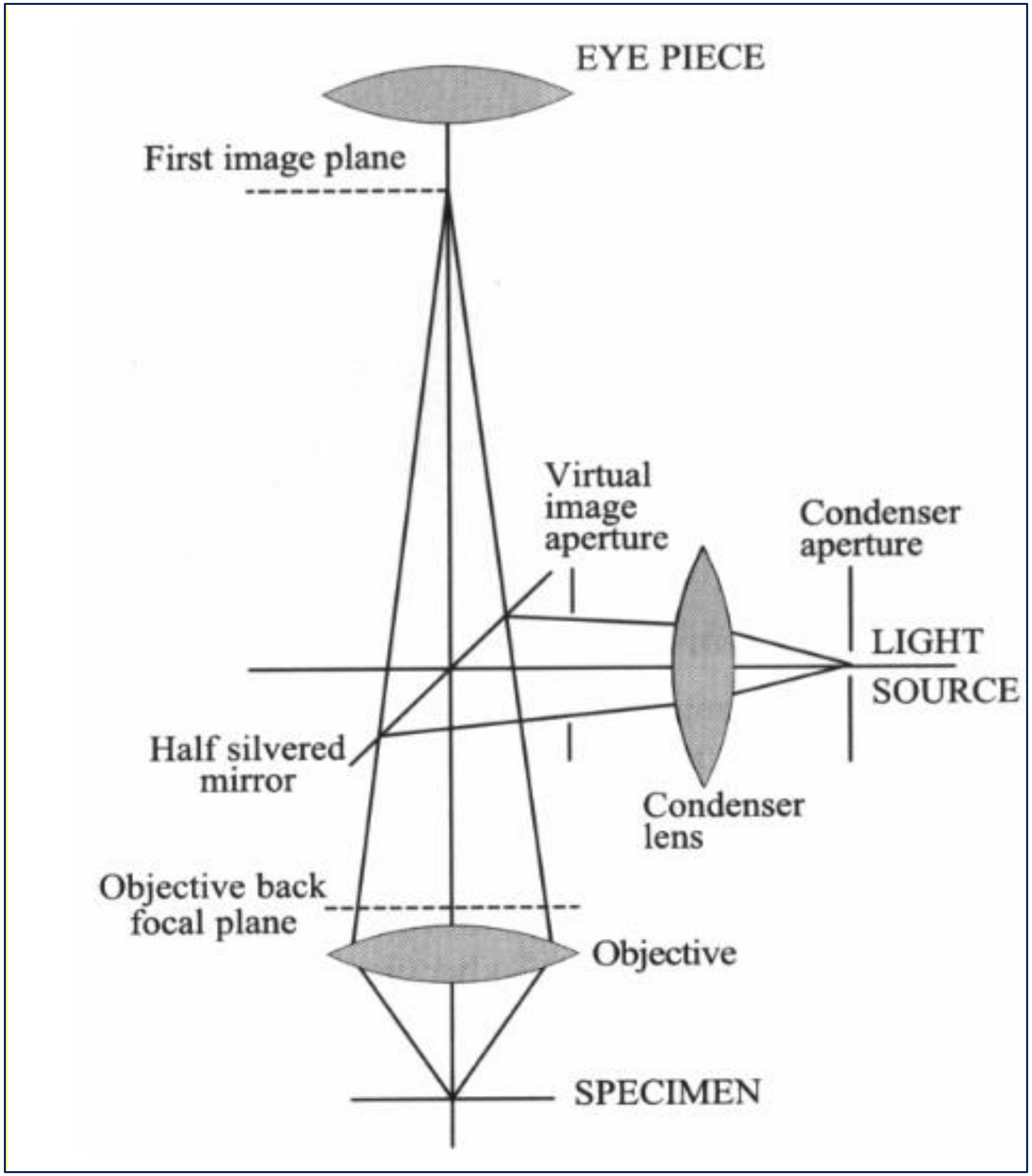


Image Formation in Reflection Light Microscope
(For thick and Opaque samples)



Similar to transmission optical microscope. Different arrangement of components

Vertical illumination Reflected light



Total magnification of Optical Microscope

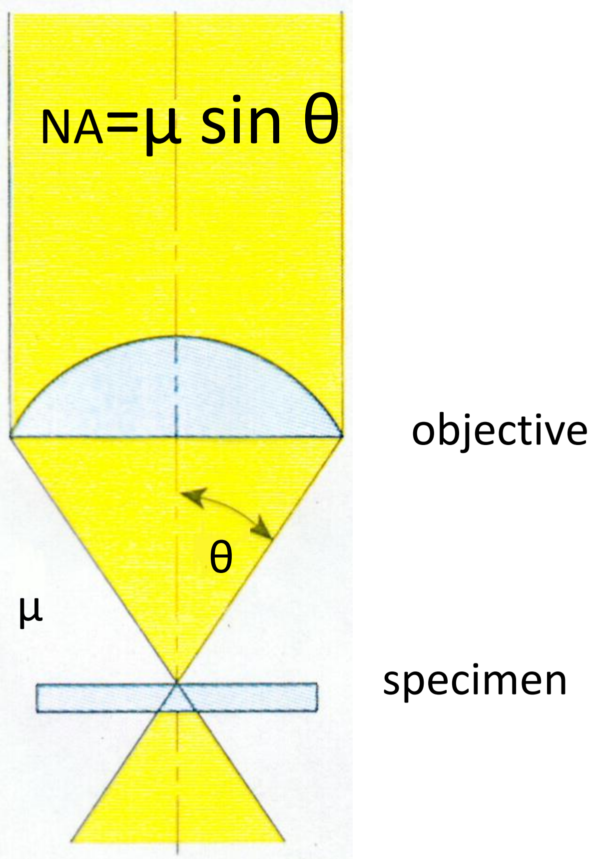
$$\frac{1}{u}+\frac{1}{v}=\frac{1}{f}$$ and $$M=\frac{v-f}{f}=\frac{v}{u}$$

$$M=M_1M_2=\frac{(v_1-f_1)(v_2-f_2)}{f_1f_2}$$

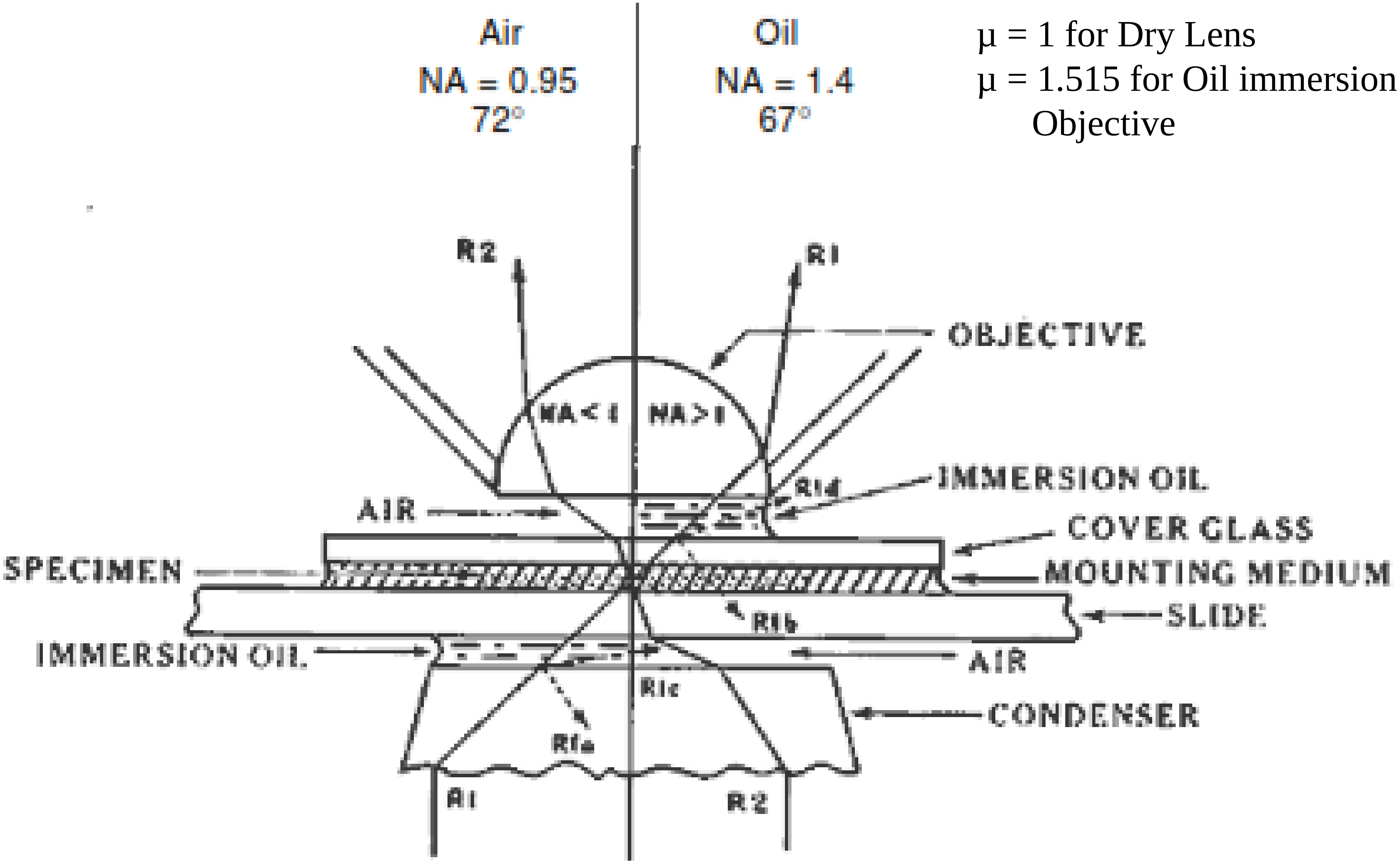
$$M_{total}=M_{objective}\cdot M_{tubelens}\cdot M_{eyepiece}$$

Numerical aperture

- NA: numerical aperture
- μ refractive index
- θ half angle of cone of specimen light accepted by objective lens
- measure of light collecting ability
- It indicates the resolving power of a lens

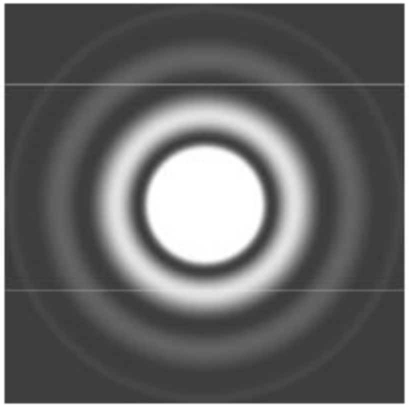


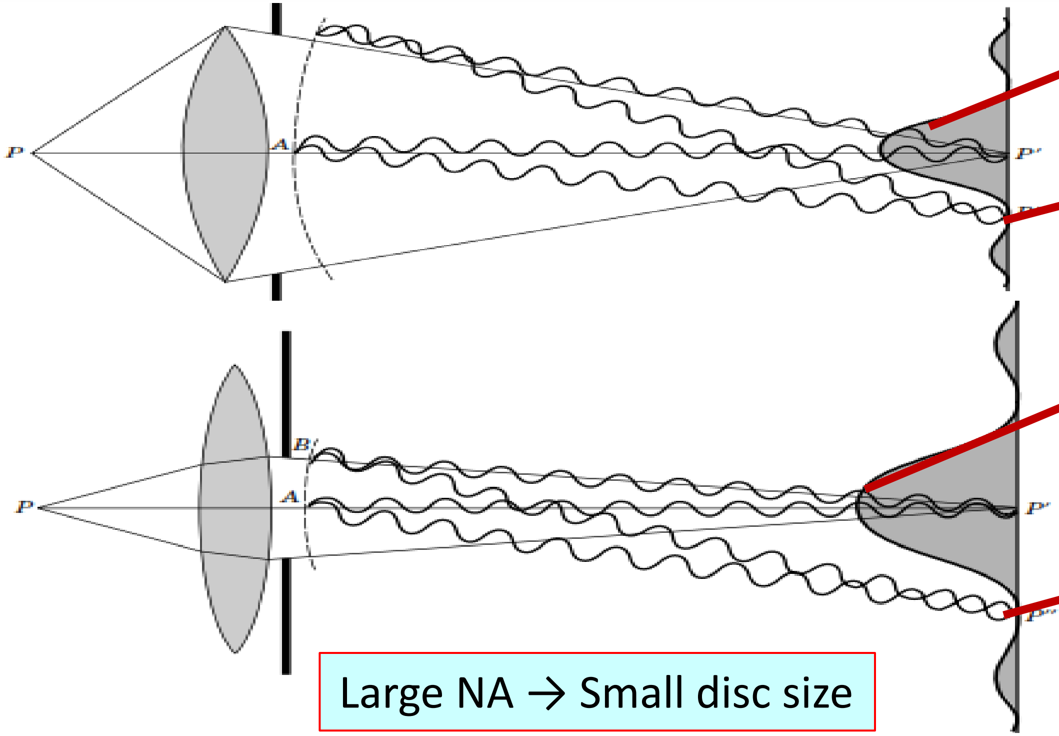
μ = 1 for Dry Lens
μ = 1.515 for Oil immersion
Objective



Resolution of Optical Microscope

- Minimum Distance between 2 points at which they can be visibly distinguished as 2 separate points
- Theoretically controlled by diffraction of light
- Ability to distinguish between two closely spaced Airy Disks in a diffraction pattern
- Image of a point produced by a lens is an extended spot surrounded by a series of rings





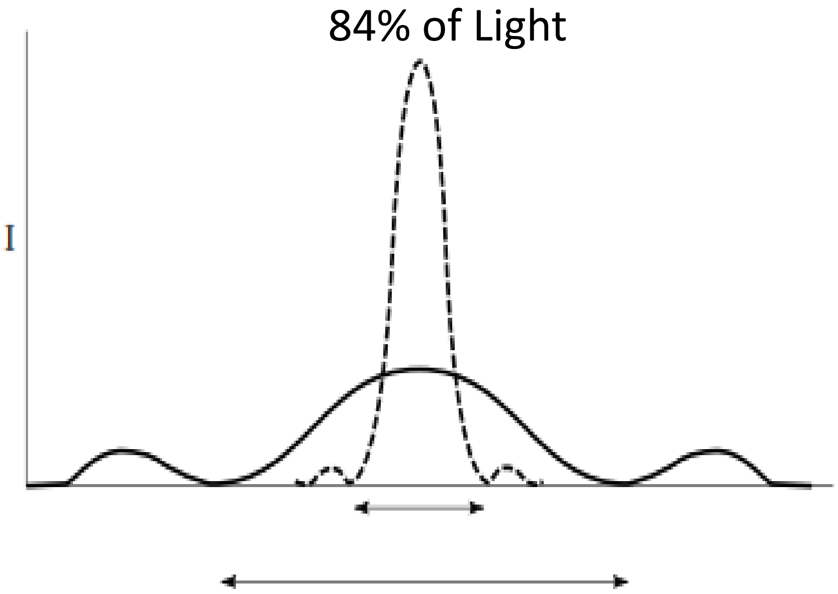
Constructive Interference

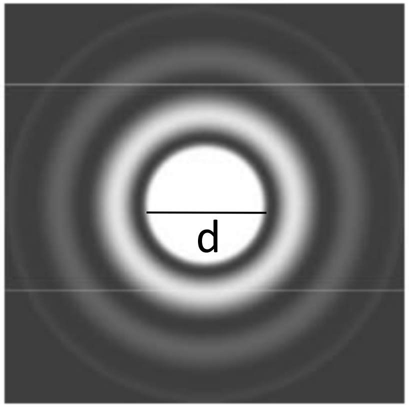
Destructive Interference

Constructive Interference

Destructive Interference

Large NA → Small disc size



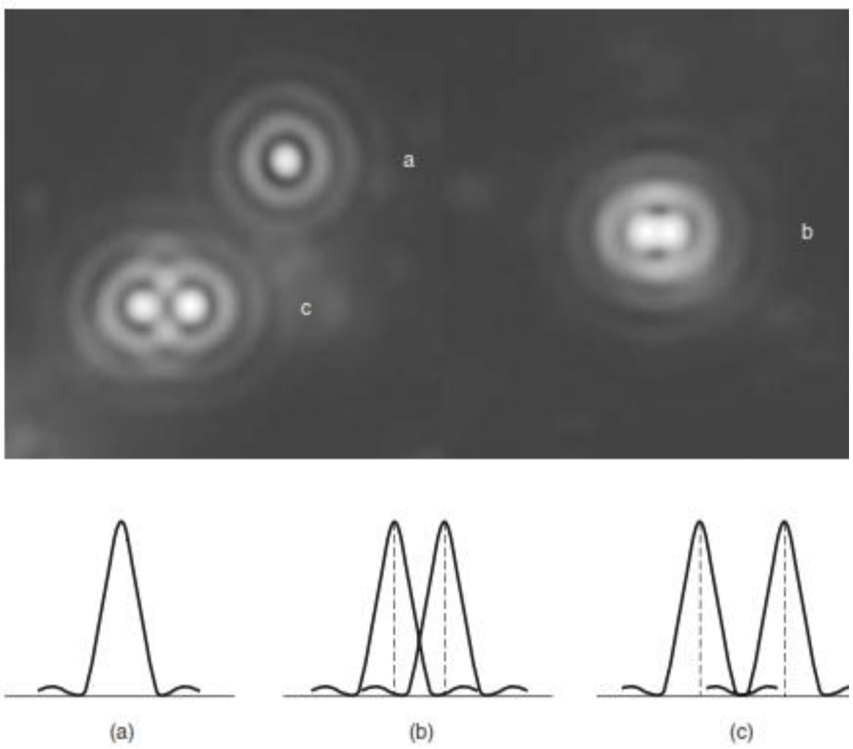


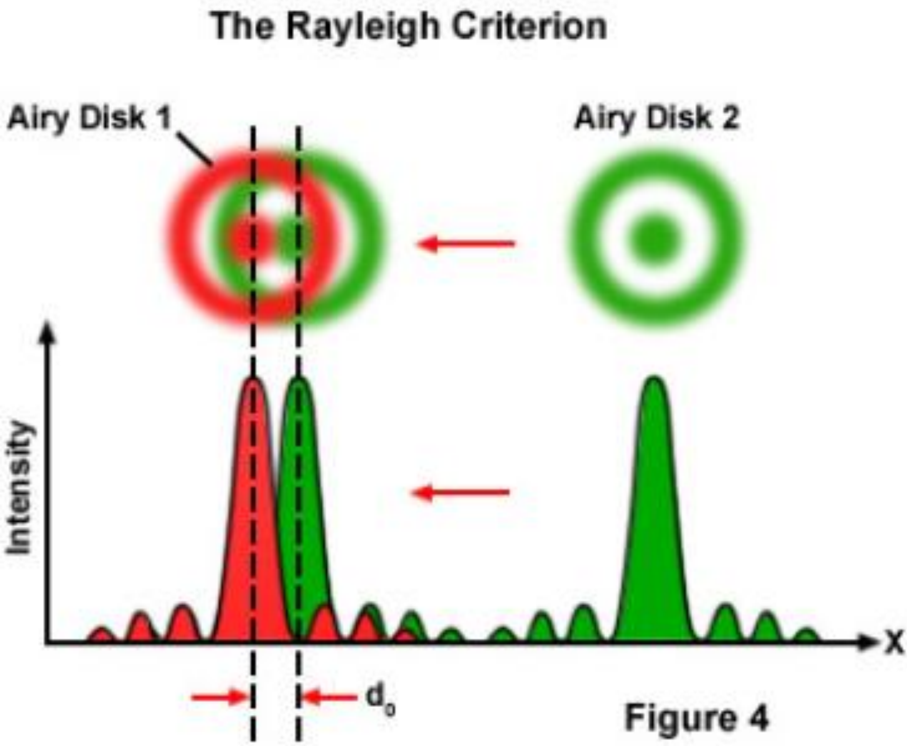
Abbe Equation

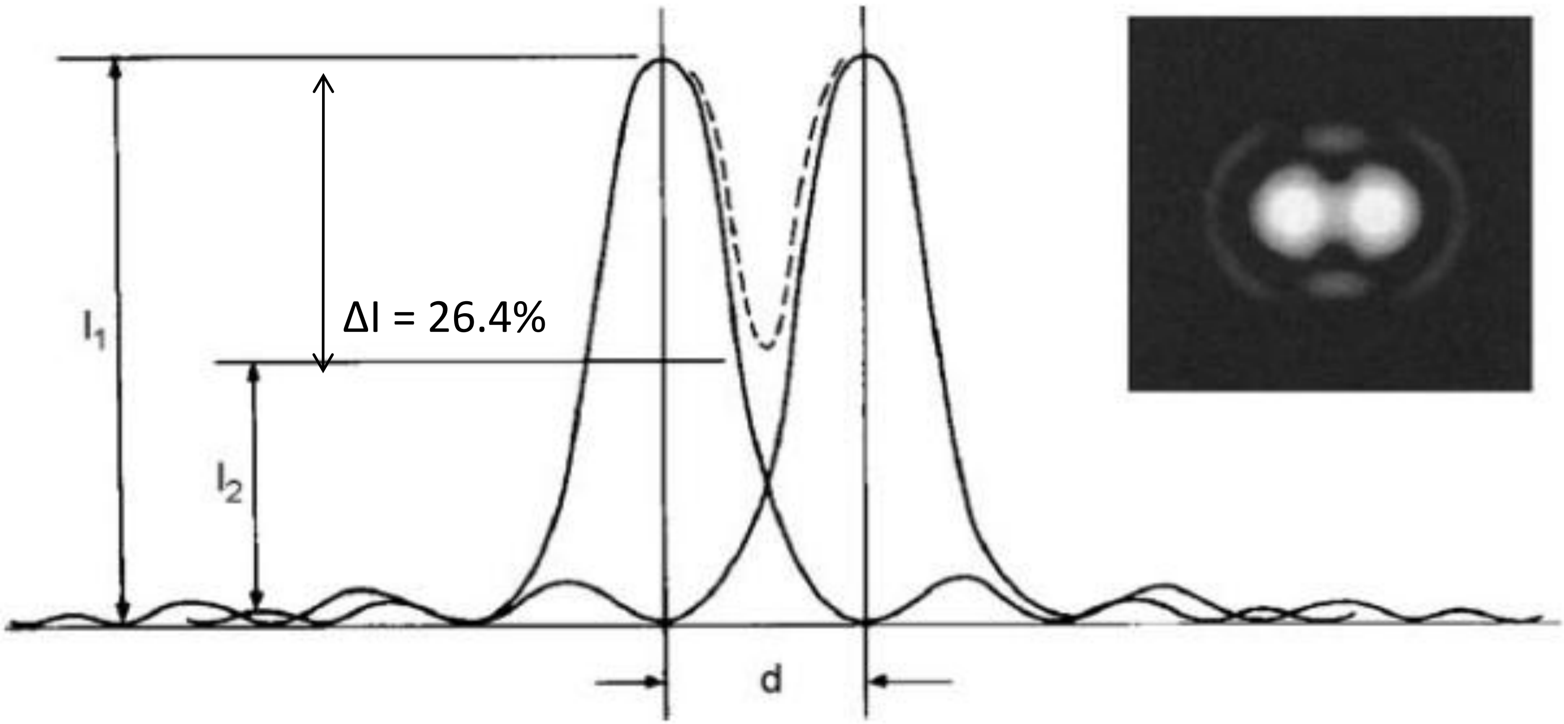
$$r = \frac{d}{2} = \frac{1.22\lambda}{2NA}$$

Rayleigh Criteria

Two adjacent object points are defined as being resolved when the central diffraction spot (Airy disk) of one point coincides with the first diffraction minimum of the other point in the image plane







Intensity distribution of two Airy disks with a distance d/2

$$\textbf{Resolution (R)} = \frac{d}{2} = \frac{1.22\lambda}{2NA} = \frac{0.61\lambda}{NA}$$

Self Luminous Body

$$\textbf{Resolution (R)} = \frac{d}{2} = \frac{1.22\lambda}{NA_{Con} + NA_{Obj}}$$

Non Luminous Body

How can you improve resolution?

$$R = \frac{d}{2} = \frac{1.22\lambda}{2NA} = \frac{0.61\lambda}{NA}$$

- ☐ Improved resolving power means smaller d/2
- ☐ Increase N.A. (not feasible in optical microscopy)
- ☐ Reduce λ of light (limited by electromagnetic spectrum (~400 – 700 nm)

Resolution Limit of a Light Microscope

- ☐ You can decrease λ to 400 nm (violet light) BUT usually kept at 550 nm (Green Light)
- ☐ N.A. is limited to ~1.4(oil) and 0.95 (Air).
- ☐ Theoretical limit for maximum resolution in an optical microscope is around ~240nm (Air) and ~ 160 nm (Oil Immersion Objective)
- ☐ Practical limit for maximum resolution in an optical microscope is around ~260 nm (Air) and ~174 nm (Oil Immersion Objective, μ = 1.515)

Magnification

- The overall magnification is given as the product of the lenses and the distance over which the image is projected:

$$M = \frac{D \cdot M_1 \cdot M_2}{250mm}$$

where:

D = projection (tube) length (usually = 250 mm)

M1, M2 = magnification of objective and ocular

- For a compound microscope, magnification is the product of the magnifications for each lens.

Effective magnification (M_{eff}):

- M_{eff} = Max Resolution of eye/ Max Resolution of Optical Microscope
- Resolution of eye 0.2 mm
- Max. resolution of Optical Microscope 0.0002mm
- M_{eff} = 1000 X
- M's > M_{eff} make the image bigger, but do not provide any additional details. This is termed "empty magnification"

Brightness

- ☐ Brightness = Intensity of light.
- ☐ Related to the N.A. and the magnification (M)

$$Brightness = \frac{(NA)^2}{M^2}$$

- ☐ In a Reflected Light Microscope Brightness is more dependent on NA

$$Brightness = \frac{(NA)^4}{M^2}$$

Contrast

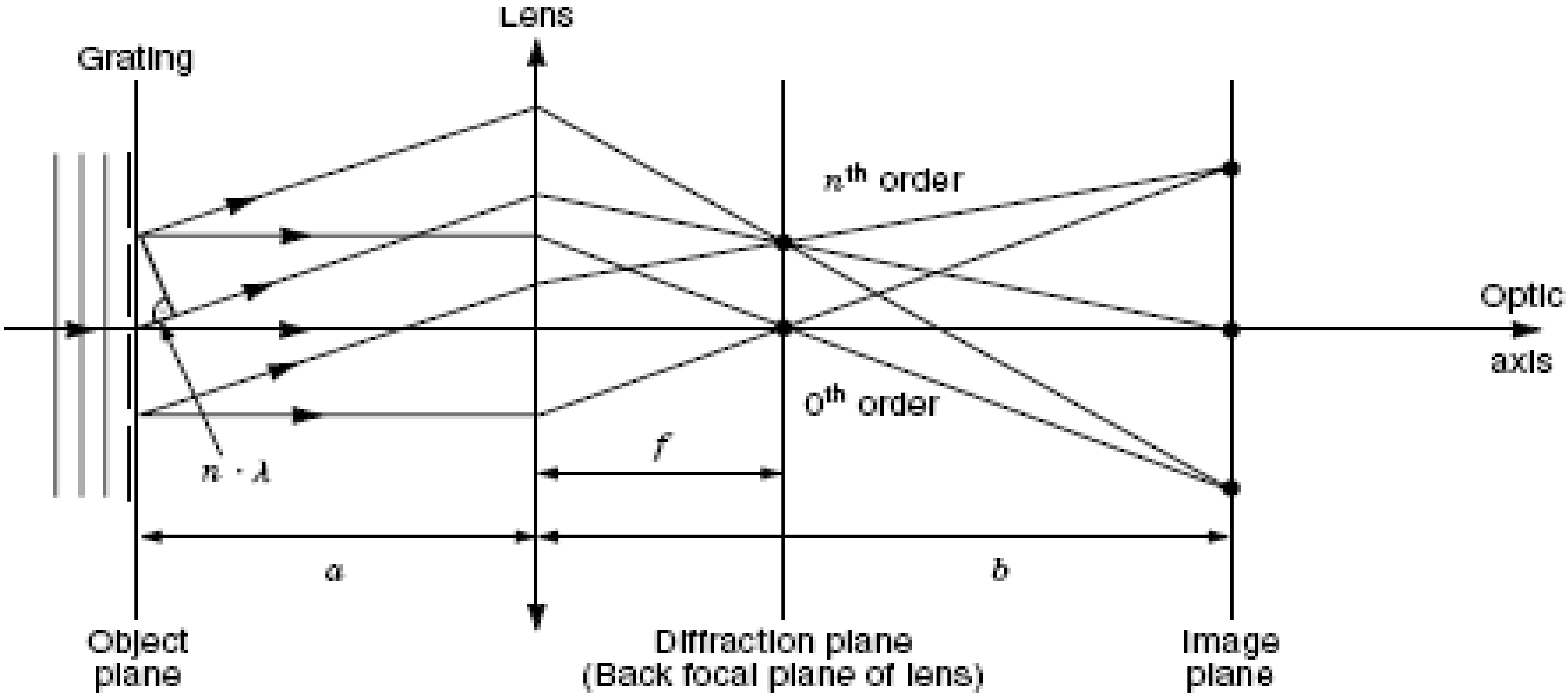
- ☐ The relative change in light intensity (I) between an object and its background.

$$Contrast = \frac{I_{object} - I_{background}}{I_{background}}$$

Depth of Field

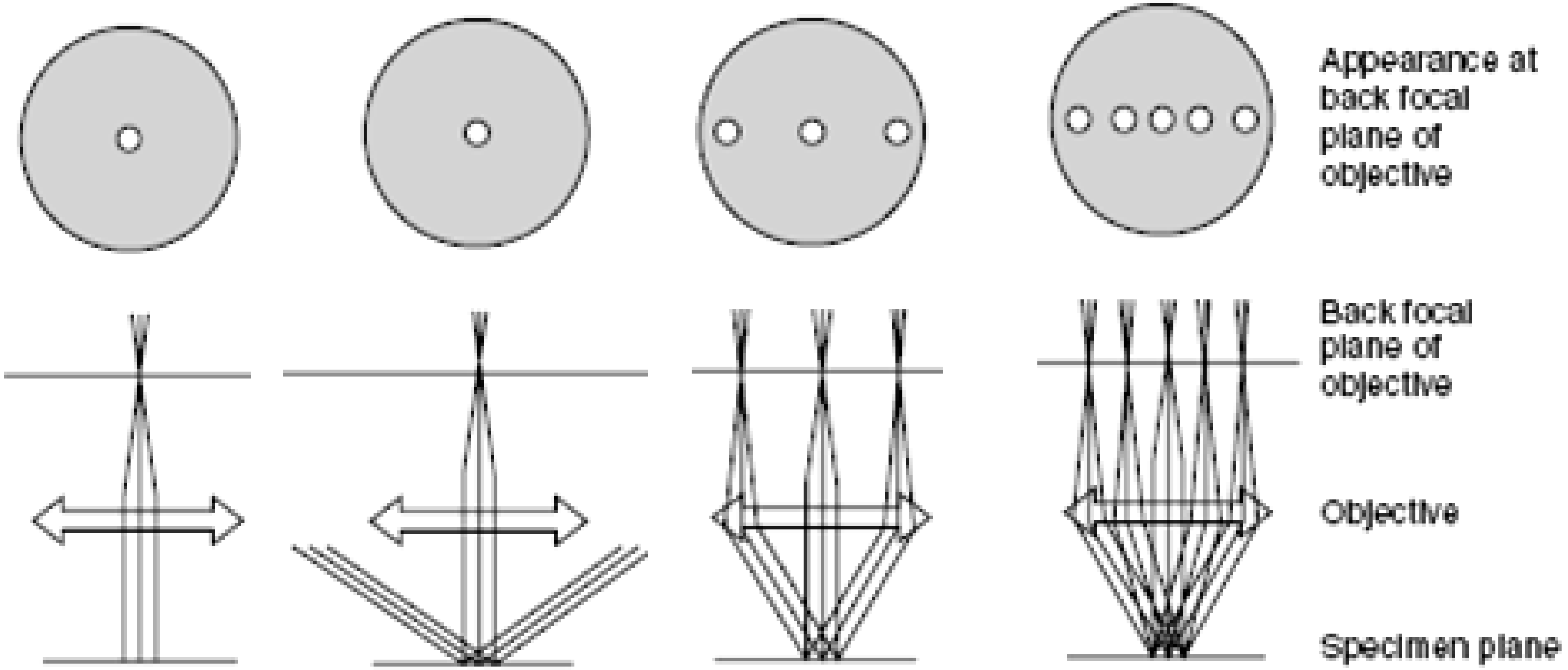
Depth of Field: $D_{ob} = \frac{0.61\lambda}{NA_2}$

Abbe's theory for image formation



- Interference between 0th and higher-order diffracted rays in the image plane generates image contrast and determines the limit of spatial resolution that can be provided by an objective
- If light from only a single diffraction order is collected by the lens (only the 0th order is collected), there is no interference, and no image is formed
- larger the number of diffraction orders collected by the objective, the sharper and better resolved (the greater the information content) are the details in the image.

Generation of Image by Interference



- If a specimen does not diffract light or if the objective does not capture the diffracted light from an object, no image is formed in the image plane.
- If portions of two adjacent orders are captured, an image is formed, but the image may be barely resolved and indistinct.
- If multiple orders of diffracted light are captured, a sharply defined image is formed.
- This theory is the basis for determining the spatial resolution of the light microscope.

Contrasting methods of microscopy

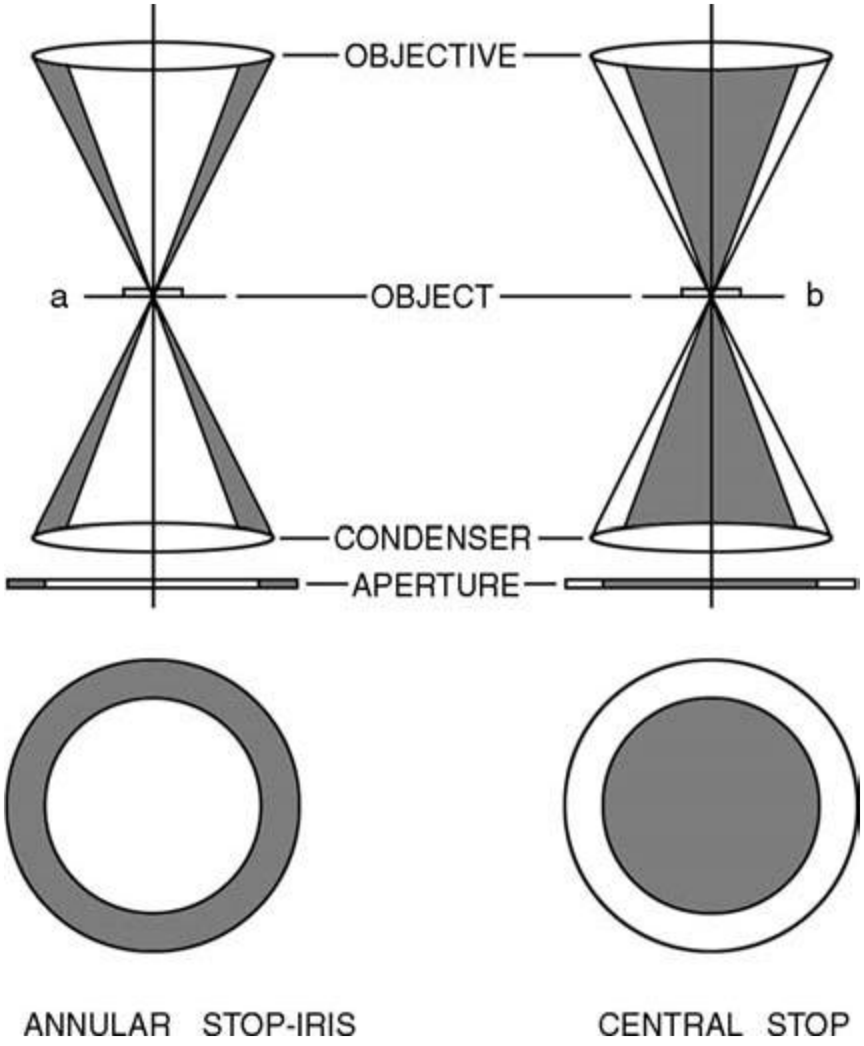
- ❑ Several contrasting methods of microscopy are: Brightfield, Darkfield, Pol contrast, Phase contrast, Interference contrast etc.
- ❑ Method of illumination depends on the specimen
  - ✓ Amplitude object in brightfield
  - ✓ Phase object in phase- or interference contrast
  - ✓ Anisotropic an birefringent substances in Pol contrast
  - ✓ Objects whose structures are based on changes of the refractive index in darkfield

- ❑ Brightness contrast arises from different degrees of absorption at different points in the specimen.
- ❑ Color contrast can also arise from absorption when the degree of absorption depends on the wavelength and varies from point to point in the specimen.
- ❑ Phase contrast arises from a shift in the phase of the light as a result of interaction with the specimen.
- ❑ Polarization-dependent phase contrast arises when the phase shift depends on the plane of polarization of the incident light.
- ❑ Fluorescence contrast arises when the incident light is absorbed and partially reemitted at a different wavelength.

BRIGHT FIELD & DARK FIELD IMAGING

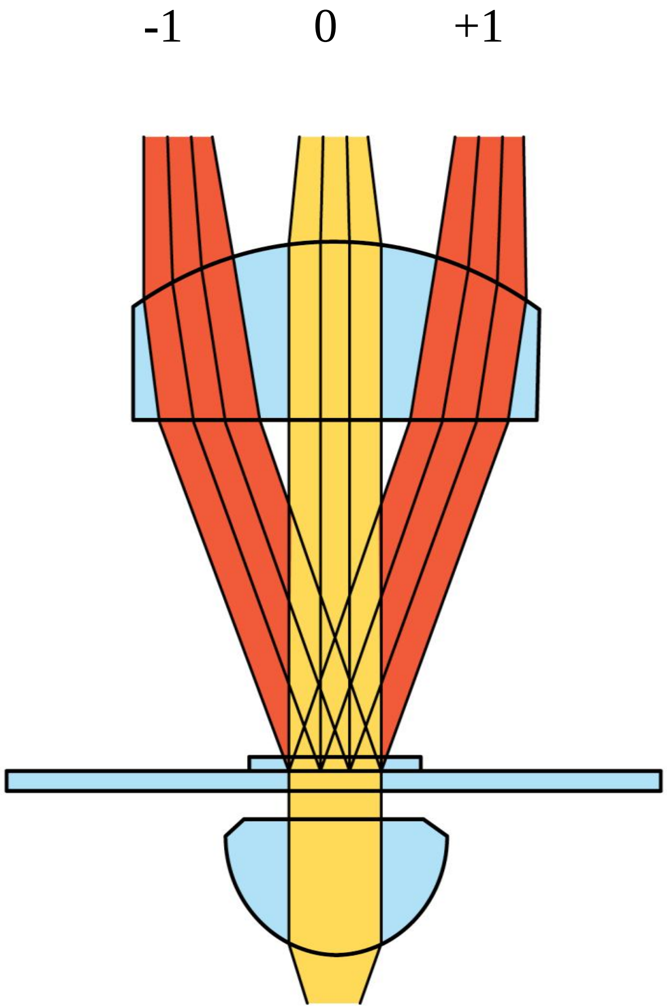
Bright field

Dark field



Bright field

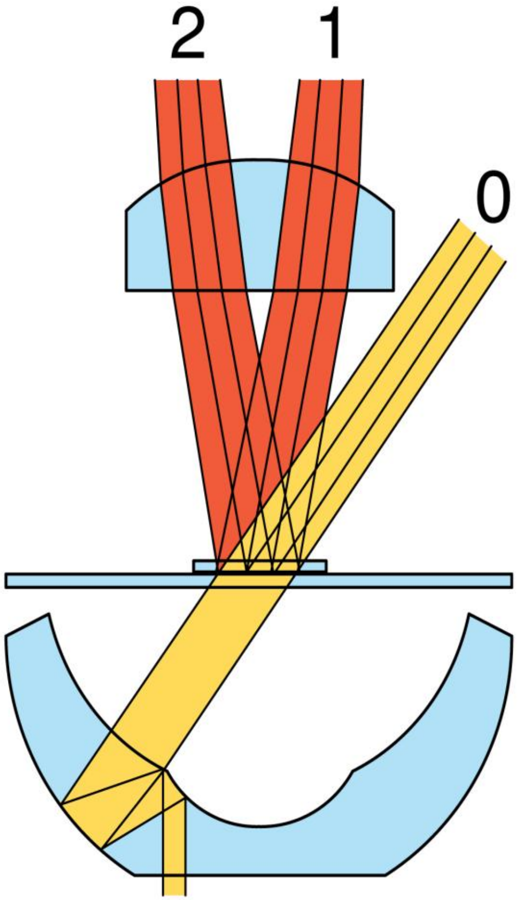
- ☐ The direct light reaches the objective
- ☐ Diffraction, refraction and absorption of light forms the microscopic image
- ☐ Brightness, resolution, contrast and depth of field are the quality-parameters of the image
- ☐ Surfaces of the sample that are perpendicular to the incident light appear bright
- ☐ Surfaces oblique to the incident light reflect less light back into the objective and appear darker
- ☐ The natural colors of materials can also be observed in this mode



The 1st, 2nd ... order are produced by diffraction. Together with the direct 0^{th} order light they form the microscopic image.

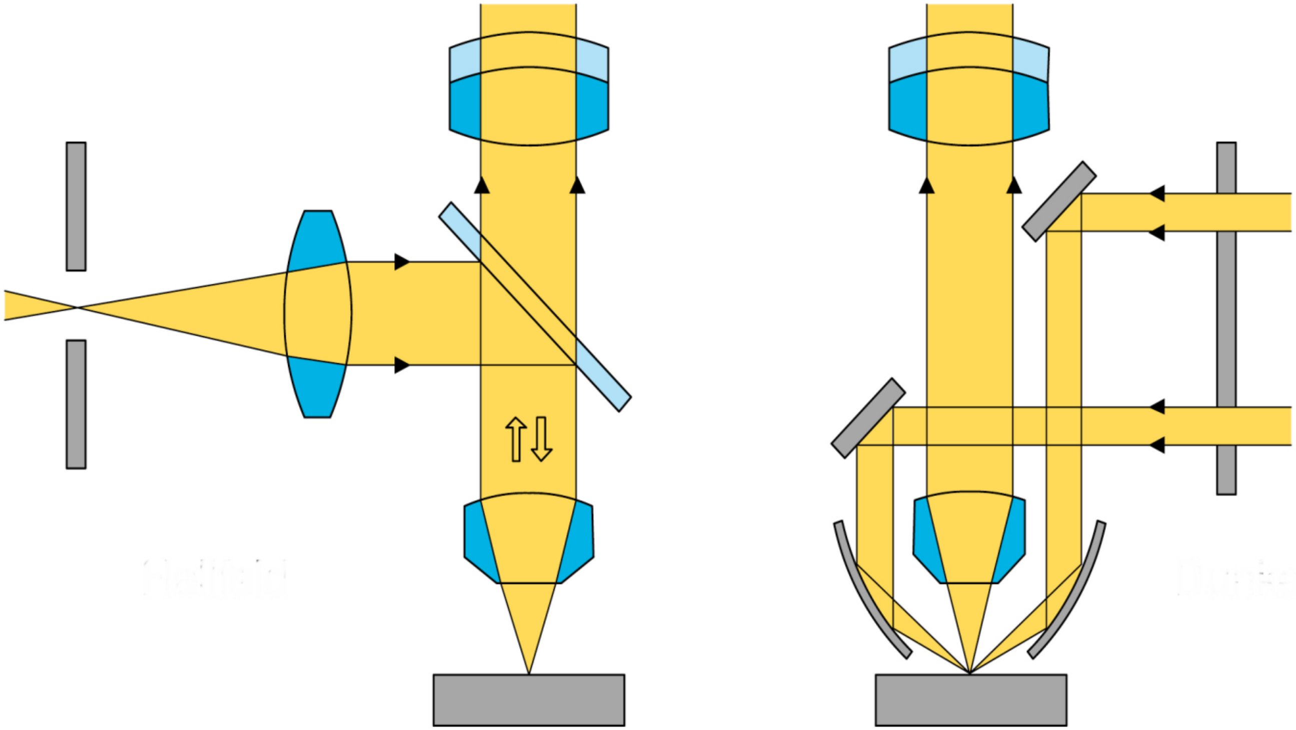
Dark field

- Direct light doesn't reach the objective
- only the diffracted light forms the image.
- well suited for all kinds of line-structures (edges, cracks etc.) and objects whose structures are based on changes of refractive index.
- We see the edges brightly against a dark background
- Detection of particles which are smaller than the resolving power



The 0th order no longer reaches the objective. Only the diffracted light is used for image formation.

Brightfield & Darkfield imaging in a reflected light microscope

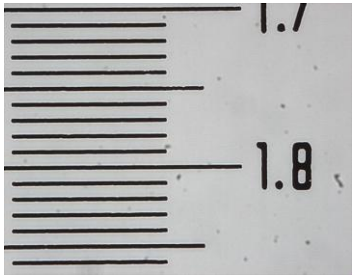


central stop

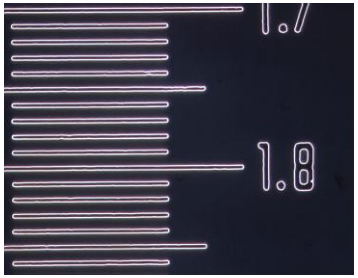
light source

DF-Objective

Brightfield

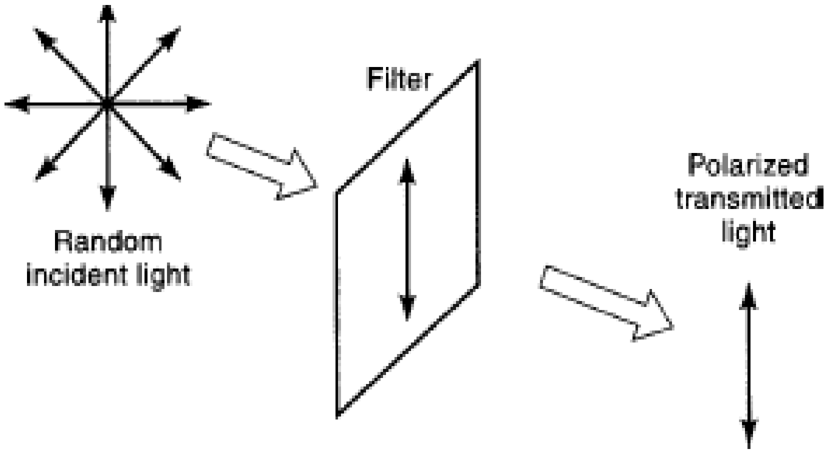


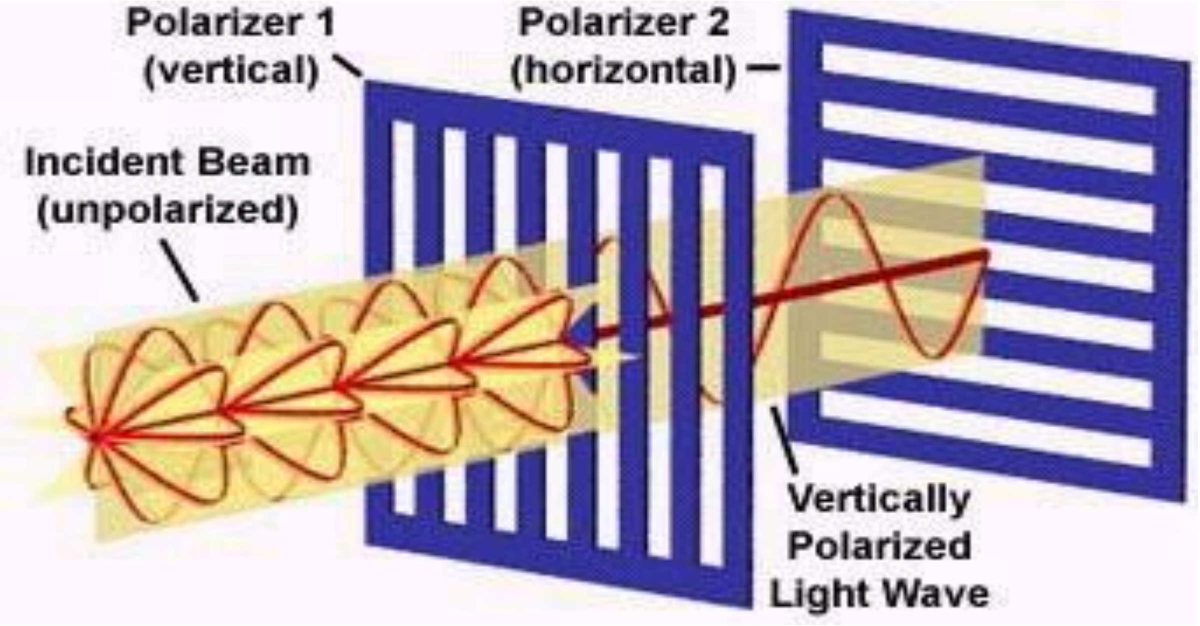
Darkfield



Linear Polarization

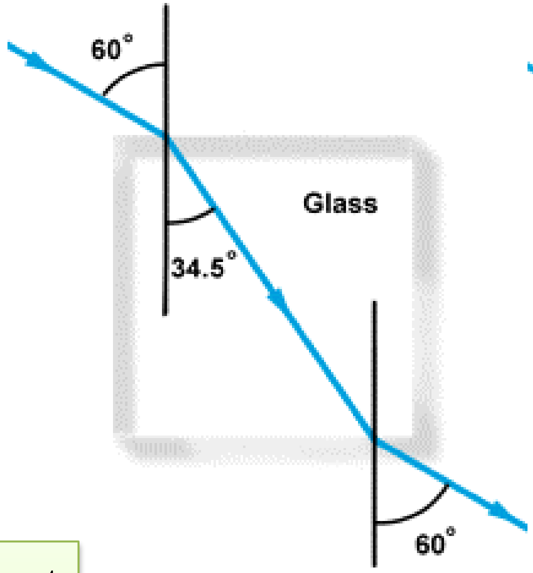
- ❑ Electro-magnetic waves vibrate in certain planes.
- ❑ Light which contains only rays of the same vibration direction is called linearly polarized light.
- ❑ Without aid, the human eye is not able to distinguish between polarized and natural light.

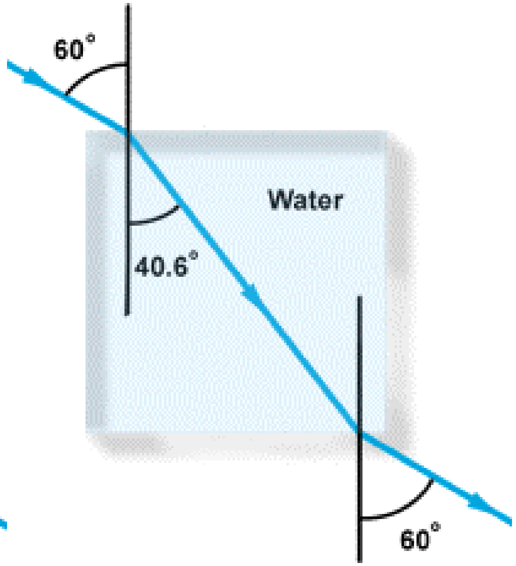




Birefringent

Refractive index (n) = C/V
Where, C =light speed
V =velocity of light in the medium

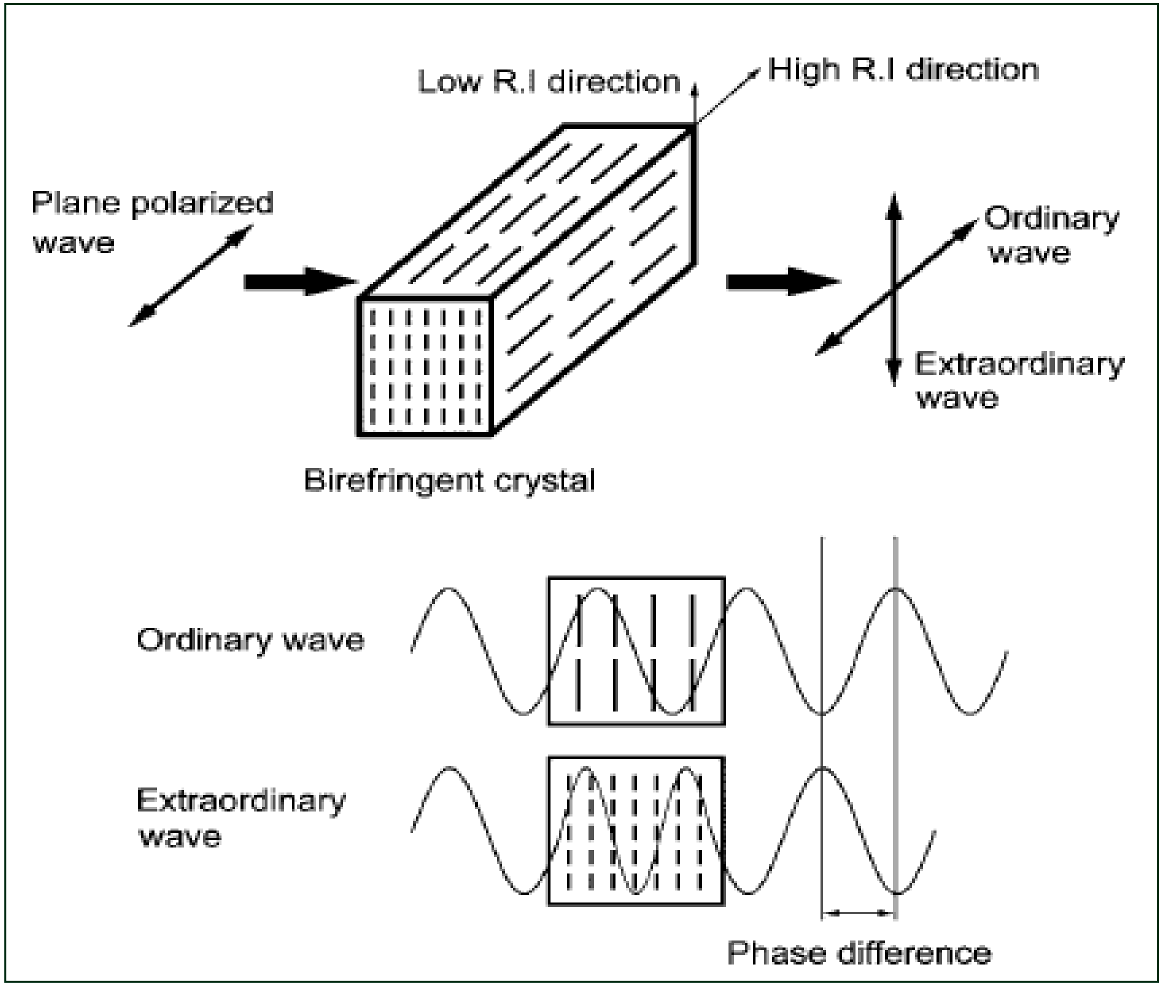


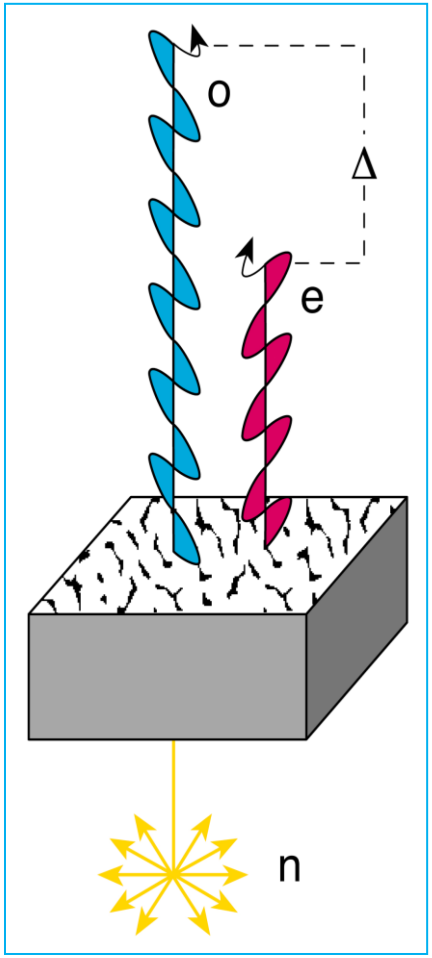


- Birefringent substances are transparent crystals exhibiting optical anisotropy (Shows Double Refraction)
- Each light ray is split up into two part-rays of different velocities.
- Different refractive indices for the ordinary and the extraordinary ray.
- They vibrate perpendicularly to each other

Material	Refractive Index (n)
Air	1.0003
Water	1.33
Glycerin	1.47
Immersion Oil	1.515
Glass	1.52
Flint	1.66
Zircon	1.92
Diamond	2.42
Lead Sulfide	3.91

Birefringence

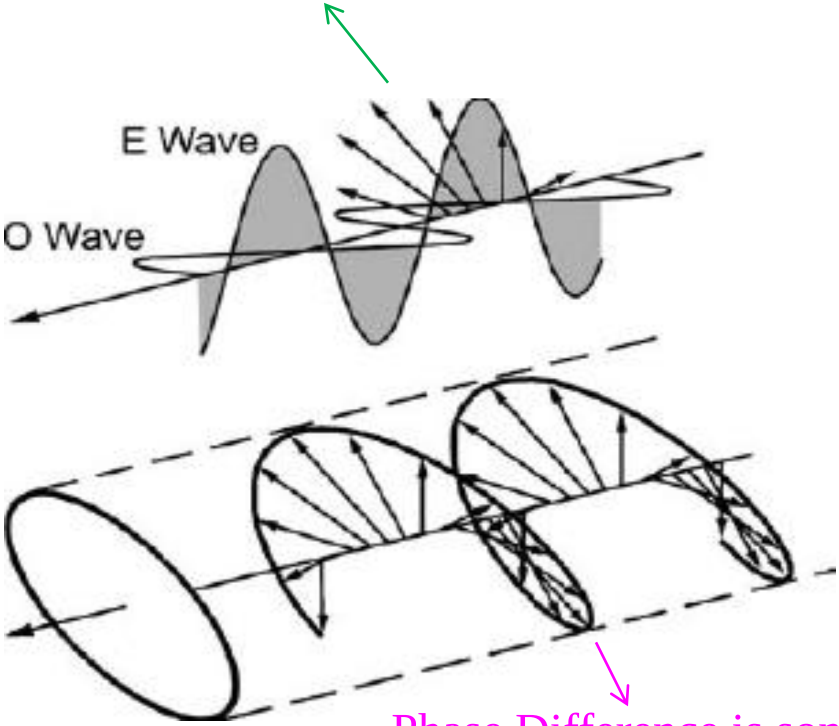




Δ: phase difference
o: Ordinary Ray
e: Extraordinary Ray

Resultant polarized light by vector addition of two plane-polarized light waves

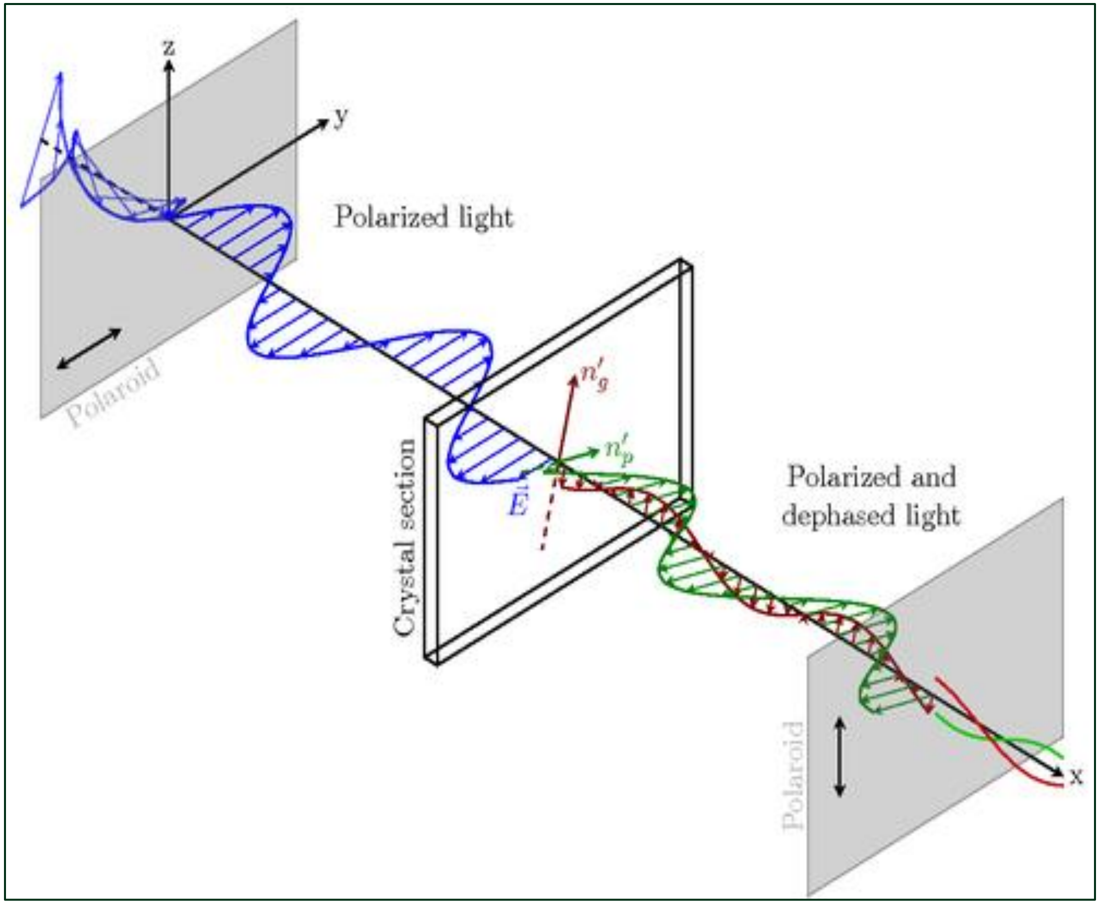
Phase Difference is λ/2



Phase Difference is some other value

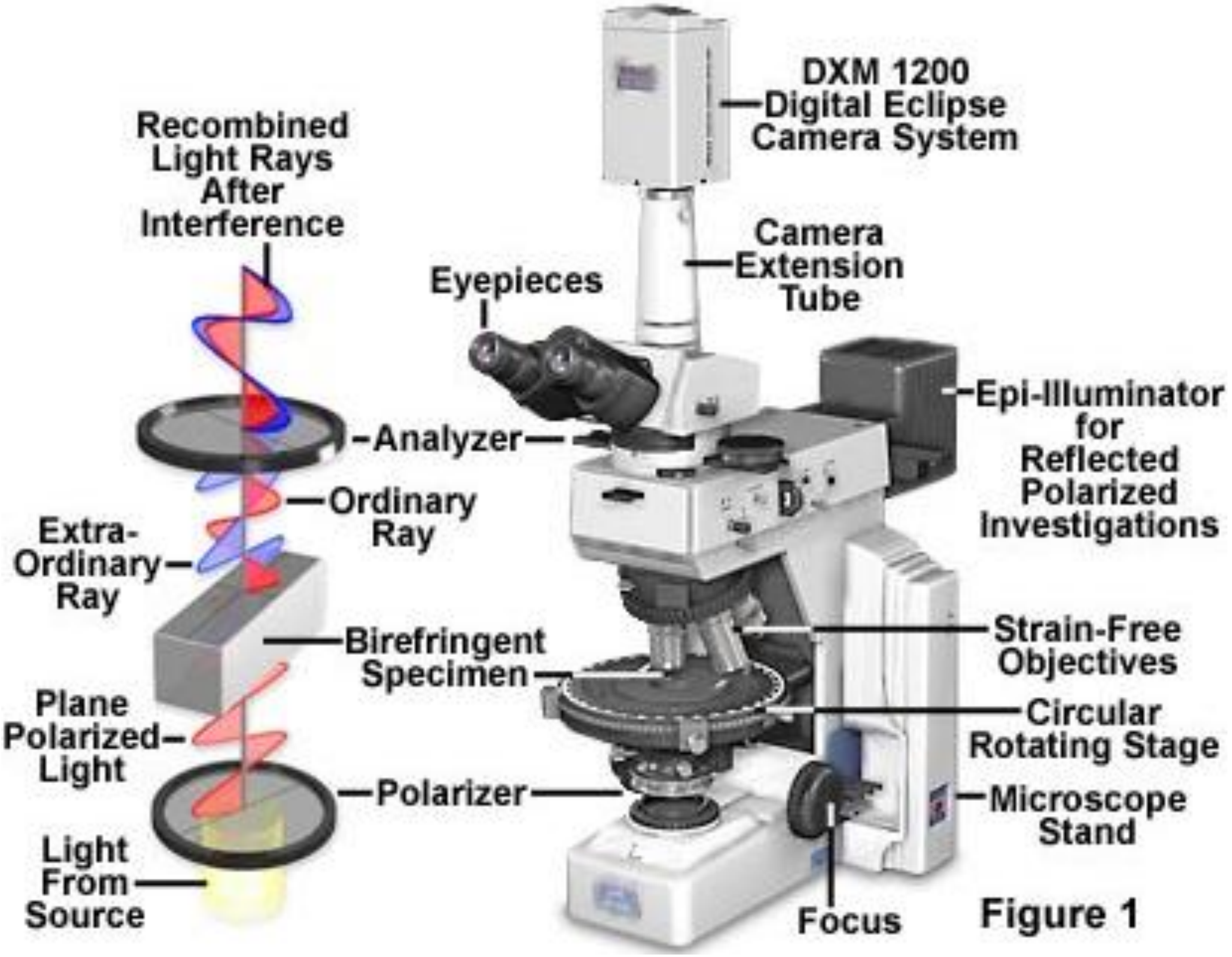
Polarized Light Microscopy

- Examines specimens which exhibit optical anisotropy (Birefringence substances)
- Crossed polarizers (Polarizer, Analyzer)
- Crossed polarizer block the passage of light
- For anisotropic material, image will be formed
- For an isotropic material, light will be extinguished after crossing analyzer



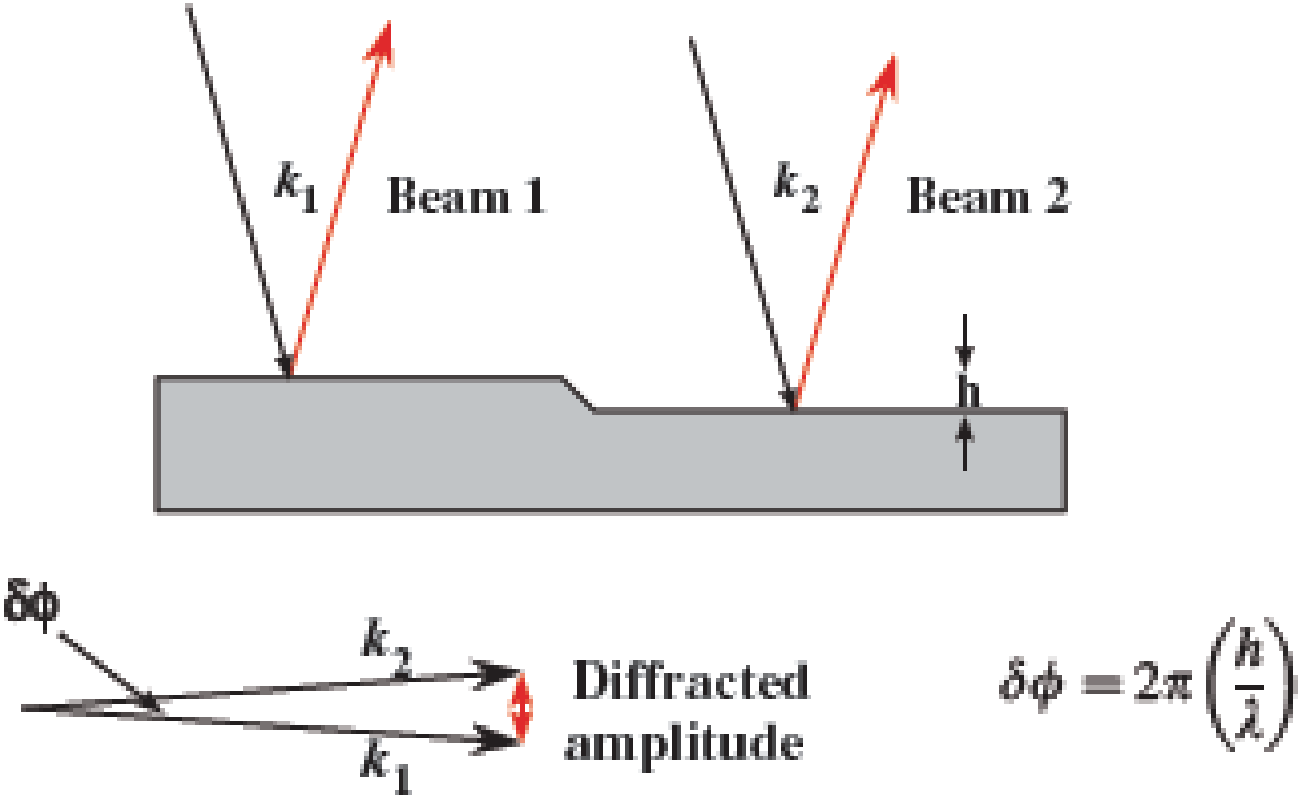
Light behaviour in a petrographic microscope with light polarizing device. Only one incident waavelength is shown (monochromatic light), the magnetic field perpendicular to the electric one is not shown

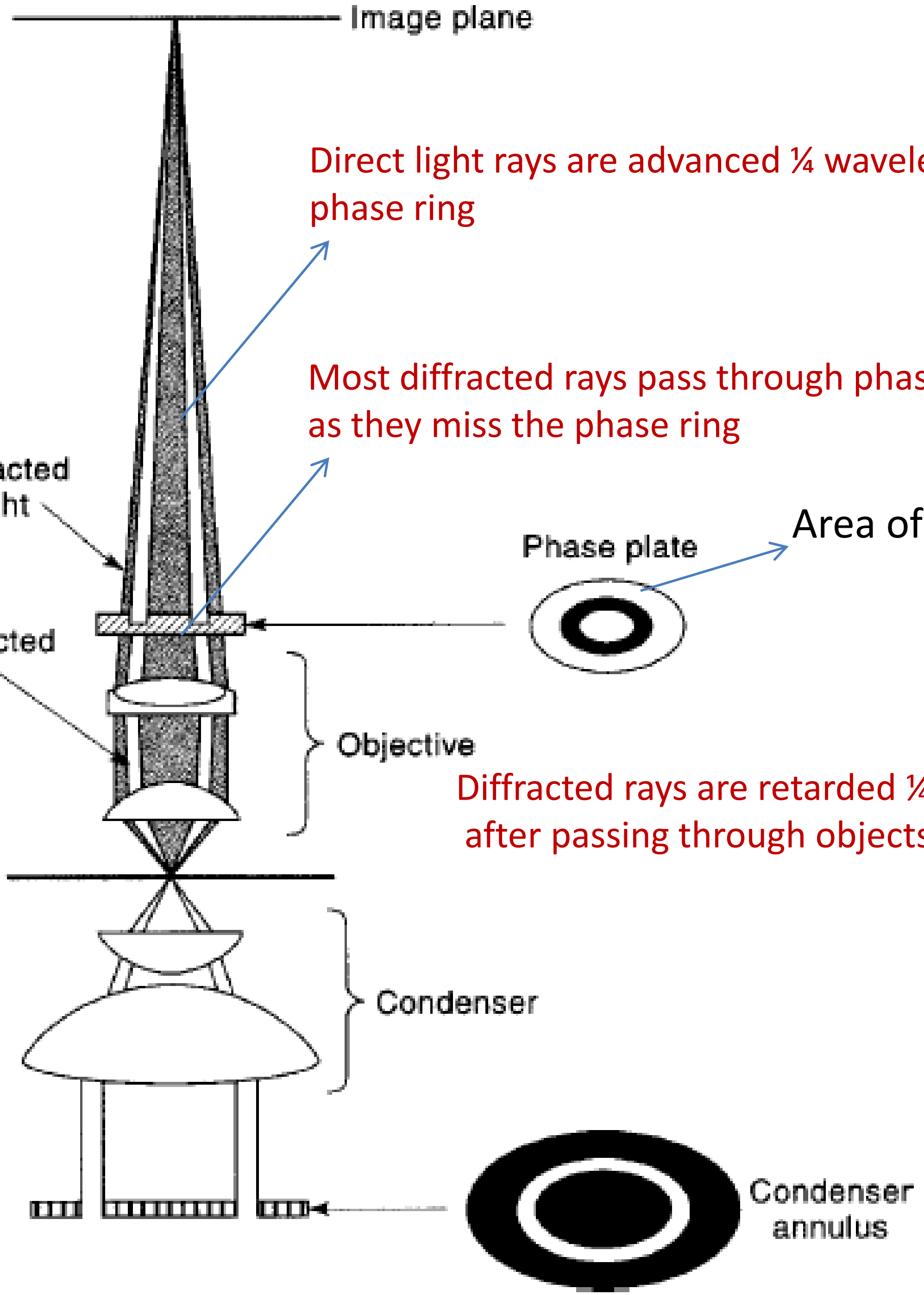
Polarized light Microscope Configuration



Phase contrast

- ❑ A sensitive method to convert phase differences into visible brightness differences (Amplitude difference)
- ❑ Mainly useful for polymers
- ❑ Special phase contrast objectives
- ❑ Illumination with annular diaphragms





Direct light rays are advanced ¼ wavelength after passing through phase ring

Most diffracted rays pass through phase plate unchanged as they miss the phase ring

Area of Reduced Thickness

Diffracted rays are retarded ¼ wavelength after passing through objects

Sample preparation for optical microscopy

Metallography:

- ✓ A systematic method to examine microstructure of materials (mainly metallic materials).
- ✓ Can also be used to examine ceramics, polymers and semiconductors.

(1) Sectioning

Why sectioning?

1. Size limitation of specimen to be examined under optical microscope.
2. Locate area needs to be selected from a large sample.

Abrasive Cutting: It is the most common sectioning method.

Electric Discharge Machining (EDM):

- ☐ Electrically conductive materials can be produced via EDM.
- ☐ Cutting is accomplished by an electric discharge between an electrode and the sample submerged in a dielectric fluid.

Microtomy:

- ☐ Useful for preparing soft materials such as polymer samples.
- ☐ Steel, glass or diamond knives in a microtome can cut samples into very thin sections.

(2) Mounting

Required when

(1) the sample is small or too oddly shaped to be handled.

(2) The sample edge area needs to be examined

Thermal Mounting:

The sample is encased in thermosetting or thermoplastic polymers at high temperature and pressure

Cold Mounting:

The sample is encased in epoxy type materials. Type of epoxy depends upon material being analyzed.

Adhesive Mounting: The sample is glued to a piece of a large holder

Clamp Mounting: The sample is fixed in mechanical clamping devices

(2) Grinding

- ❑ Removes the damage from the surface produced by sectioning.
- ❑ Grinding also produces damage which must be minimized by subsequent grinding with finer abrasives.
- ❑ At the end of grinding phase, the only grinding damage present must be from the last grinding step.
- ❑ Such damage will be removed by polishing.

Grinding Materials: Abrasive paper (covered with silicon carbide grit).

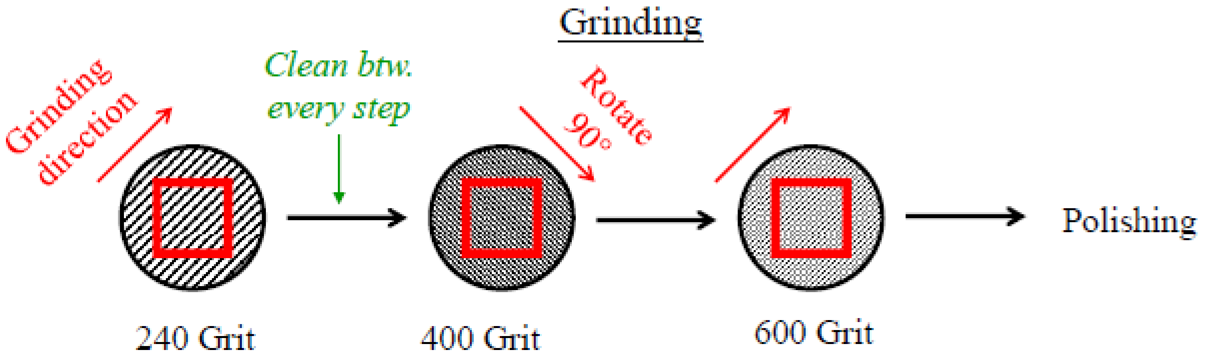
Commonly a series of abrasive papers are used from coarse to fine.

Typical Grit Sequence: 120-, 240-, 320-, 400-, 600-, 1200-, 2400-, etc.

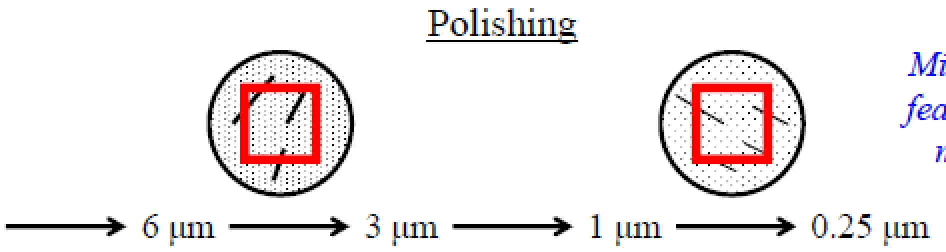
- ❑ The initial grit size depends on the surface roughness and depth of damage from sectioning.
- ❑ Surfaces cut with abrasive cutoff saws generally start with 120- to 240- grit surface finishes.
- ❑ Surfaces cut by EDM or diamond saws generally start with 320- to 400- grit surface finishes.

(4) Polishing

- After being ground to a 600-grit finish (or better), the sample is polished to produce a flat and scratch-free surface with high reflectivity.
- **Coarse polishing:** abrasives in the range of 30 µm to ~3 µm using diamond grits of the appropriate size.
- **Fine polishing:** abrasives in the range of 1µm or less using diamond grits of the appropriate size.
- **Final polishing:** 0.25-0.05 µm diamond, silica, or alumina slurries.



Check under LOM after each step

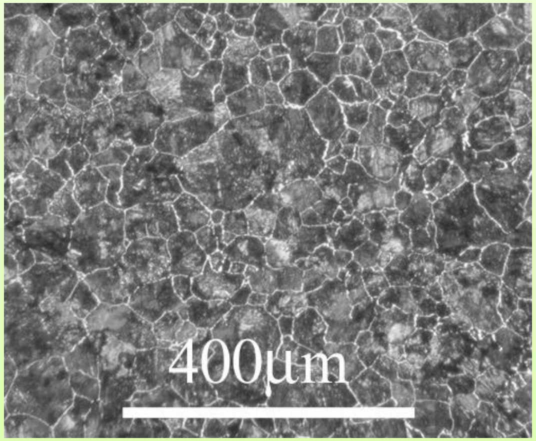


Microstructural features become more visible

(4) Etching

- Using chemicals to selectively dissolve the surface of a material in order to reveal microstructural details
- Grain boundaries are more susceptible to etching.
- May be revealed as dark lines.
- Due to change in crystal orientation across GB.

- Etching is basically a controlled corrosion process. Results from electrolytic action between surface areas of different potential.
- Electrolytic activity results from local physical or chemical heterogeneities which render some features anodic and others cathodic under the specific etching conditions.
- Chemical Etchants produce contrast by
  - – Crystal faceting
  - – Selective phase dissolution.
- Common chemical etchants have three components:
  - – A corrosive agent (acids)
  - – modifier (alcohol, glycerin…)
  - – An oxidizer (hydrogen peroxide, Fe3+, Cu2+…)



Reflected light micrographs of Fe-1.0%C steel

Scanning Electron Microscopy

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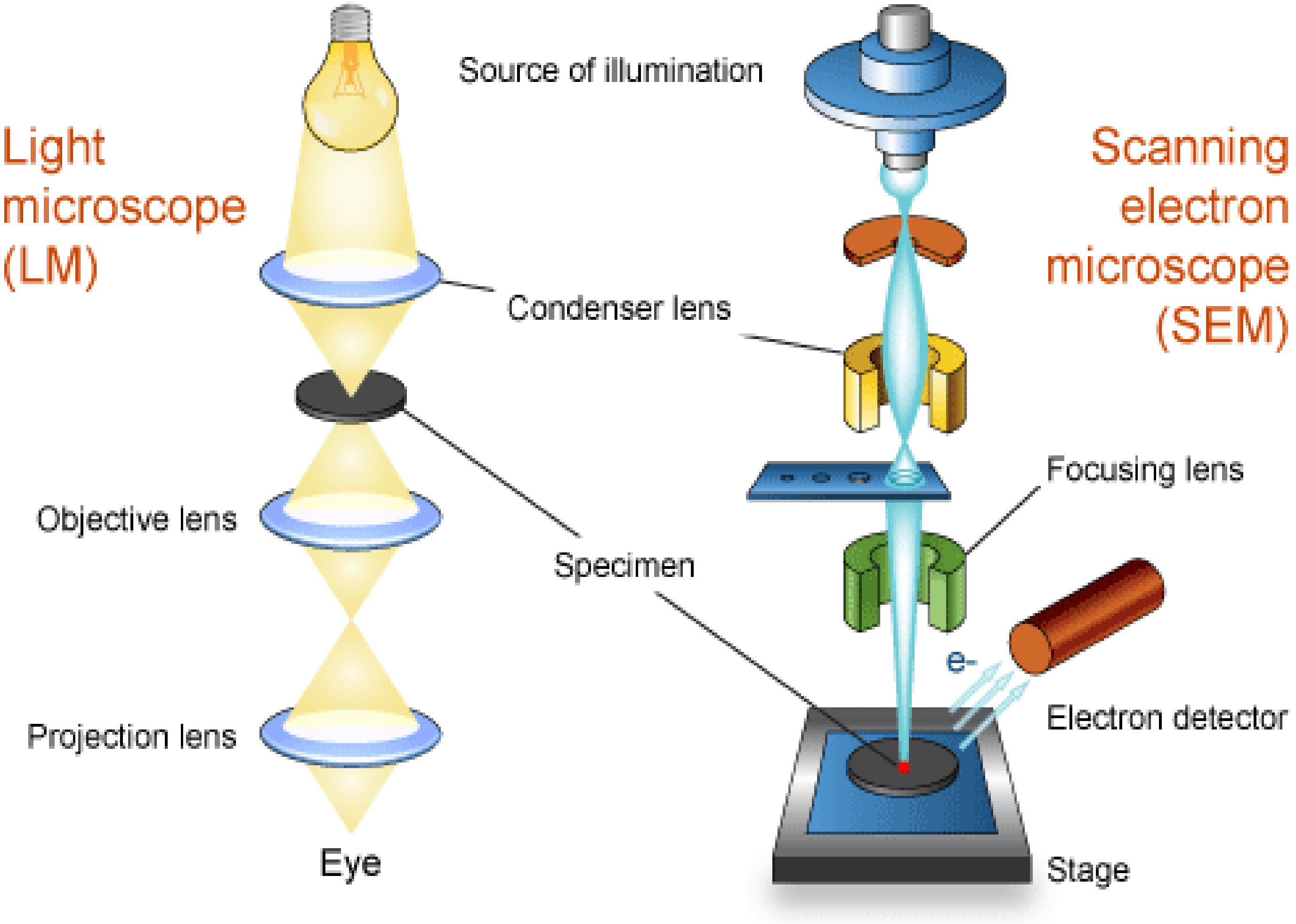
Salient features of Scanning Electron Microscopy

- ☐ Electrons are used to create images of the surface of specimen topology
- ☐ Resolution of objects of nearly 1 nm
- ☐ Magnification upto 500000X (250 times > light microscopes)
- ☐ secondary electrons (SE), backscattered electrons (BSE) are utilized for imaging
- ☐ specimens can be observed in high vacuum, low vacuum and in Environmental SEM specimens can be observed in wet condition.
- ☐ Gives 3D views of the exteriors of the objects like cells, microbes or surfaces

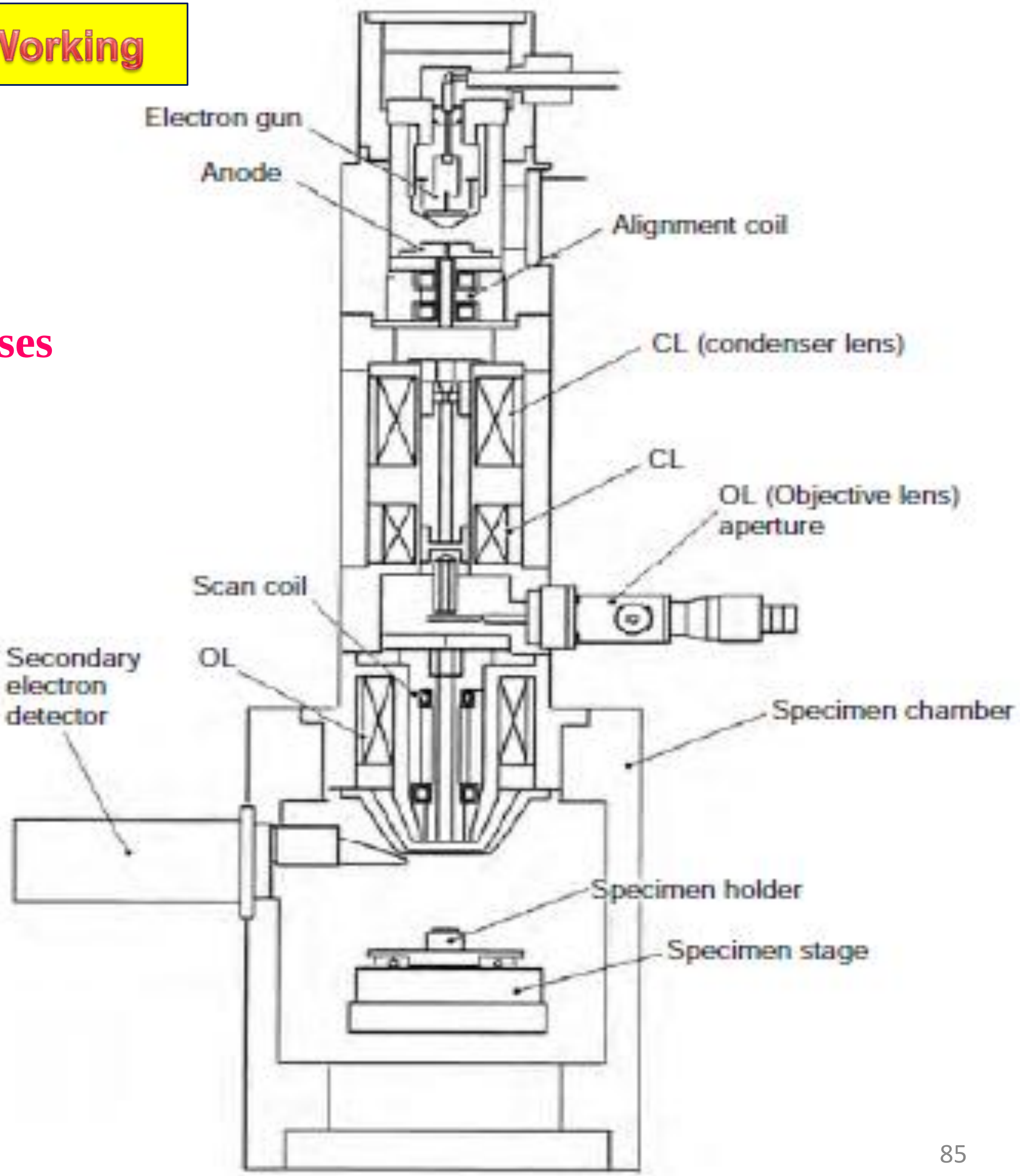
Light Microscope VS Scanning Electron Microscope



	Optical	SEM
Illumination	Light Beam	Electron Beam
Wave Length	2000-7000 Å	0.05Å
Lens	Optical lenses for magnification	Electrostatic lens for demag crossover and electromagnetic lens for magnification
Magnification	10X-20X	10X-2,00,000X
Depth of Focus	1 microns	30 µm at 1000X
Resolution	Visible region on 2000Å	50Å
Focusing	Mechanical	Electrical
Obtainable image	Transmitted and Reflected	Several
Contrast	Color and brightness controlled	Shape and chemical property controlled

SEM Construction & Working

- Electron source
- Electromagnetic Lenses
- Deflection coils
- Scanners
- Electron detectors



Electron Source

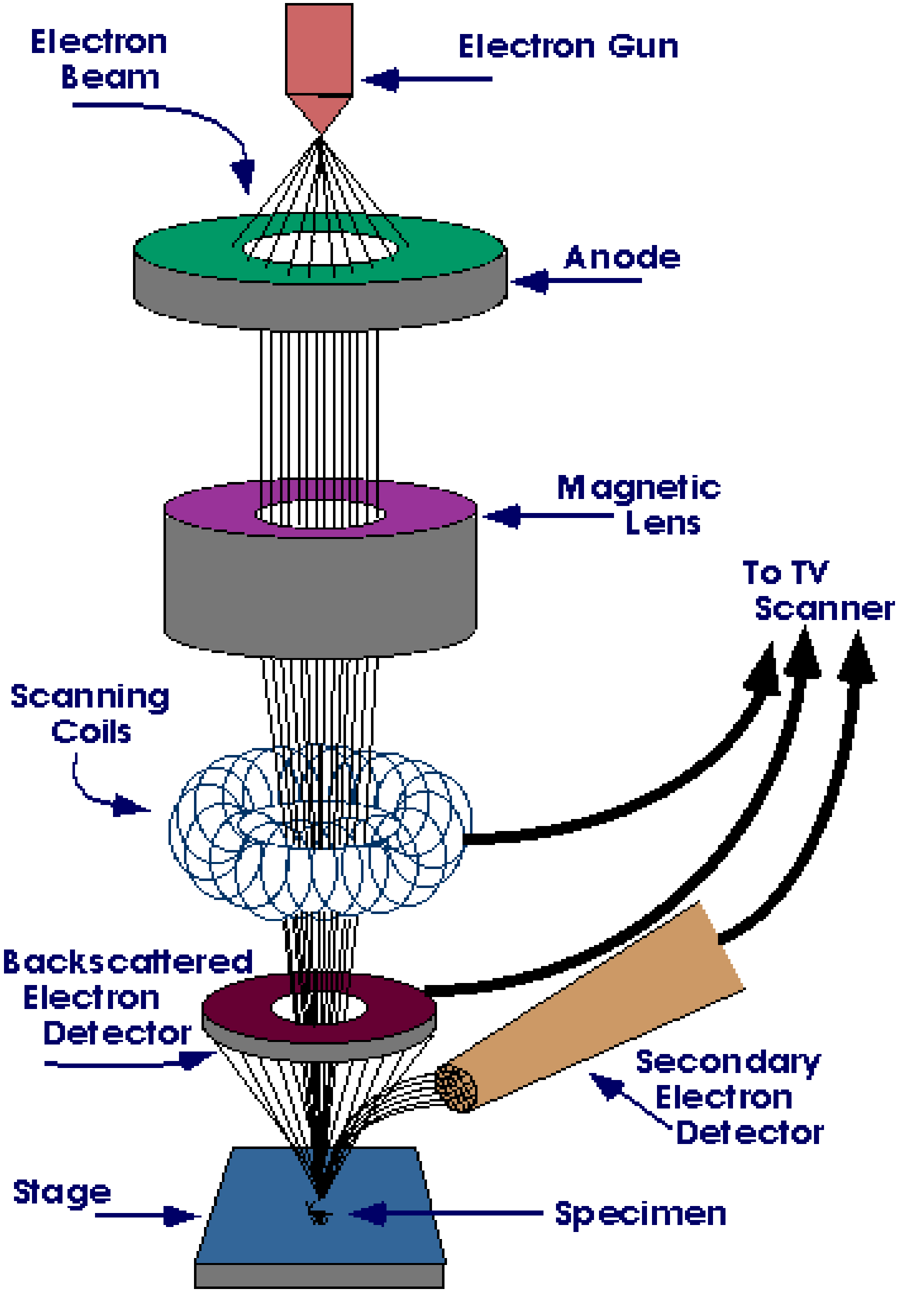
We want many electrons per time unit per area (high current density) and as small electron spot as possible.

Traditional guns: Thermionic electron gun (electrons are emitted when a solid is heated)

- W-wire, LaB6-crystal

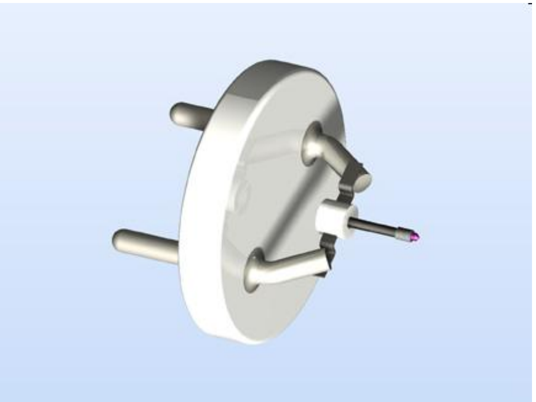
Modern: Field emission guns (FEG) (cold guns, a strong electric field is used to extract electrons)

- Single crystal of W, etched to a thin tip

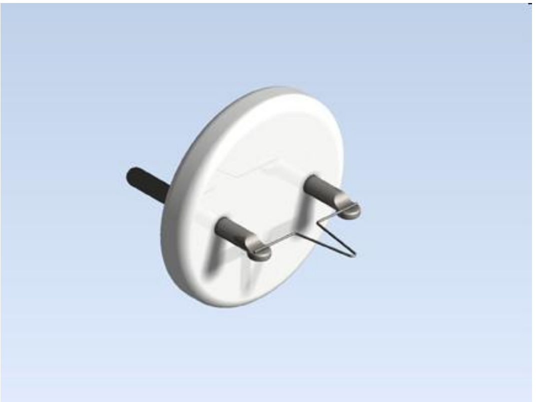


Thermionic Electron Gun

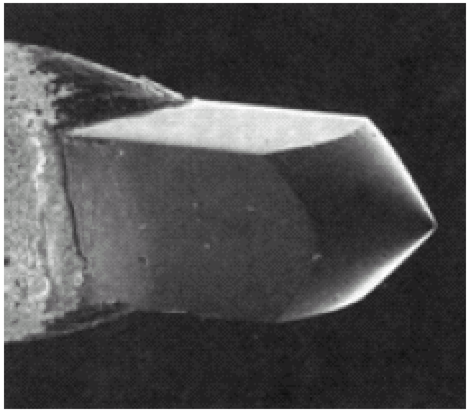
- Commonly used electron source
- Cheap and does not require relatively high vacuum
- Electrons are emitted from a heated tungsten filament / LaB6 and then accelerated towards an anode; a divergent beam of electrons emerges from the anode hole



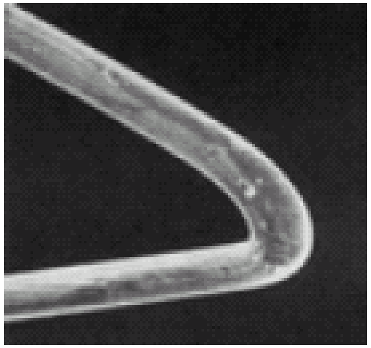
Single crystal of LaB_6



Tungsten wire



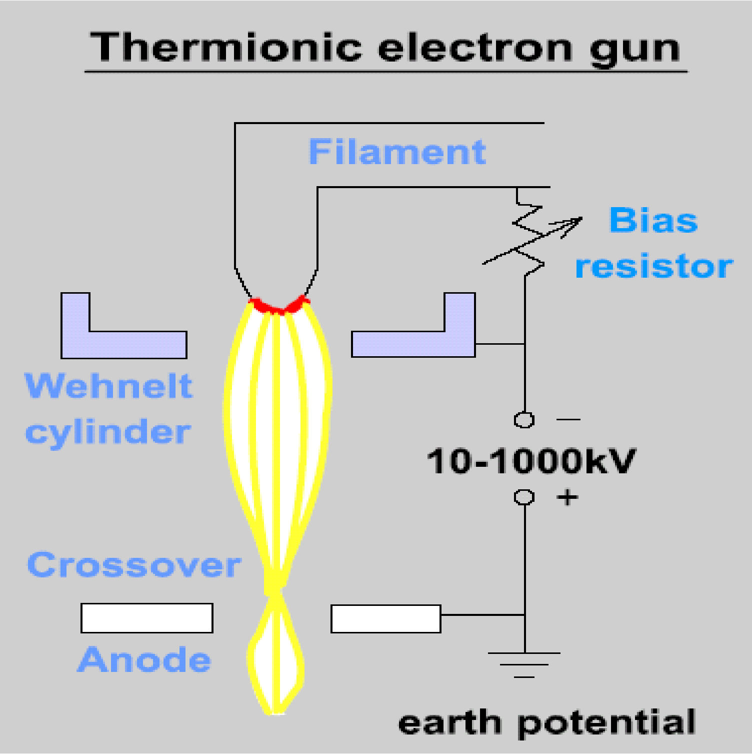
LaB_6



W

Functioning of Thermionic Electron Gun

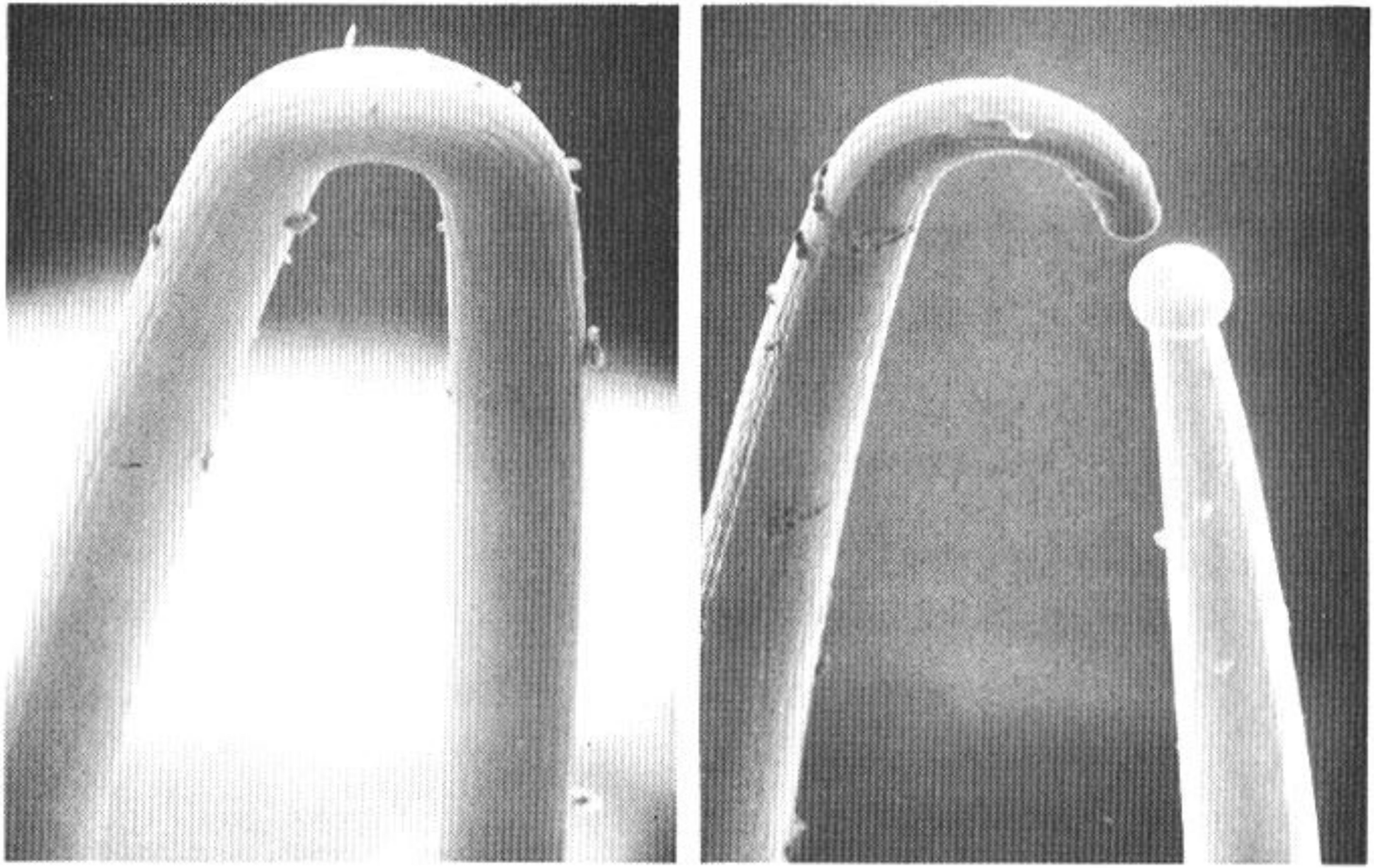
- ❑ An positive electrical potential is applied to the anode.
- ❑ The filament (cathode) is heated until a stream of electrons is produced .
- ❑ A negative electrical potential (~500 V) is applied to the Whenelt Cap.
- ❑ A collection of electrons occurs in the space between the filament tip and Whenelt Cap. This collection is called a space charge.
- ❑ Those electrons at the bottom of the space charge (nearest to the anode) can exit the gun area through the small (<1 mm) hole in the Whenelt Cap .
- ❑ These electrons then move down the column to be later used in imaging



Spot Size:

30 µm for W

5 µm for LaB_6



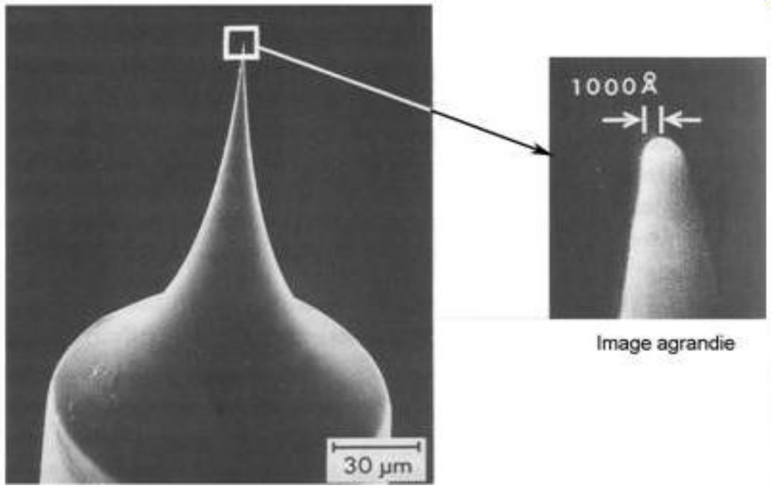
(a) (b)

Scanning electron micrograph of W filament: (a) unused, (b) failed

Field Emission Gun (FEG)

- In recent years cold field-emission and thermally-assisted field emission guns have become increasingly common.
- FEG requires a different gun design as well as much better vacuum in the gun area (~10e-8 Pa instead of the ~10e-5 Pa)
- With field emission guns we get a smaller spot and higher current densities compared to thermionic guns
- In these a very fine point on the pointed filament is formed.
- Electrons are emitted by tunnelling through the potential barrier at the tip surface when a very high potential field gradient is formed at the surface.

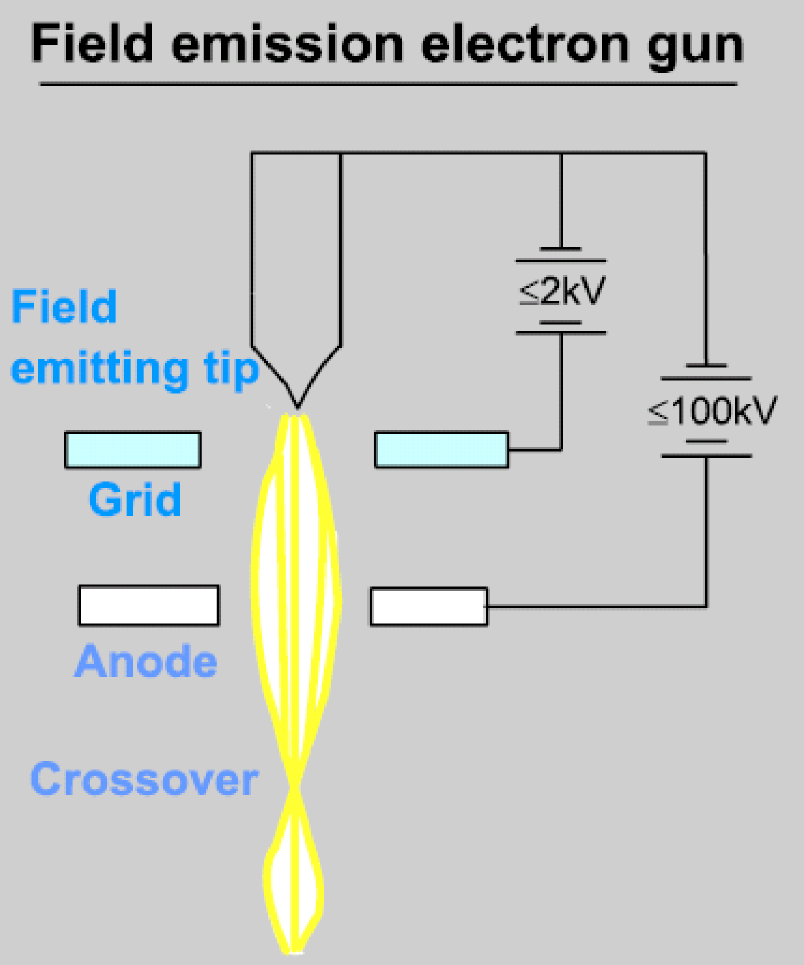
A simple tungsten tip can be very sensitive to surface contamination. More than any other cathode design, the field emission tip is extremely sensitive to the size, shape and surface condition

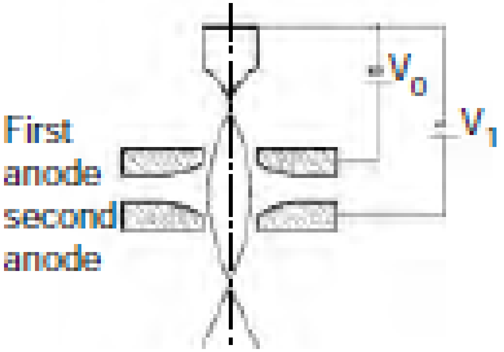


Field Emission Tip

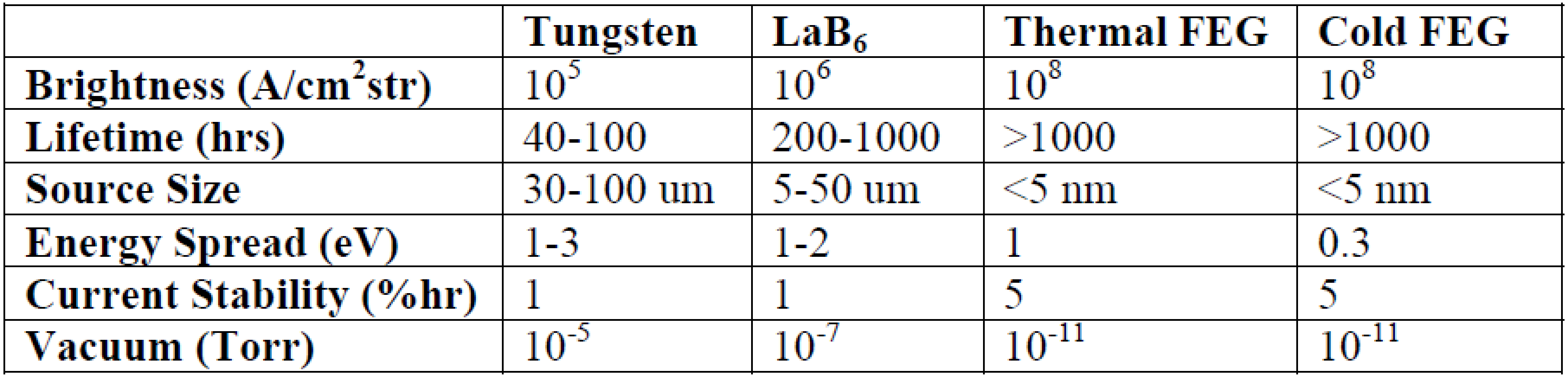
Functioning of the Field Emission Gun

- ❑ Consists of a small single-crystal tungsten needle that is put in a strong extraction voltage (2-5 kV).
- ❑ In the case of a cold FEG, the needle is so sharp that electrons are extracted directly from the tip.
- ❑ In the case of a thermal FEG, the tip is heated to 2000K for few seconds to clean the adsorbed gas on tip. It also stabilizes the emission of electron beam at low vacuum





Comparision between TEG and FEG



	Tungsten	LaB_6	Thermal FEG	Cold FEG
Brightness (A/cm^{2}str)	10^5	10^6	10^8	10^8
Lifetime (hrs)	40-100	200-1000	>1000	>1000
Source Size	30-100 um	5-50 um	<5 nm	<5 nm
Energy Spread (eV)	1-3	1-2	1	0.3
Current Stability (%hr)	1	1	5	5
Vacuum (Torr)	10^{-5}	10^{-7}	10^{-11}	10^{-11}

- Electron probes of sizes down to ~ 6 nm are attainable with conventional thermionic emission sources, although smaller probes ~ 2 nm can be achieved using field emission sources

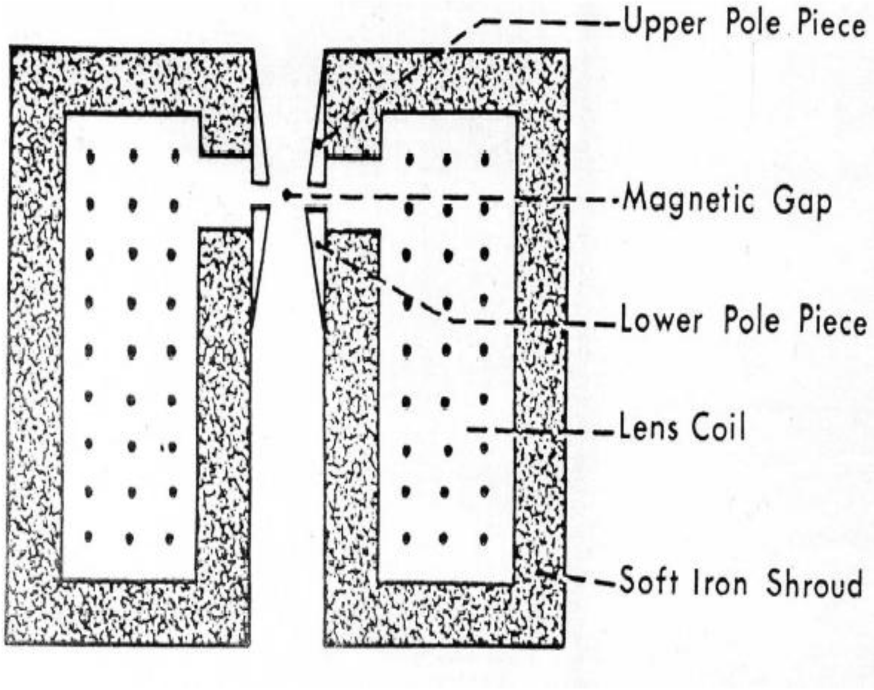
- Unlike the thermionic gun, the FEG does not produce a small cross-over directly below the emitter, but the electron trajectories seemingly originate inside the tip itself, forming a virtual source of electrons for the microscope.

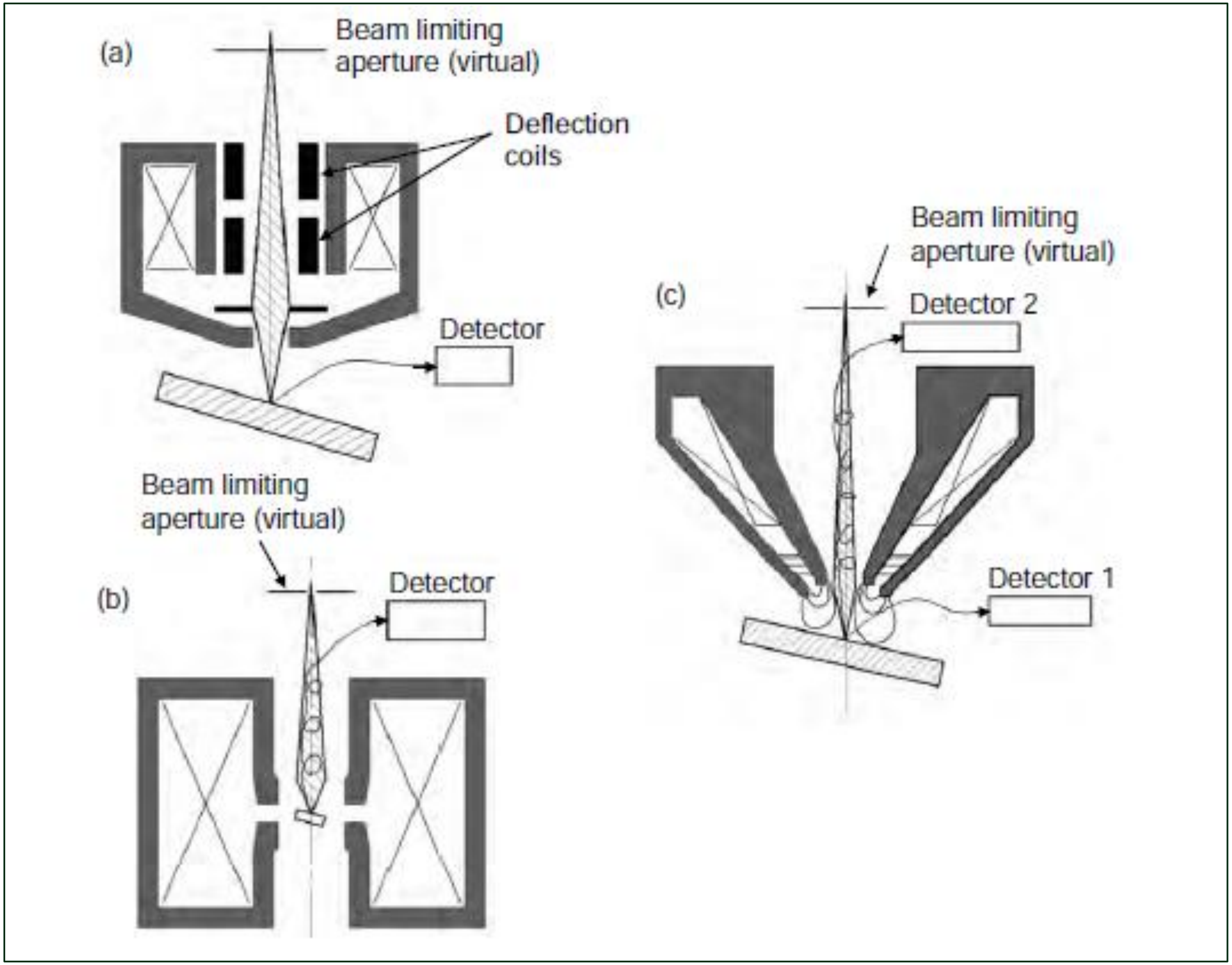
Electron Lenses

- Magnetic Lenses are used because of less aberrations and good focus.
- As electrons are deflected by the electromagnets, the trajectories of electrons can be adjusted by the current applied to the coils(electromagnets).
- Electron lenses can be used to magnify or demagnify (SEM Lenses always demagnifies) the electron beam diameter, because their strength is variable, which results in a variable focal length

Condenser Lenses

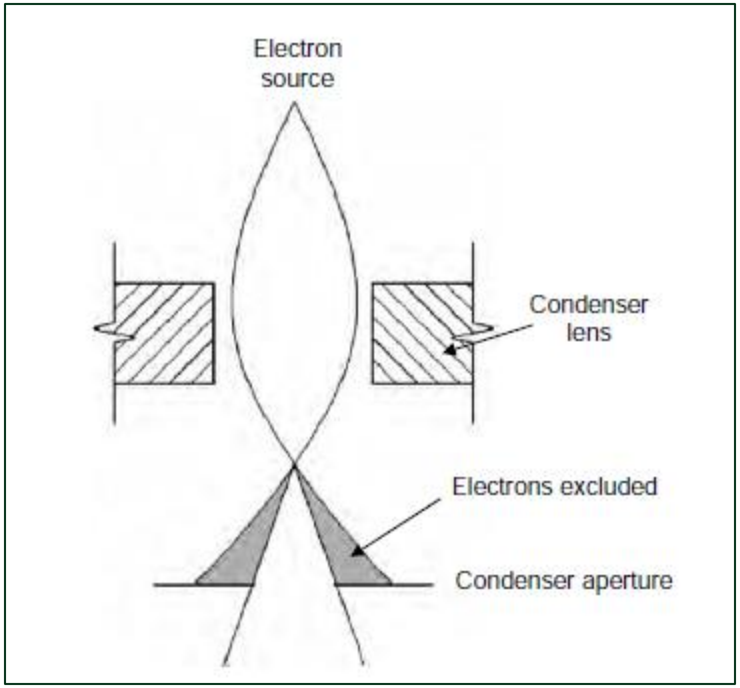
- Hole at the center of pole pieces
- Coil of several thousand turns of wire through which a current (0-1A) is passed which creates a magnetic field
- To concentrate field further a soft iron pole piece is inserted into the bore of the objective lens
- Appropriate aperture size is chosen to exclude inhomogeneous and scattered electrons
- A second condenser lens is often used to provide additional control on the electron beam

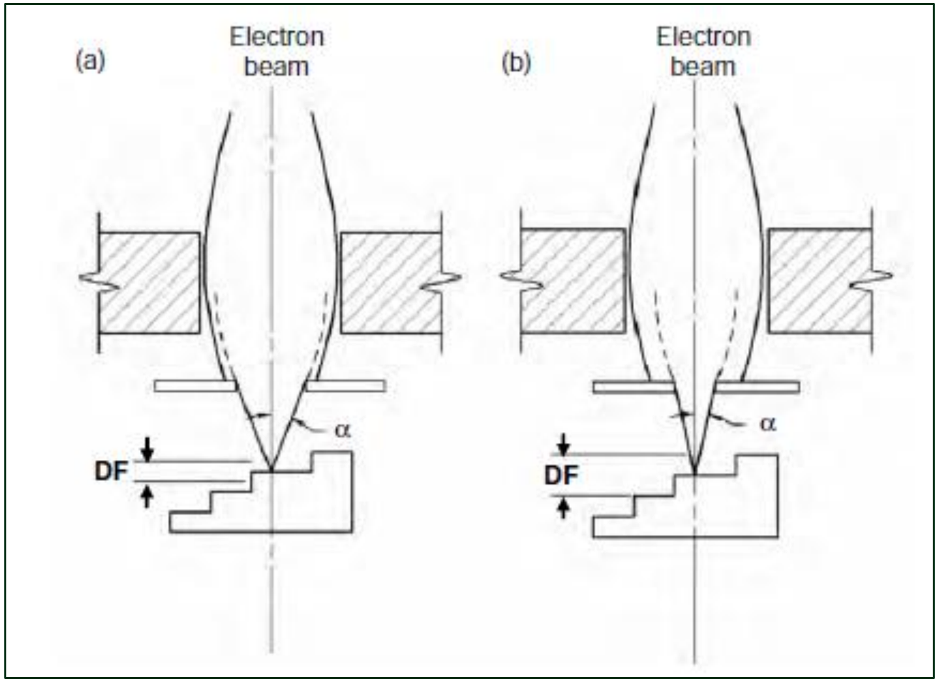




Objective lens configurations: (a) asymmetric pinhole lens, which has large lens aberration; (b) symmetric immersion lens, in which small specimen can be observed with small lens aberration; and © snorkel lens, where the magnetic field extends o the specimen providing small lens aberration on large specime

Types of Apertures used in electron microscopy





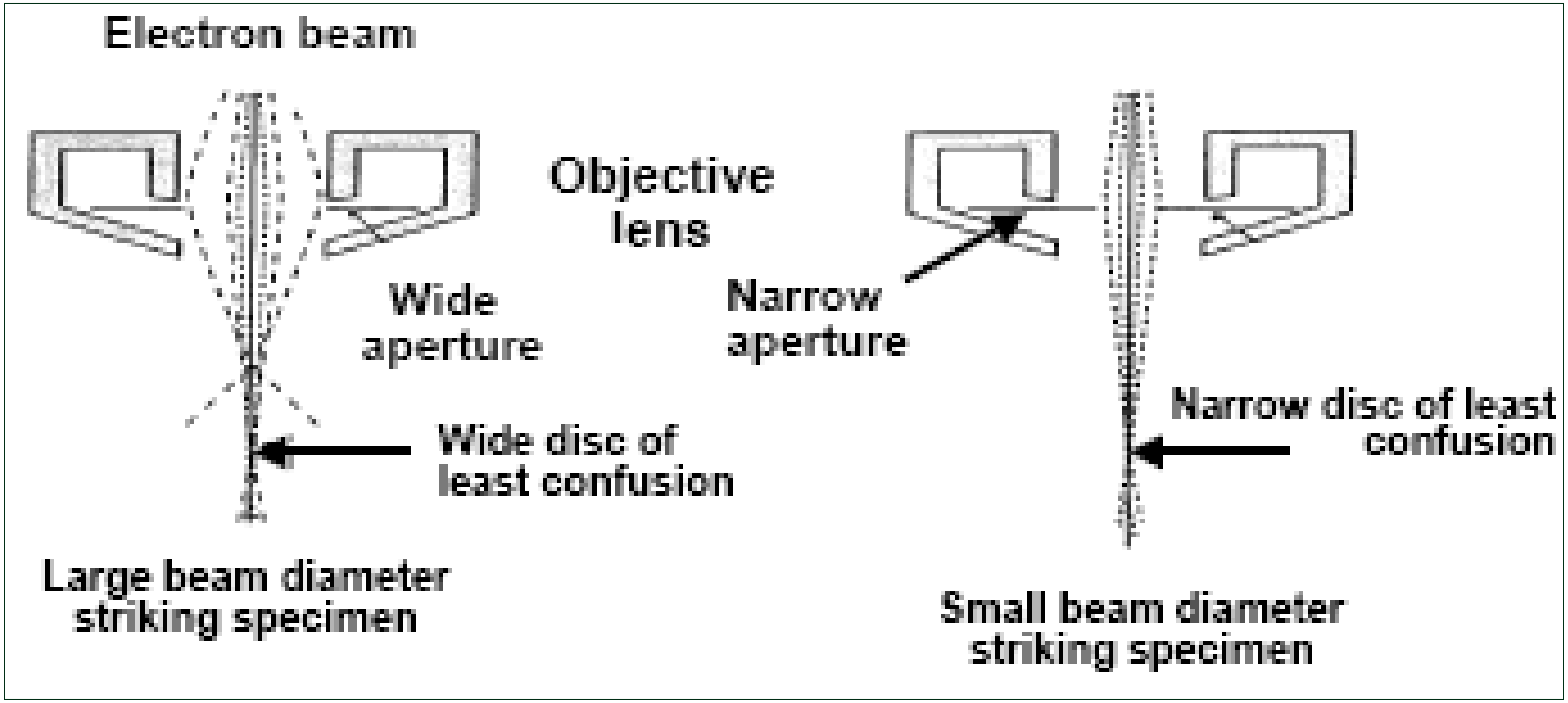
Virtual Aperture

- ✓ Reduces e-beam diameter
- ✓ Placed above the final lens
- ✓ Can be kept clean for long time as far away from specimen chamber
- ✓ Seen in modern SEM

Real Aperture

- ✓ Reshapes the beam and has the same effect as virtual
- ✓ Placed at base of objective/final lens
- ✓ Seen in conventional SEM
- ✓ Fig. (b) has more depth of field than (a)

Decreasing the aperture size will reduce the beam angle α for the same WD, resulting in an enhancement of the depth of field.



Decreasing the aperture size will result in narrow disc of least confusion

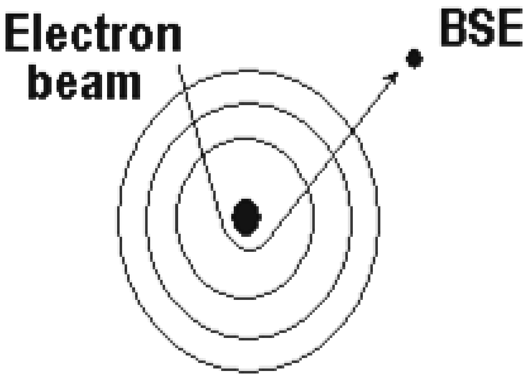
Electron Specimen Interaction

- ❑ Electrons from a source interact with electrons in specimen yielding a variety of photons and electrons via elastic and inelastic scattering processes.
- ❑ These are the “signals” that we use to make images and measure to characterize the composition of our specimens.

Elastic and inelastic scattering of electron by sample

Elastic :

- ❑ Incident electron’s direction is altered by Columbic field of nucleus (Rutherford scattering), screened by orbital electrons.
- ❑ Direction may be changed by 0-180° but velocity remains virtually constant. 80-100% of beam energy is transferred.
- ❑ Ex: Backscattering of electrons (~high energy)

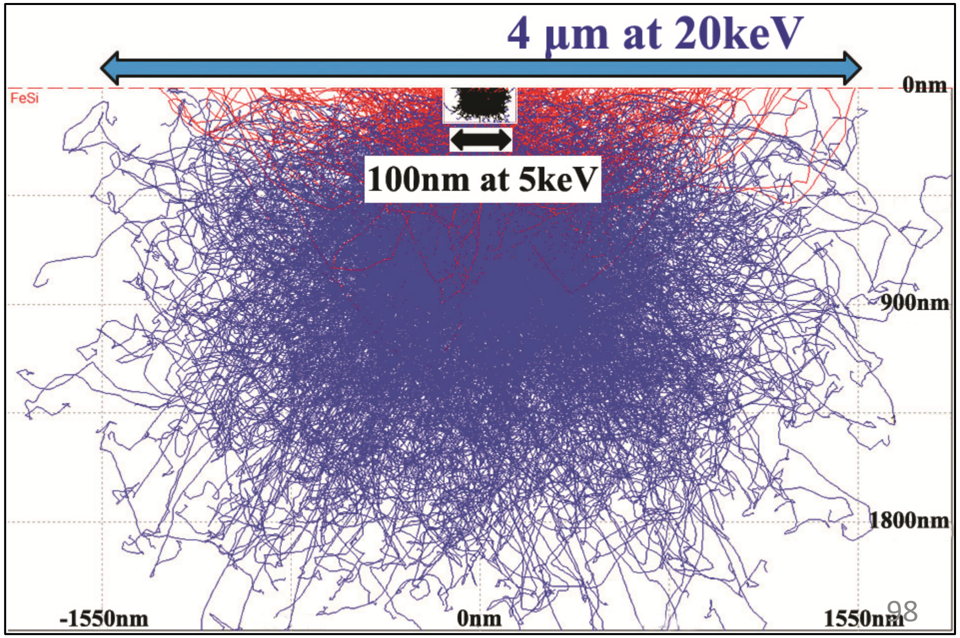


$$p(\theta) \propto \frac{1}{E_O^{\,2} \sin^4 \theta}$$

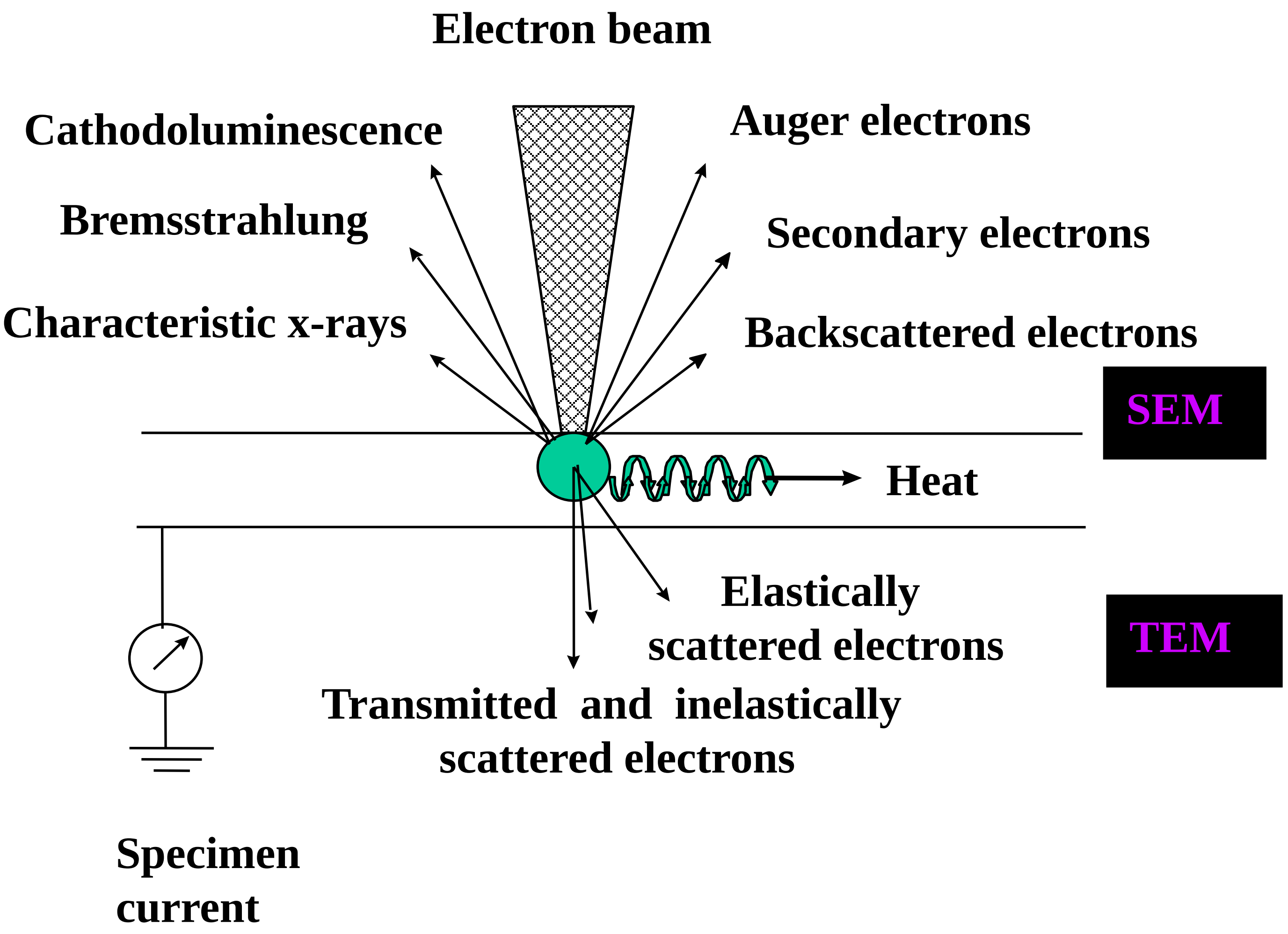
Inelastic:

- ❑ Incident electron transfers some energy (up to all, E0) to tightly bound inner-shell electrons and loosely bound outer-shell electrons
- ❑ Examples:
  - ✓ Secondary electron excitation
  - ✓ Inner-shell ionization (Auger electrons, X-rays)
  - ✓ Bremsstrahlung (continuum) X-ray generation
  - ✓ Cathodoluminescence radiation (non-metal valence shell phenomenon)
  - ✓ Photons & Plasmons

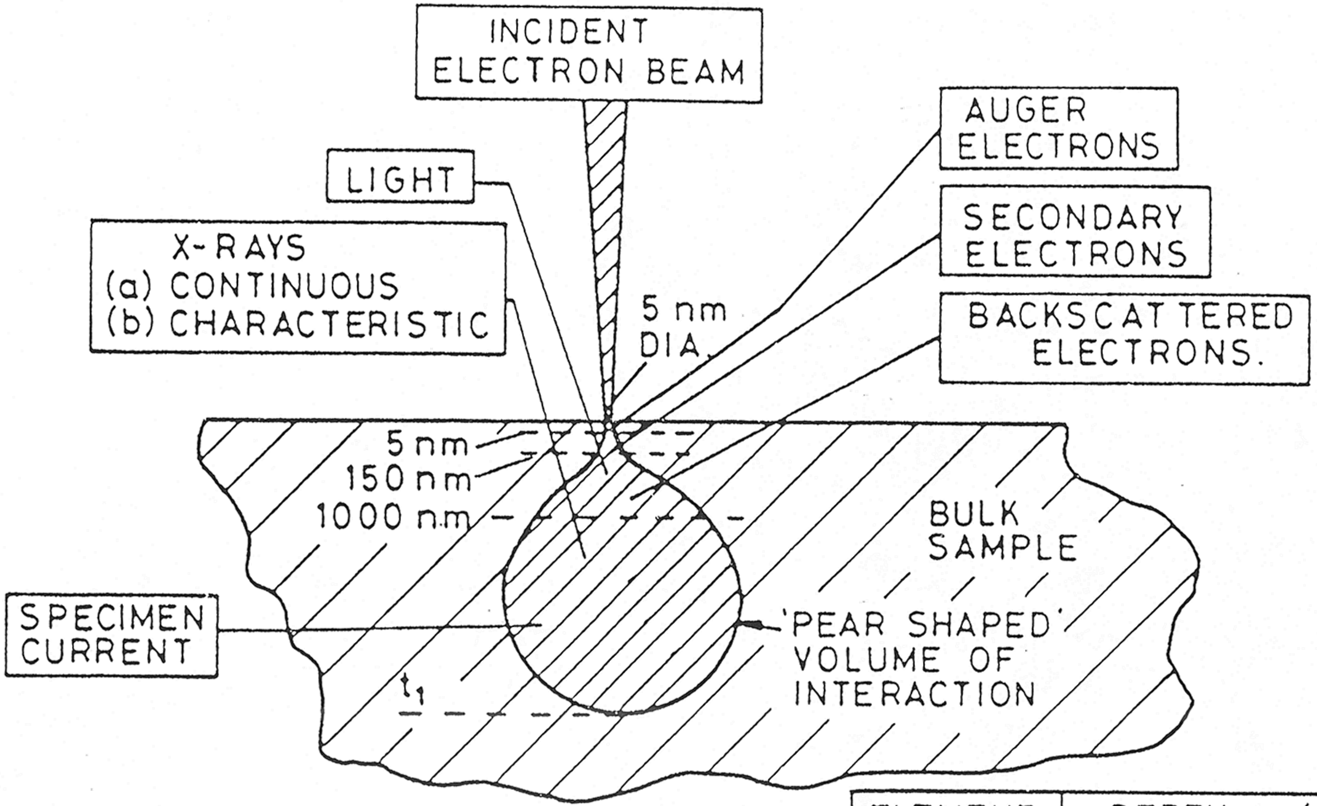
Monte Carlo simulation: Can simulate the "interaction volume" of scattered electrons for whatever kV and whatever composition material you may be interested in. (in seconds)



Specimen – Electron Beam Interaction



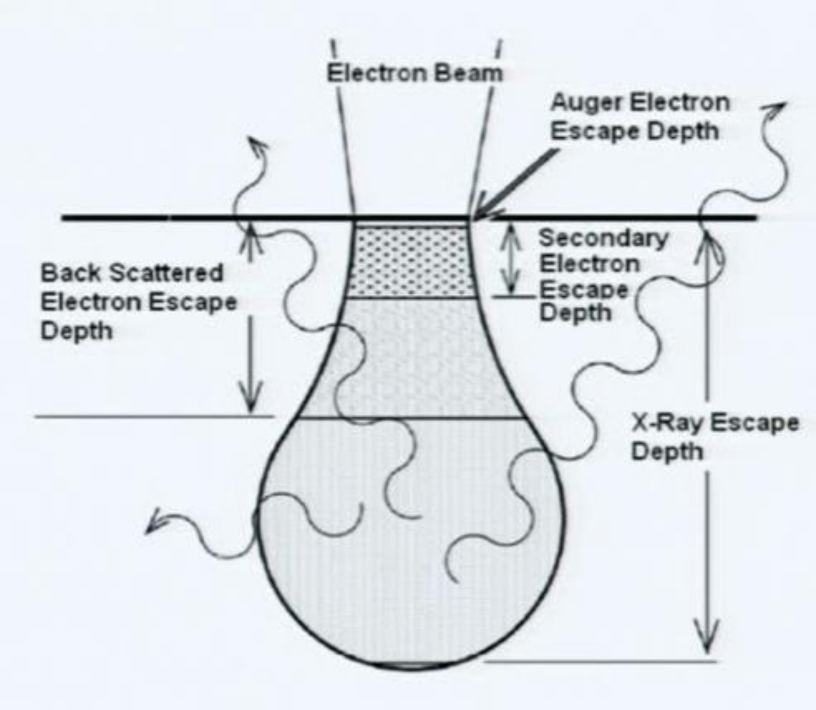
Specimen – Electron Beam Interaction

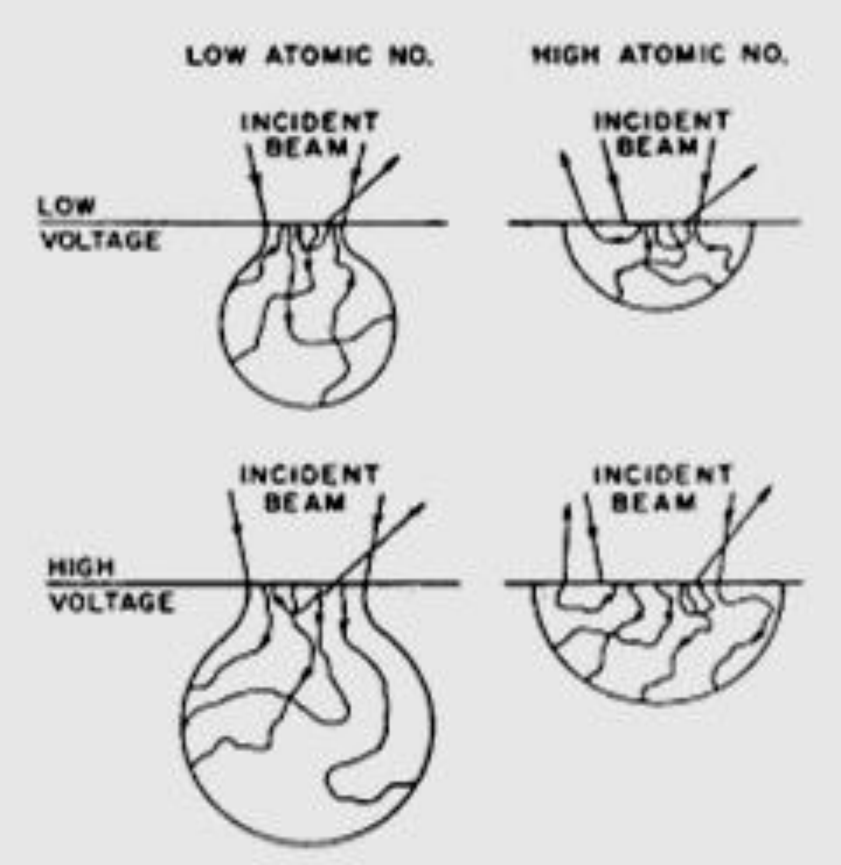


ELEMENT	DEPTH t_1 (μm)
Al	1.5
Cu	0.58
Ag	0.49
Au	0.26

Interaction Volume

- 3D volume of space beneath the sample surface over which the incident beam spreads due to elastic collisions
- 100 times more than spot size/probe size

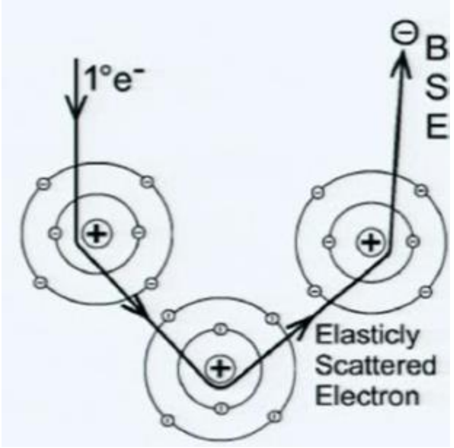


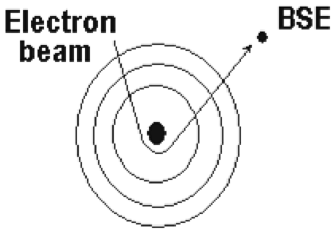


- As accelerating voltage increase beam penetration increases and hence large interaction volume.
- As atomic number increases interaction volume decreases.

Backscattered Electrons (BSEs)

- Incident electrons that reverse direction with minimal energy loss
- Caused by Elastic Scattering
- High Energies: 50-100% 0f incident beam energy (0.5- 30 kev)
- Huge Escape depths:: Typically 0.5-5 µm, may exceed 50 µm

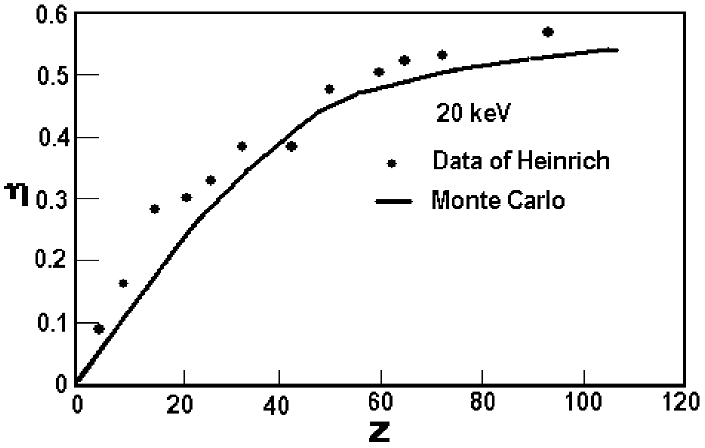




BSE Signal

Higher Z elements means:

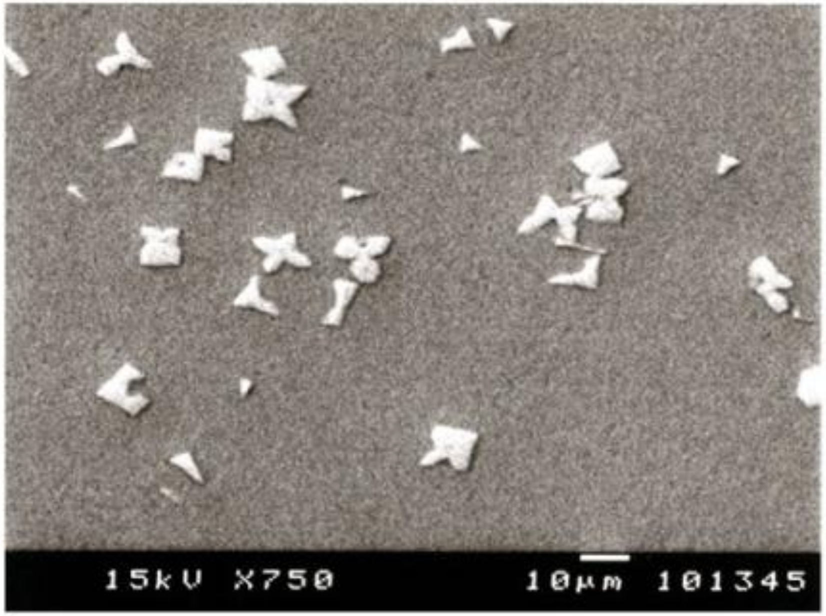
- More high energy BSEs
- Appears bright
- Eta (η) is the Backscattered coefficient which is the Ratio of No. of BSE's produced to the no. of beam electrons incident to the sample



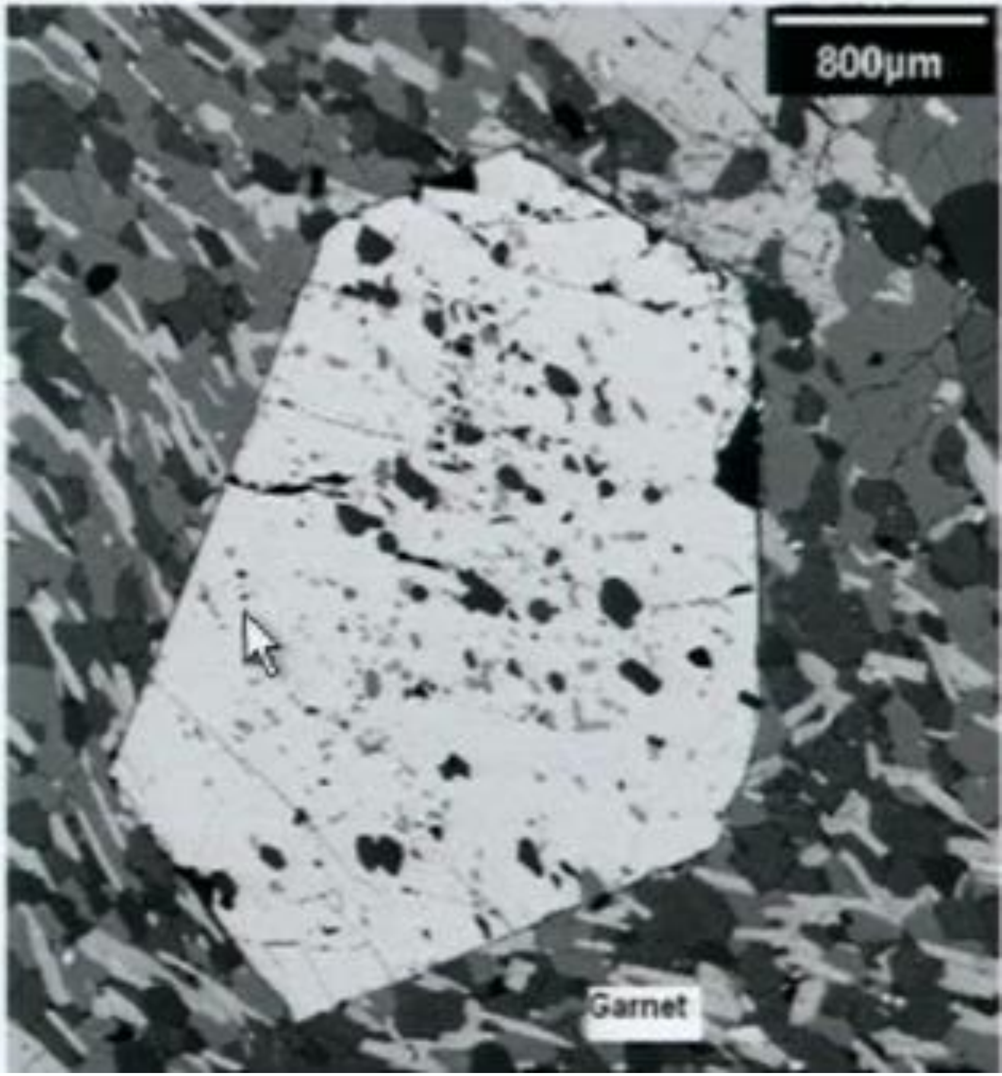
Dependence of Back Scatter Coefficient on Atomic Number

BSE Contrast (Atomic No./ Z Contrast)

- ✓ High Z –More Brighter
- ✓ This allows compositional analysis

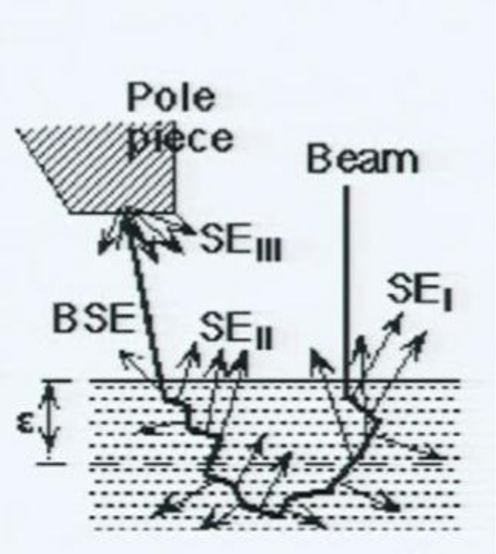


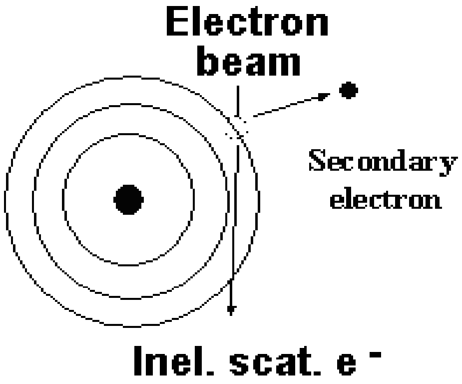
Al-2%Sc alloy with bright particles of Al_3Sc



Secondary Electrons (SEs)

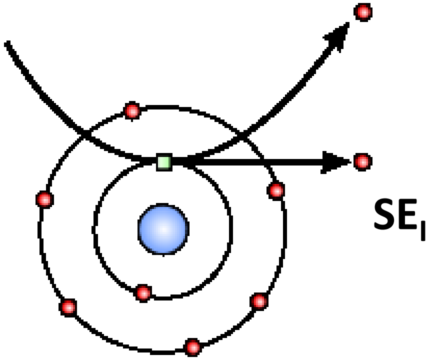
- ❑ Loosely bound electrons near the surface of the sample ejected by the incident high energy electrons
- ❑ Energy: 10 eV - 50 eV
- ❑ SE yield increases with increasing tilt of the sample with respect to the electron beam direction; increases with decreasing energy of the incident electrons





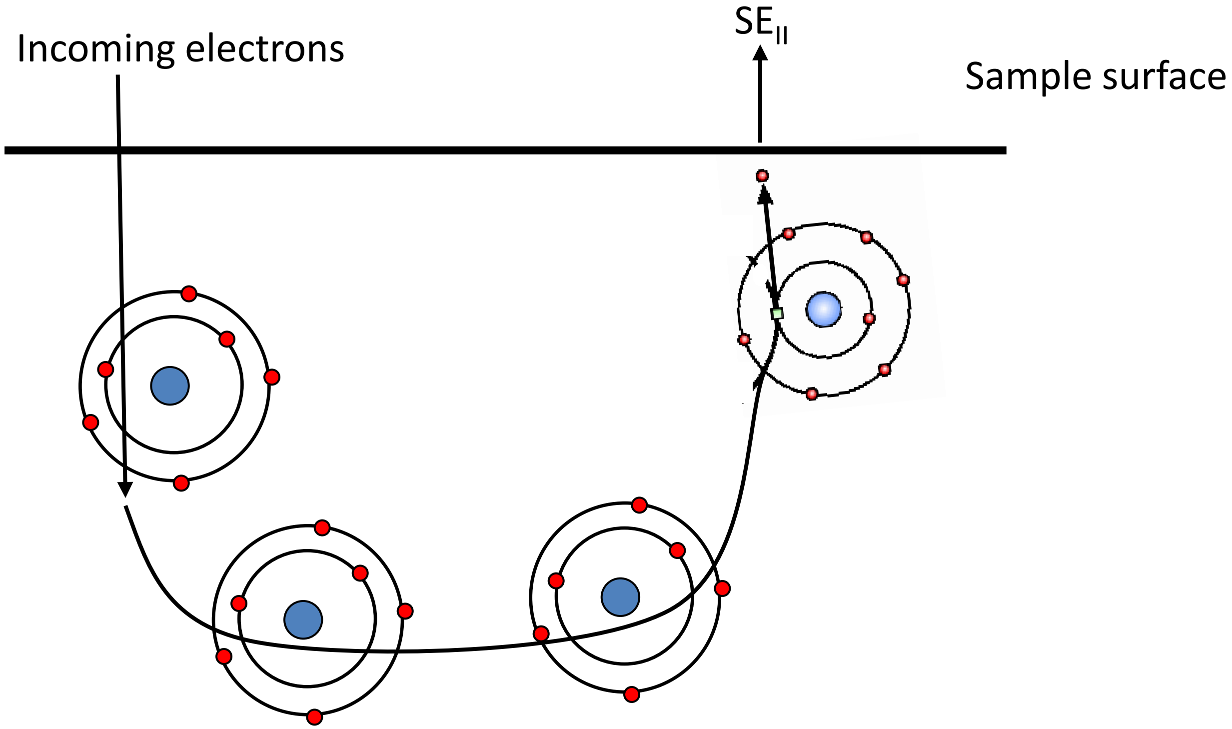
SE$_{I}$

- ❑ The secondary electrons that are generated by the incoming electron beam as they enter the surface
- ❑ High resolution signal with a resolution which is only limited by the electron beam diameter



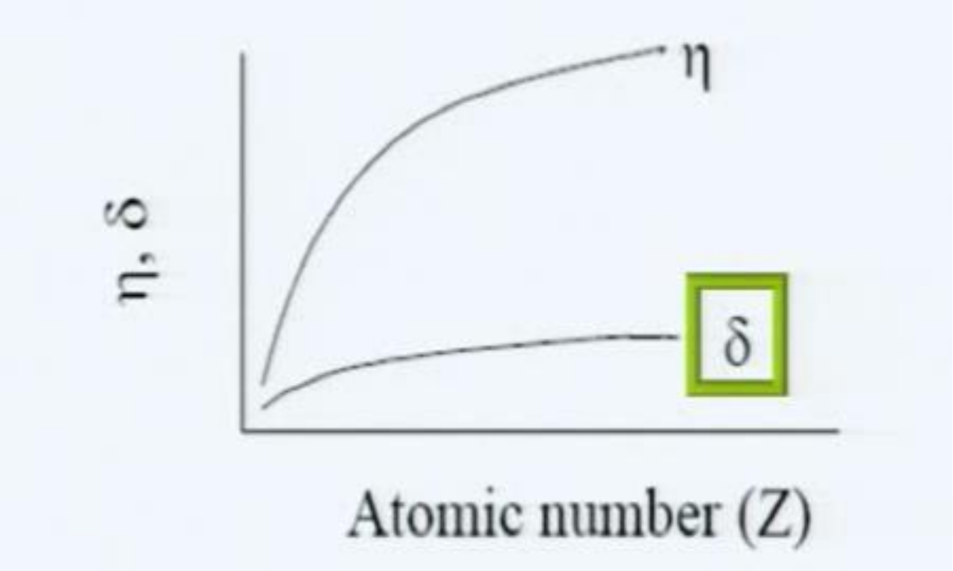
SE_{II}

- ❑ The secondary electrons that are generated by the backscattered electrons that have returned to the surface after several inelastic scattering events
- ❑ SE2 come from a surface area that is bigger than the spot from the incoming electrons → resolution is poorer than for SE1 exclusively



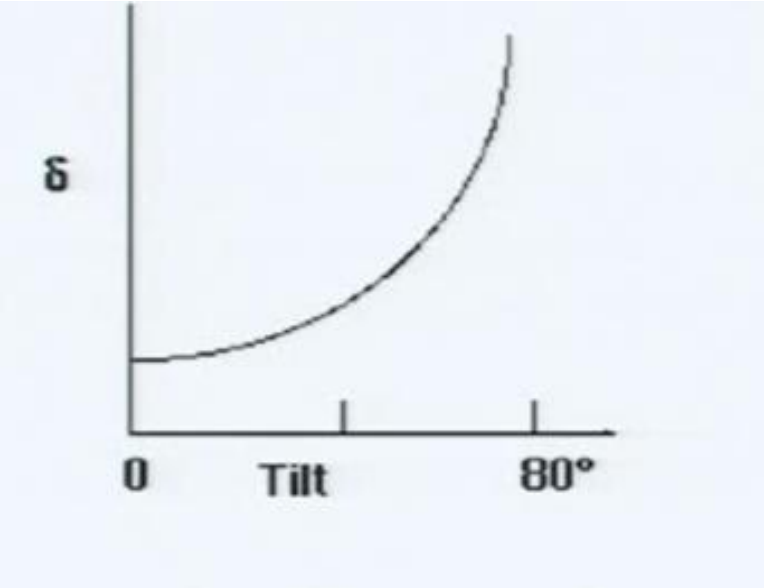
SE Signal

- ❑ Relatively Insensitive to atomic number
- ❑ Increases with decreasing beam energy because of reduced interaction volume and less BSEs
- ❑ Delta (δ) is the SE coefficient which is the Ratio of No. of SE's produced to the no. of beam electrons incident on the sample.



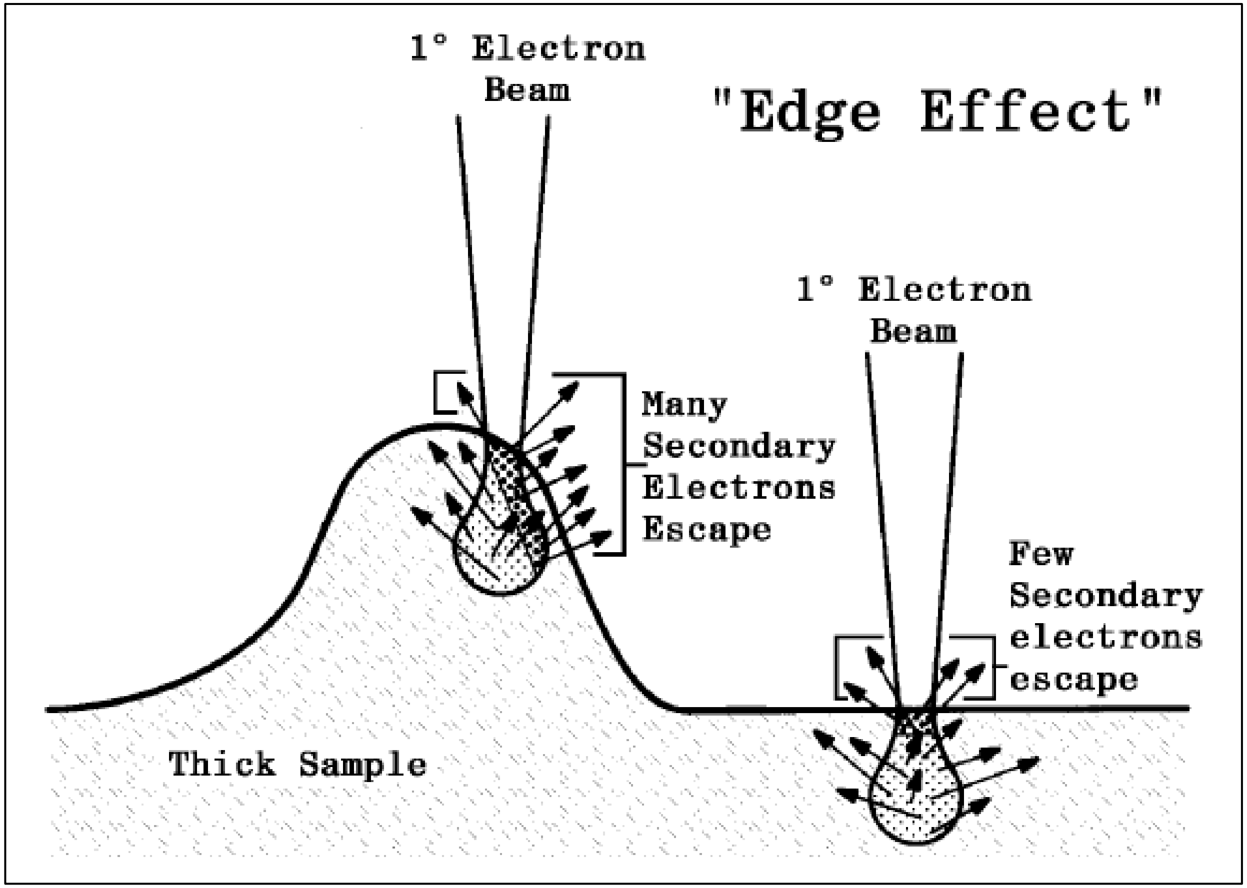
SE Contrast (Topological Contrast)

- ❑ SE's are emitted from shallow depth and have very little Z contrast
- ❑ SE contrast results from a combination of sample topography and the shape of the interaction volume (Edge Effect)

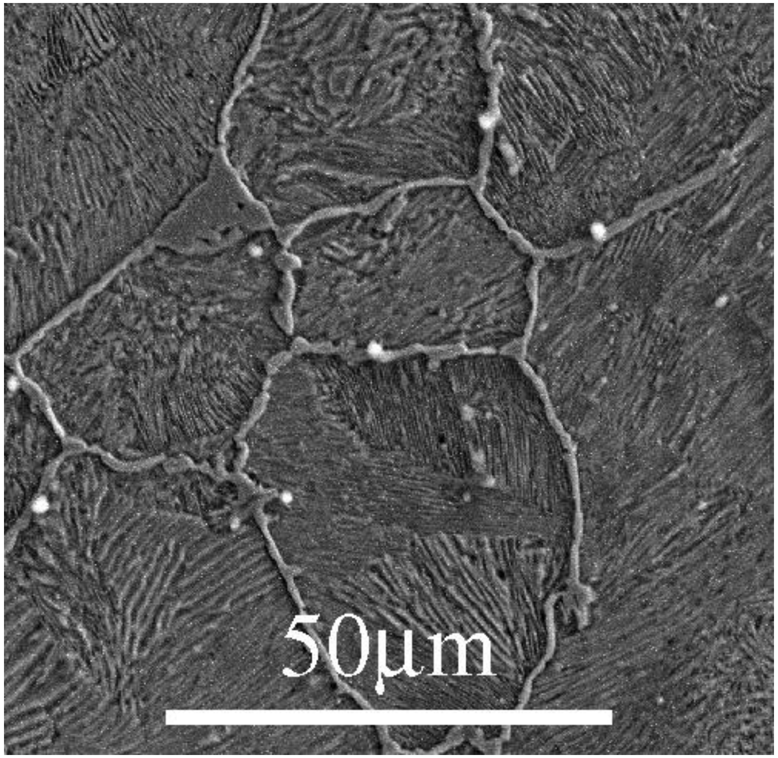


Edge Effect:

- Edges and Ridges emit more SE’s than flat or perpendicular surfaces to incident beam and thus appears brighter
- Also, tilting of e beam means greater distances near surface and increases SE2’s.

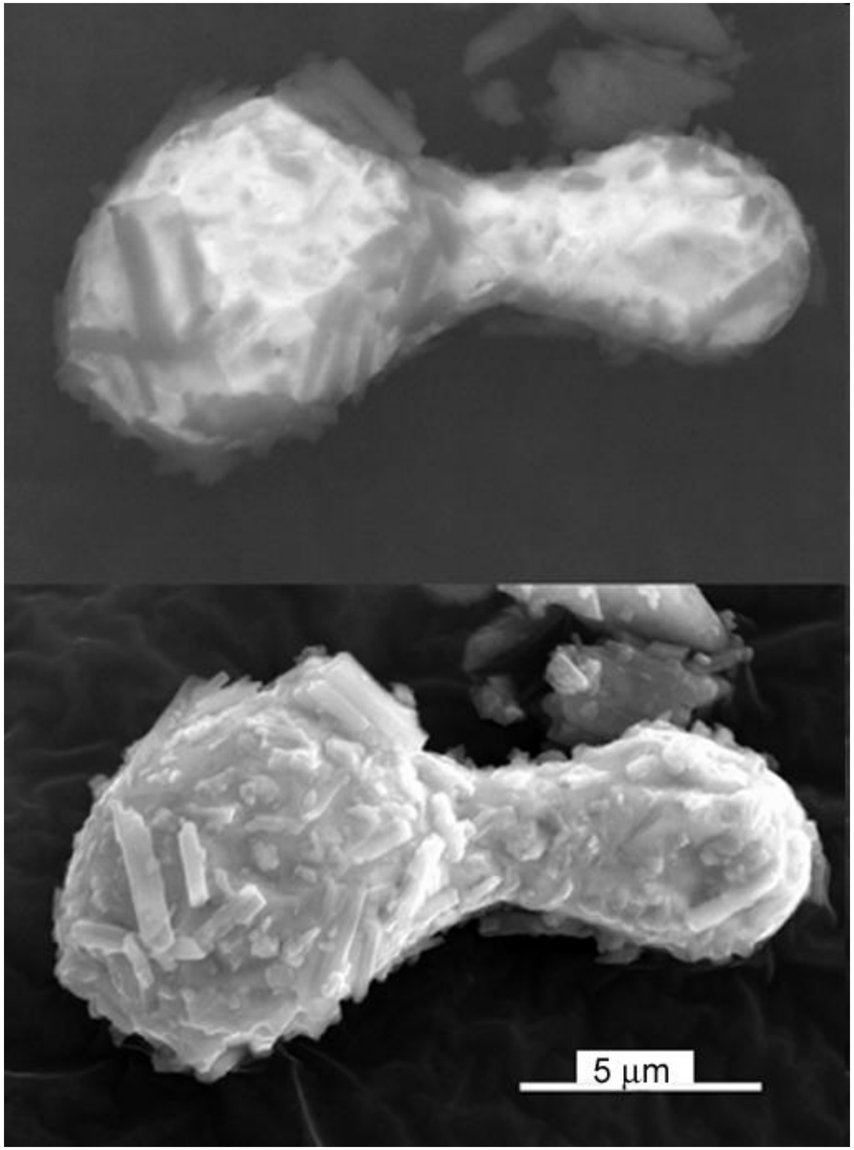


Enables to image the size, shape & structure of 3D objects



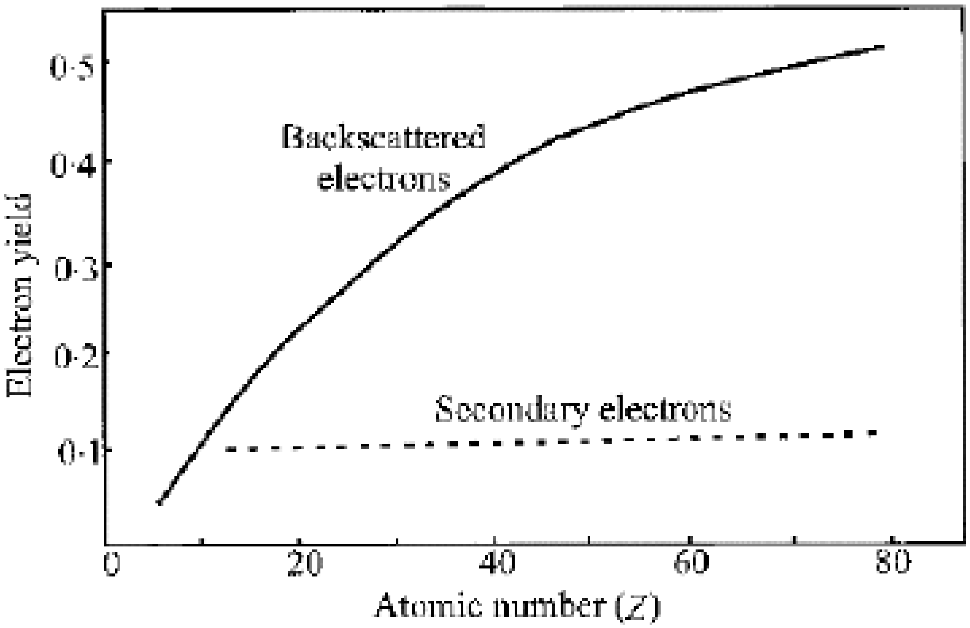
SE micrographs of Fe-1.0%C steel

SE Micrographs

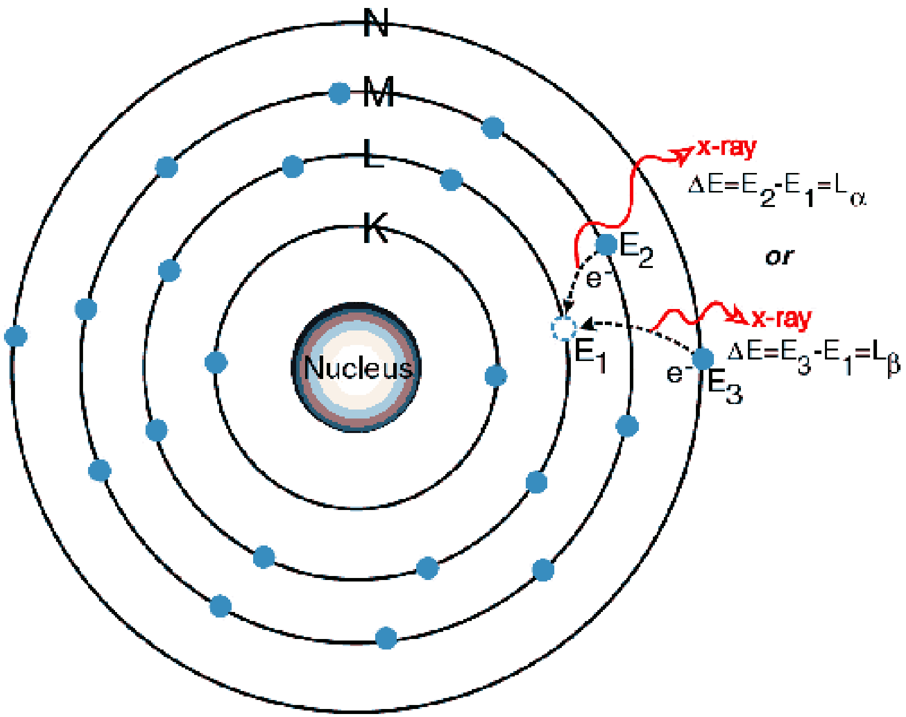


BSE vs SE micrographs

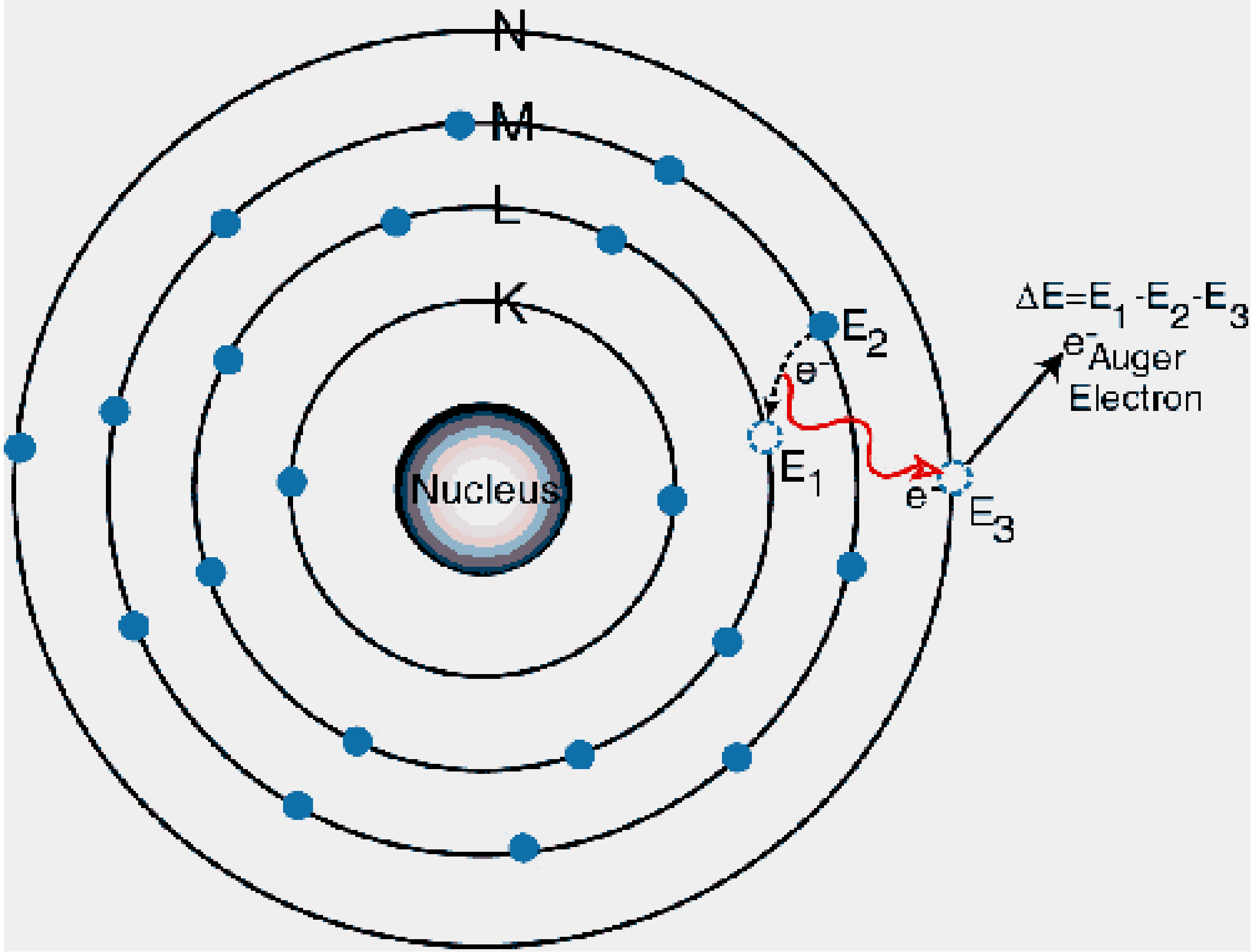
SE vs. BSE Signals



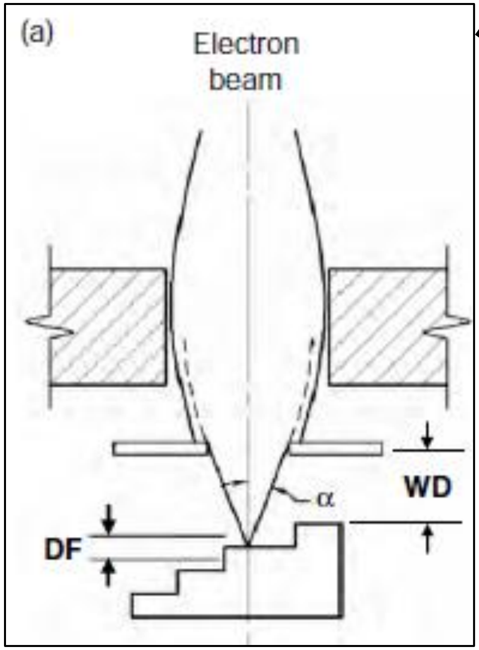
Emission of X-rays (L lines)

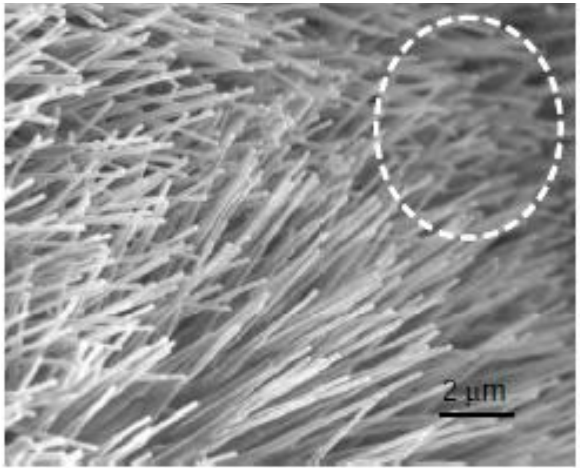


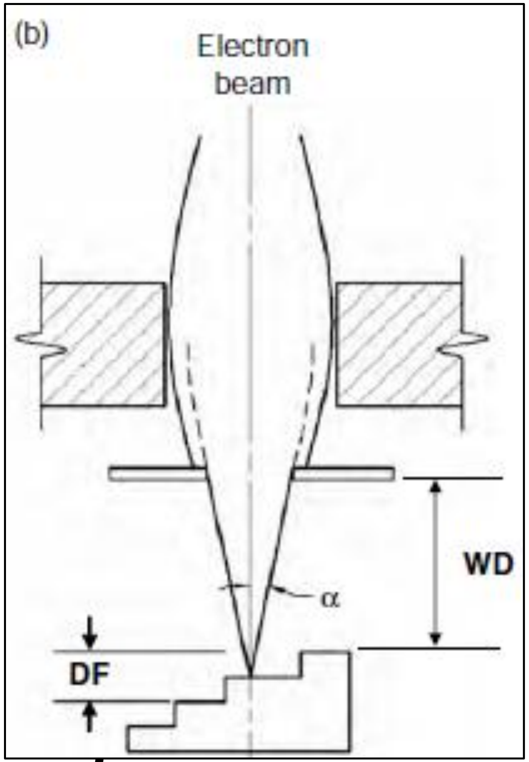
Emission of Auger Electrons

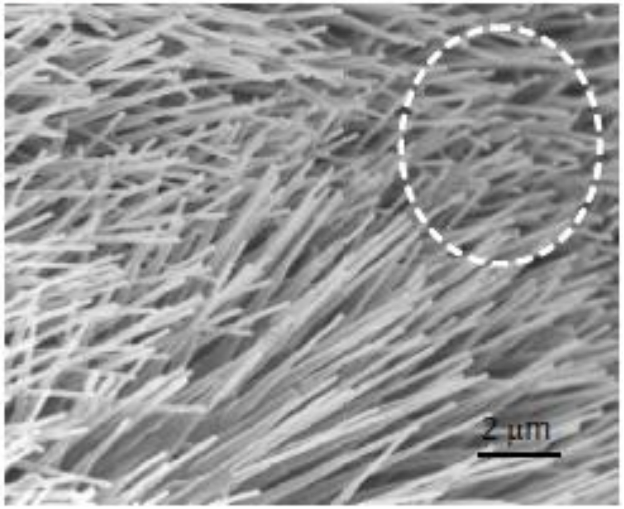


Effect of working distance on SEM Image



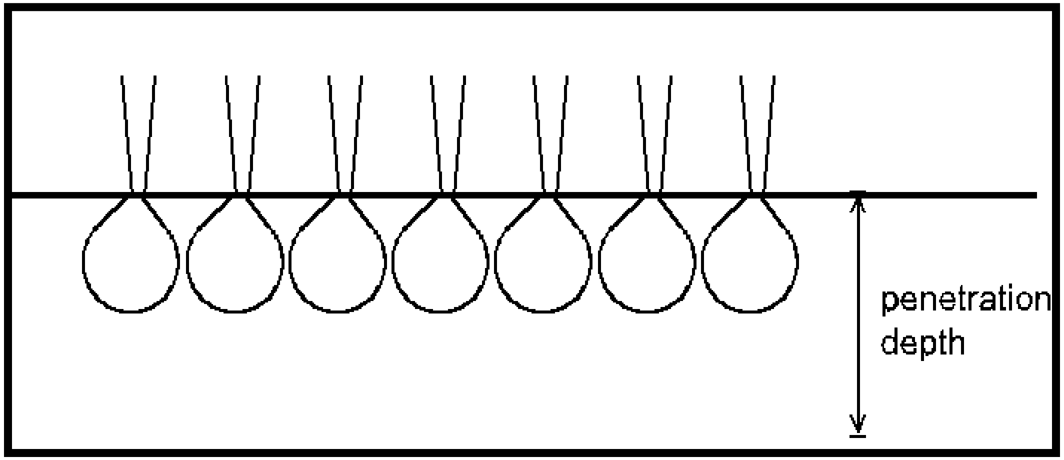




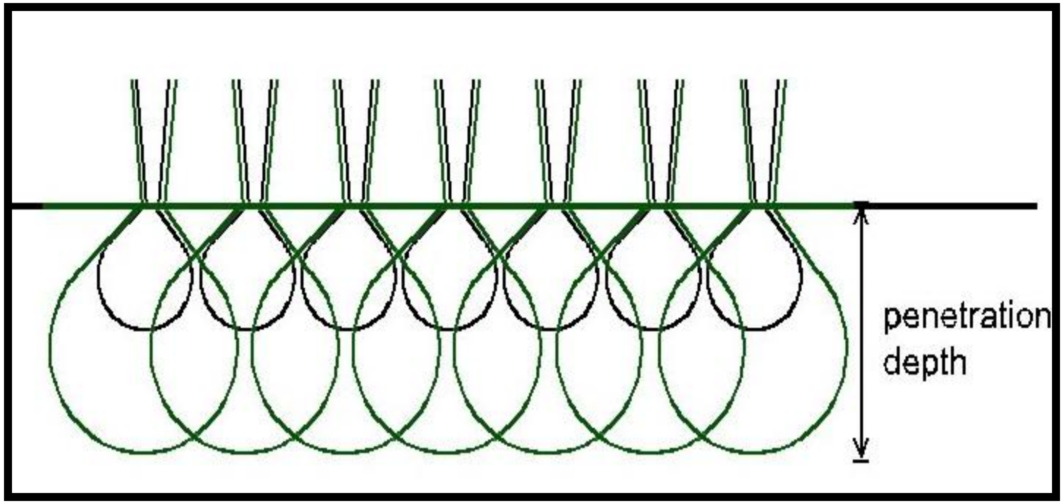


Beam diagram showing enhancement of depth of field (DF) by increasing working distance(WD). (a) Short working distance and (b) Long working distance

Effect of Spot Size on SEM Image

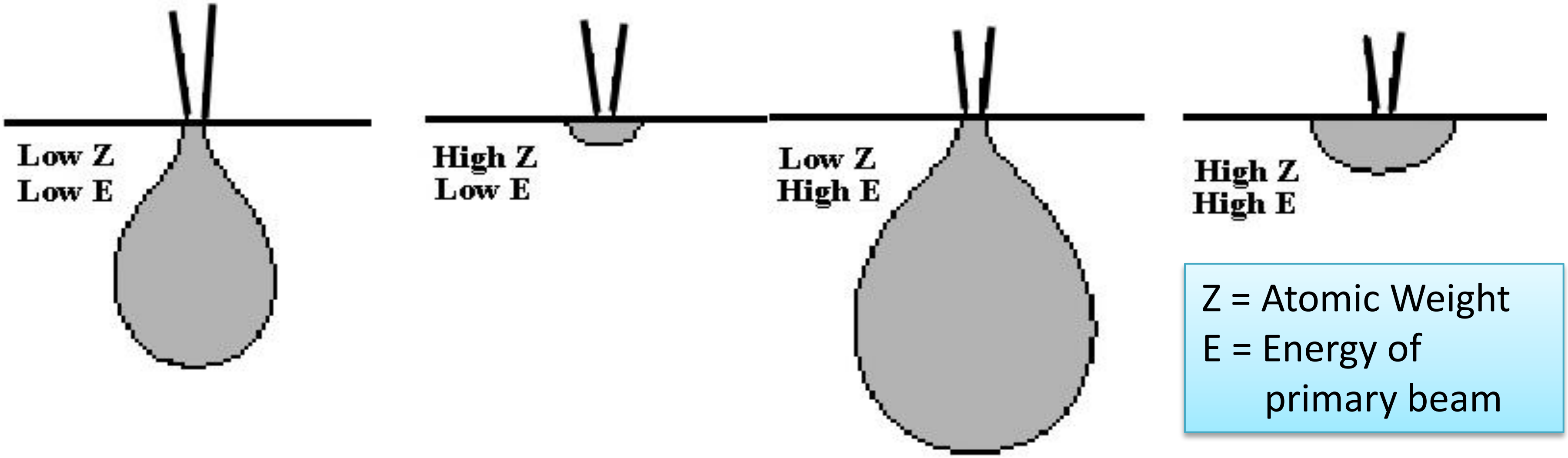


If the region of excitation remains small then signal will be produced from a small region and there will be no overlapping from adjacent regions. In this case each individual spot is resolved from its neighbors.

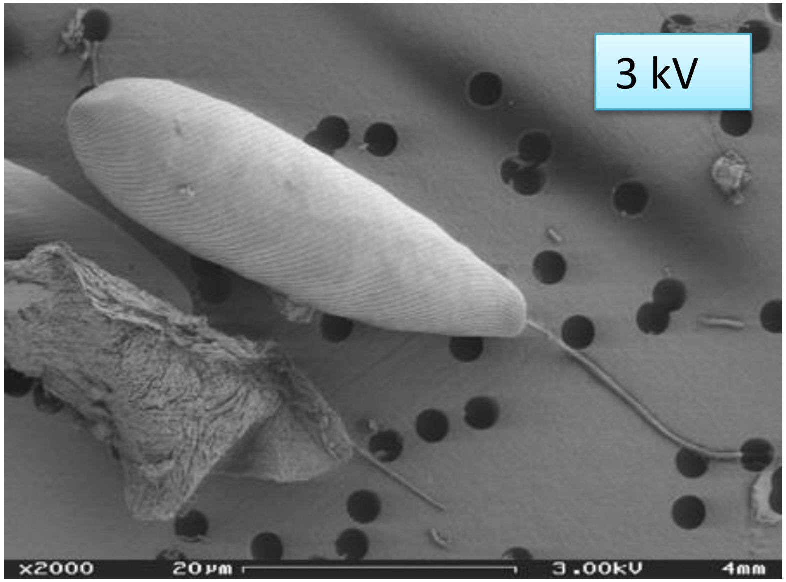


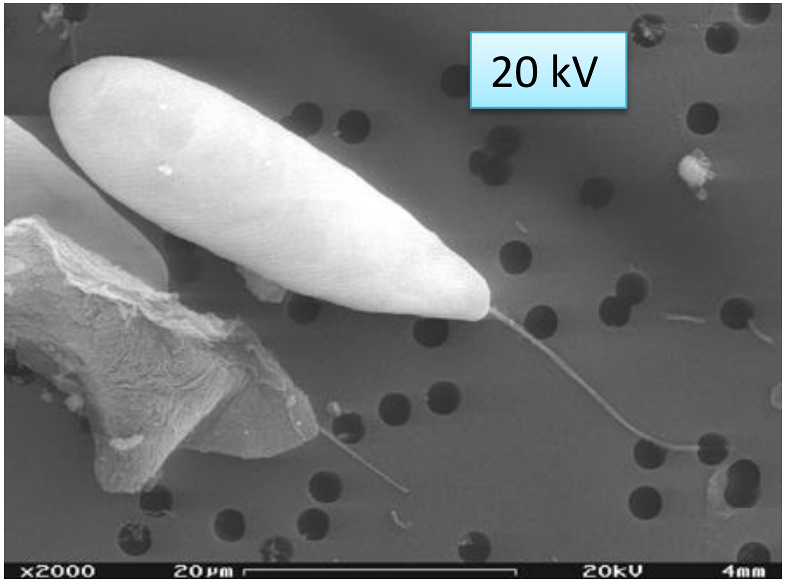
If the beam is scanned in exactly the same positions but the region of excitation is larger then the regions of signal production will also be larger and overlap with adjacent ones. Such an image would therefore not be resolved.

Effects of Accelerating Voltage on SEM Image

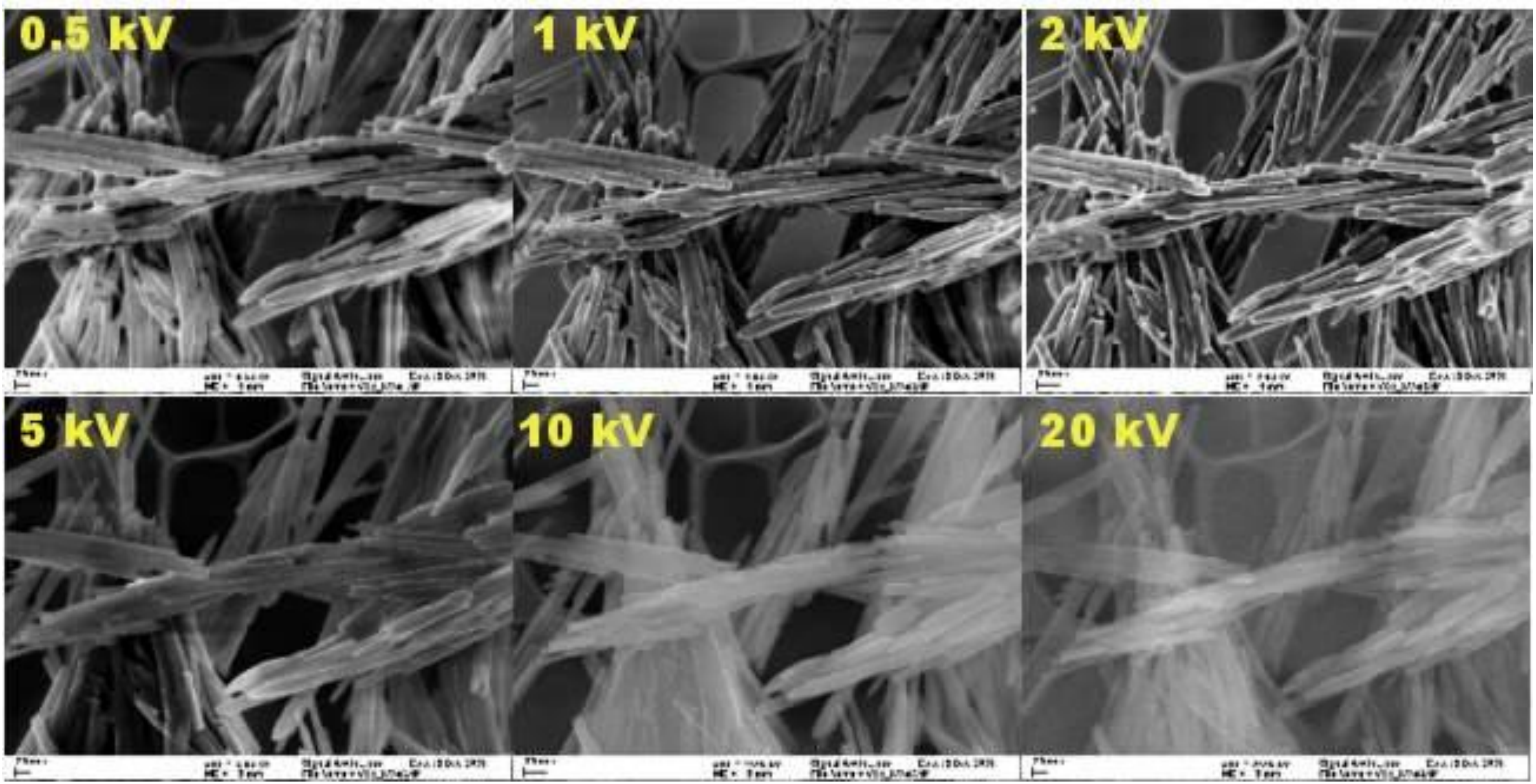


Z = Atomic Weight
E = Energy of primary beam





* More signal (brighter but reduced resolution)



Variation of image contrast with variation in accelerating potential

How do we get an image?

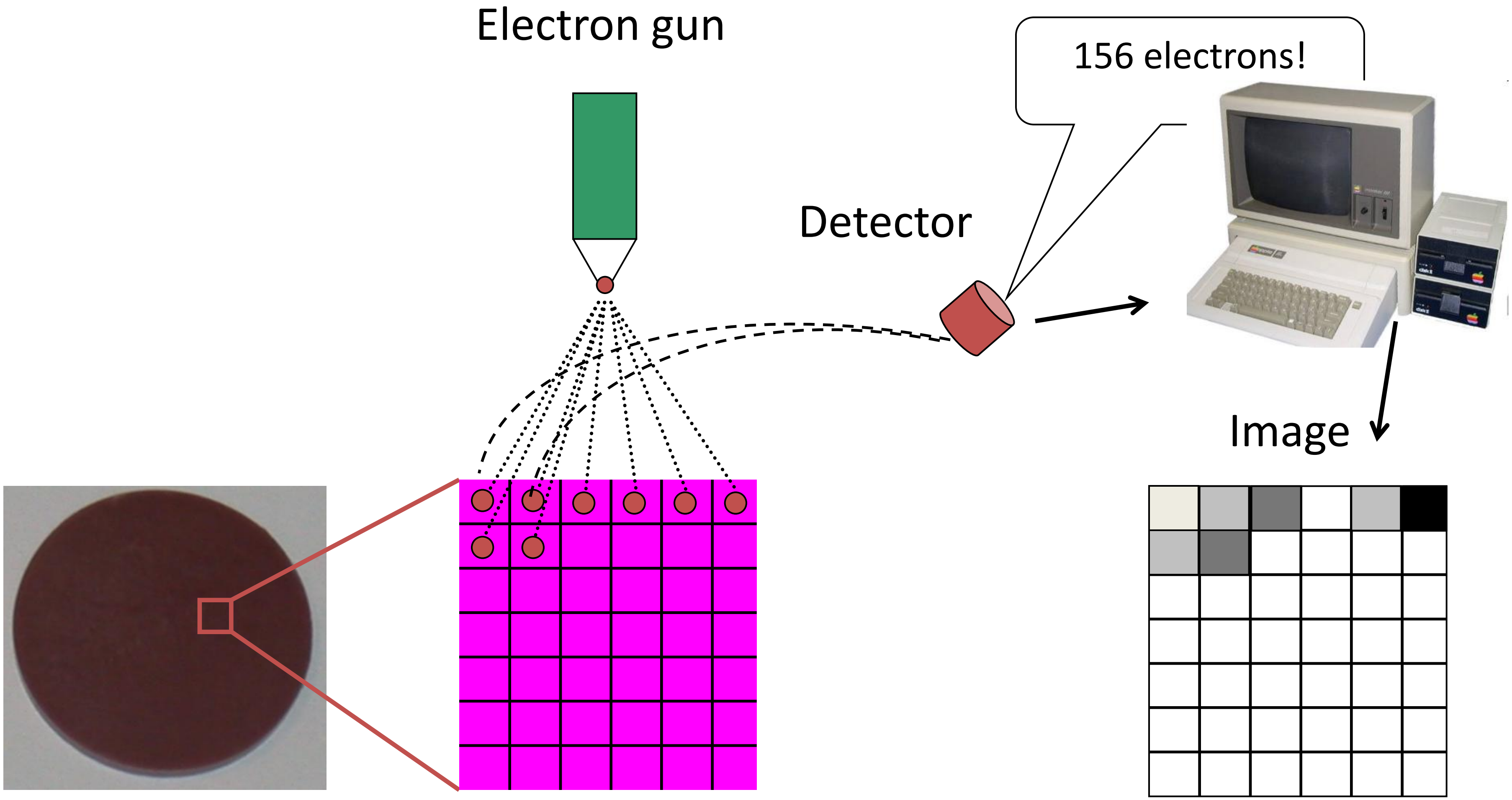
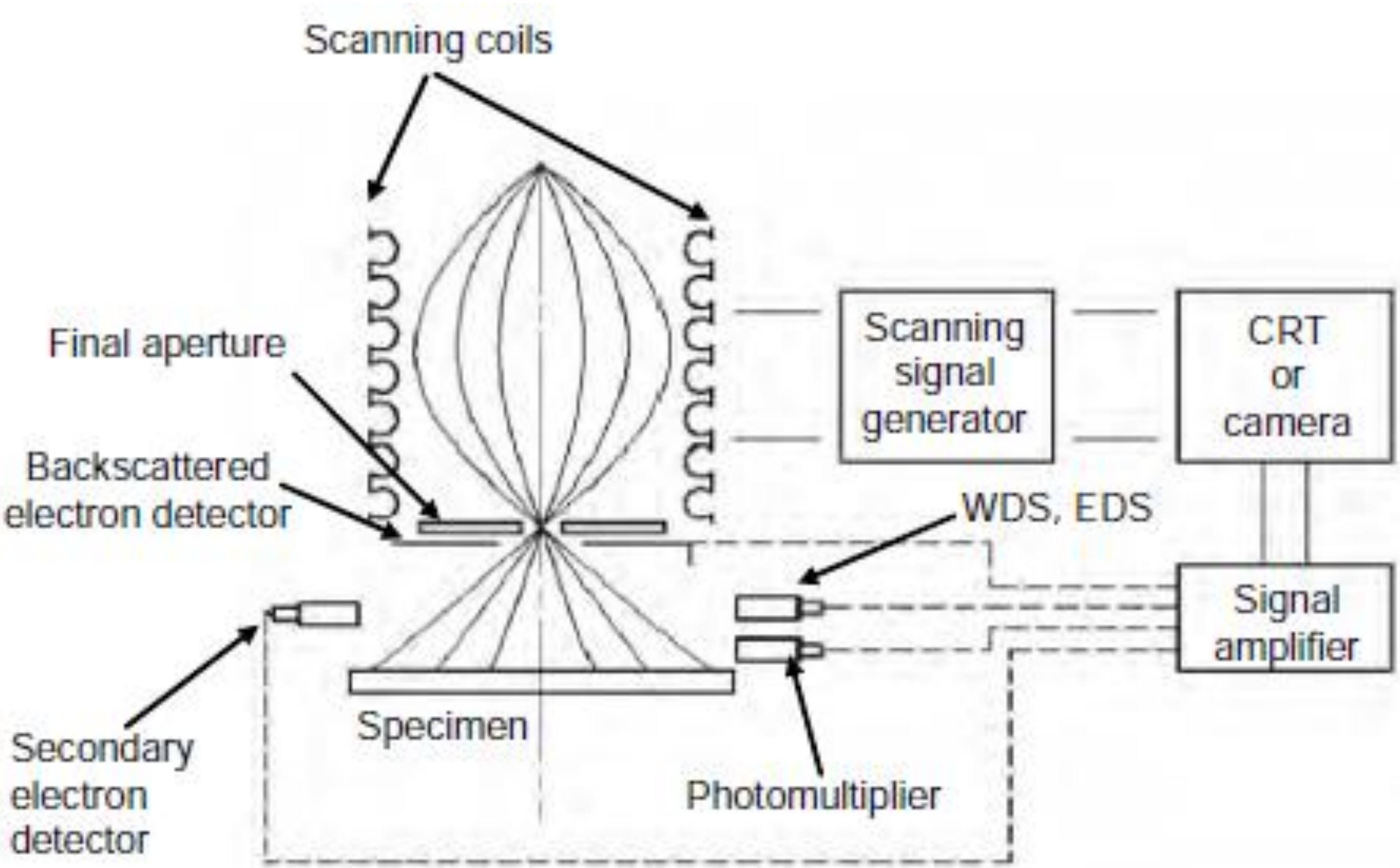


Image formation system in a typical scanning electron microscope



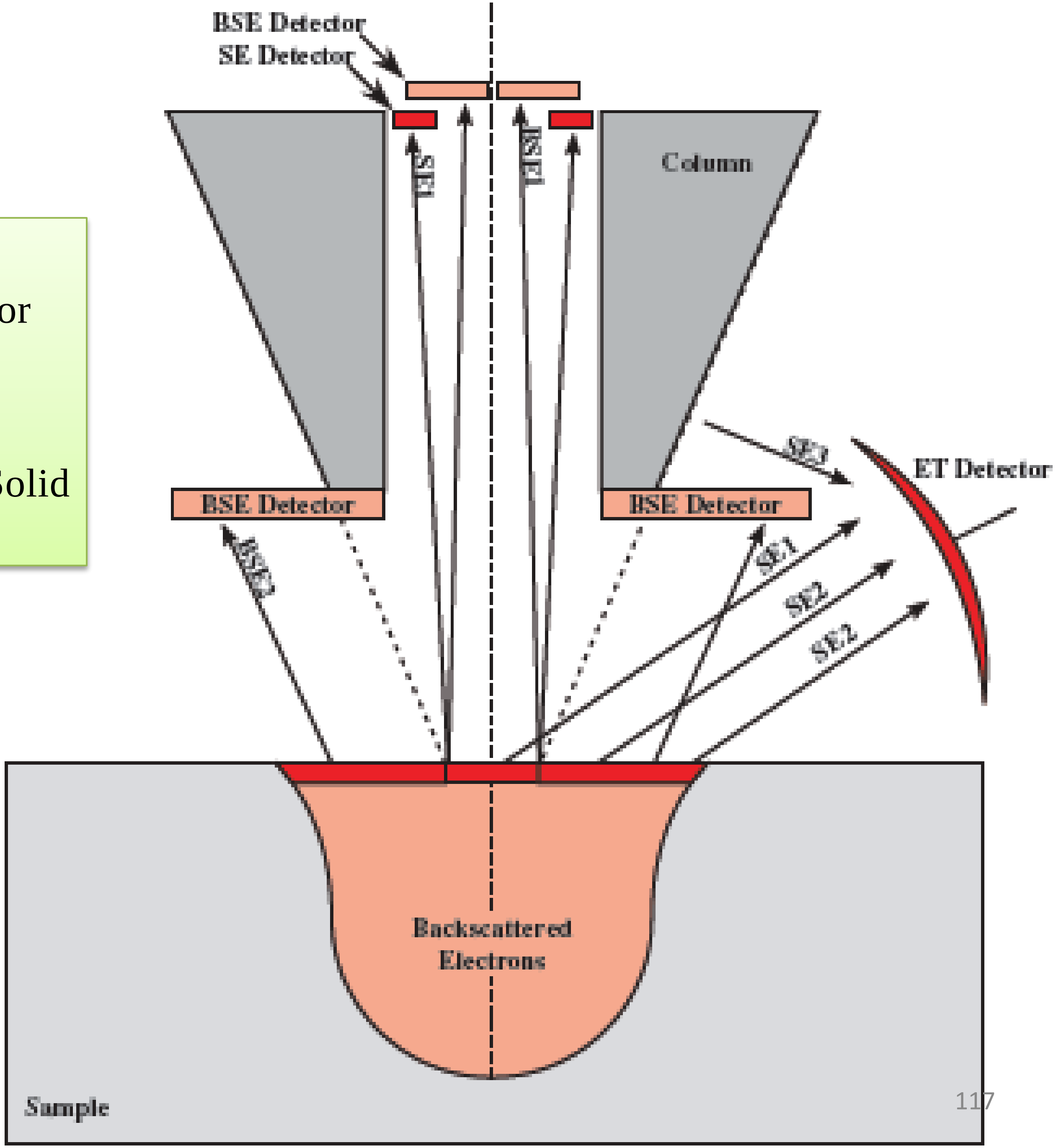
Electron Detectors

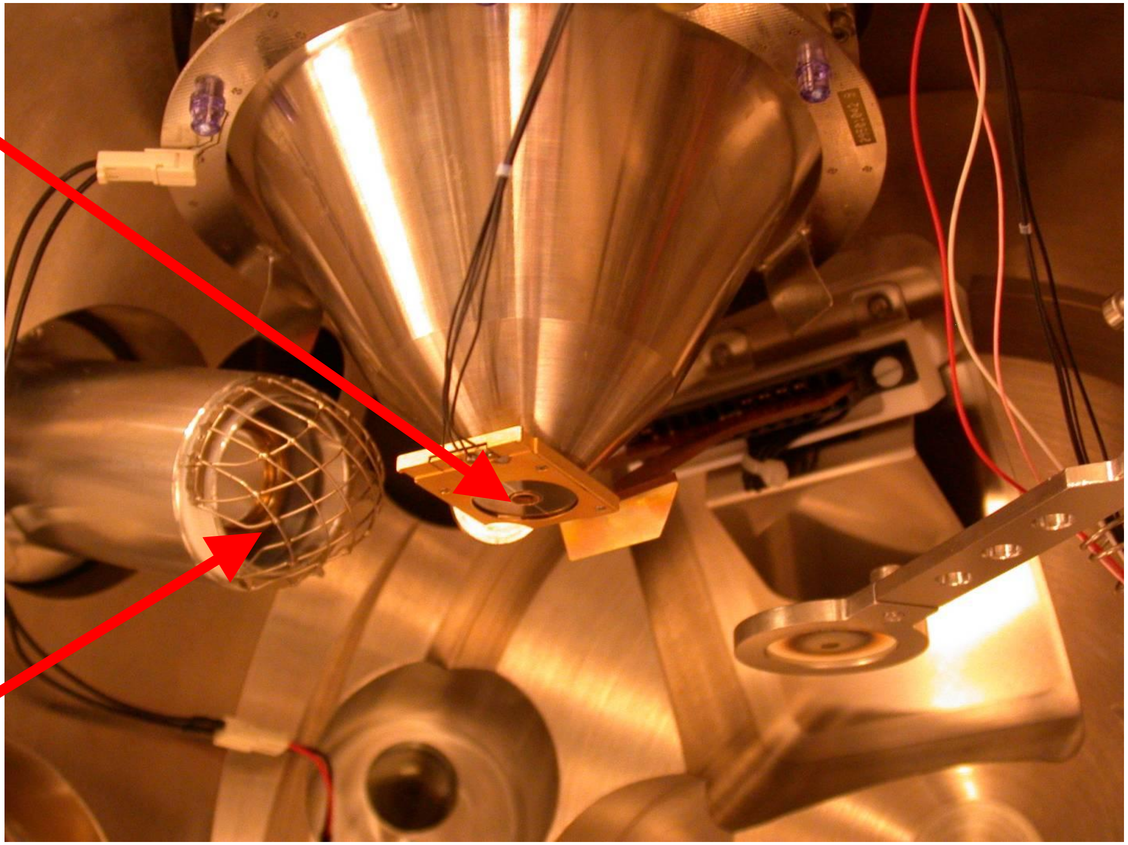
Secondary electrons:

Everhart-Thornley Detector

Backscattered electrons:

Robinsons Detector & Solid State Detector

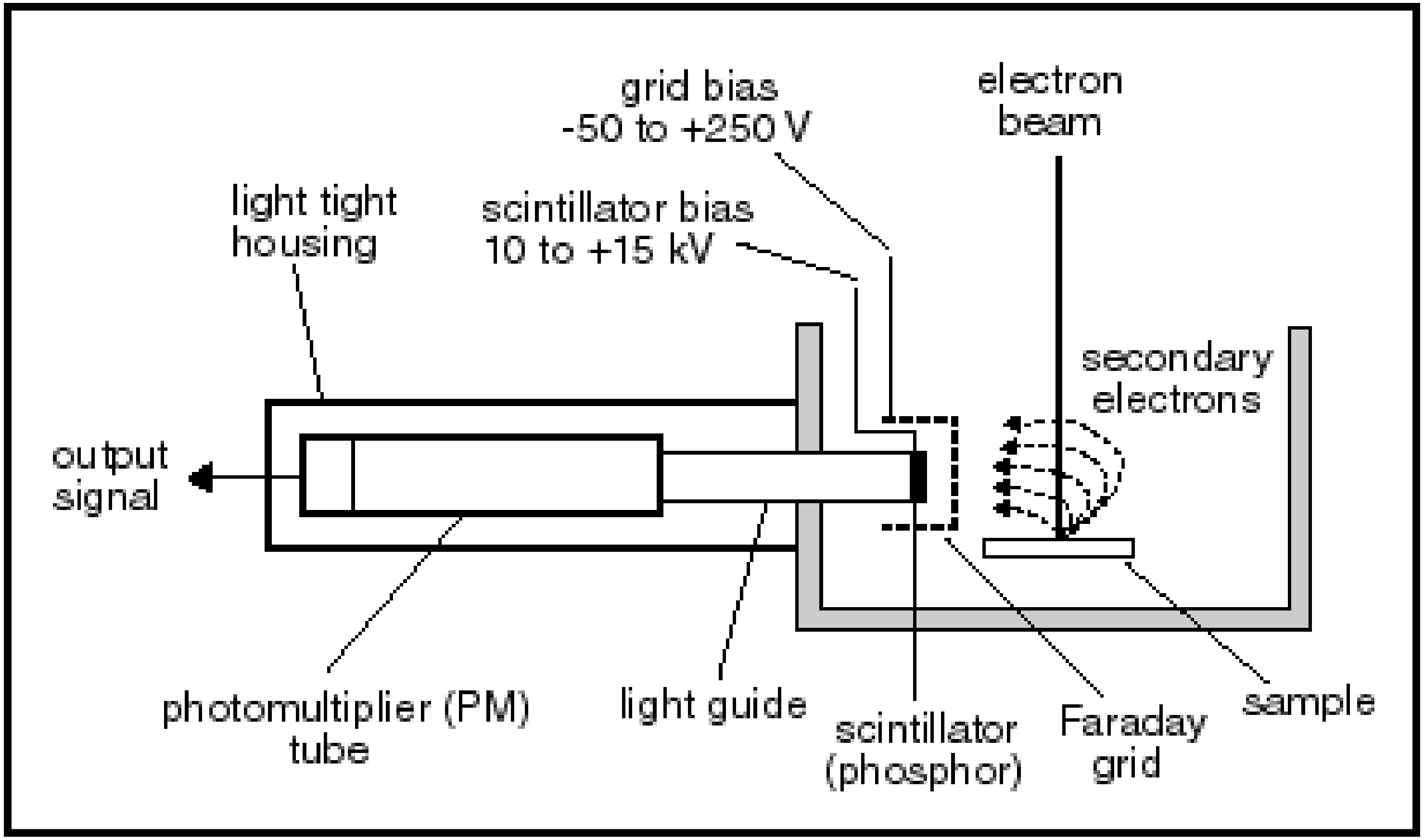




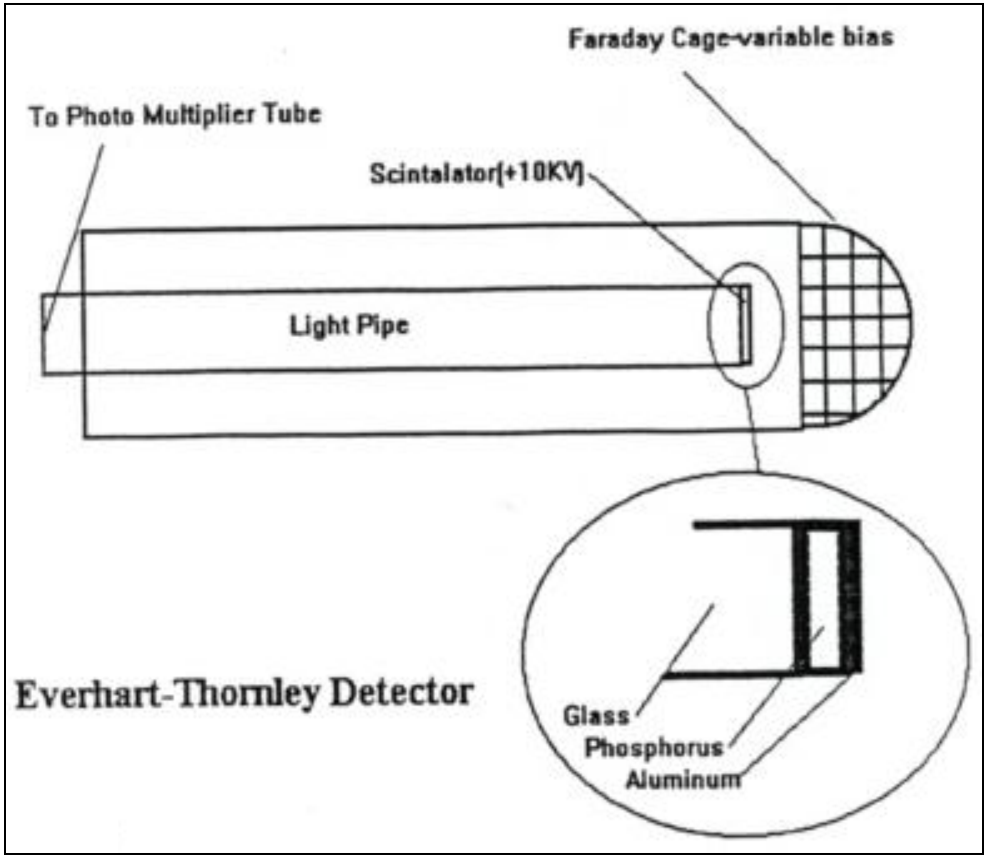
Backscattered electron detector:
(Solid-State Detector)

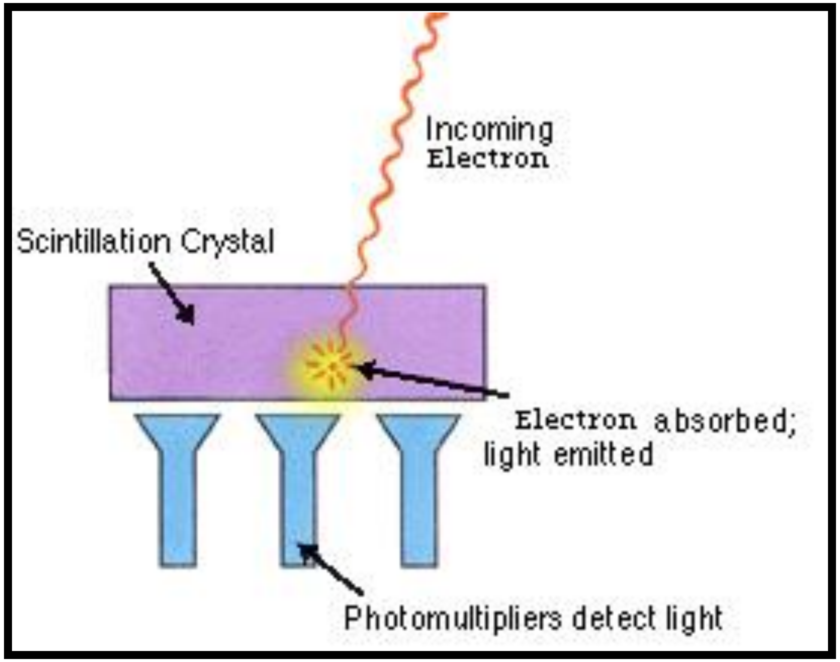
Secondary electron detector:
(Everhart-Thornley)

Secondary electron detector (Everhart-Thornley)



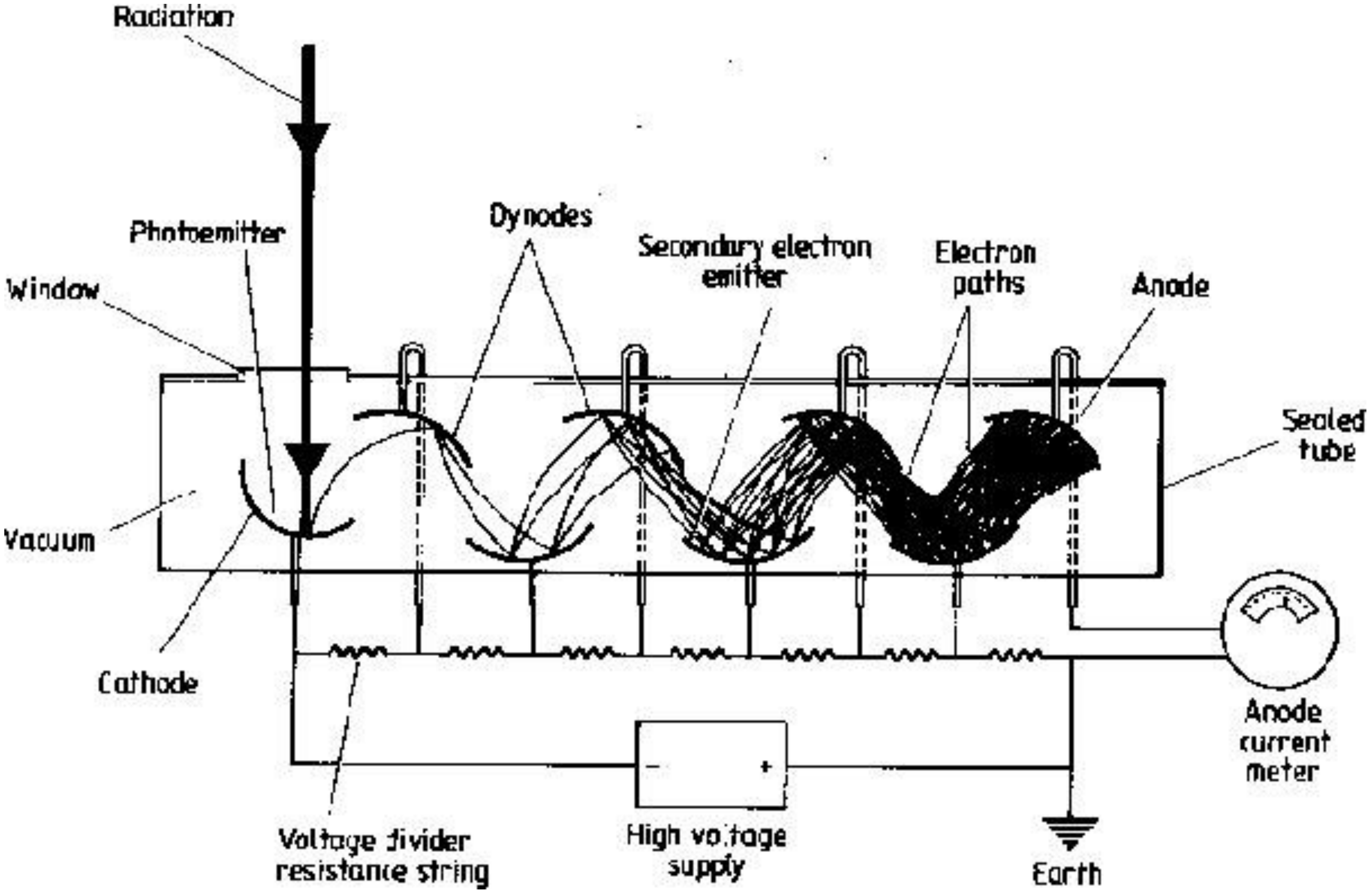
Everhart-Thornley secondary electron detector lies outside of the SEM chamber and is based on a photomultiplier tube (PMT)



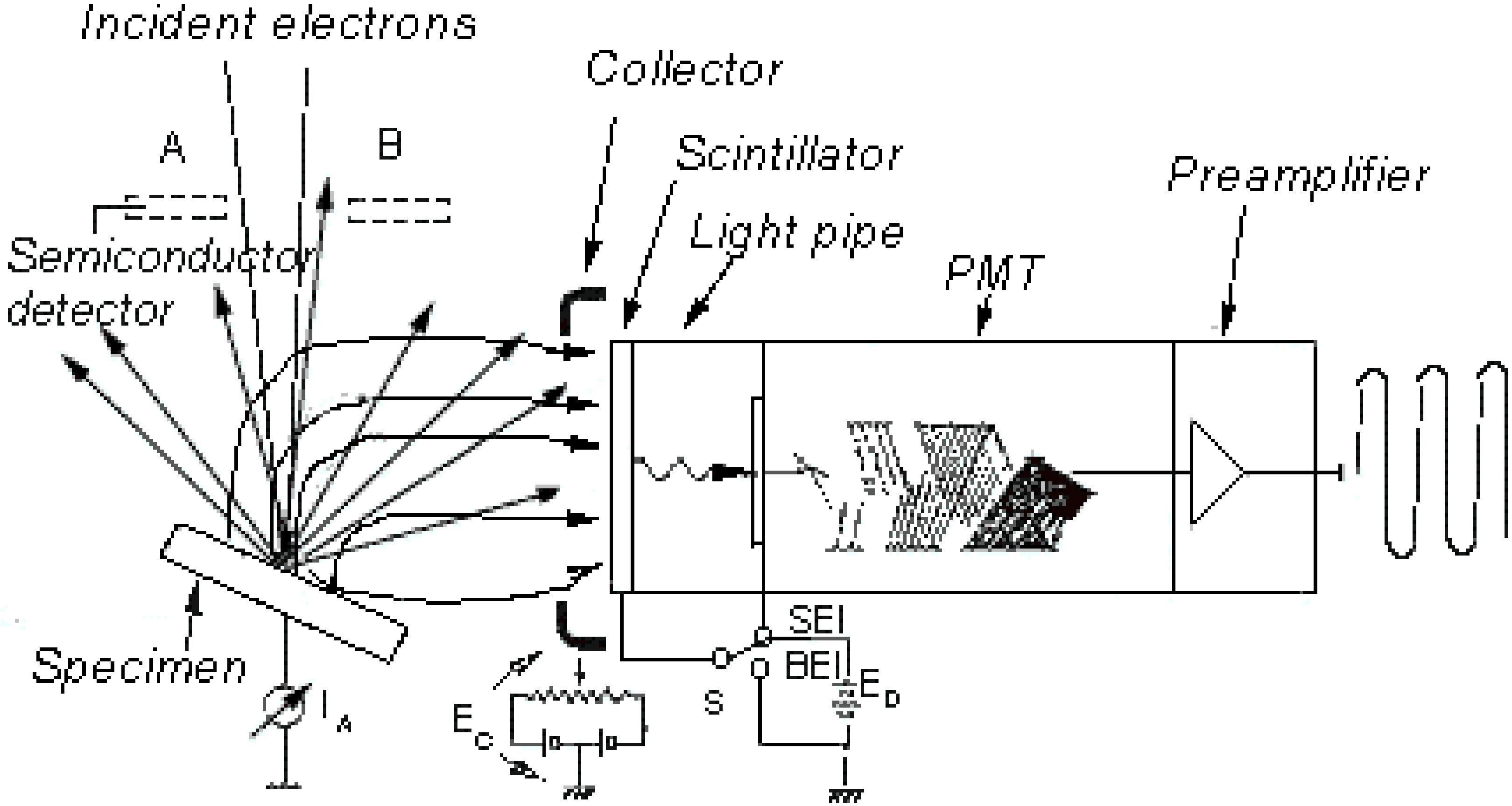


The Everhart-Thornley detector has an aluminum coating (+10-12 KeV) that serves to accelerate the secondary electrons and reflect the photons back down the light pipe.

- ✓ The scintillator is a phosphor crystal that absorbs an electron and generates a photon
- ✓ The photons produced in the scintillator are carried down a fiber optic light pipe out of the microscope.

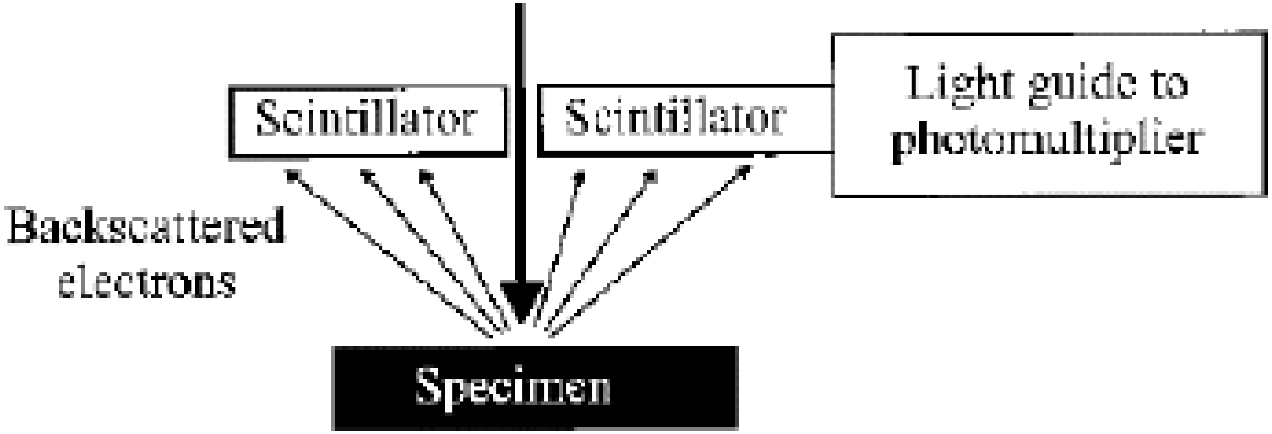


A PMT works by converting the incoming photons into electrons which are then drawn to dynodes kept at a positive bias. The dynodes are made of material with a low work function and thus give up excess electrons for every electron that strikes them. The result "multiplies" the signal contained in each photon produced by the scintillator.



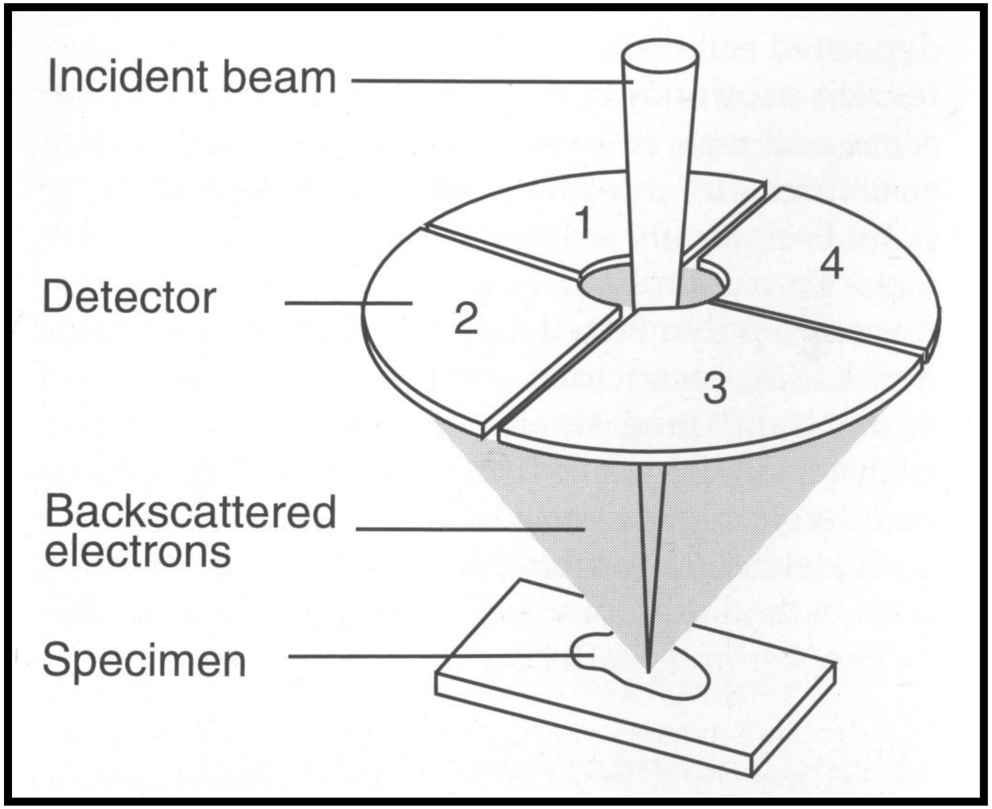
The electronic signal from the PMT is further increased by a signal amplifier. Thus an increase in "gain" is accomplished by voltage applied to the dynodes of the PMT and alters the contrast of the image.

BSE Detector (Robinson Detector)



- ✓ Rapid response time but limited working distance

BSE Detector (Solid state segmented detector)



- ✓ The most common design is a four quadrant solid state detector that is positioned directly above the specimen
- ✓ Electron impinges the semiconductor → e-hole pair → current is produced due to self biased P-N junction → current is amplified
- ✓ Slow response time & Unsuitable for rapid scan rates

Chemical Analysis in SEM

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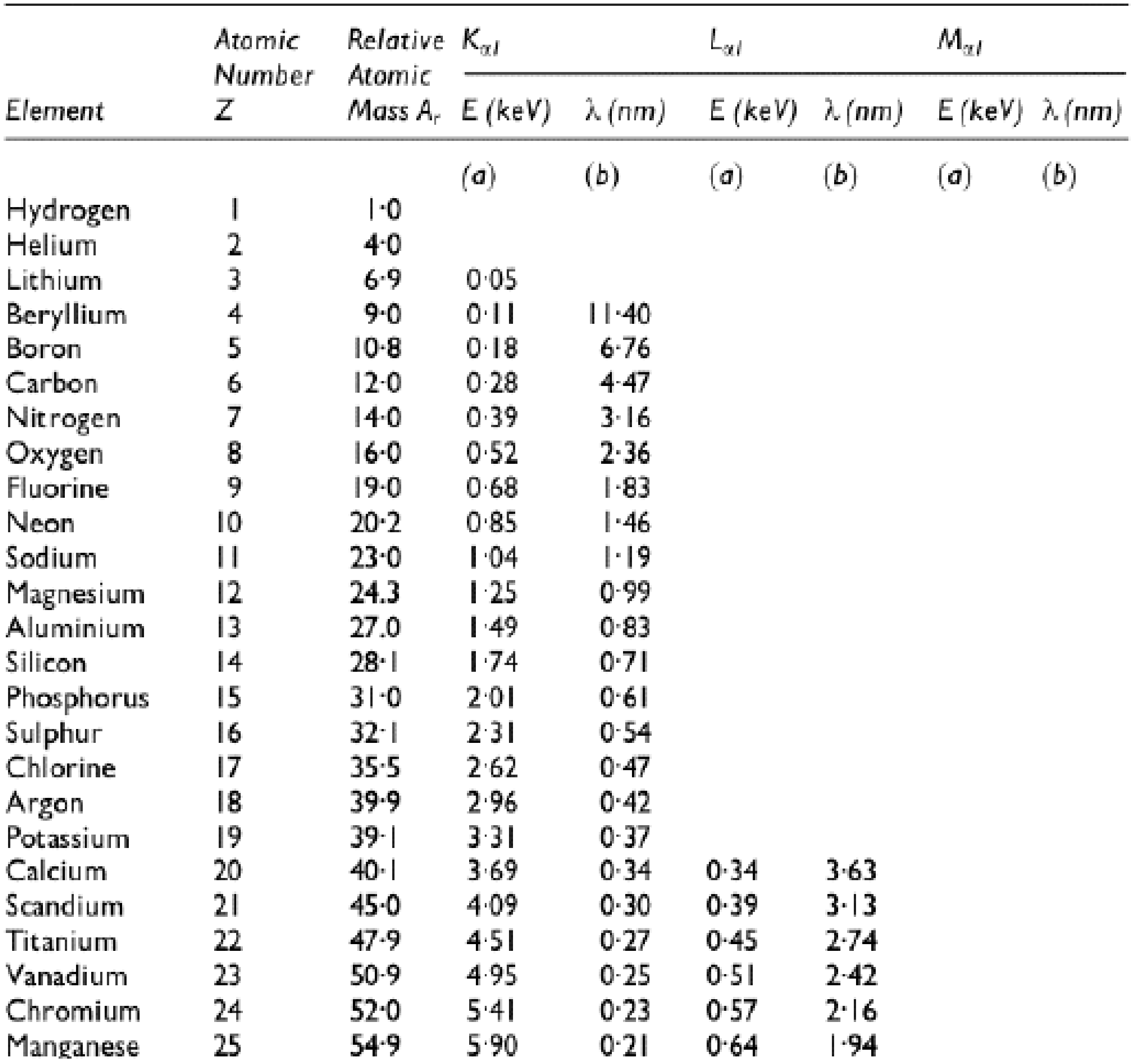
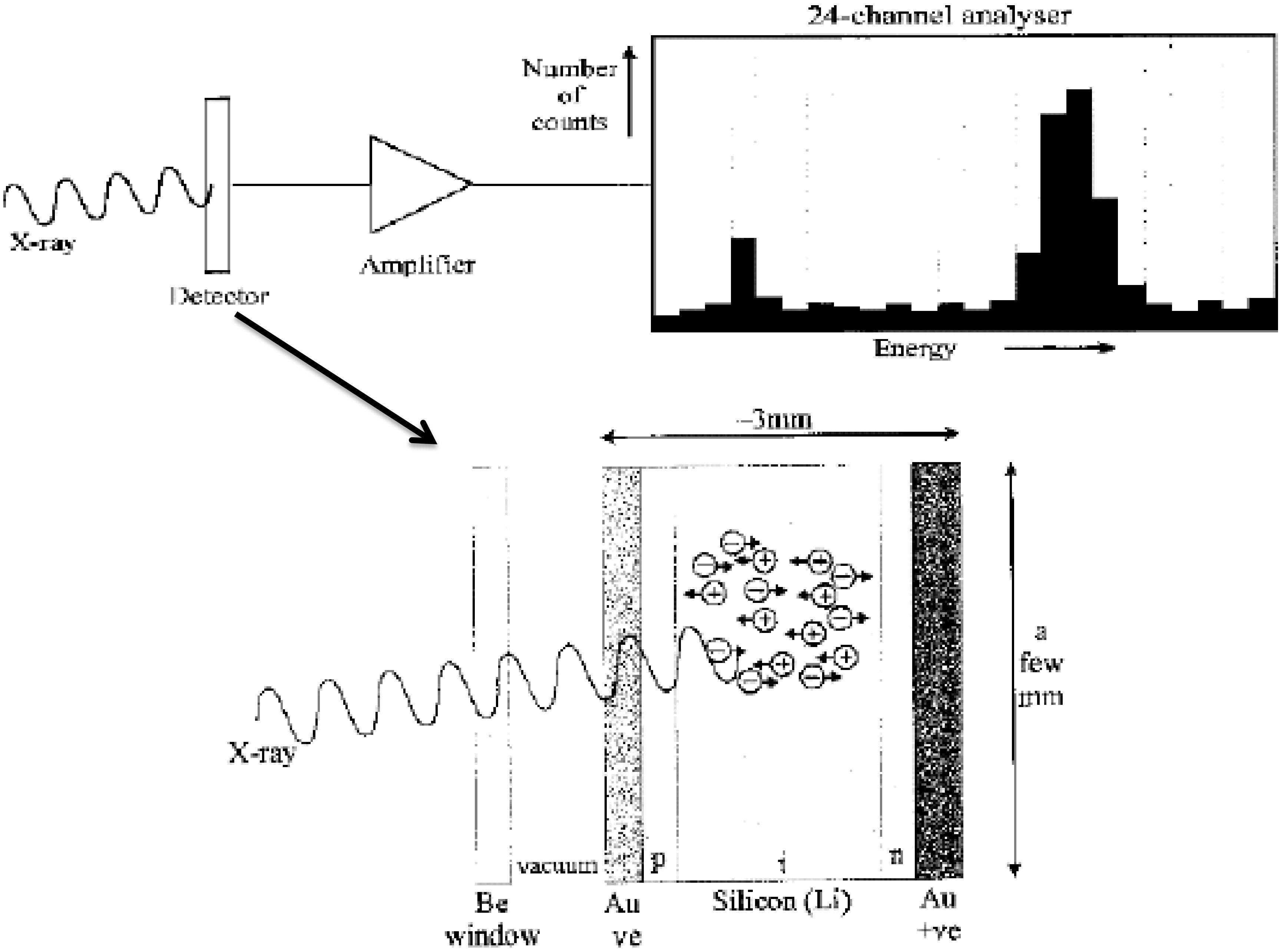
The energy and associated wavelength of the strongest K, L, M lines of the elements



Element	Atomic Number Z	Relative Atomic Mass A_r	$K_{\alpha 1}$		$L_{\alpha 1}$		$M_{\alpha 1}$	
			E (keV)	λ (nm)	E (keV)	λ (nm)	E (keV)	λ (nm)
			(a)	(b)	(a)	(b)	(a)	(b)
Hydrogen	1	1·0						
Helium	2	4·0						
Lithium	3	6·9	0·05					
Beryllium	4	9·0	0·11	11·40				
Boron	5	10·8	0·18	6·76				
Carbon	6	12·0	0·28	4·47				
Nitrogen	7	14·0	0·39	3·16				
Oxygen	8	16·0	0·52	2·36				
Fluorine	9	19·0	0·68	1·83				
Neon	10	20·2	0·85	1·46				
Sodium	11	23·0	1·04	1·19				
Magnesium	12	24.3	1·25	0·99				
Aluminium	13	27.0	1·49	0·83				
Silicon	14	28·1	1·74	0·71				
Phosphorus	15	31·0	2·01	0·61				
Sulphur	16	32·1	2·31	0·54				
Chlorine	17	35·5	2·62	0·47				
Argon	18	39·9	2·96	0·42				
Potassium	19	39·1	3·31	0·37				
Calcium	20	40·1	3·69	0·34	0·34	3·63		
Scandium	21	45·0	4·09	0·30	0·39	3·13		
Titanium	22	47·9	4·51	0·27	0·45	2·74		
Vanadium	23	50·9	4·95	0·25	0·51	2·42		
Chromium	24	52·0	5·41	0·23	0·57	2·16		
Manganese	25	54·9	5·90	0·21	0·64	1·94		

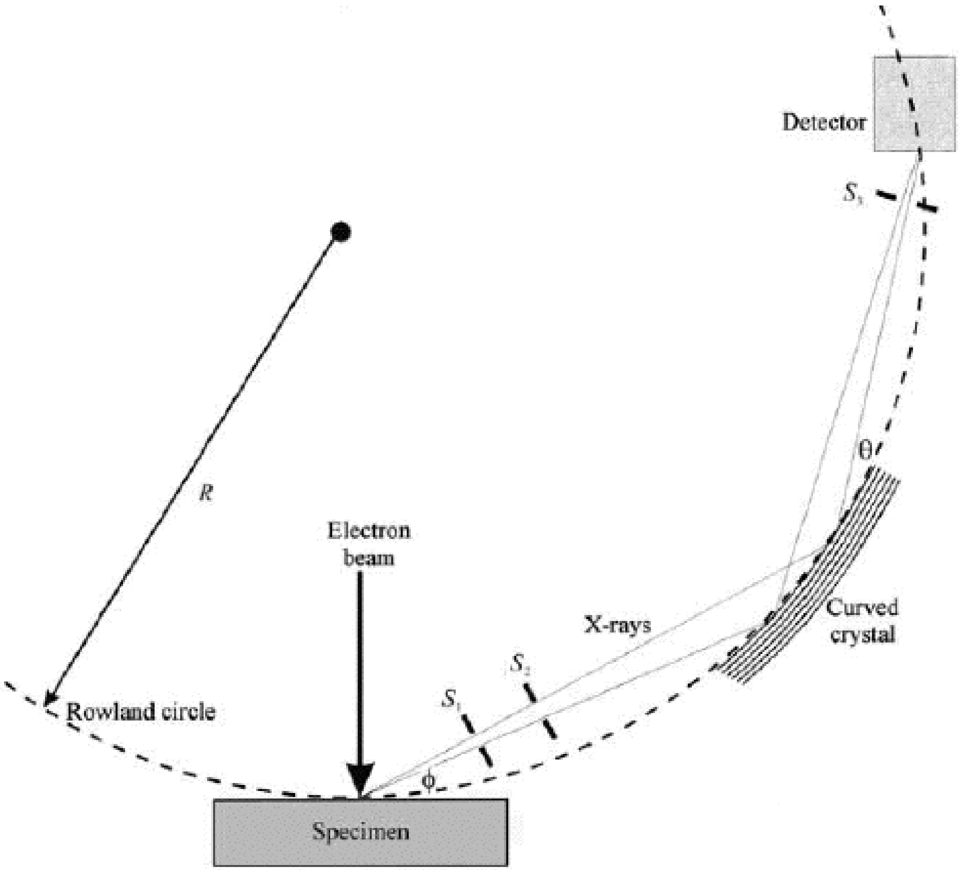
Energy-Dispersive Spectroscopy (EDS)

- ☐ Dispersive device is a semiconductor diode, fabricated from a single crystal of silicon (Li/Ge)
- ☐ Energy of incident photons release a considerable number of outer-shell (valence) electrons from the confinement of a particular atomic nucleus and creates electron-hole pairs resulting in electrical conduction by both electrons and holes for a brief period of time.
- ☐ Al Kα with energy 1.49 Kev gives rise to 390 e-hole pair in a silicon substrate. (1 e- hole pair requires 3.8ev)
- ☐ Application of reverse-bias voltage to the diode causes electrical charge to flow through the junction and is proportional to the number N of electron-hole pairs generated

24-channel analyser
Number of counts
X-ray
Detector
Amplifier
Energy
~3mm
X-ray
vacuum
p
i
n
a few mm
Be window
Au ve
Silicon (Li)
Au +ve

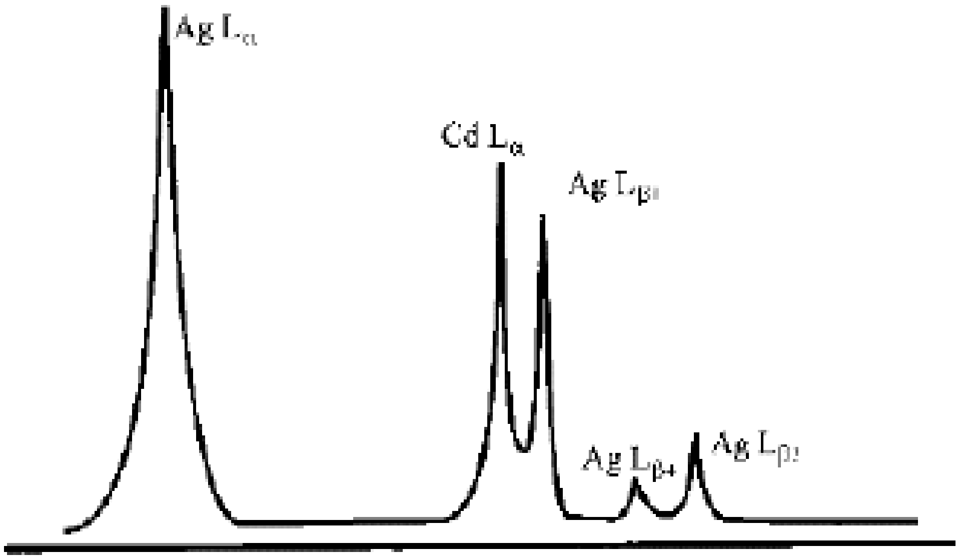
Wavelength-Dispersive Spectroscopy (WDS)

- In x-ray wavelength-dispersive spectroscopy (XWDS), characteristic x-ray are distinguished on the basis of their wavelength rather than their photon energy
- It can accurately determine the position of a single X-Ray line.
- Change θ (by moving crystal; Detector also need to be moved) and measure λ by Bragg’s Law

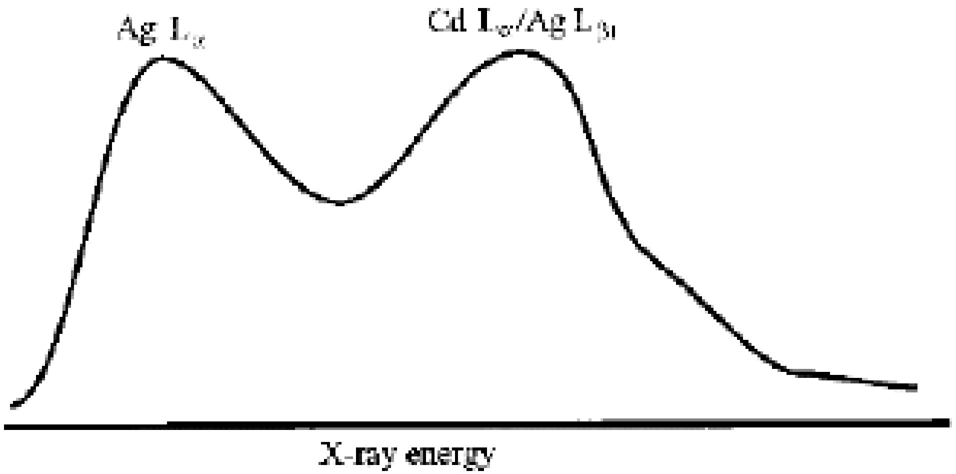


Comparison between WDS & EDS

- A big advantage of the EDS technique is the speed of data acquisition, due largely to the fact that x-rays within a wide energy range are detected and analyzed simultaneously. In contrast, the WDS system examines only one wavelength at any one time and may take several minutes to scan the required wavelength range.
- EDS detector can be brought very close (within a few mm) of the specimen, allowing about 1% of the emitted x-rays to be analyzed, whereas the WDS analyzing crystal needs room to move and subtends a smaller (solid) angle, so that much less than 1% of the x-ray photons are collected
- EDS is less costly than WDS
- WDS can clearly analyze low Z elements and elements present at low concentration which EDS can’t do



WDS



EDS

Transmission Electron Microscopy

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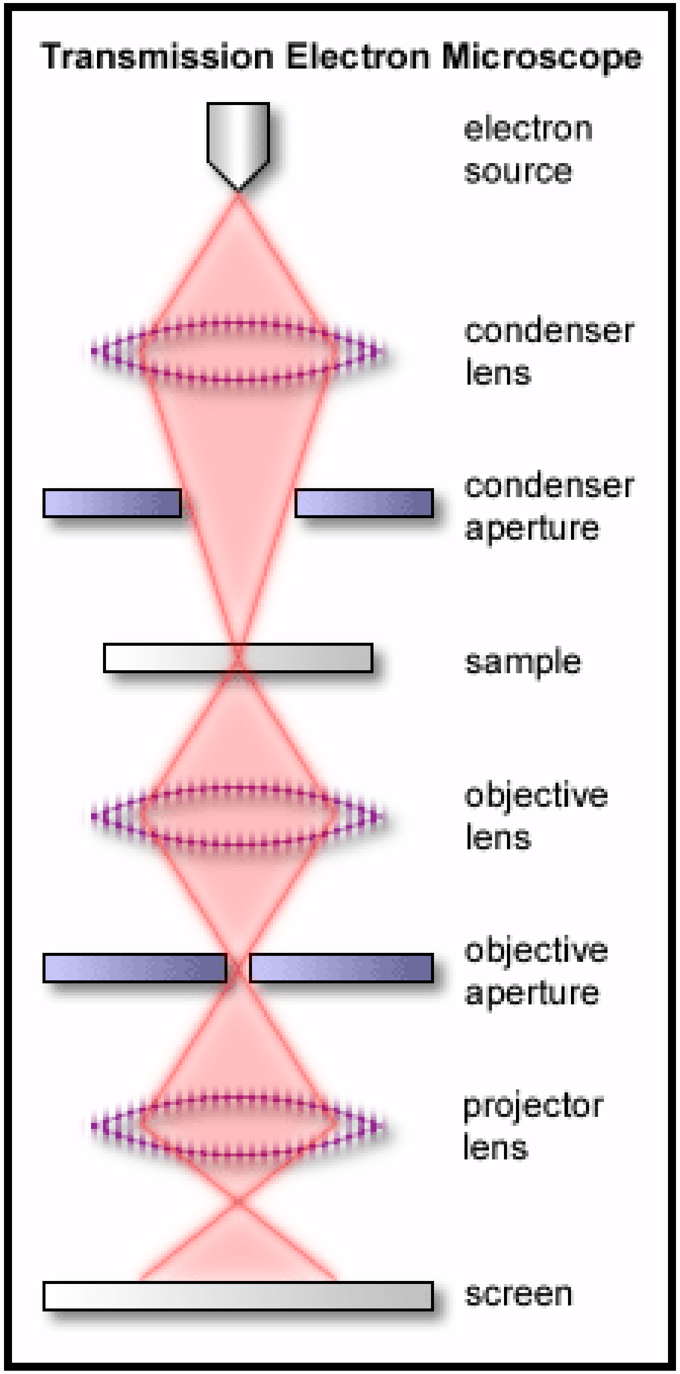
Comparison between SEM & TEM

- SEM is based on scattered electrons while TEM is based on transmitted electrons.
- The sample in TEM has to be cut thinner whereas there is no such need with SEM sample.
- SEM allows for large amount of sample to be analysed at a time whereas with TEM only small amount of sample can be analysed at a time.
- SEM is used for surfaces, powders, polished & etched microstructures, IC chips, chemical segregation whereas TEM is used for imaging of dislocations, tiny precipitates, grain boundaries and other defect structures in solids
- TEM has much higher resolution than SEM.

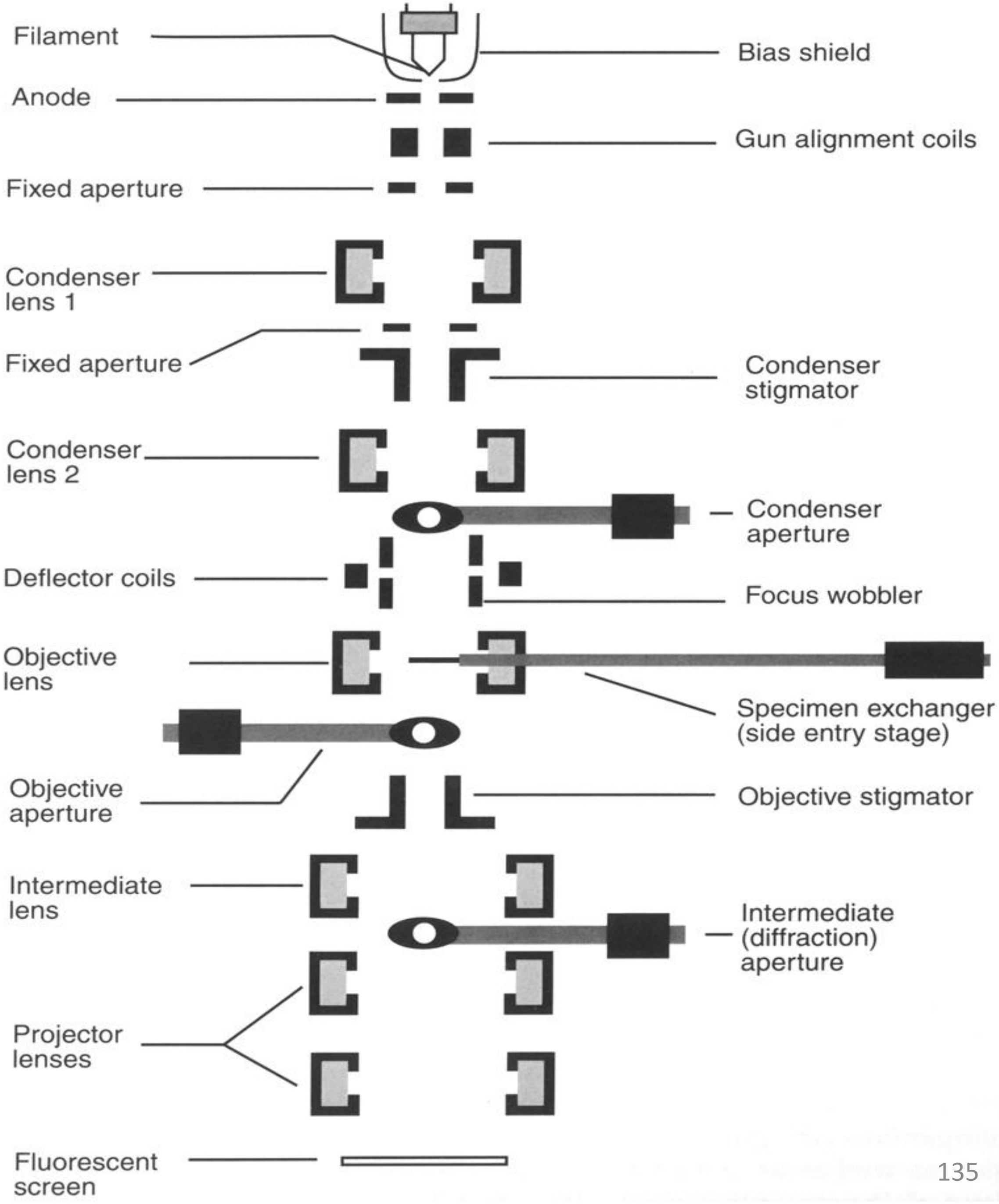
DESIGN OF TRANSMISSION ELECTRON MICROSCOPE

A simplified ray diagram of a TEM consists of an electron source, condenser lens with aperture, specimen, objective lens with aperture, projector lens and fluorescent screen.



Components of a TEM Column

In actuality a modern TEM consists of many more components including a dual condenser system, stigmators, deflector coils, and a combination of intermediate and dual projector lens



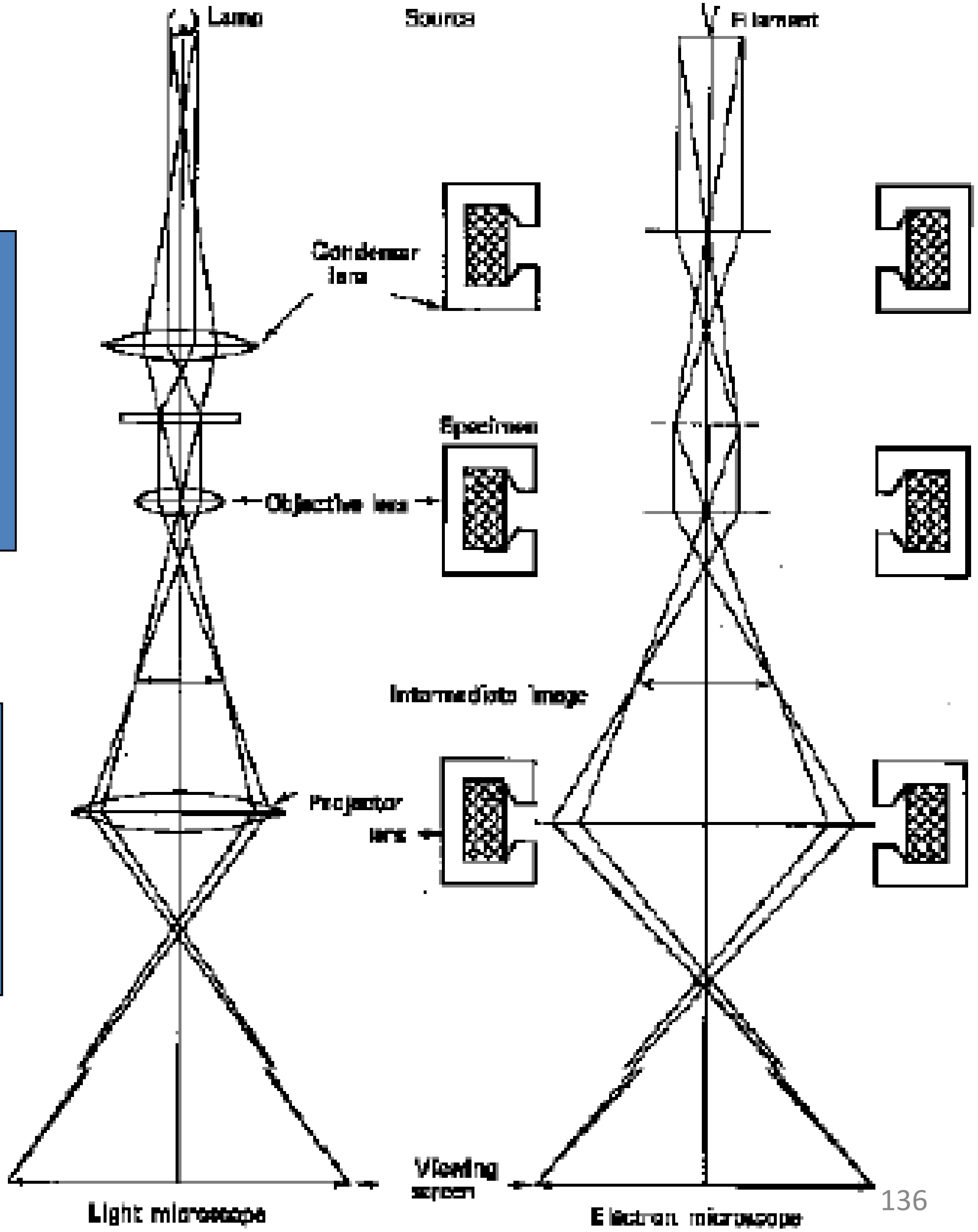
COMPARISION OF LIGHT AND ELECTRON MICROSCOPE

LIGHT MICROSCOPE

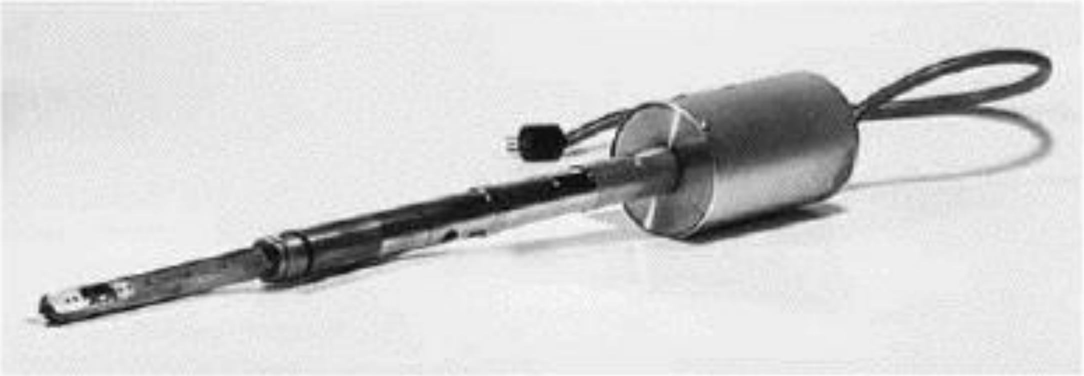
Optical glass lens, Small depth of Field, lower magnification, do not Require vacuum, Low price.

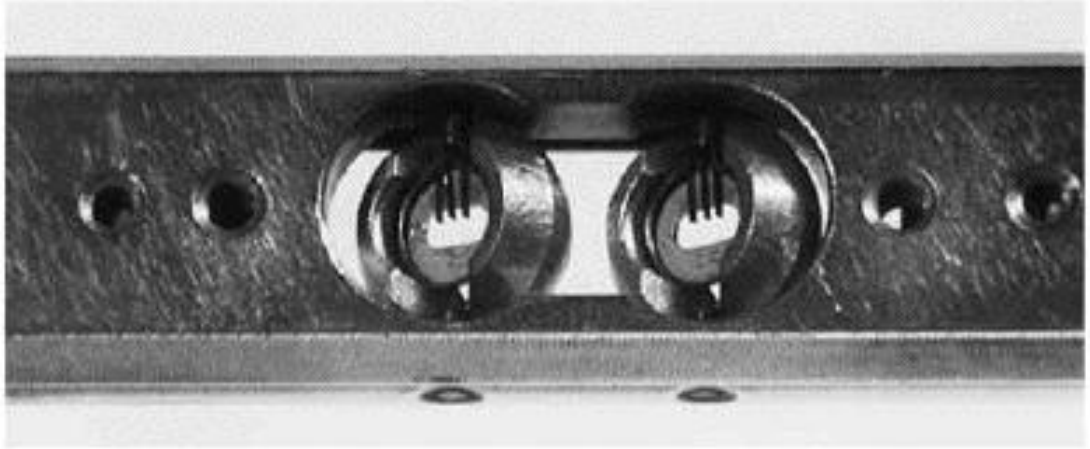
ELECTRON MICROSCOPE

Magnetic lens, Large depth of field, Higher magnification and better Resolution, Operates in HIGH vacuum, Price tag.



Sample Holder of TEM





Fluorescent Screen

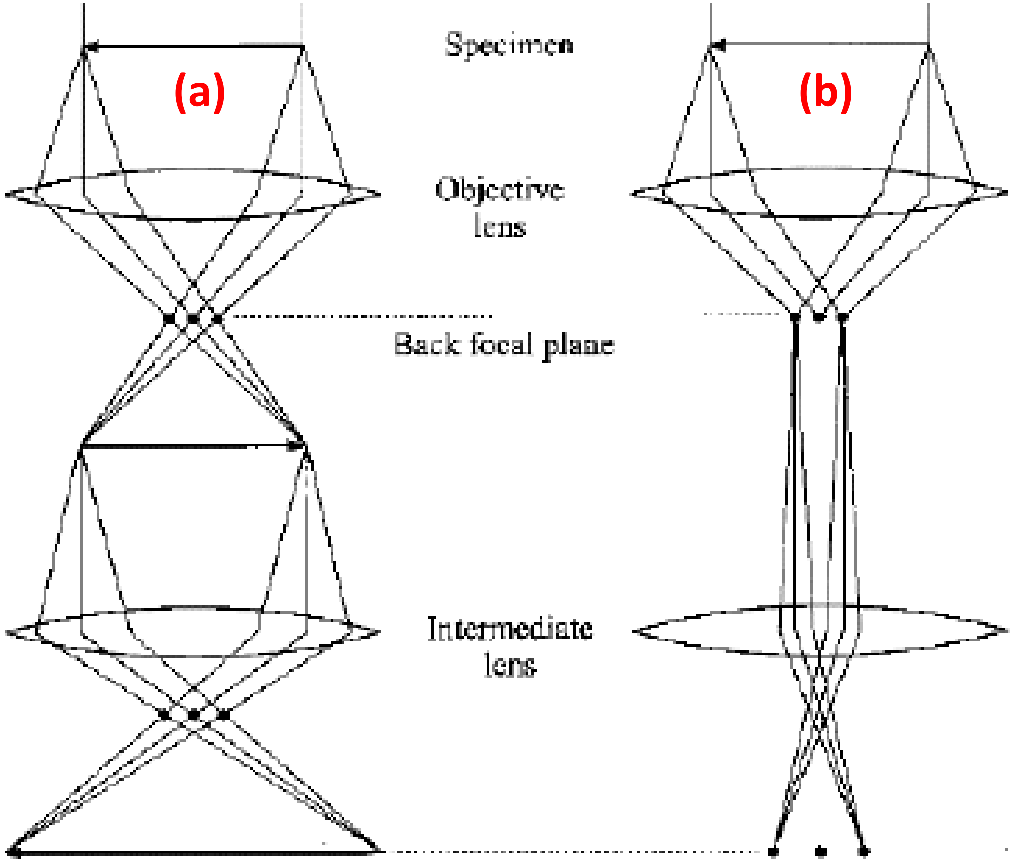
- Fluorescence: Property of emitting radiation under the influence of electromagnetic or electron beam bombardment.

- In the TEM, screen coated with a material in the visible range, eg zinc sulphide, is installed beneath the projector lens in the path of the electron beam.

- Screen emits visible light when bombarded with electrons.

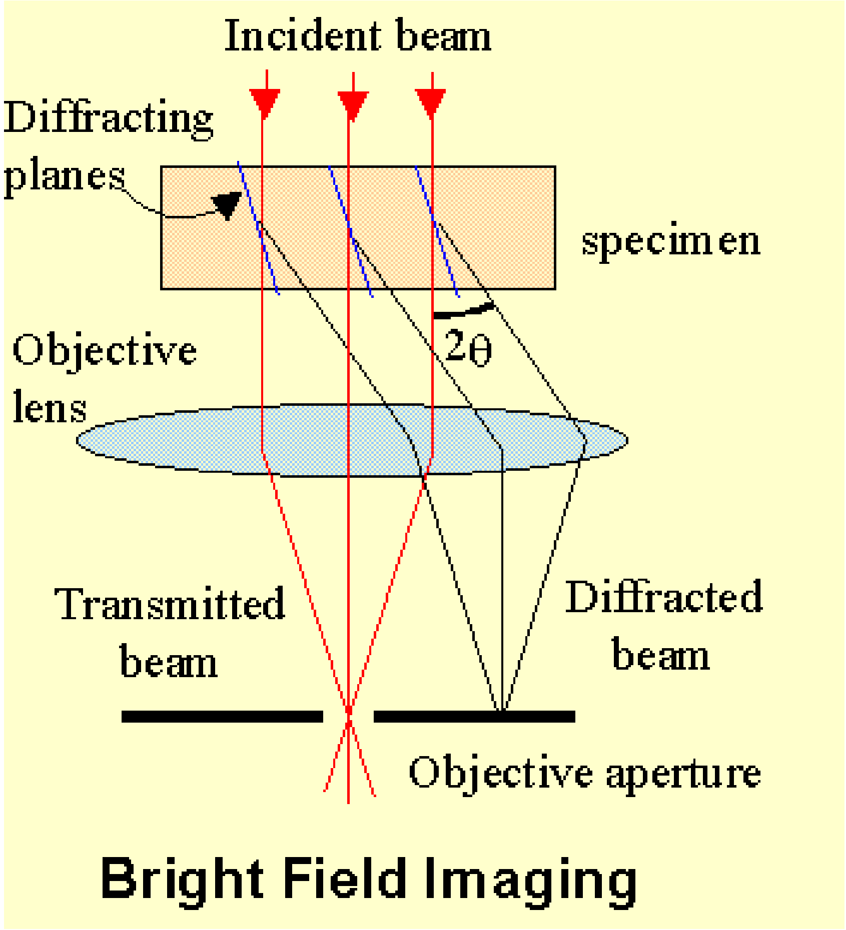
- The resolution of the fluorescent screen is limited to 70-100µm by the grain size of the fluorescent material and by light scattering within this material.

Imaging Mode(a) & Diffraction Mode(b)

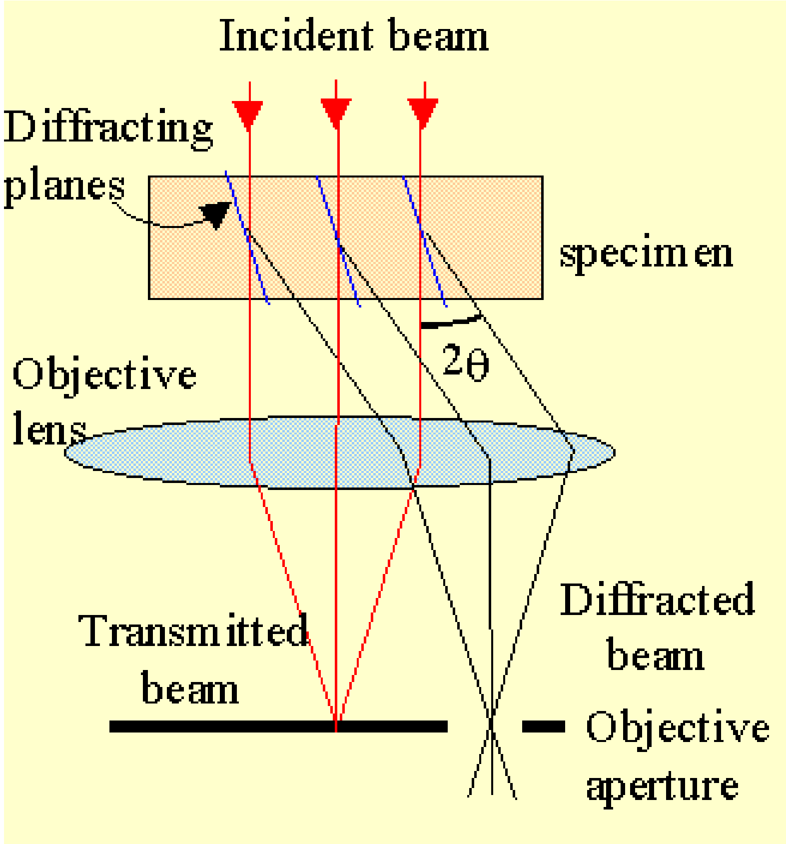


- ❑ The image of the specimen in conventional microscopy, is formed selectively allowing only the transmitted beam (Bright Field Imaging) or one of the diffracted beams (Dark Field Imaging) down to the microscope column by means of an aperture.
- ❑ The origin of the image contrast is the variation of intensities of transmitted and diffracted beams due to the differences in diffraction conditions depending on the microstructural features on the electron path.

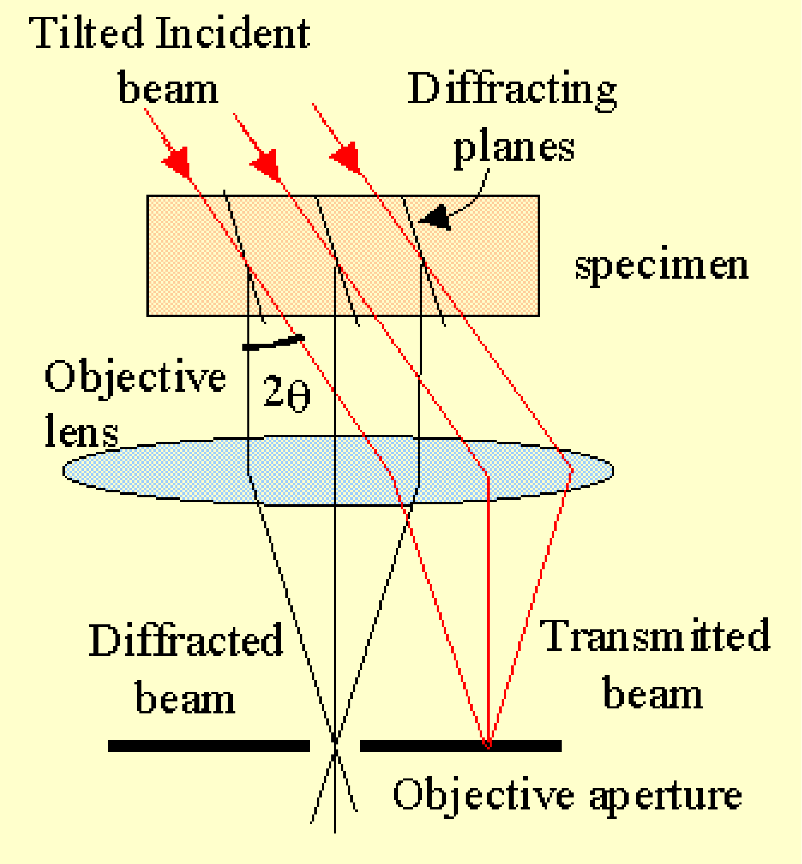
Bright field imaging allowing transmitted beam



Bright field imaging allowing diffracted beam



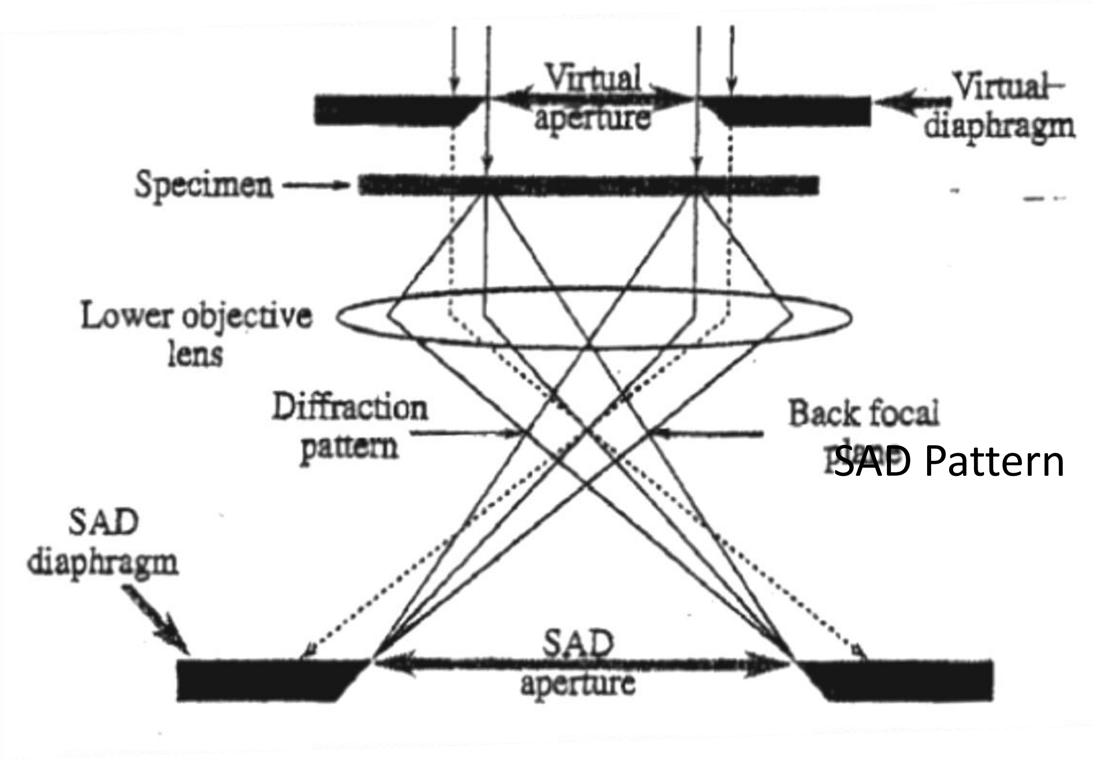
Off-axis Dark Field

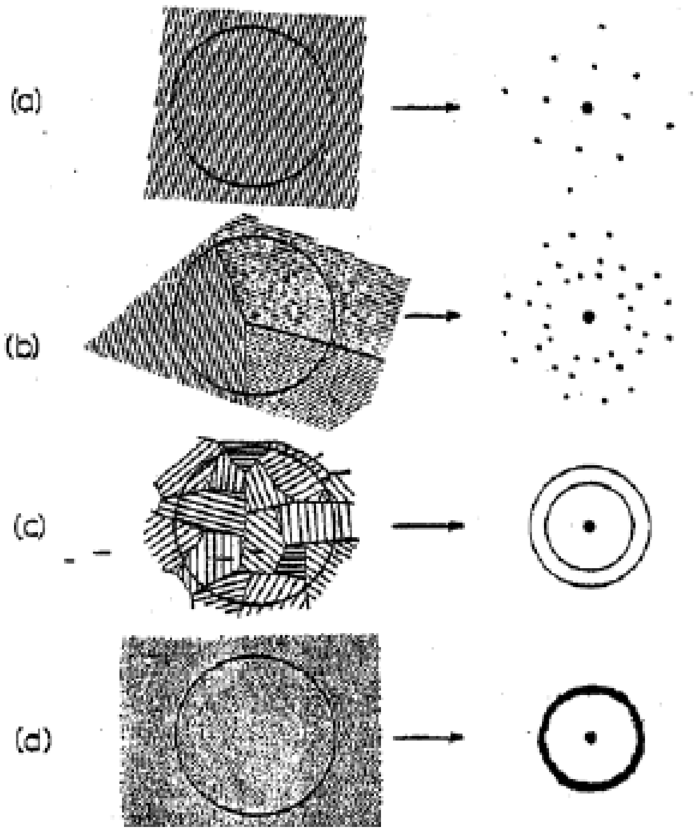


On-axis Dark Field

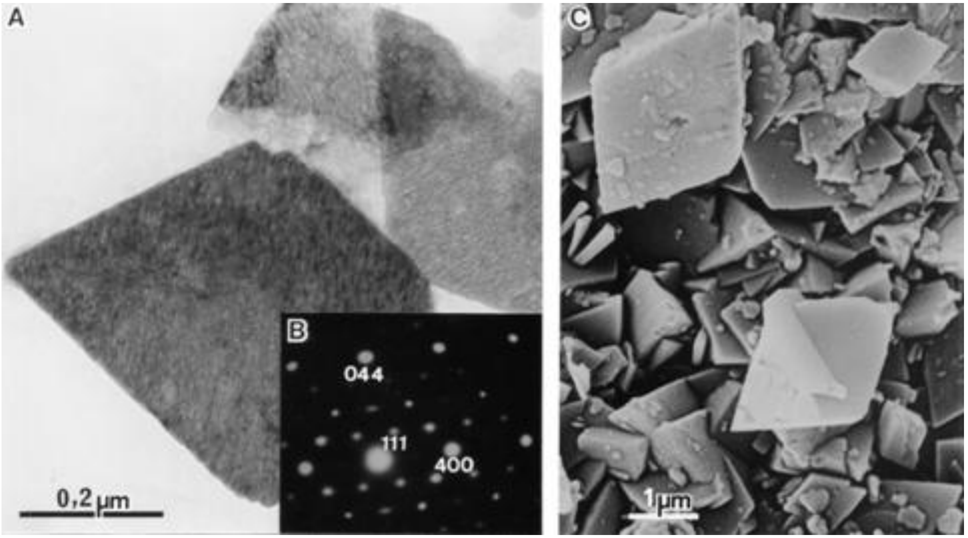
SAD Aperture

SAD Pattern

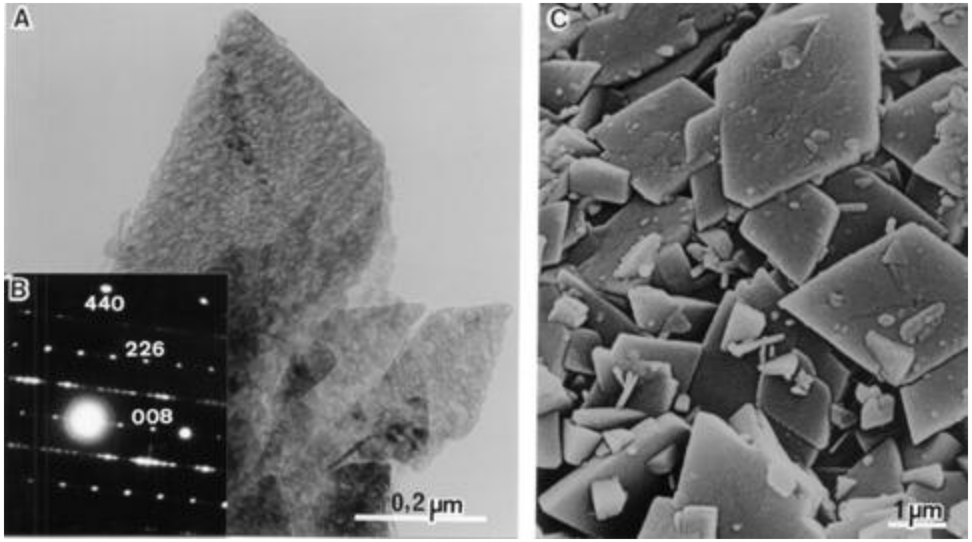




The types of diffraction pattern which arises from different specimen microstructures. (a) A single perfect crystal; (b) A small number of grins-notice that even with only three grains the pots begin to appear to form circles; (c) A large number of randomly oriented grains-the spots have now merged into rings; (d) An amorphous specimen merely gives rise to a diffuse halo, indicating that on average the atoms are similar distances apart



$\gamma\text{-Al}_2\text{0}_3$ (A) TE micrograph; (B) SAD pattern; (C) SE micrograph.



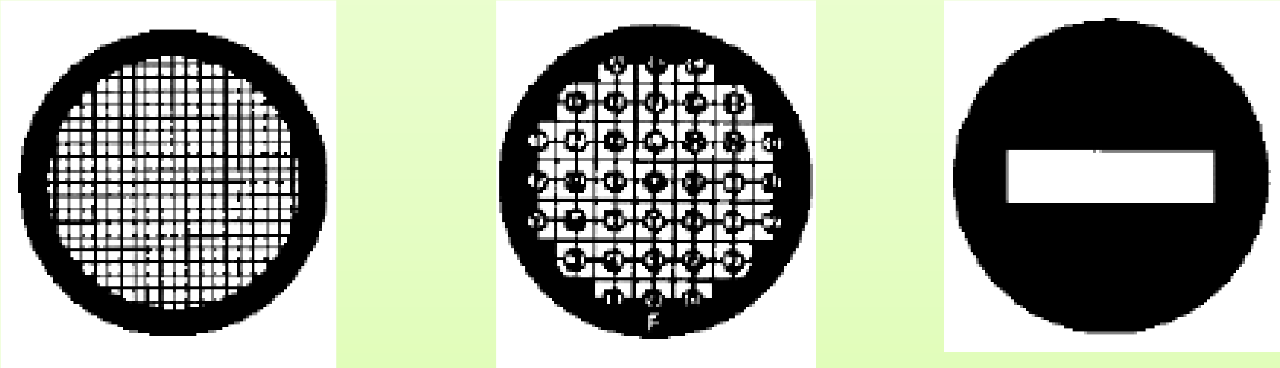
δ-Al203 (A) TE micrograph; (B) SAD pattern; (C) SE micrograph.

SPECIMEN PREPARATION METHODS

Specimens are usually in one or two forms:

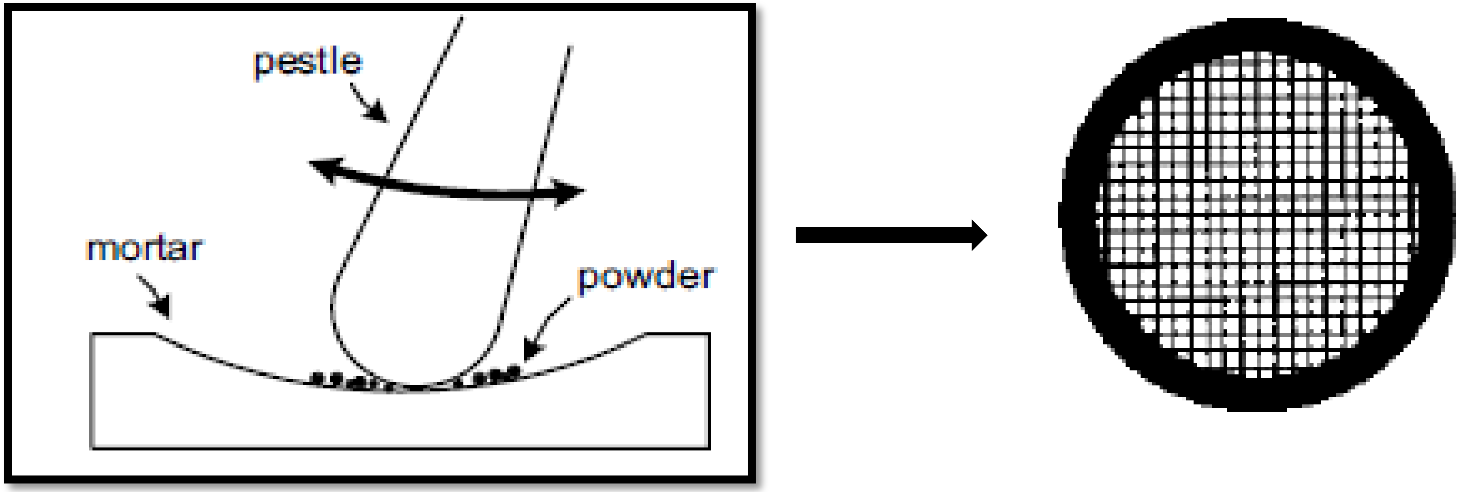
- Powder
- Thin foil
- Replica

Types of Grid



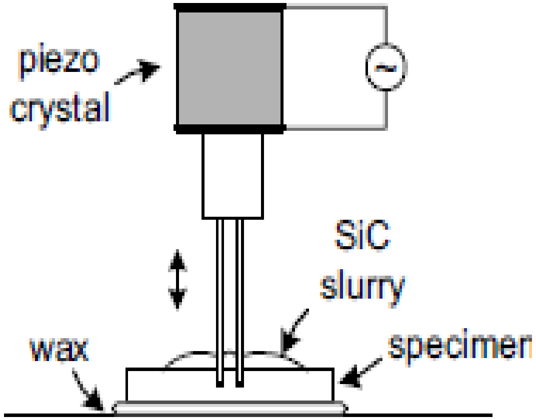
Three types of grid for TEM specimens. (a) A plain mesh Grid, (b) A ‘finder’ grid marked with identification letters and (c) A slot grid for large specimens

Powder Sample



Thin foil preparation

Initial size reduction involves mechanical method

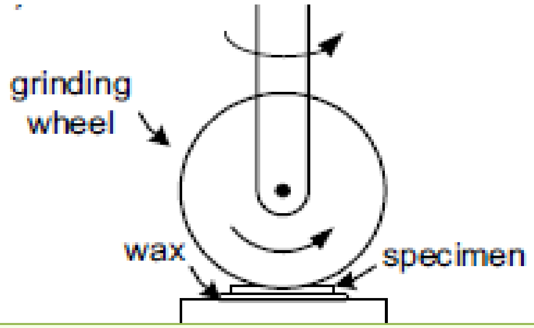


1. **Cut the specimen to < 1mm thin and 3mm dia (soft material- Mechanical Punch & Hard material use Ultrasonic Drill)**

- ✓ *piezoelectric* crystal that changes slightly in length when a voltage is applied between electrodes on its surfaces

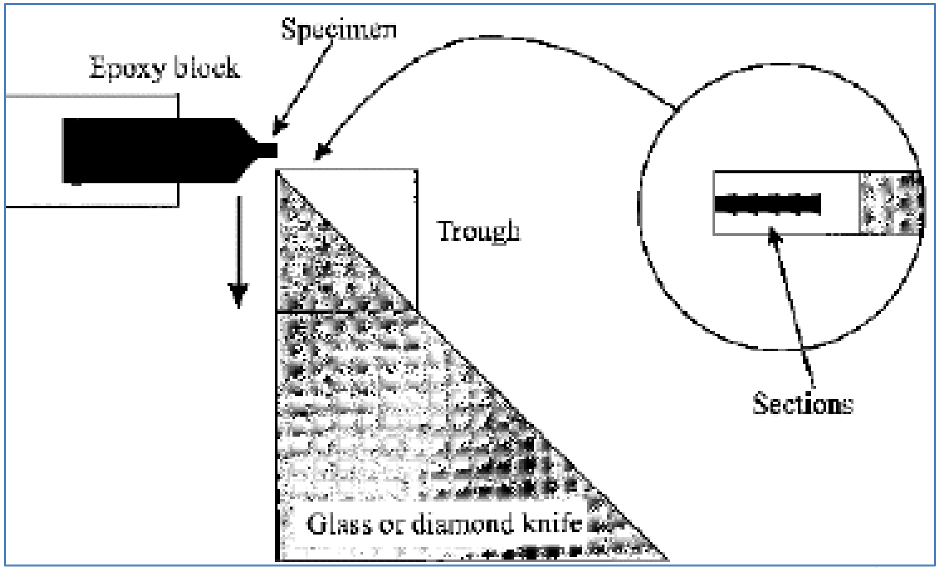
Upon applying a high-frequency ac voltage, the tube oscillates vertically thousands of times per second, driving SiC particles against the sample and cutting an annular groove in the slice

2. Disk is then thinned further by polishing with abrasive paper (coated with diamond or silicon carbide particles) or by using a dimple grinder

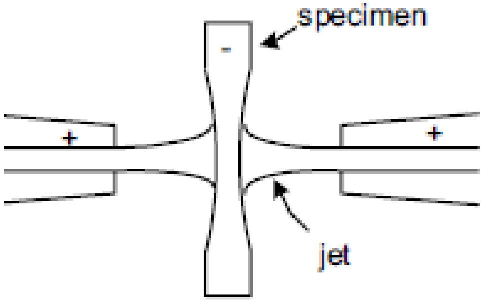


- Metal wheel rotates rapidly against the surface (covered with a SiC slurry or diamond paste)
- Specimen disk is rotated slowly about a vertical axis.
- The result is a dimpled specimen of 10 µm to 50 µm thickness at the center but greater (100 µm to 400 µm) at the outside, which provides the mechanical strength needed for easy handling.

- In the case of biological tissue, a common procedure is to use an ultramicrotome to directly cut slices of 100 nm or more in thickness. The tissue block is lowered onto a glass or diamond knife that cleaves the material apart . The ultramicrotome can also be used to cut thin slices of the softer metals, such as aluminum.



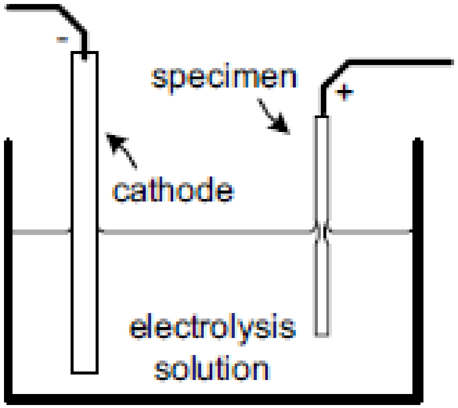
3. **Chemically thinning**: A chemical solution dissolves the original surface and reduces the specimen thickness to a value suitable for TEM imaging.



- ✓ In the simplest case, a thin piece of material is floated onto the surface of a chemical solution that attacks its lower surface; the sample is retrieved (e.g, by picking up by a TEM grid held in tweezers) before it dissolves completely.
- ✓ More commonly, a jet of chemical solution is directed at one or both surfaces of a thin disk. As soon as a small hole forms in the center (detected by the transmission of a light beam), the polishing solution is replaced by rinse water.

4. **Electrochemical thinning :** Carried out with a direct current flowing between the specimen (at a negative potential) and a positive electrode, immersed in a chemical solution.

- ✓ **Only used for conducting samples**

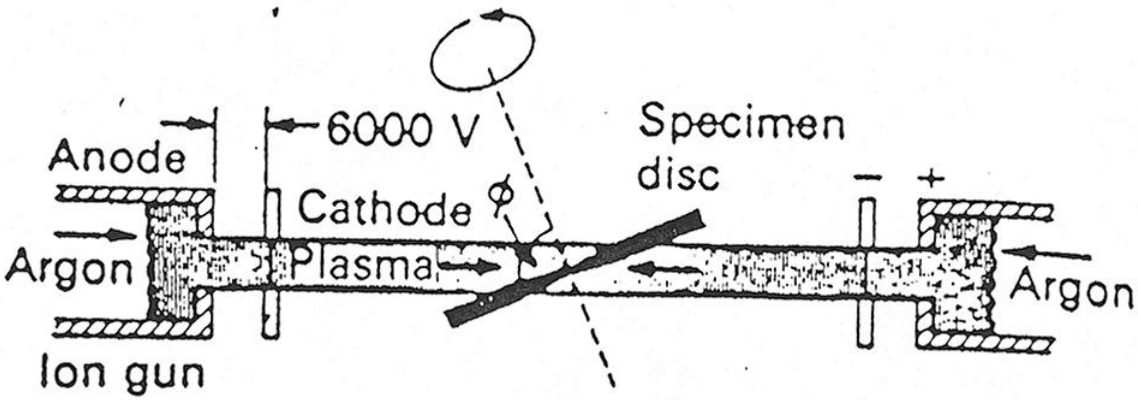


Window-frame method: Specimen is in the form of a thin sheet (1 cm or more in height and width) whose four edges are previously painted with protective lacquer to prevent erosion at the edge. When partially immersed in the electrolytic solution, thinning is most rapid at the liquid/air interface, which perforates first

Jet Thinning: Apply a dc voltage between the specimen and jet electrodes.

When thinning metals, glycerin is sometimes added to the solution to make the liquid more viscous, helping to give the thinned specimen a polished (microscopically smooth) surface.

5. **Ion Milling/Ion-beam Milling:** Used for chemically inert material



Schematic diagram of typical ion-beam thinning equipment

6. Replication: These are prepared by different techniques

- ✓ Surface or Carbon replica
- ✓ “Extraction” replica

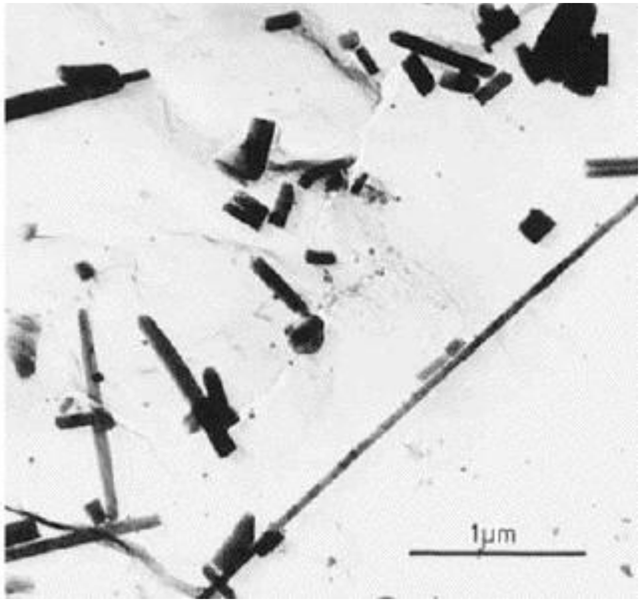
Surface Or Carbon Replica:

This is produced from a specimen.

- ✓ The specimen surface is coated with a cellulose acetate film (e.g., collodion) to produce a negative impression of the surface features.
- ✓ The plastic film is stripped from the specimen surface and coated with a layer of carbon (about 10 to 20 nm thick). The carbon-coating process takes place in a vacuum evaporator unit.
- ✓ The plastic is then removed (dissolved) from the carbon replica by solvent.
- ✓ Before the replica is observed in the microscope, it is usually shadowed (sputtered) with carbon or a heavy element to enhance the topographical features of the surface.

“Extraction” replica:

- ✓ The metallographic specimen is etched beforehand to put particles and carbides in relief.
- ✓ Carbon film is deposited on the surface of the etched specimen.
- ✓ The carbon film itself is not physically stripped from the specimen surface, but etched or “floated” away from the surface so that those particles attached to the deposited carbon film will be extracted from the specimen.



X-Ray Diffraction Technology

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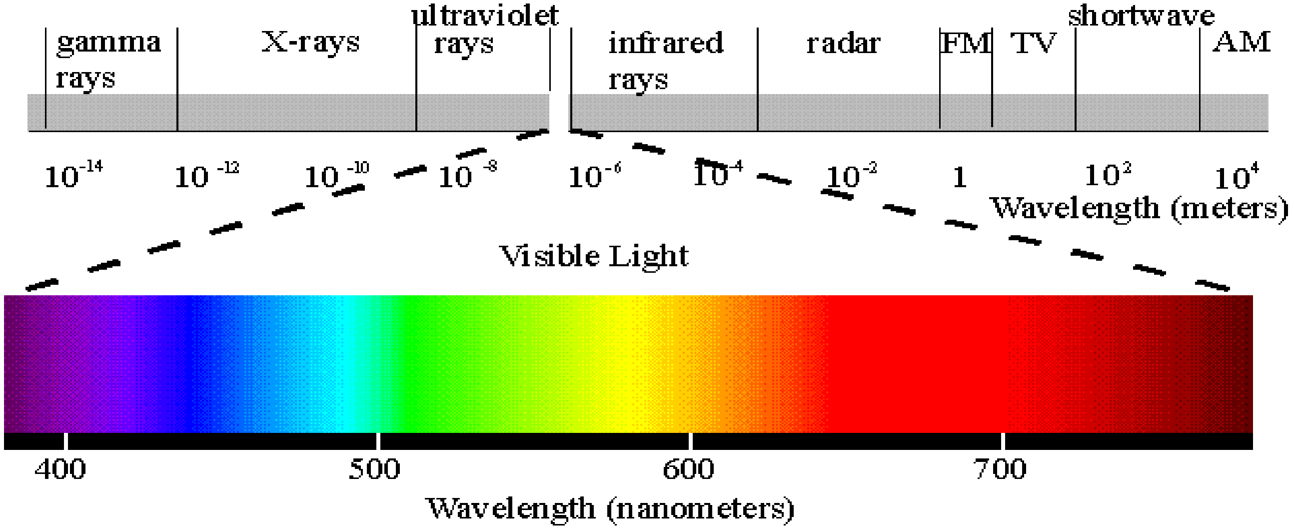
X-Ray

- X-rays were discovered in 1895 by the German physicist Wilhelm Conrad Röntgen and were so named because their nature was unknown at the time.
- He was awarded the Nobel prize for physics in 1901.

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

W.C. Röntgen
(1845-1923)

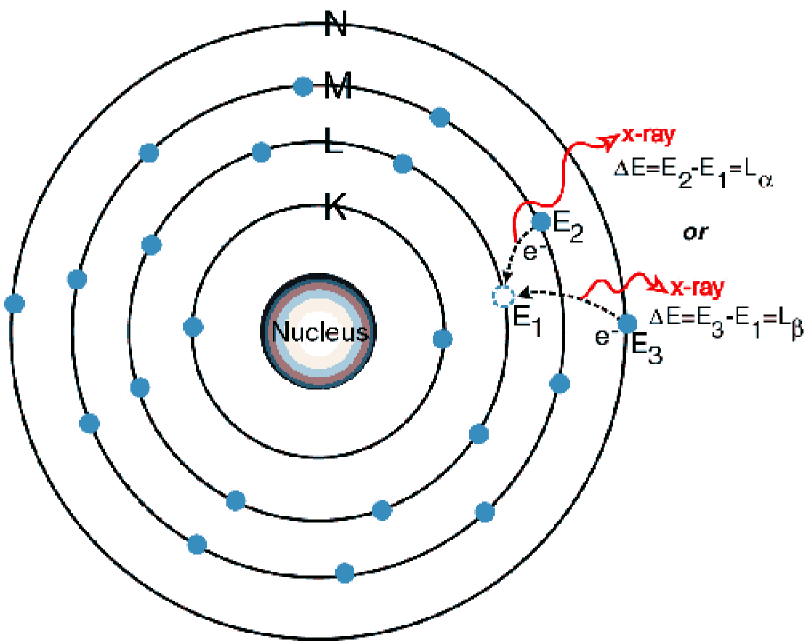


Energy of Photons:

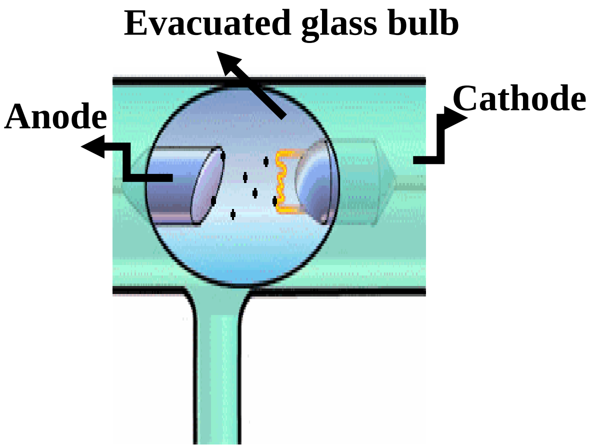
$$E = \frac{hc}{\lambda}$$

Production of X-Rays

- Visible light photons and X-ray photons are both produced by the movement of electrons in atoms. Electrons occupy different energy levels, or orbitals, around an atom's nucleus.
- When an electron drops to a lower orbital, it needs to release some energy; it releases the extra energy in the form of a photon. The energy level of the photon depends on how far the electron dropped between orbitals.

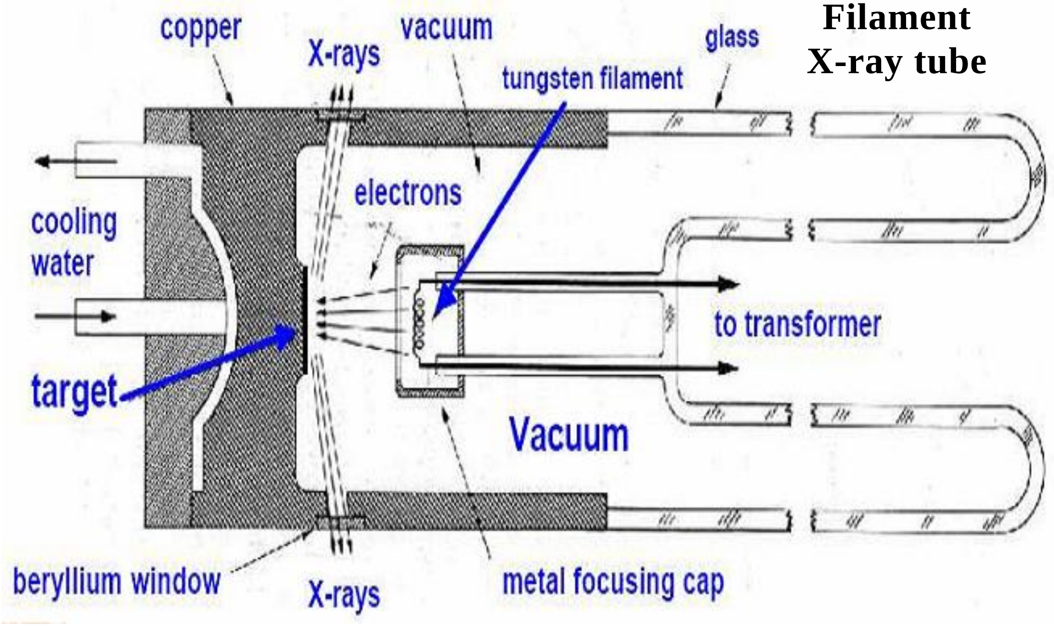


- X-rays are produced when any electrically charged particle of sufficient kinetic energy is rapidly decelerated. Electrons are usually used for this purpose.
- When a high voltage is applied between the electrodes, streams of electrons (cathode rays) are accelerated from the cathode (W or any high melting point element) to the anode and produce X rays as they strike the anode.



Filament X-ray tube

- Filament tube consists of an evacuated glass envelope which insulates the anode at one end from the cathode at the other, the cathode being a tungsten filament and the anode a water-cooled block of copper containing the desired target metal (mainly Mo, Cu, Co, Cr, Fe) as a small insert at one end.



- One lead of the high-voltage transformer is connected to the filament and the other to ground, the target being grounded by its own cooling water connection.
- The filament is heated by a filament current of about 3 amp and emits electrons which are rapidly drawn to the target by the high voltage across the tube.
- A small metal cup maintained at the same high (negative) voltage as the filament is present surrounding the filament. It repels the electrons and tends to focus them into a narrow region of the target, called the focal spot.
- X-rays are emitted from the focal spot in all directions and escape from the tube through two or more windows in the tube housing. Since these windows must be vacuum tight and yet highly transparent to x-rays, they are usually made of beryllium, aluminum, or mica.

X-Ray Spectrum

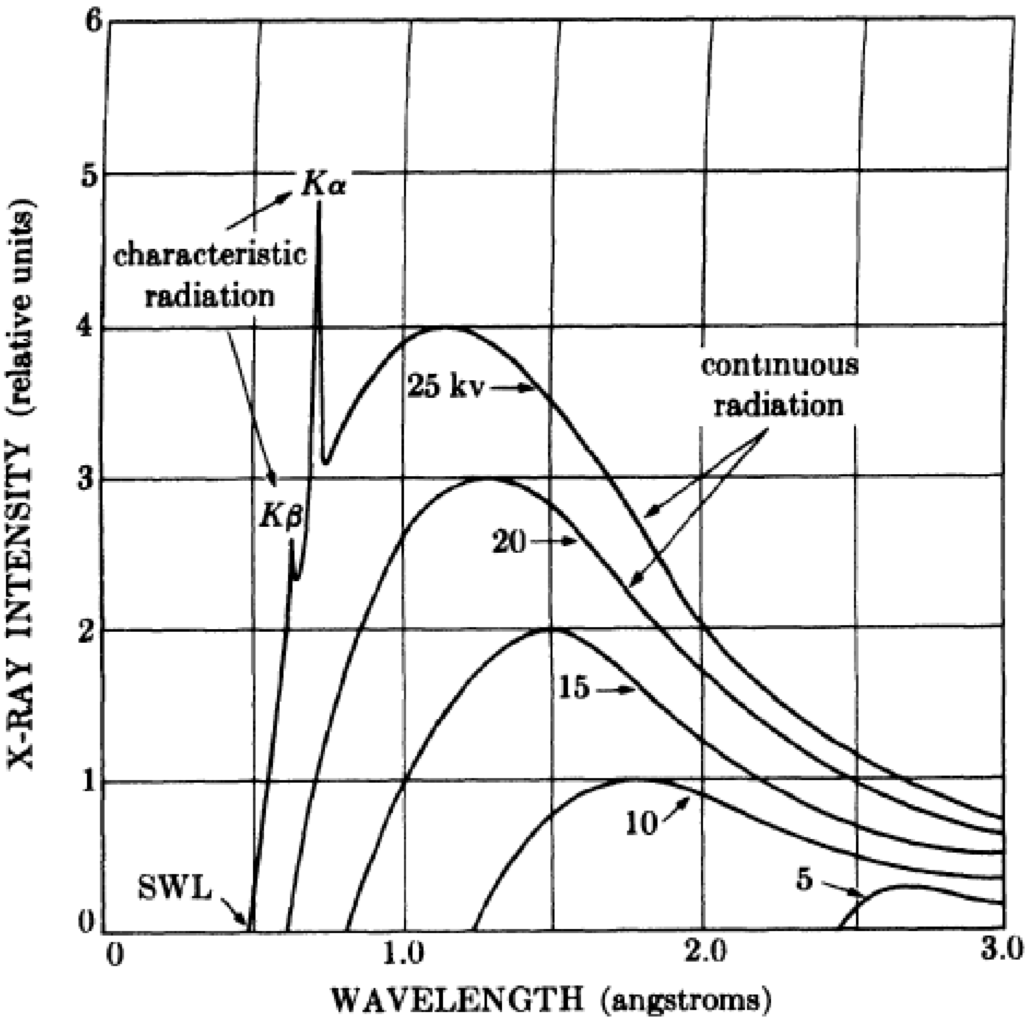
- ☐ X-rays result from fast electron irradiation of metal targets (Cu, Co, Cr, Mo) under vacuum.
- ☐ Types of X-rays:
  - ✓ Characteristic: X-rays from core-level ionization
  - ✓ Continuous/ Heterochromatic/white: X-ray from deceleration of electrons

- ☐ If e is the charge on the electron (4.80 X 10^{-10} esu) and the voltage (in esu) across the electrodes, then the kinetic energy (in ergs) of the electrons on impact is given by the equation: $KE = eV = \frac{1}{2}mv^2$

Where m is the mass of the electron (9.11 X 10^{-28} gm) and v its velocity just before impact.

- ☐ Most of the kinetic energy of the electrons striking the target is converted into heat, less than 1 percent being transformed into x-rays.
- ☐ Rays coming from the target consist of a mixture of different wavelengths, and the variation of intensity with wavelength is found to depend on the tube voltage.

- The intensity is zero up to a certain wavelength, called the short-wavelength limit (λ_{SWL}), increases rapidly to a maximum and then decreases, with no sharp limit on the long wavelength side.
- When the tube voltage is raised, the intensity of all wavelengths increases, and both the λ_{SWL} and the position of the maximum shift to shorter wavelengths.
- Smooth curves corresponding to applied voltages of 20 kv or less in the case of a Mo target, represents heterochromatic/continuous/white radiation, since it is made up of rays of many wavelengths.



X-ray spectrum of molybdenum as a function of applied voltage

Continuous Spectrum

- The continuous spectrum is due to the rapid deceleration of the electrons hitting the target since, any decelerated charge emits energy.
- Not every electron is decelerated in the same way, however; some are stopped in one impact and give up all their energy at once, while other are deviated this way and that by the atoms of the target, successively losing fractions of their total kinetic energy until it is all spent.
- Those electrons which are stopped in one impact will give rise to photons of maximum energy, i.e., to x-rays of minimum wavelength. Such electrons transfer all their energy eV into photon energy.

$$\boxed{\begin{aligned} &eV = h\gamma_{\max} \\ &\lambda_{SWL} = \frac{hc}{eV} = \frac{12{,}400}{eV} \end{aligned}}$$

- If an electron is not completely stopped in one encounter but undergoes a glancing impact which only partially decreases its velocity, then only a fraction of its energy eV is emitted as radiation and the photon produced has energy less than $h\gamma_{\max}$. In terms of wave motion, the corresponding x-ray has a wavelength longer than λ_{SWL} .
- The totality of these wavelengths, ranging upward from λ_{SWL}, constitutes the continuous spectrum.

Intensity of Continuous Spectrum

$$I_{cont.spetrum} = AizV^{m}$$

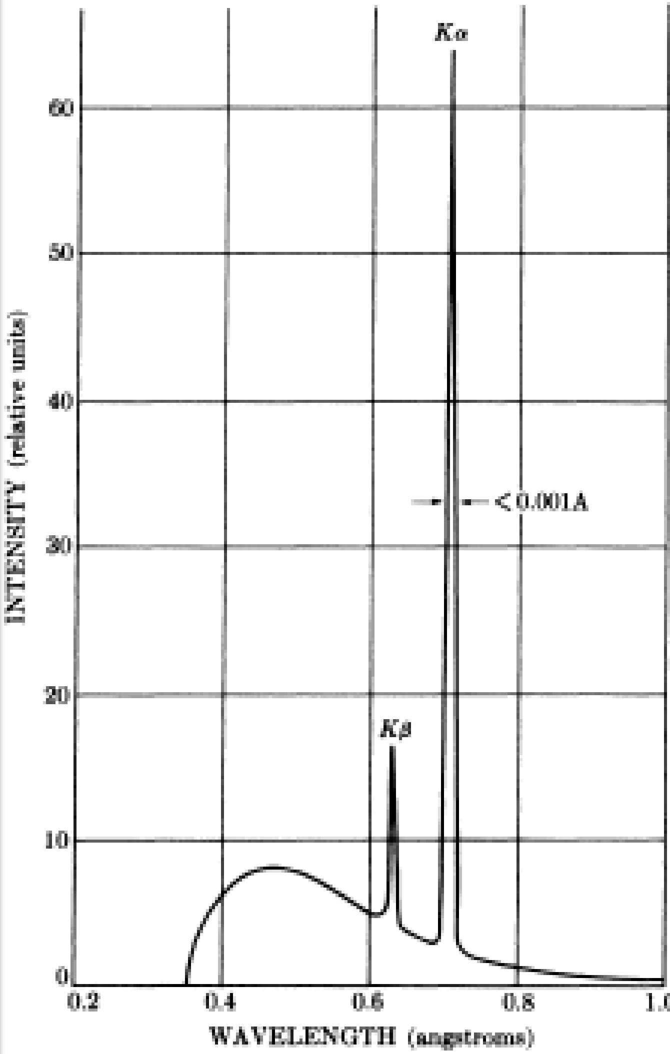
Where A is a proportionality constant and m is a constant with a value of about 2

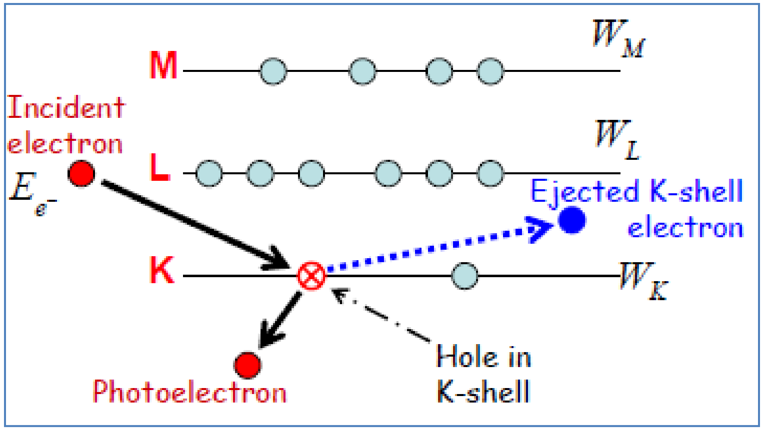
Higher atomic number (Z) elements and high voltages are required to generate high intensity X-rays

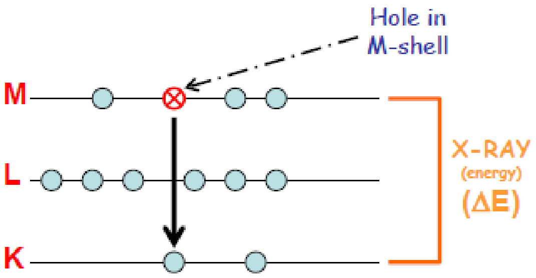
Characteristics Spectrum

- When the voltage on an x-ray tube is raised above a certain critical value, characteristic of the target metal, sharp intensity maxima appear at certain wavelengths, superimposed on the continuous spectrum.
- Since they are so narrow and since their wavelengths are characteristic of the target metal used, they are called characteristic lines.
- The origin of the characteristics spectrum lies in the atoms of the target metal itself. If one of the electrons bombarding the target has sufficient kinetic energy, it can knock an electron out of the K shell, leaving the atom in an excited, high-energy state.
- One of the outer electrons immediately falls into the vacancy in the K shell, emitting energy in the process, and the atom is once again in its normal energy state. The energy emitted is in the form of radiation of a definite wavelength and is, in fact, characteristic K radiation.
- The K-shell vacancy may be filled by an electron from any one of the outer shells, thus giving rise to a series of K lines; K_α and $K_ß$ lines.

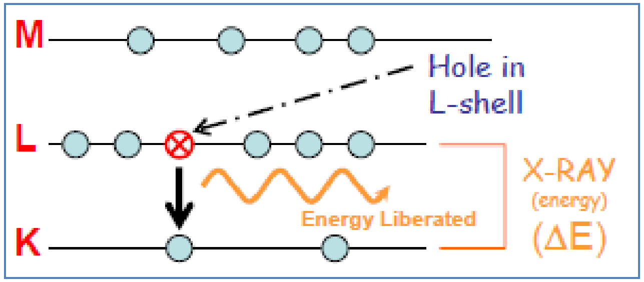
- These characteristics lines fall into several sets, referred to as K, L, M, etc., in the order of increasing wavelength, all the lines together forming the characteristic spectrum of the metal used as the target.
- For a molybdenum target the K lines have wavelengths of about 0.7A, the L lines about 5A, and the M lines still higher wavelengths.
- Ordinarily only the K lines are useful in x-ray diffraction, the longer-wavelength lines being too easily absorbed.
- There are several lines in the K set, but only the three strongest are observed in normal diffraction work. These are the $K_{\alpha1}$, $K_{\alpha2}$, $K_{ß1}$ and for molybdenum their wavelengths are: $K_{\alpha1} = 0.70926Å$, $K_{\alpha2} = 0.71354Å$ and $K_{ß1} = 0.63225Å$.
- The intensity of any characteristic line: $I_{K\ line} = Bi(V - V_K)^n$, where B is a proportionality constant, I is the current, V_K is the K excitation voltage, and n is a constant with a value of about 1.5.
- The intensity of a characteristic line can be quite large but at the same time these are also very narrow (< 0.001A wide) measured at half their maximum intensity.







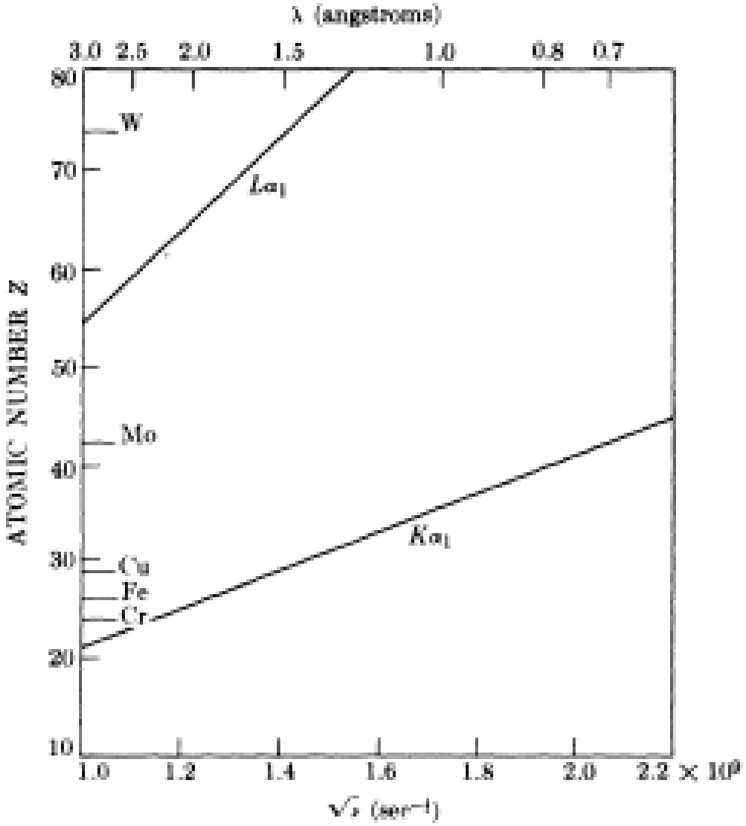
K_β X-ray



Kα X-ray

Moseley's law

- The wavelength of any particular line decreases as the atomic number of the emitter increases.
- In particular, Moseley's law shows a linear relation between the square root of the line frequency γ and the atomic number Z : $\sqrt{\gamma} = C(Z - \sigma)$, where C and σ are constants.



Monochromatic and Broad Spectrum of X-rays

- X-rays can be created by bombarding a metal target with high energy (> 10^4) electrons.
- Some of these electrons excite electrons from core states in the metal, which then recombine, producing highly monochromatic X-rays. These are referred to as characteristic X-ray lines.
- Other electrons, which are decelerated by the periodic potential of the metal, produce a broad spectrum of X-ray frequencies.
- Depending on the diffraction experiment, either or both of these X-ray spectra can be used.

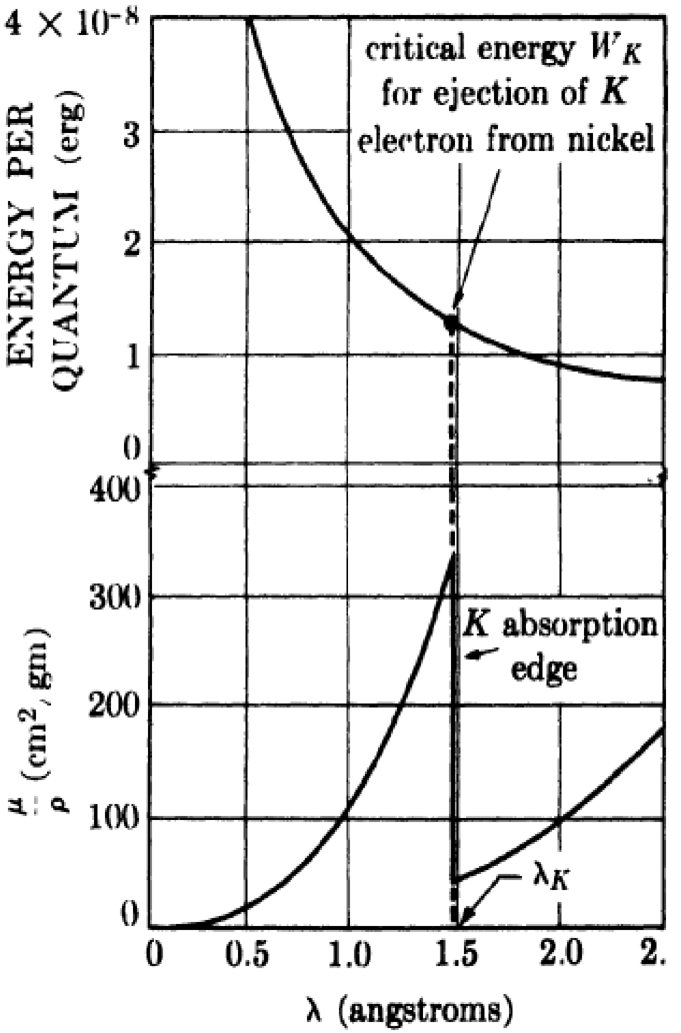
Absorption of X-rays

- When x-rays encounter any form of matter, they are partly transmitted and partly absorbed.
- Fractional decrease in the intensity I of an x-ray beam as it passes through any homogeneous substance is proportional to the distance traversed, x.
- In differential form,

$$-\frac{dI}{I} = \mu dx$$

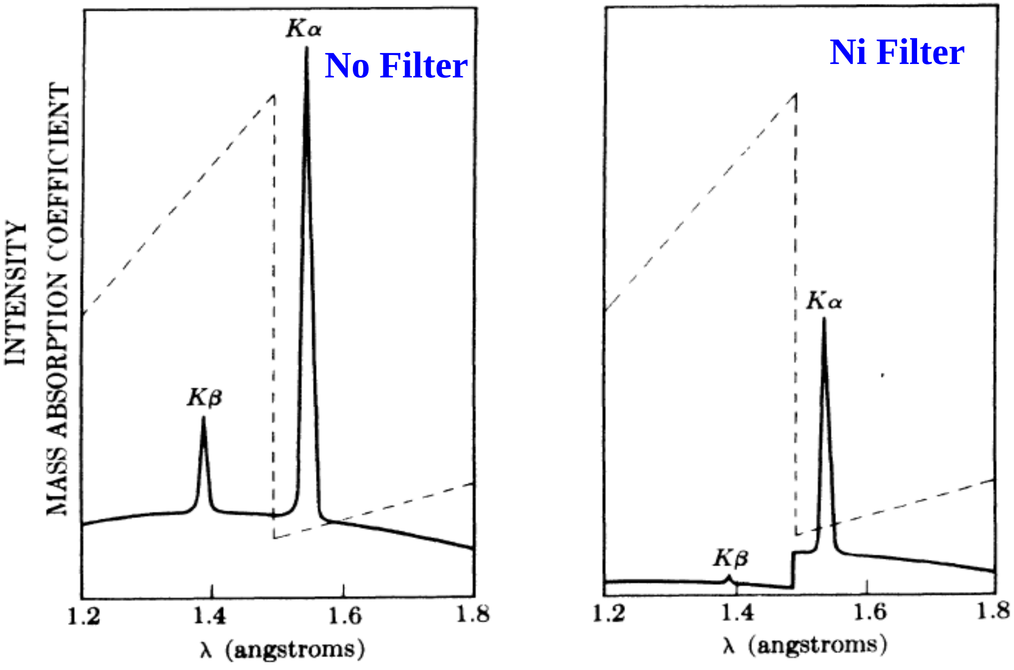
where the proportionality constant μ is called the linear absorption coefficient and is dependent on the substance considered, its density, and the wavelength of the x-rays.

- On integration, $I_x = I_0 e^{-\mu x}$
  where I_o = intensity of incident x-ray beam and I_x = intensity of transmitted beam after passing through a thickness x.
- The linear absorption coefficient μ is proportional to the density ρ, which means that the quantity μ / ρ is a constant of the material and independent of its physical state (solid, liquid, or gas). $I_x = I_0 e^{-(\mu/\rho)\rho x}$
- This latter quantity, called the mass absorption coefficient.
- Mass absorption coefficient is the weighted average of the mass absorption coefficients of its constituent elements.
$$\frac{\mu}{\rho} = w_1\left(\frac{\mu}{\rho}\right)_1 + w_2\left(\frac{\mu}{\rho}\right)_2 + ...$$
- The absorption coefficient varies with wavelength in the following way. $\frac{\mu}{\rho} = k\lambda^3 z^3$
  where k = a constant, with a different value for each branch of the curve, and Z = atomic number of absorber.
- Absorption edges correspond to the binding energies for different types of inner shell electrons

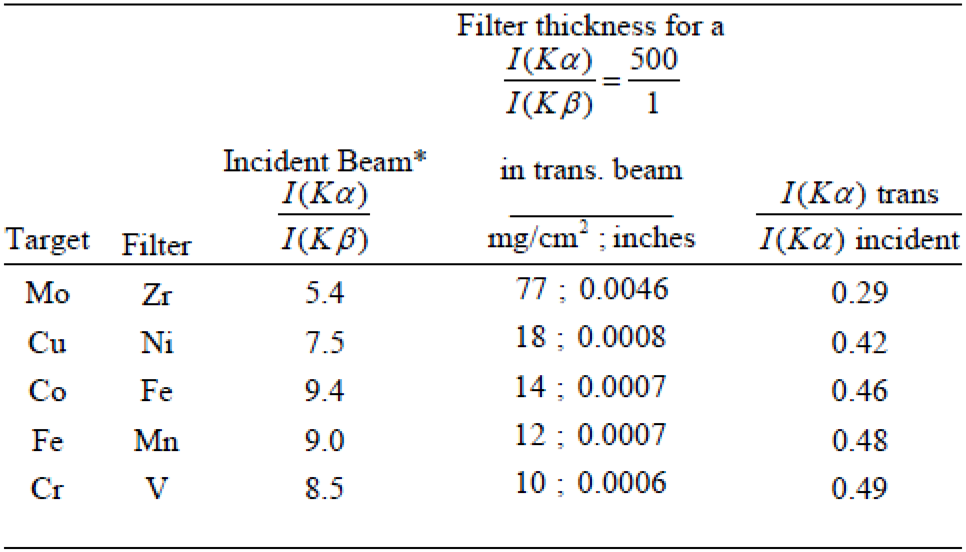


Good aspects/uses of absorption: X-ray Filters

- We can conduct XRD experiments without adversely influencing our health by using X-ray absorbing shields (e.g., lead aprons, leaded glass, etc.).
- We can also utilize absorption to improve our XRD experiments.
- "Filtering" of unwanted X-rays
- If we place a thin foil with atomic number (Z-1) in a beam of X-rays generated with a target of atomic number Z, the K_β peak of the target radiation will be almost completely absorbed and the background intensity around the K_α peak will also be attenuated (i.e., reduced).



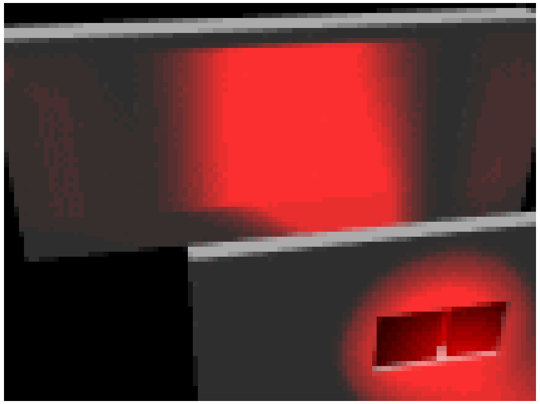
Filters for common target metals



Target	Filter	Incident Beam* $\frac{I(K\alpha)}{I(K\beta)}$	Filter thickness for a $\frac{I(K\alpha)}{I(K\beta)} = \frac{500}{1}$ in trans. beam mg/cm^2 ; inches	$\frac{I(K\alpha)\text{ trans}}{I(K\alpha)\text{ incident}}$
Mo	Zr	5.4	77 ; 0.0046	0.29
Cu	Ni	7.5	18 ; 0.0008	0.42
Co	Fe	9.4	14 ; 0.0007	0.46
Fe	Mn	9.0	12 ; 0.0007	0.48
Cr	V	8.5	10 ; 0.0006	0.49

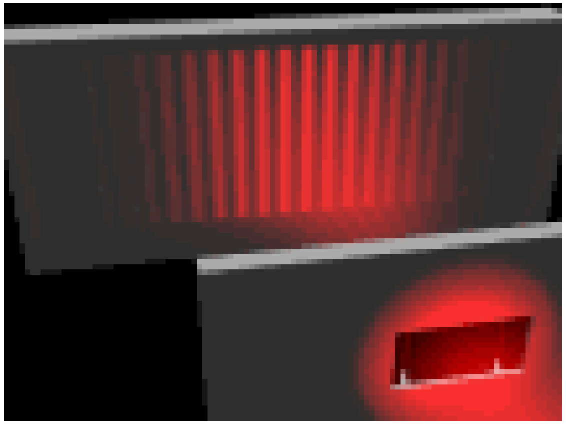
Diffraction

- Diffraction is a wave phenomenon in which the apparent bending and spreading of waves when they meet an obstruction.
- Diffraction occurs with electromagnetic waves, such as light and radio waves, and also in sound waves and water waves.
- The most conceptually simple example of diffraction is double-slit diffraction, that’s why firstly we remember light diffraction.

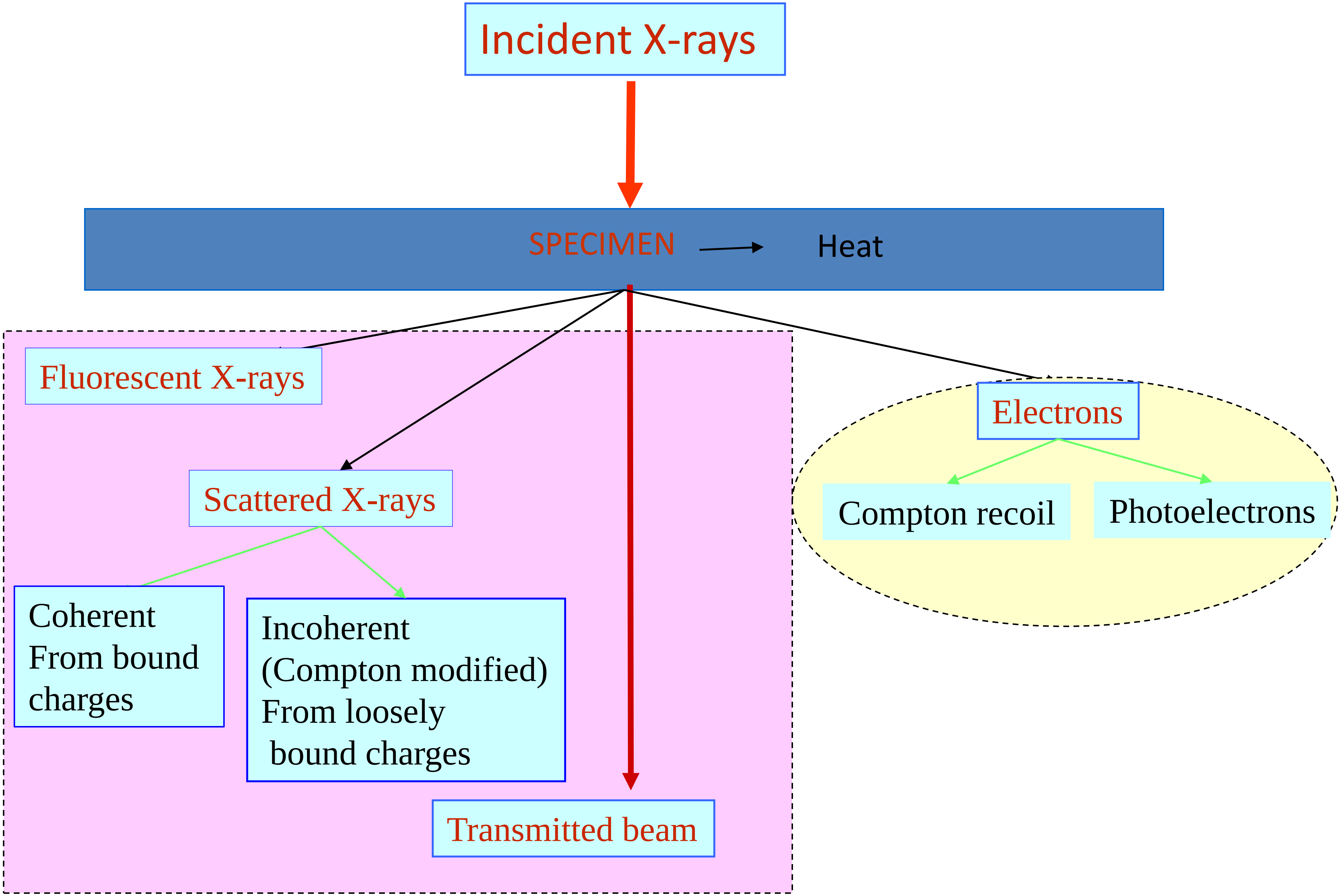


Width b: (500-1500 nm)
λConstant: (600 nm)
Distance d: Constant

- Light diffraction is caused by light bending around the edge of an object. The interference pattern of bright and dark lines from the diffraction experiment can only be explained by the additive nature of waves; wave peaks can add together to make a brighter light, or a peak and a through will cancel each other out and result in darkness.



Thus Young’s light interference experiment proves that light has wavelike properties.



Incident X-rays

SPECIMEN → Heat

Fluorescent X-rays

Scattered X-rays

Coherent
From bound
charges

Incoherent
(Compton modified)
From loosely
bound charges

Transmitted beam

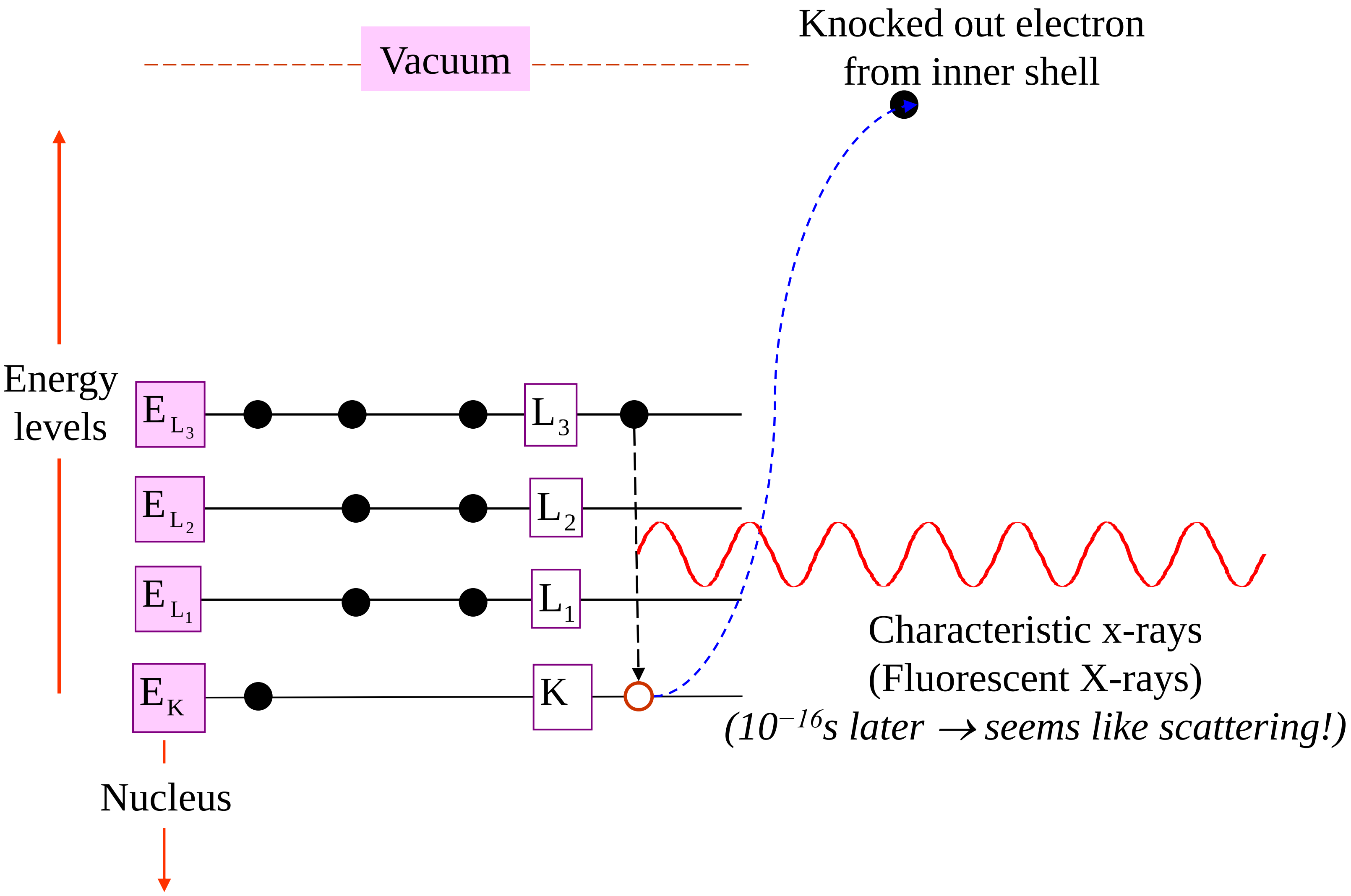
Electrons

Compton recoil

Photoelectrons

- *X-rays can also be refracted (refractive index slightly less than 1) and reflected (at very small angles)*
- *Refraction of X-rays is neglected for now.*

Fluorescent X-rays



Vacuum

Knocked out electron
from inner shell

Energy
levels

E_{L_3} L_3

E_{L_2} L_2

E_{L_1} L_1

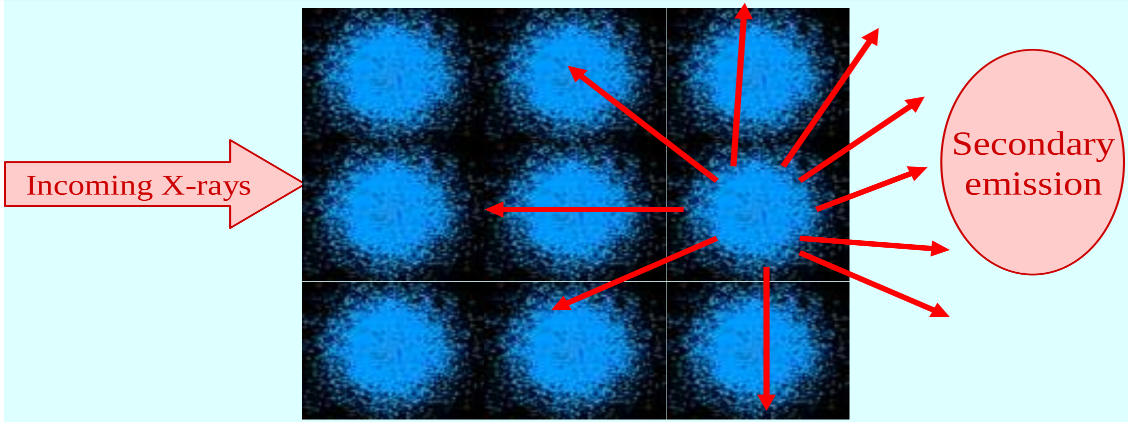
E_K K

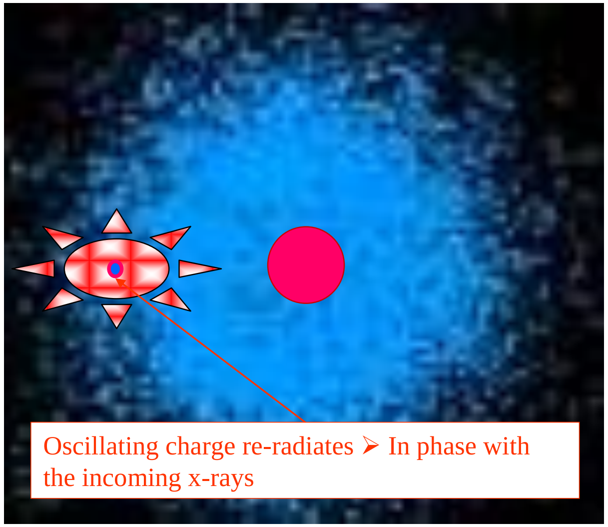
Nucleus

Characteristic x-rays
(Fluorescent X-rays)
(10^{-16}s later → seems like scattering!)

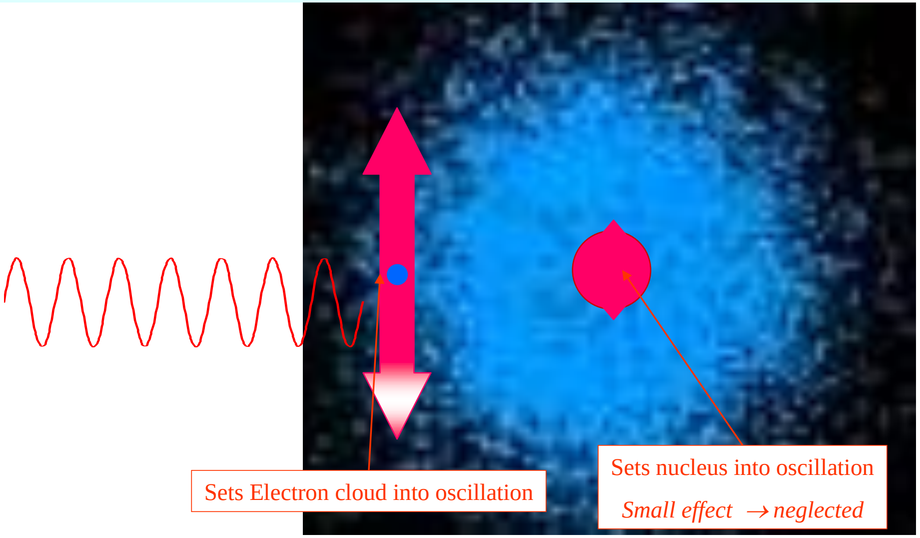
Scattered X-rays: Coherent Scattering

- A beam of X-rays directed at a crystal interacts with the electrons of the atoms in the crystal
- The electrons oscillate under the influence of the incoming X-Rays and become secondary sources of EM radiation
- The secondary radiation is in all directions
- The waves emitted by the electrons have the same frequency as the incoming X-rays ⇒ coherent
- The emission can undergo constructive or destructive interference




Oscillating charge re-radiates ➢ In phase with the incoming x-rays

Schematics


Sets Electron cloud into oscillation

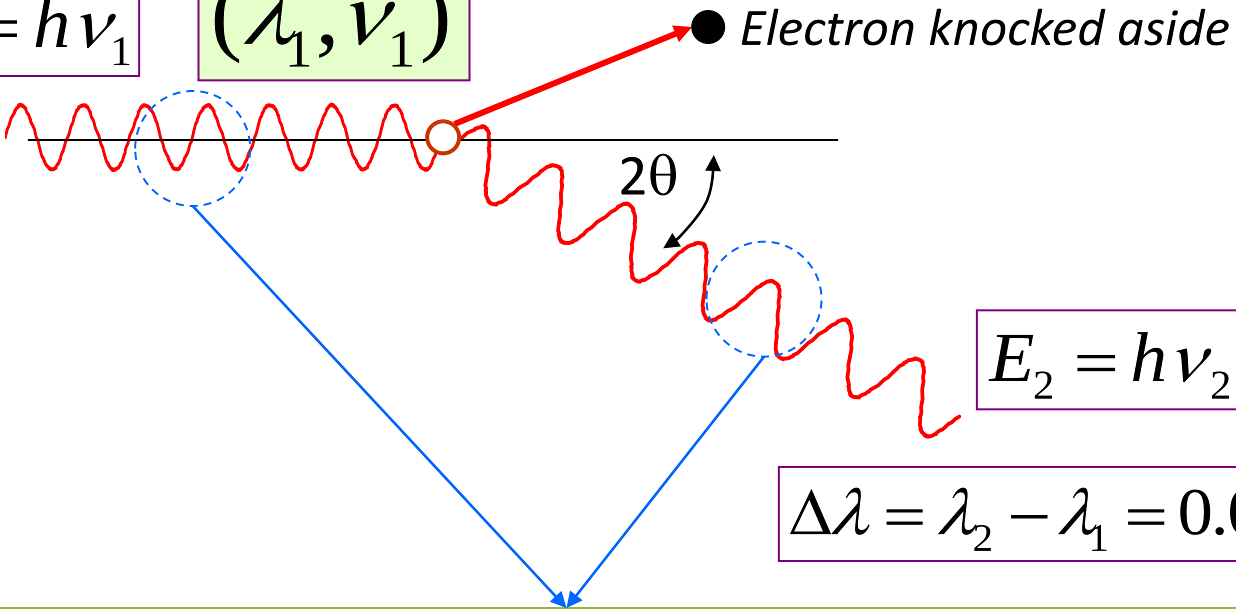
Sets nucleus into oscillation

Small effect → *neglected*

Incoherent Scattering (Compton modified)

Here the particle picture of the electron & photon comes in handy

$E_1 = h\nu_1$ (λ_1, ν_1)



$E_2 = h\nu_2$ (λ_2, ν_2)

$$\Delta\lambda = \lambda_2 - \lambda_1 = 0.0243(1 - Cos 2\theta)$$

No fixed phase relation between the incident and scattered waves
Incoherent → does not contribute to diffraction

(Darkens the background of the diffraction patterns)

BRAGG's EQUATION

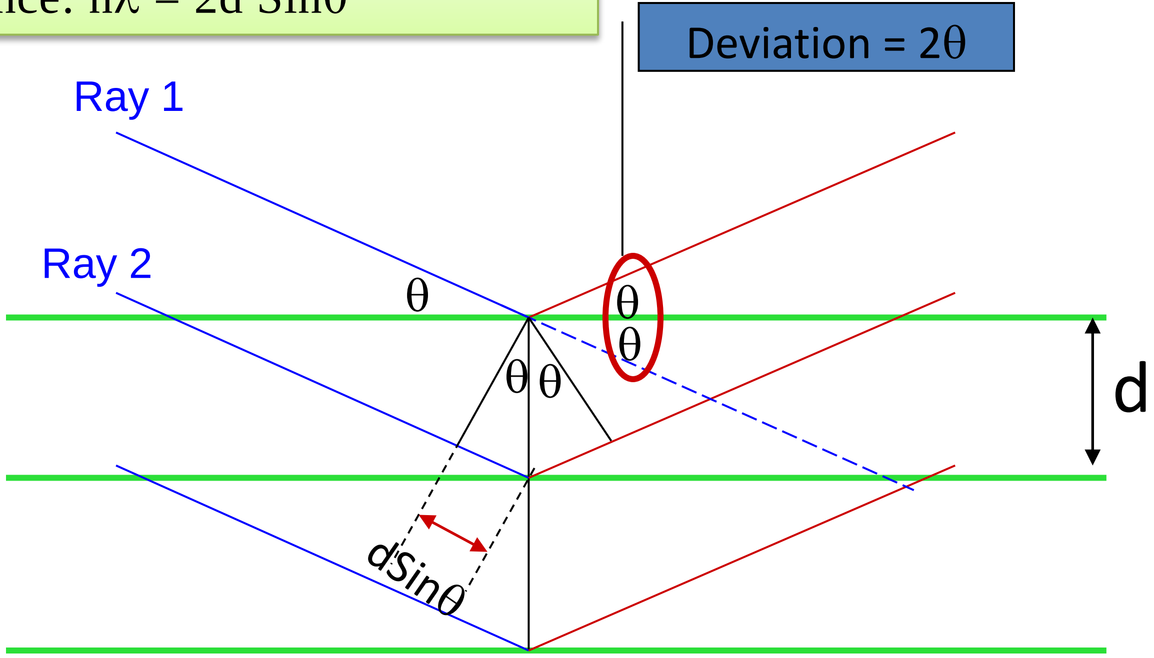
Bragg Law

Two geometrical facts are worth remembering:

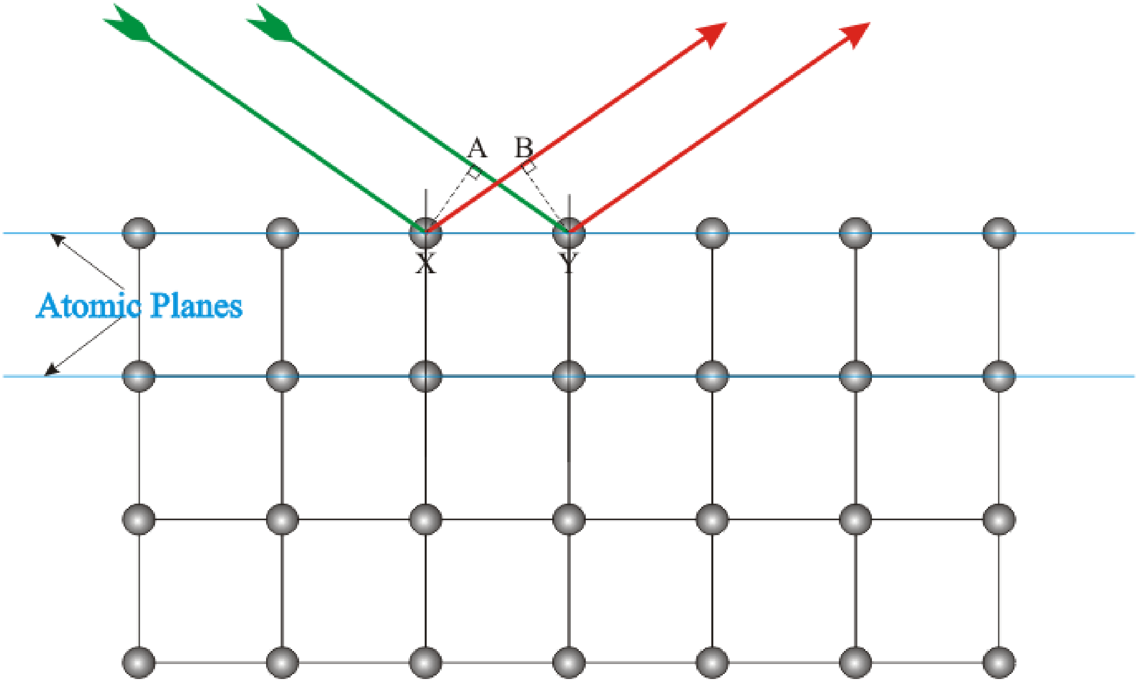
(1) The incident beam, the normal to the reflecting plane, and the diffracted beam are always coplanar.

(2) The angle between the diffracted beam and the transmitted beam is always 2θ. This is known as the diffraction angle, and it is this angle, rather than θ, which is usually measured experimentally.

- The path difference between ray 1 and ray 2 = 2d Sinθ
- For constructive interference: nλ = 2d Sinθ



Deviation = 2θ

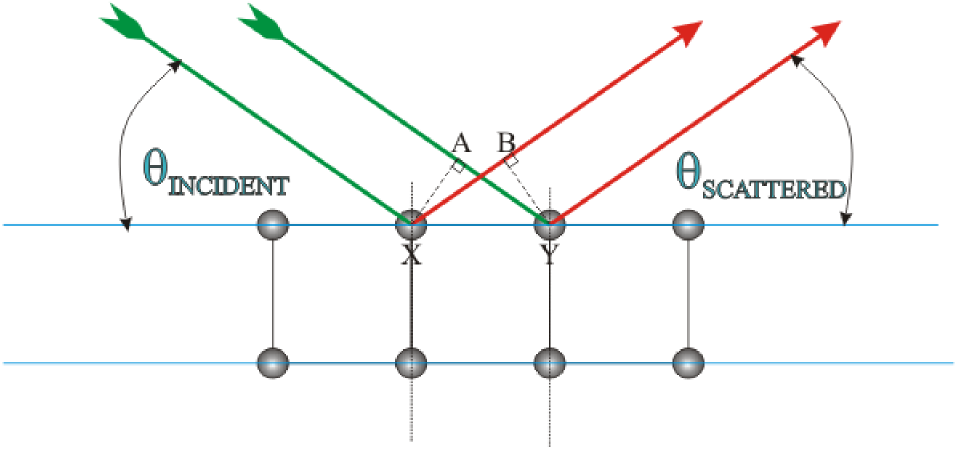


Extra path traveled by incoming waves → AY

Extra path traveled by scattered waves → XB

These can be in phase if and only if → $\theta_{\text{incident}} = \theta_{\text{scattered}}$

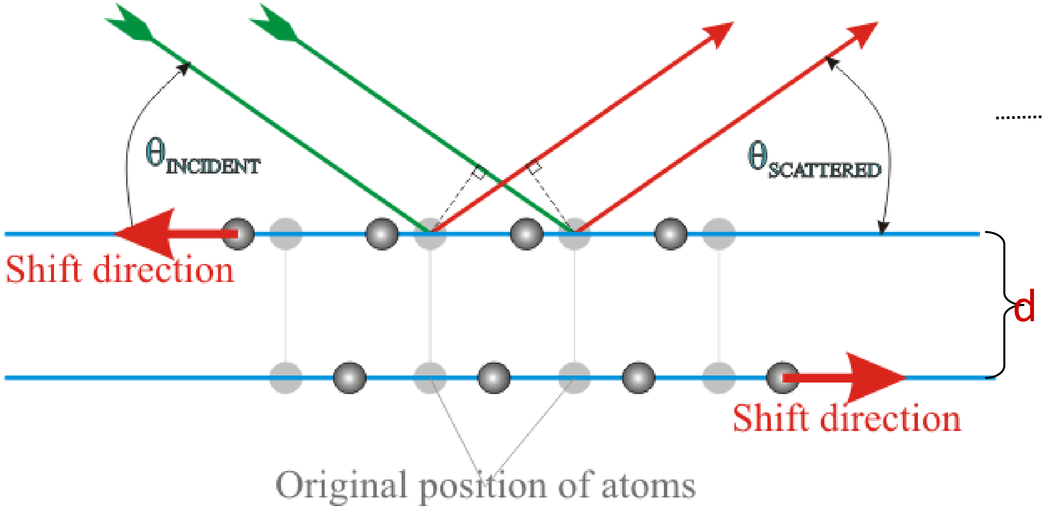
But this is still reinforced scattering *and NOT reflection*



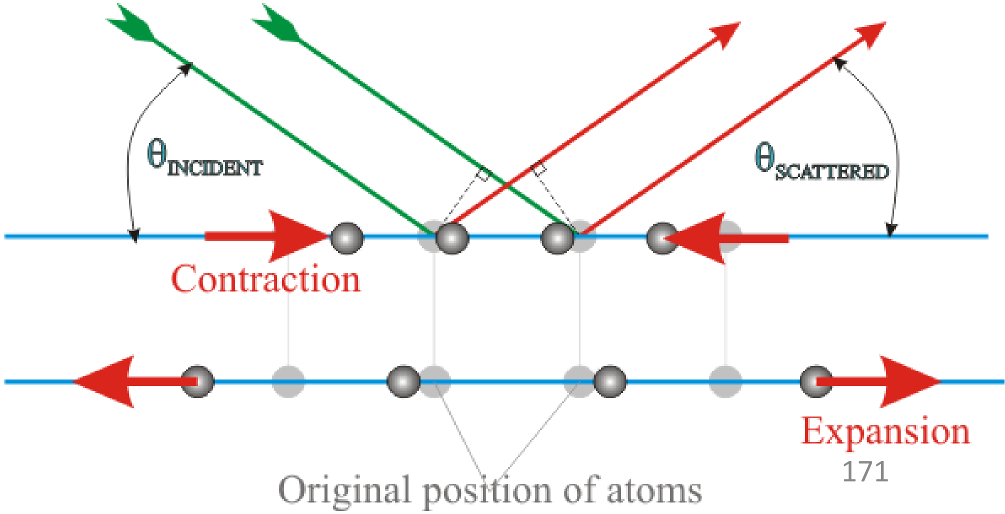
Note that in the Bragg’s equation:

- The interatomic spacing (a) along the plane does not appear
- Only the interplanar spacing (d) appears

⇒ Change in position or spacing of atoms along the plane should not affect Bragg’s condition !!



Note: shift (systematic) is actually not a problem!



Note: shift is actually not a problem! → Why is 'systematic' shift not a problem?

$$\boxed{n\lambda = AY + YB}$$

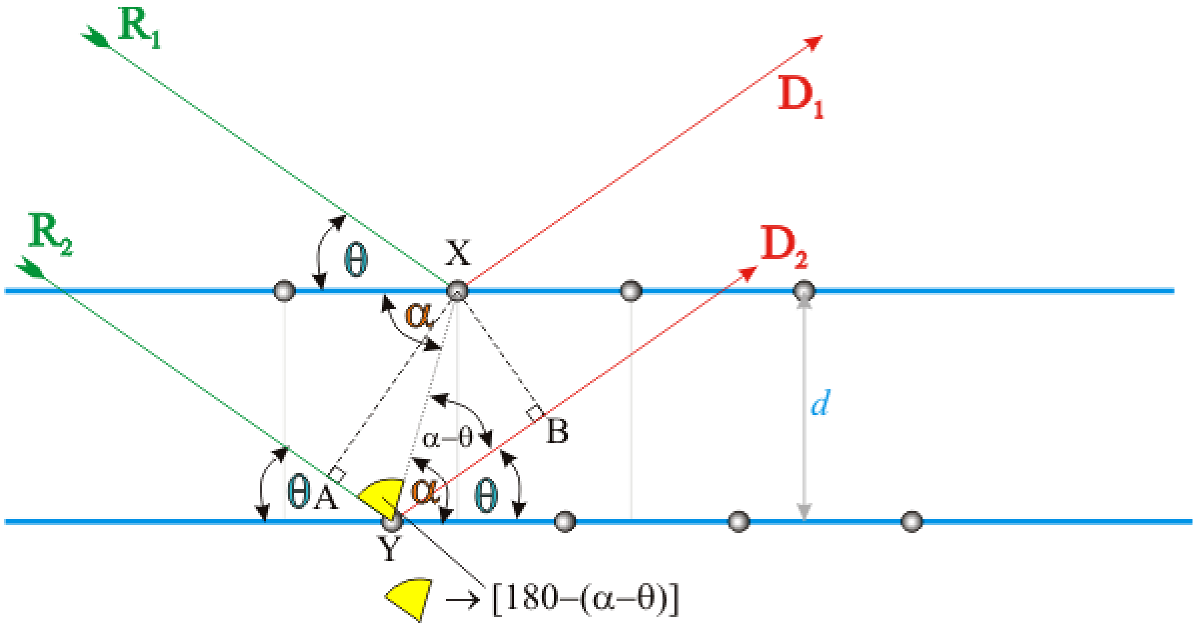
$$\boxed{AY = XY\,Cos[180-(\alpha+\theta)] = -XY\,Cos(\alpha+\theta)}$$

$$\boxed{YB = XY\,Cos(\alpha-\theta)}$$

$$\boxed{n\lambda = AY + YB = XY\,[Cos(\alpha-\theta) - Cos(\alpha+\theta)] = XY\,[2\,Sin\alpha\,Sin\theta]}$$

$$\boxed{n\lambda = \frac{d}{Sin\alpha}[2\,Sin\alpha\,Sin\theta] = 2\,d\,Sin\theta} \longrightarrow \boxed{n\lambda = 2\,d\,Sin\theta}$$

$$\boxed{\frac{d}{XY} = Sin(\alpha)}$$



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

Reflection versus Scattering

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

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

- In XRD nth order reflection from (h k l) is considered as 1st order reflection from (nh nk nl)

$$\boxed{n\lambda = 2d_{hkl}\sin\theta} \longrightarrow \boxed{\lambda = 2\frac{d_{hkl}}{n}\sin\theta} \longrightarrow \boxed{\lambda = 2d_{nh\,nk\,nl}\sin\theta}$$

Diffraction Methods

- As diffraction occurs only at specific Bragg angles, the chance that a reflection is observed when a crystal is irradiated with monochromatic X-rays at a particular angle is small (added to this the diffracted intensity is a small fraction of the beam used for irradiation).
- The probability to get a diffracted beam (with sufficient intensity) is increased by either varying the wavelength (λ) or having many orientations (rotating the crystal or having multiple crystallites in many orientations).
- The three methods used to achieve high probability of diffraction are shown below.

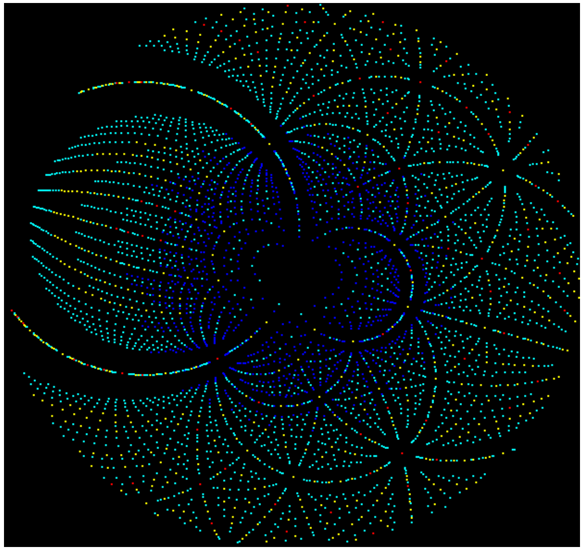
Monochromatic X-rays	Many θs (orientations) Powder specimen	POWDER METHOD	$\lambda \rightarrow$ fixed $\theta \rightarrow$ variable
Panchromatic X-rays	Single θ	LAUE TECHNIQUE	$\lambda \rightarrow$ variable $\theta \rightarrow$ fixed
Monochromatic X-rays	θ Varied by rotation	ROTATING CRYSTAL METHOD	$\lambda \rightarrow$ fixed $\theta \rightarrow$ rotated

Powder Method

- ☐ The Laue method is mainly used to determine the orientation of large single crystals while radiation is reflected from, or transmitted through a fixed crystal.

- ☐ The diffracted beams form arrays of spots, that lie on curves on the film.

- ☐ The Bragg angle is fixed for every set of planes in the crystal. Each set of planes picks out and diffracts the particular wavelength from the white radiation that satisfies the Bragg law for the values of d and θ involved.

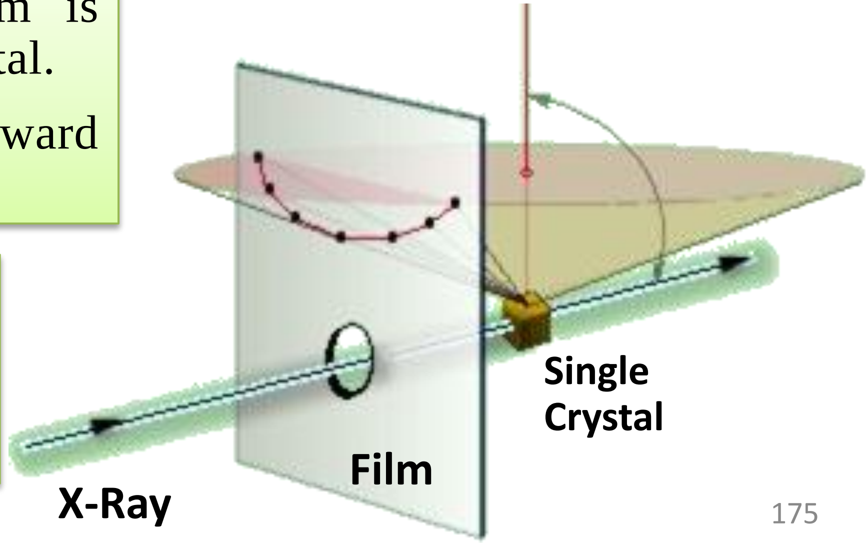


Back-reflection Laue Method

- ☐ In the back-reflection method, the film is placed between the x-ray source and the crystal.

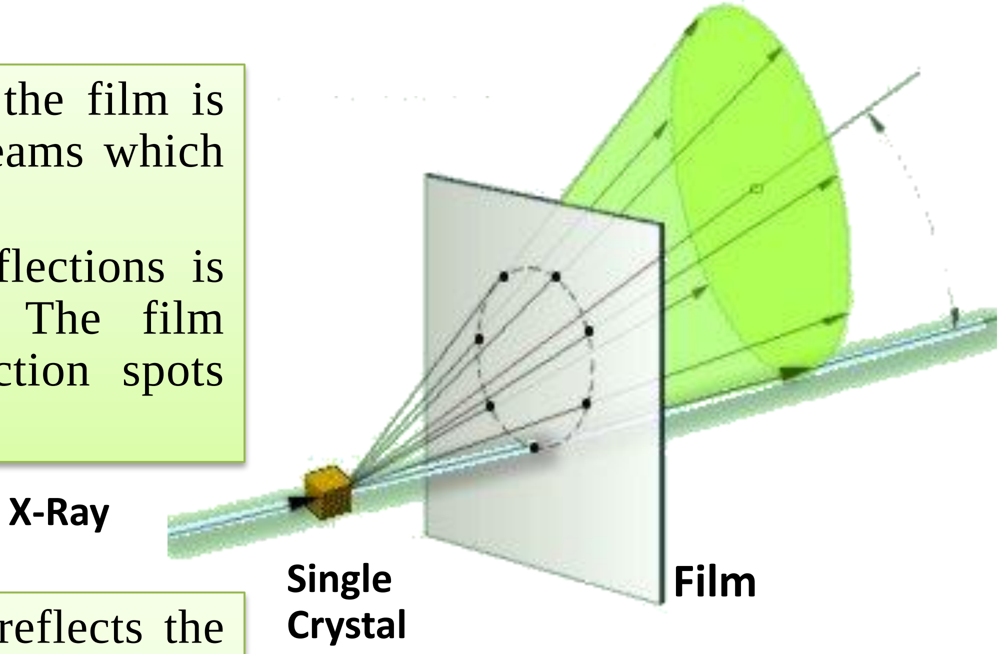
- ☐ The beams which are diffracted in a backward direction are recorded.

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



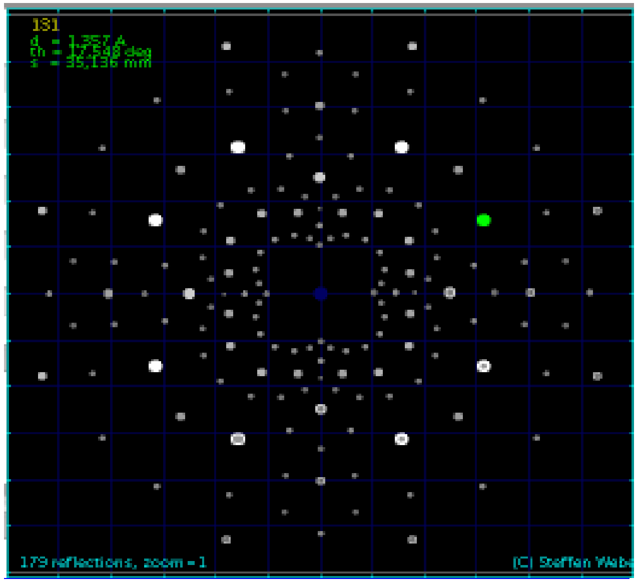
Transmission Laue Method

- ❑ In the transmission Laue method, the film is placed behind the crystal to record beams which are transmitted through the crystal.
- ❑ One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an ellipse.



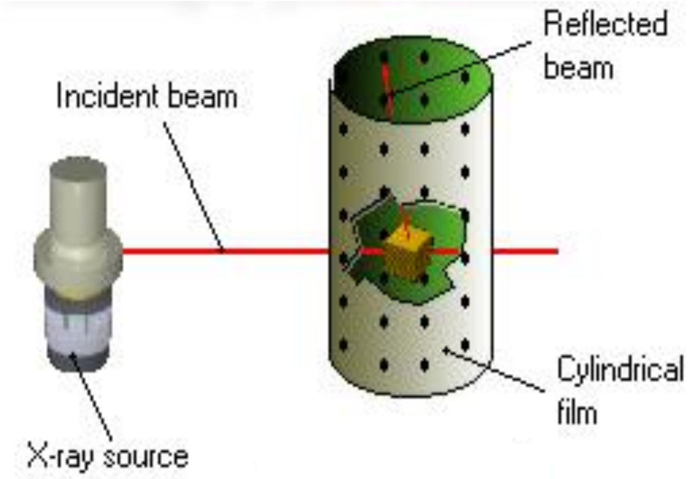
Laue Pattern

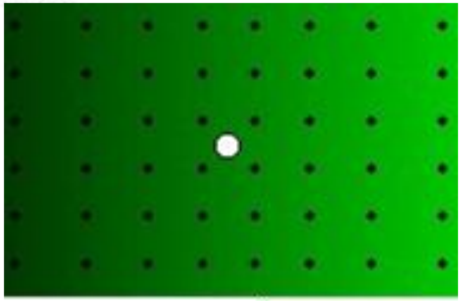
- ❑ The symmetry of the spot pattern reflects the symmetry of the crystal when viewed along the direction of the incident beam. Laue method is often used to determine the orientation of single crystals by means of illuminating the crystal with a continuos spectrum of X-rays.
- ❑ Although the Laue method can also be used to determine the crystal structure, several wavelengths can reflect in different orders from the same set of planes, with the different order reflections superimposed on the same spot in the film. This makes crystal structure determination by spot intensity diffucult.



Rotating Crystal Method

- In the rotating crystal method, a single crystal is mounted with an axis normal to a monochromatic x-ray beam. A cylindrical film is placed around it and the crystal is rotated about the chosen axis.
- As the crystal rotates, sets of lattice planes will at some point make the correct Bragg angle for the monochromatic incident beam, and at that point a diffracted beam will be formed.
- The reflected beams are located on the surface of imaginary cones. By recording the diffraction patterns (both angles and intensities) for various crystal orientations, one can determine the shape and size of unit cell as well as arrangement of atoms inside the cell.





Film

- Lattice constant of the crystal can be determined by means of this method; for a given wavelength if the angle θ at which a reflection occurs is known, d_{hkl} can be determined.

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

Powder Method

- ❑ If a powdered specimen is used, instead of a single crystal, then there is no need to rotate the specimen, because there will always be some crystals at an orientation for which diffraction is permitted. Here a monochromatic X-ray beam is incident on a powdered or polycrystalline sample.

- ❑ This method is useful for samples that are difficult to obtain in single crystal form.

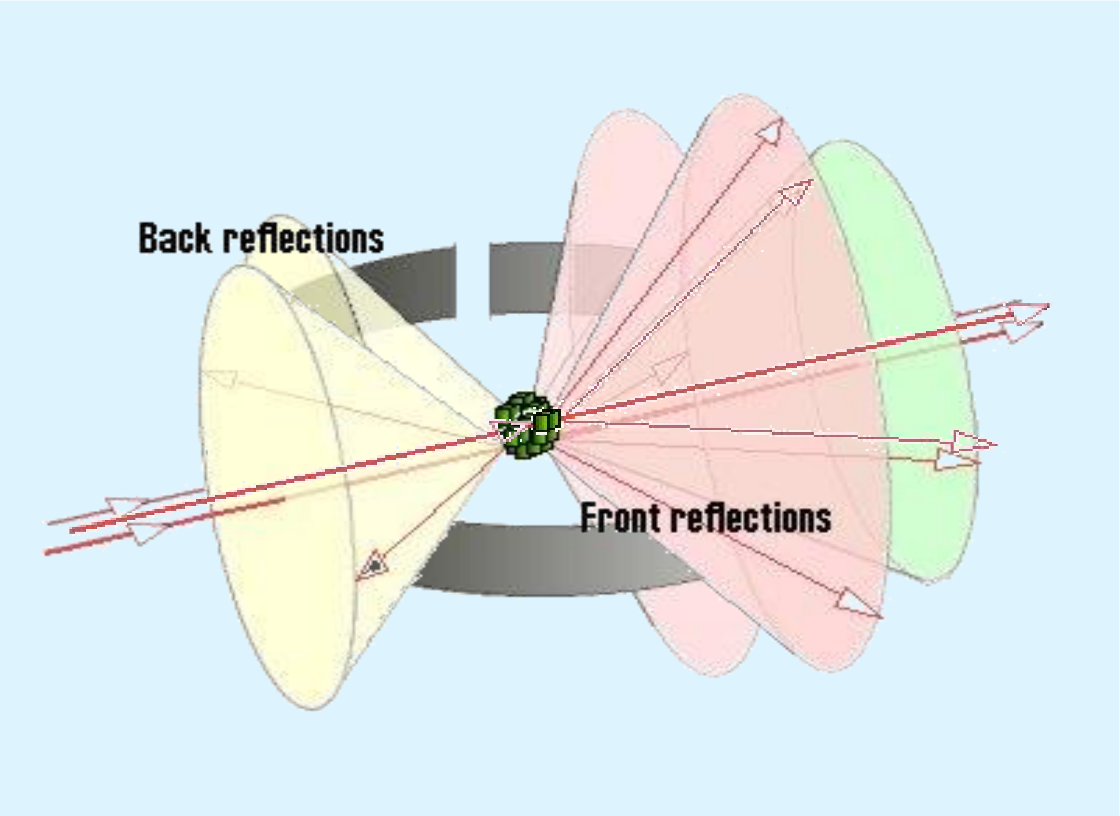
- ❑ In the powder method the specimen has crystallites (or grains) in many orientations (usually random).

- ❑ Monochromatic X-rays are irradiated on the specimen and the intensity of the diffracted beams is measured as a function of the diffracted angle.

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

- ❑ For every set of crystal planes, by chance, one or more crystals will be in the correct orientation to give the correct Bragg angle to satisfy Bragg's equation. Every crystal plane is thus capable of diffraction. Each diffraction line is made up of a large number of small spots, each from a separate crystal. Each spot is so small as to give the appearance of a continuous line.

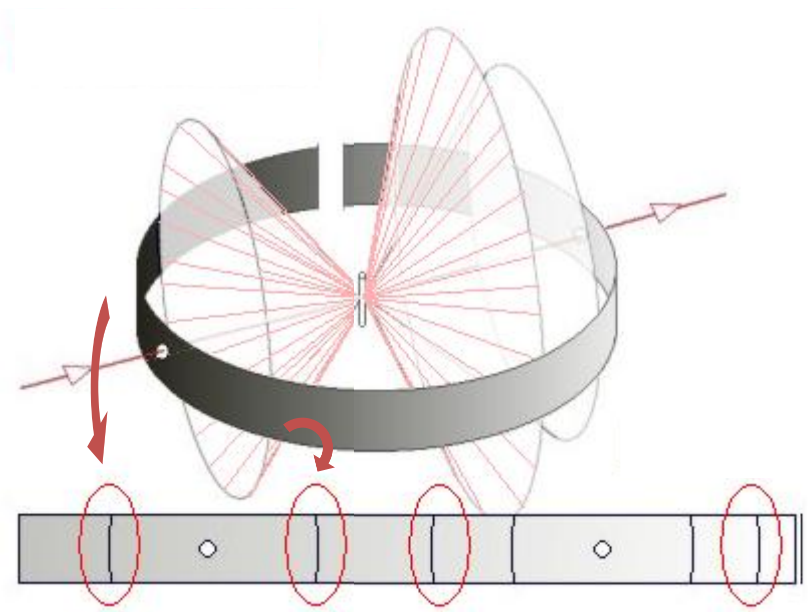
- ❑ If the sample consists of some tens of randomly orientated single crystals, the diffracted beams are seen to lie on the surface of several cones. The cones may emerge in all directions, forwards and backwards.



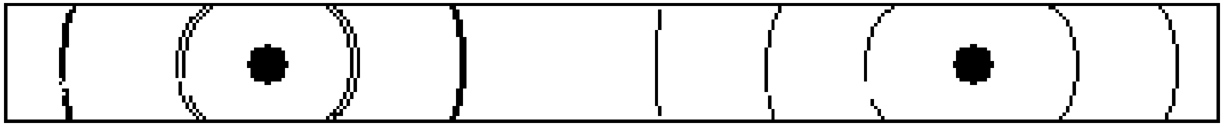
- If a monochromatic x-ray beam is directed at a single crystal, then only one or two diffracted beams may result.
- A sample of some hundreds of crystals (i.e. a powdered sample) show that the diffracted beams form continuous cones. A circle of film is used to record the diffraction pattern as shown. Each cone intersects the film giving diffraction lines. The lines are seen as arcs on the film.

Debye Scherrer Camera

- ❑ A very small amount of powdered material is sealed into a fine capillary tube made from glass that does not diffract x-rays.
- ❑ The specimen is placed in the Debye Scherrer camera and is accurately aligned to be in the centre of the camera. X-rays enter the camera through a collimator.
- ❑ The powder diffracts the x-rays in accordance with Braggs law to produce cones of diffracted beams. These cones intersect a strip of photographic film located in the cylindrical camera to produce a characteristic set of arcs on the film.



When the film is removed from the camera, flattened and processed, it shows the diffraction lines and the holes for the incident and transmitted beams.



Intensity of the Scattered waves

Bragg's equation tells us about the position of the intensity peaks (in terms of θ) → but tells us nothing about the intensities. The intensities of the peaks depend on many factors as considered here.

Scattering by a crystal can be understood in three steps

A

Electron

Polarization factor

To understand the scattering from a crystal leading to the 'intensity of reflections' *(and why some reflections go missing),* three levels of scattering have to be considered:

1) scattering from electrons
2) scattering from an atom
3) scattering from a unit cell

Click here to know the details

B

Atom

Atomic scattering factor (f)

- Structure Factor (F): The resultant wave scattered by all atoms of the unit cell
- The Structure Factor is independent of the shape and size of the unit cell; but is dependent on the position of the atoms/ions etc. within the cell

C

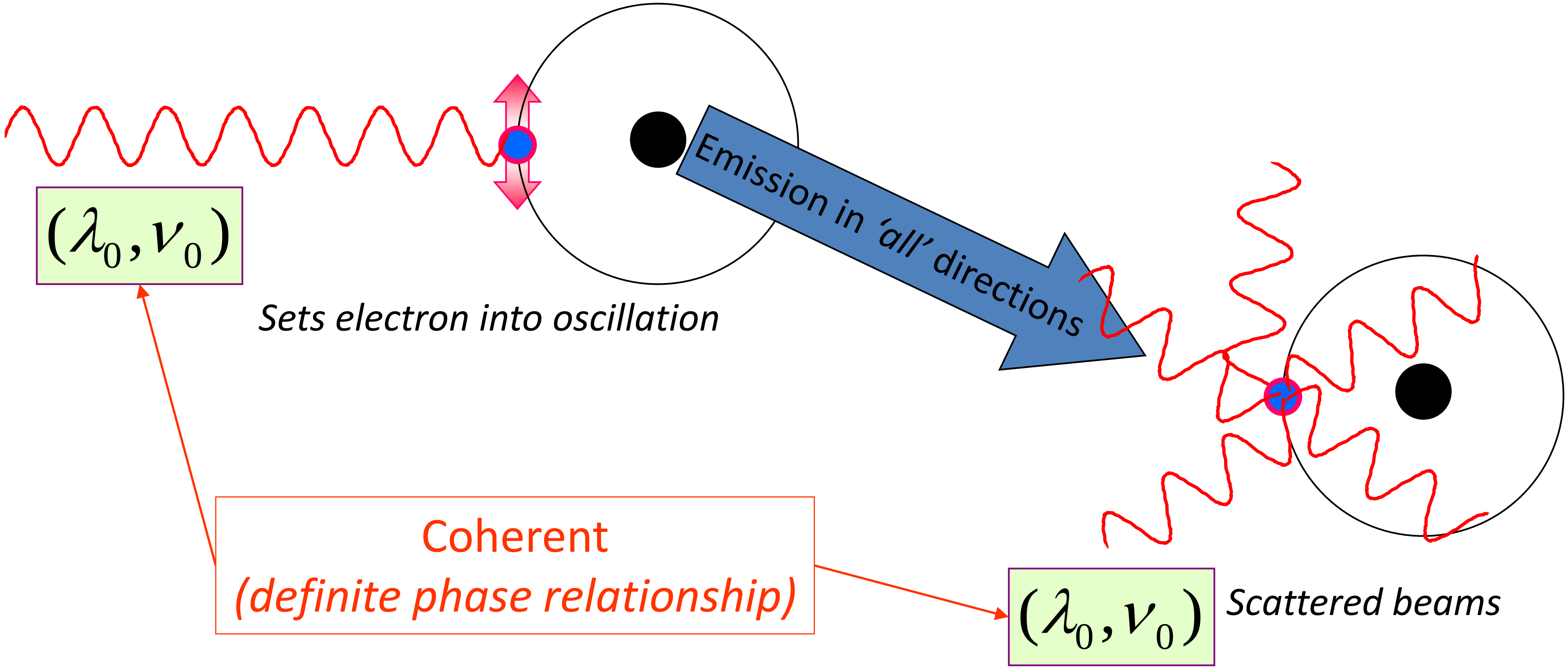
Unit cell (uc)

Structure factor (F)

Structure factor calculations
&
Intensity in powder patterns

A

Scattering by an Electron



(λ_0, ν_0)

Sets electron into oscillation

Emission in 'all' directions

Coherent

(definite phase relationship)

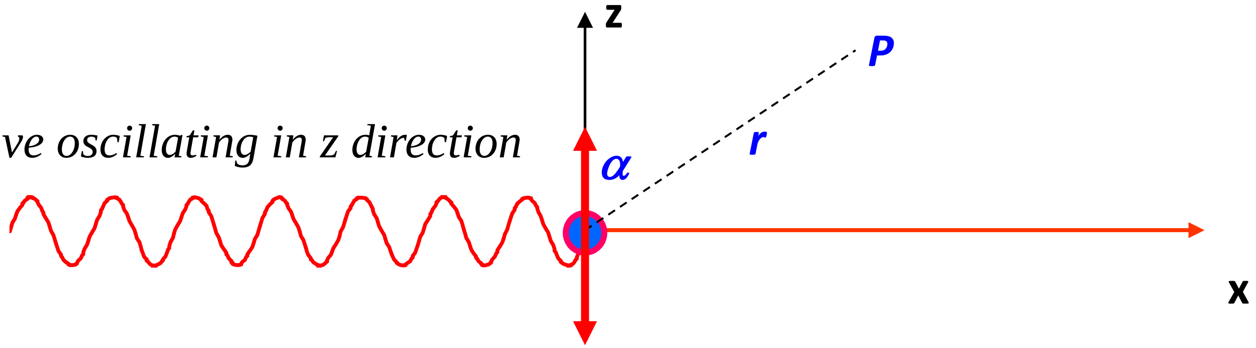
(λ_0, ν_0)

Scattered beams

- ❑ The electric field (E) is the main cause for the acceleration of the electron
- ❑ The moving particle radiates most strongly in a direction perpendicular to its motion
- ❑ The radiation will be polarized along the direction of its motion

For an polarized wave

For a wave oscillating in z direction

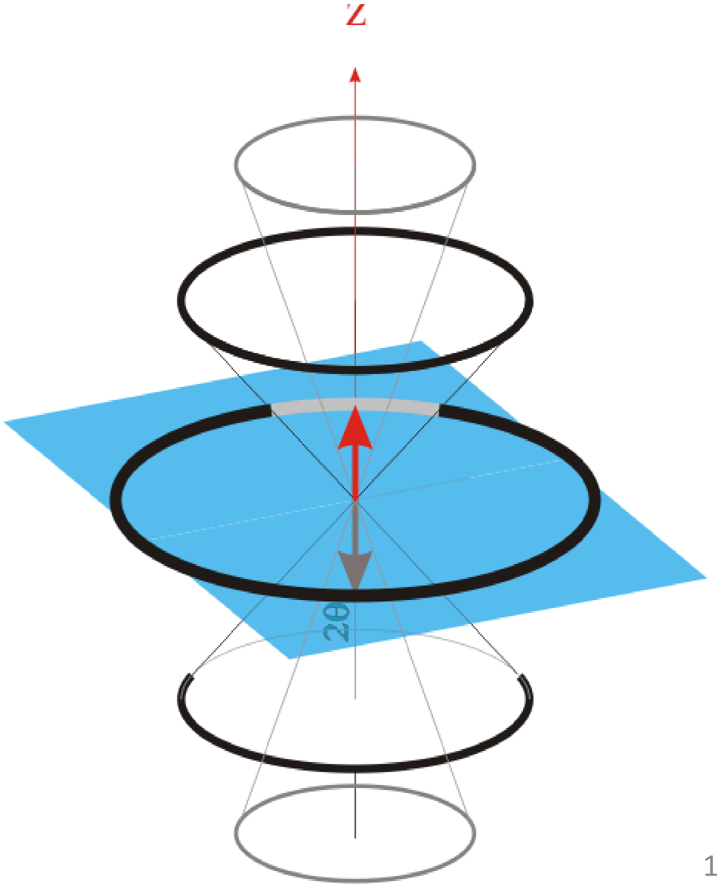


Intensity of the scattered beam due to an electron (I) at a point P such that r >> λ

$$I = I_0 \frac{e^4}{m^2 c^4}\left(\frac{Sin^2\alpha}{r^2}\right)$$

The reason we are able to neglect scattering from the protons in the nucleus

The scattered rays are also plane polarized



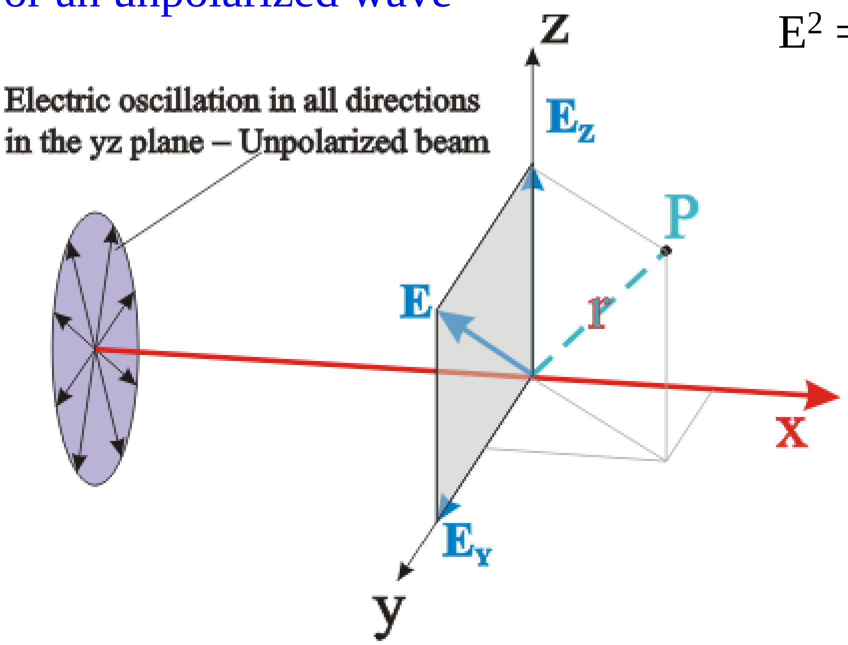
For an unpolarized wave

E is the measure of the amplitude of the wave

E^2 = Intensity

$$\boxed{E^2 = E_y^2 + E_z^2}$$

$$\boxed{\frac{I_0}{2} = I_{0y} = I_{0z}}$$

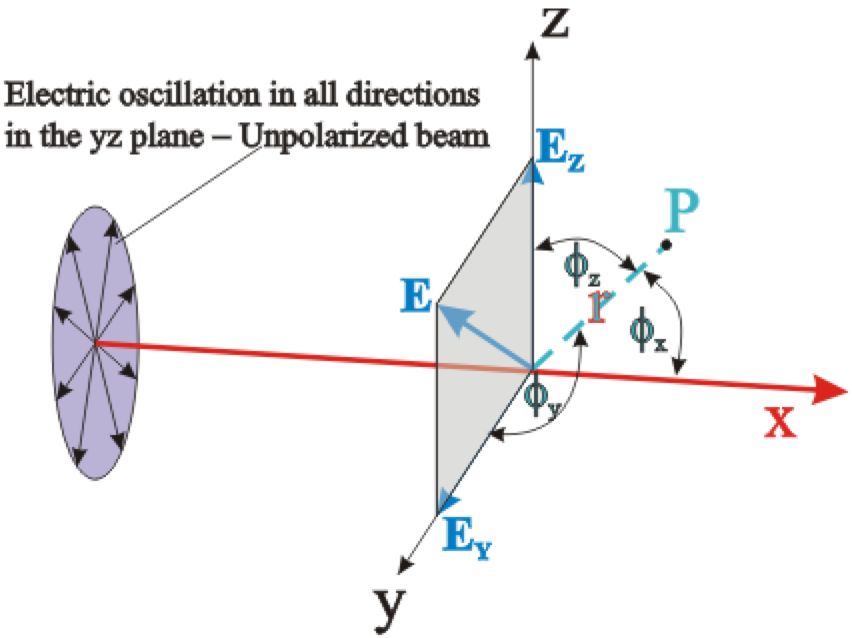


I_{Py} = Intensity at point P due to $\mathbf{E}_y$

$$\boxed{I_{Py} = I_{0y} \frac{e^4}{m^2c^4}\left(\frac{Sin^2(\phi_y)}{r^2}\right)}$$

I_{Pz} = Intensity at point P due to $\mathbf{E}_z$

$$\boxed{I_{Pz} = I_{0z} \frac{e^4}{m^2c^4}\left(\frac{Sin^2(\phi_z)}{r^2}\right)}$$



Total Intensity at point P due to **Ey** & **Ez**

$$\boxed{I_P = I_0 \frac{e^4}{m^2c^4}\left(\frac{Sin^2(\phi_y) + Sin^2(\phi_z)}{r^2}\right)}$$

$$I_P = I_0 \frac{e^4}{m^2c^4}\left(\frac{Sin^2(\phi_y)+Sin^2(\phi_z)}{r^2}\right)$$

$$\left[Sin^2(\phi_y)+Sin^2(\phi_z)\right]=\left[1-Cos^2(\phi_y)+1-Cos^2(\phi_z)\right]=\left[2-Cos^2(\phi_y)-Cos^2(\phi_z)\right]$$

$$\left[Cos^2(\phi_x)+Cos^2(\phi_y)+Cos^2(\phi_z)\right]=1$$

Sum of the squares of the direction cosines =1

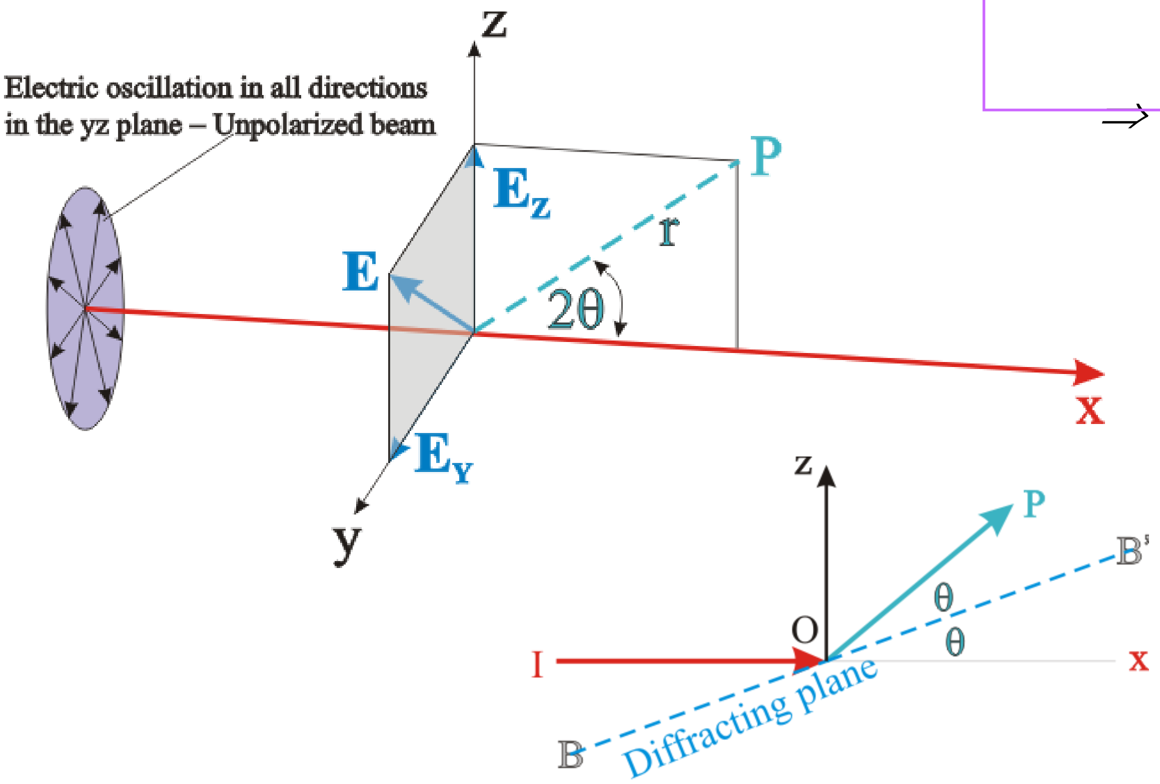
Hence

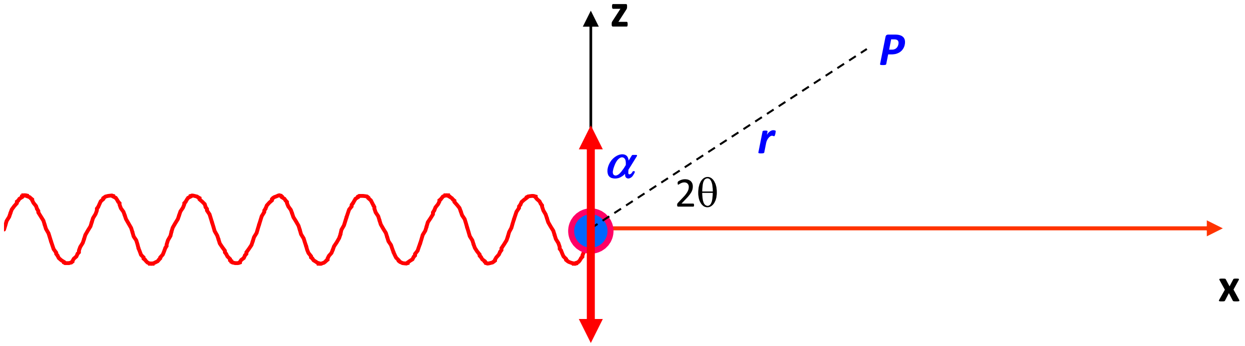
$$\left[2-Cos^2(\phi_y)-Cos^2(\phi_z)\right]=\left[2-\left(1-Cos^2(\phi_x)\right)\right]=\left[\left(1+Cos^2(\phi_x)\right)\right]$$

$$\rightarrow I_P = I_0 \frac{e^4}{m^2c^4}\left(\frac{\left(1+Cos^2(\phi_x)\right)}{r^2}\right)$$

In terms of 2θ

$$I_P = I_0 \frac{e^4}{m^2c^4}\left(\frac{\left(1+Cos^2(2\theta)\right)}{r^2}\right)$$





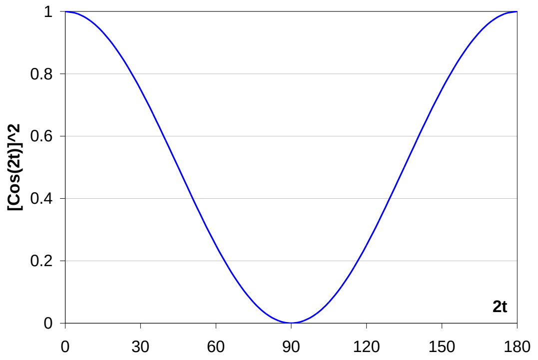
- In general P could lie anywhere in 3D space.
- For the specific case of Bragg scattering:

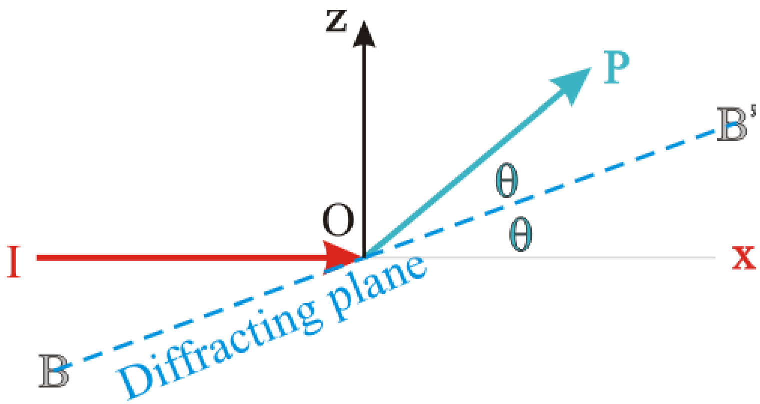
The incident direction → IO

The diffracted beam direction → OP

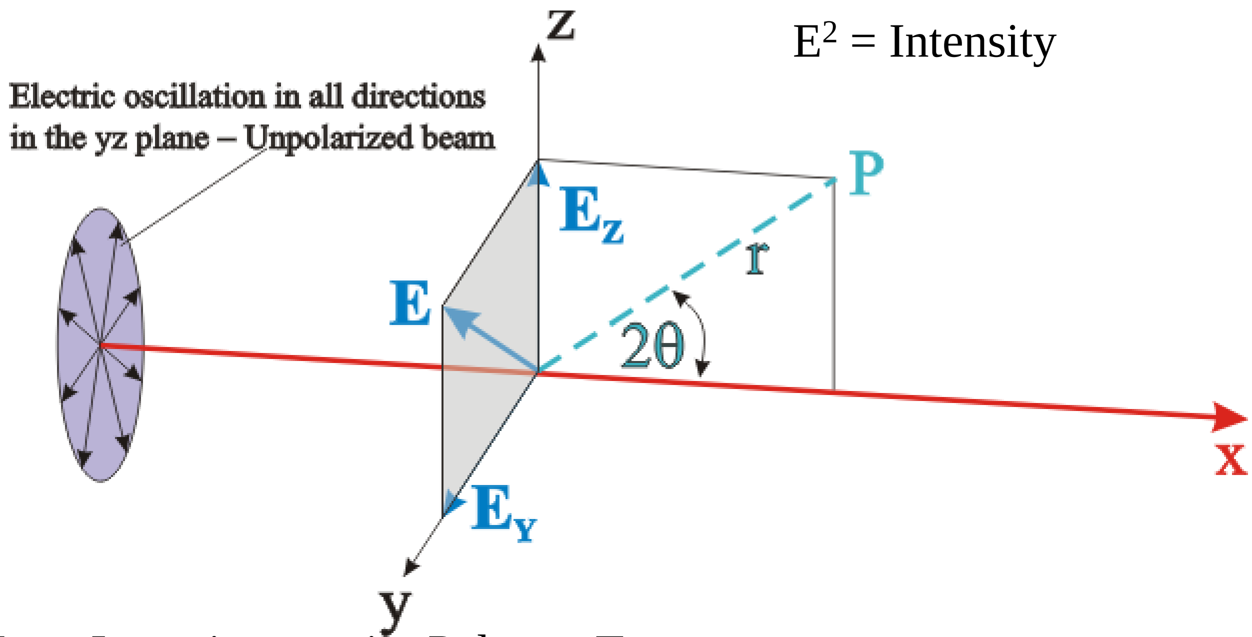
The trace of the scattering plane → BB'
Are all coplanar ⇒ OP is constrained to be on the xz plane

$$I = I_0 \frac{e^4}{m^2c^4}\left(\frac{Cos^2 2\theta}{r^2}\right)$$





For an unpolarized wave



E is the measure of the amplitude of the wave
E^2 = Intensity

$$\boxed{E^2 = E_y^2 + E_z^2}$$

$$\boxed{\frac{I_0}{2} = I_{0y} = I_{0z}}$$

I_{Py} = Intensity at point P due to $\mathbf{E}_y$

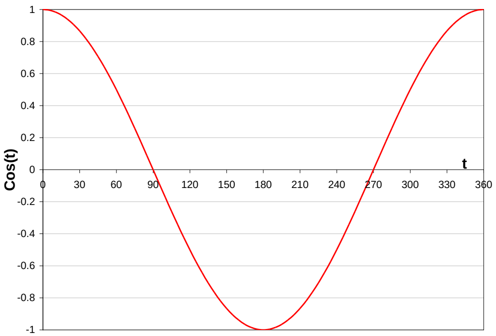
$$\boxed{I_{Py} = I_{0y}\frac{e^4}{m^2c^4}\left(\frac{Sin^2\left(\pi/2\right)}{r^2}\right) = I_{0y}\frac{e^4}{m^2c^4}\left(\frac{1}{r^2}\right)}$$

The zx plane is ⊥ to the y direction: hence, $\alpha = 90°$

I_{Pz} = Intensity at point P due to $\mathbf{E}_z$

$$\boxed{I_{Pz} = I_{0z}\frac{e^4}{m^2c^4}\left(\frac{Sin^2\left(\pi/2 - 2\theta\right)}{r^2}\right) = I_{0z}\frac{e^4}{m^2c^4}\left(\frac{Cos^2(2\theta)}{r^2}\right)}$$

$$I_P = I_{Py} + I_{Pz} = \frac{e^4}{m^2c^4}\left(\frac{I_{0y} + I_{0z}Cos^2(2\theta)}{r^2}\right)$$



$$I_P = \frac{I_0}{2}\frac{e^4}{m^2c^4}\left(\frac{1 + Cos^2(2\theta)}{r^2}\right)$$

⇒ Scattered beam is not unpolarized

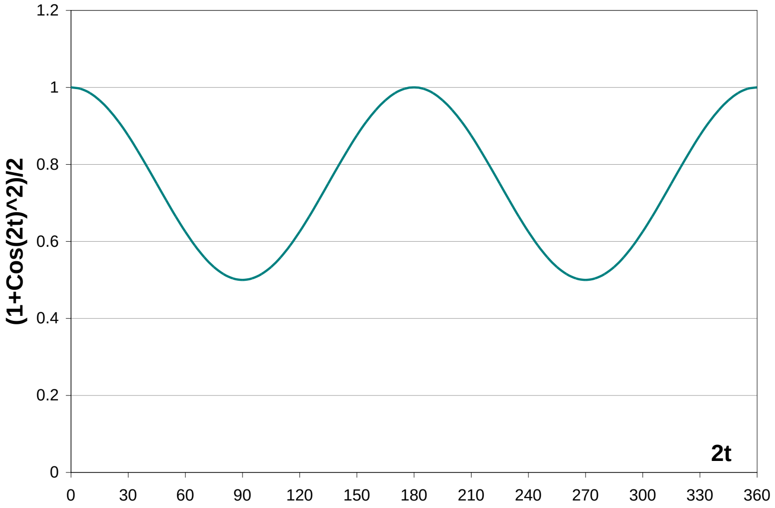
Very small number

- *Forward and backward scattered intensity higher than at 90 °*
- *Scattered intensity minute fraction of the incident intensity*

$$I_P = \frac{I_0}{r^2}\frac{e^4}{m^2c^4}\left(\frac{1 + Cos^2(2\theta)}{2}\right)$$

Polarization factor

Comes into being as we used unpolarized beam



B

Scattering by an Atom

Scattering by an atom ∝ [Atomic number, (path difference suffered by scattering from each e−, λ)]

Scattering by an atom ∝ [Z, (θ, λ)]

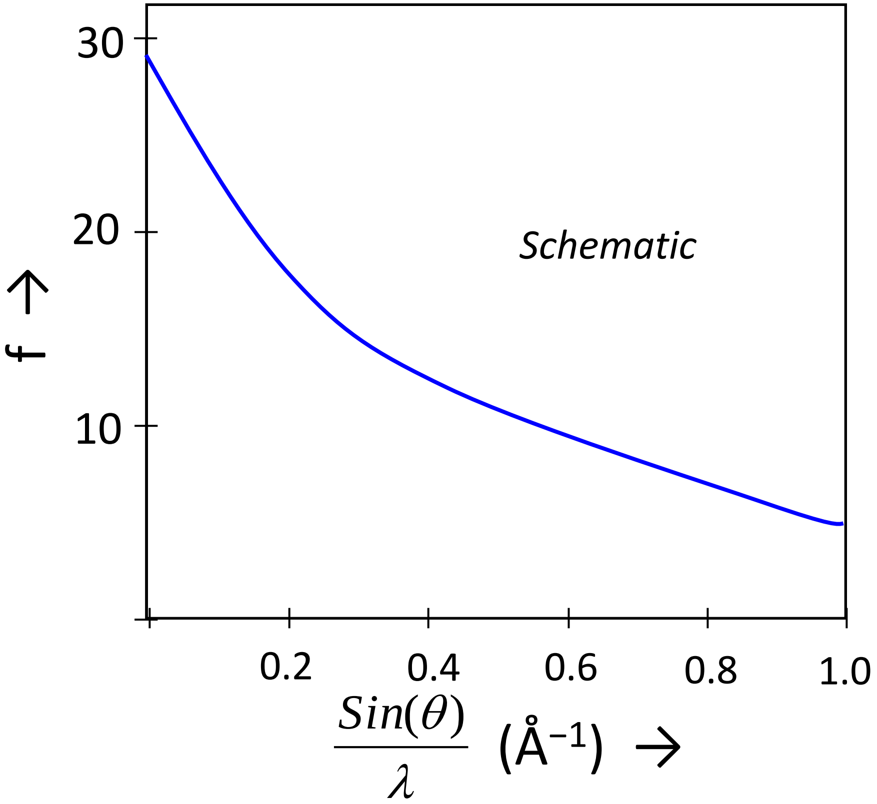
$$\frac{Sin(\theta)}{\lambda}$$

- *Angle of scattering leads to path differences*
- *In the forward direction all scattered waves are in phase*

$$f = \text{Atomic Scattering Factor}$$

$$= \frac{\text{Amplitude of wave scattered by an atom}}{\text{Amplitude of wave scattered by an electron}}$$

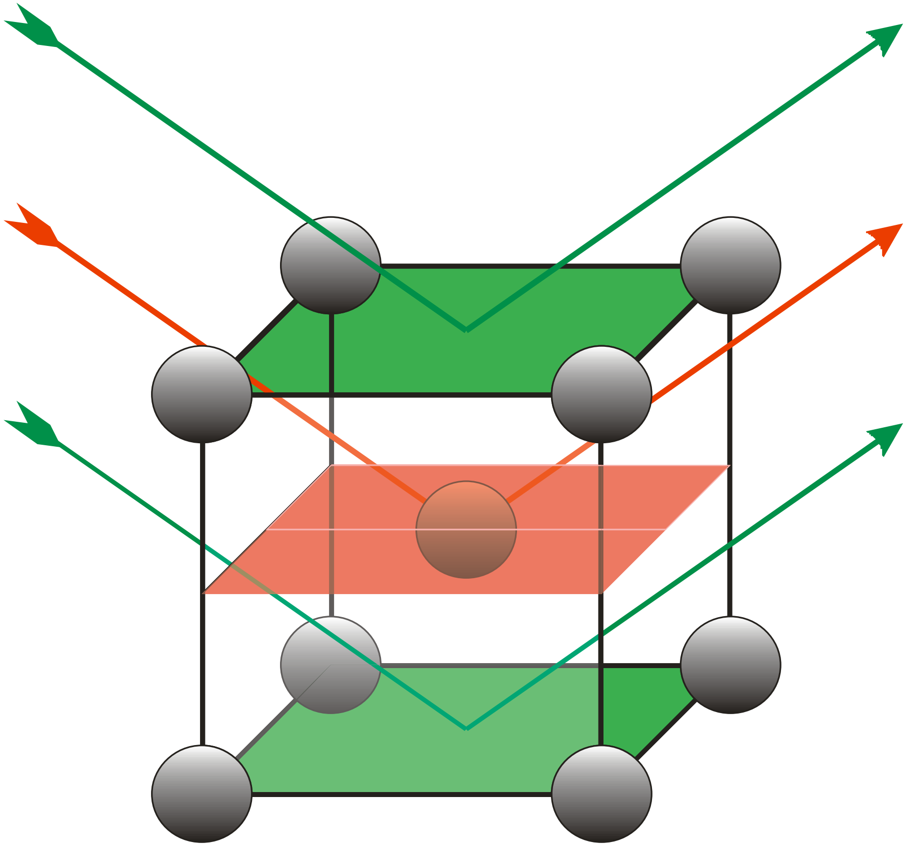
	Coherent scattering	Incoherent (Compton) scattering
Z ↑	↑	↓
Sin(θ) / λ ↓	↑	↓

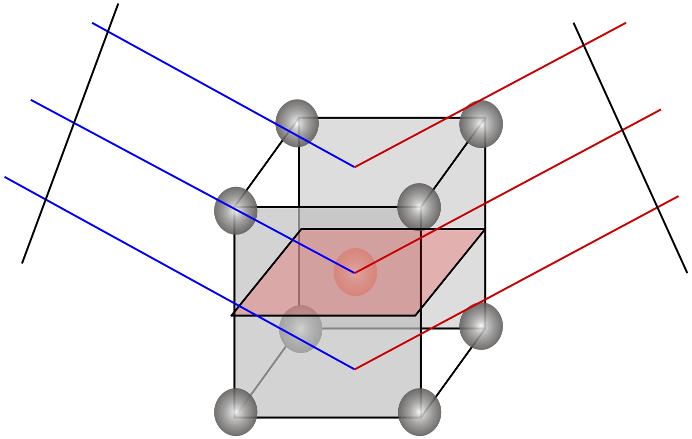


C

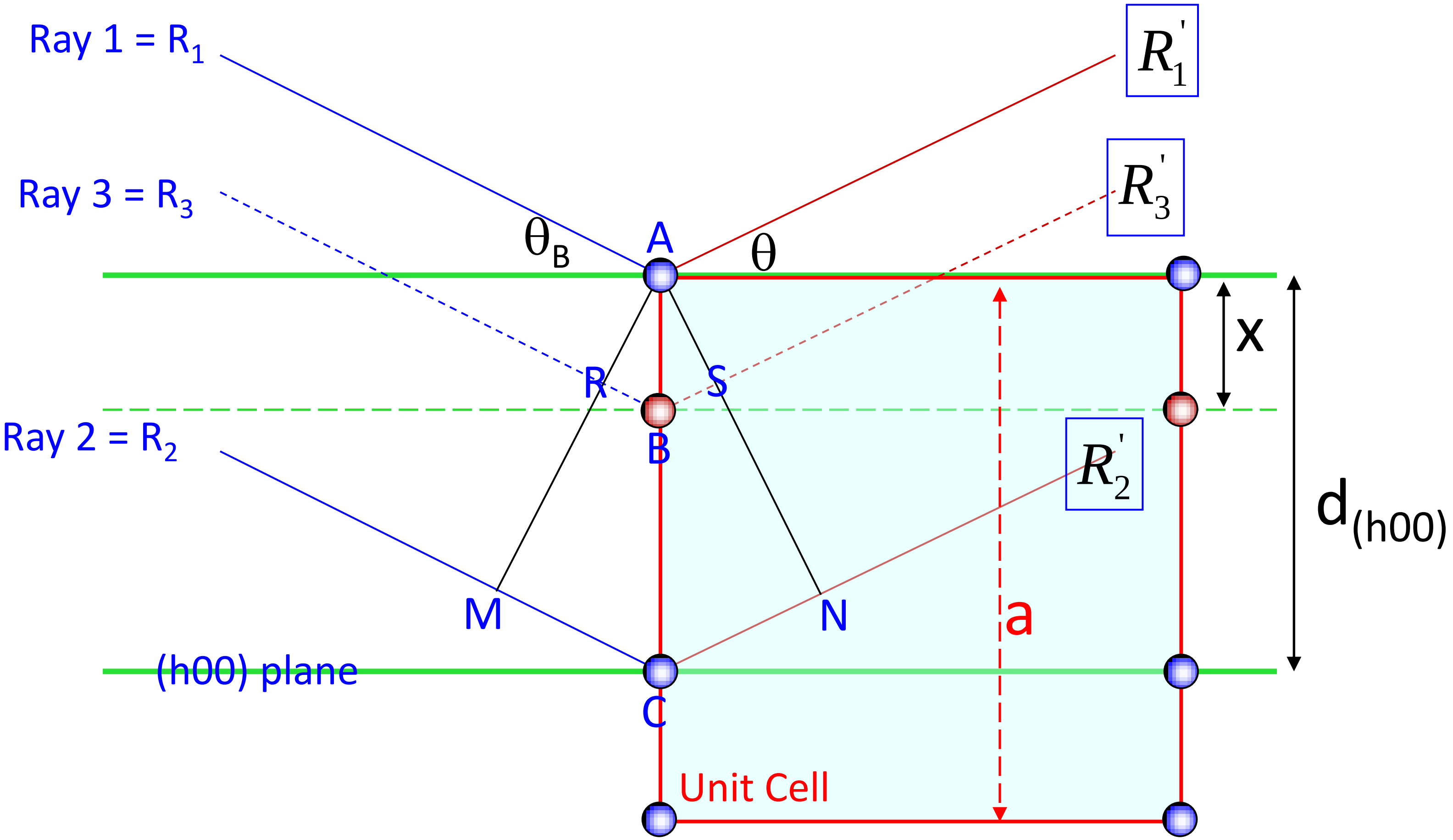
Scattering by the Unit cell (uc)

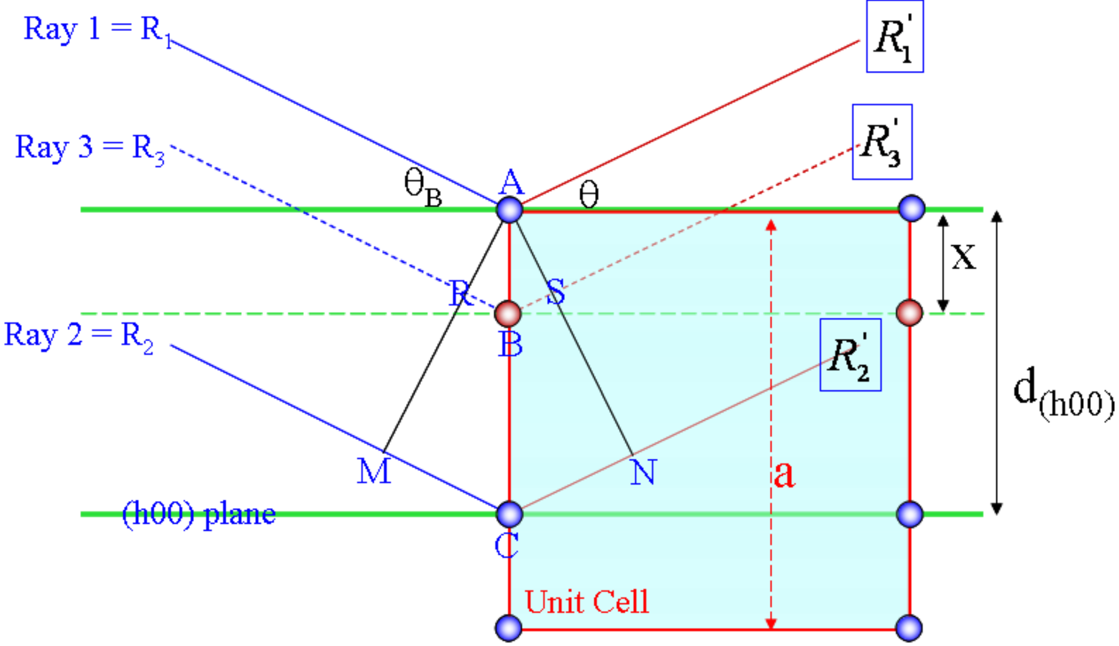
- Coherent Scattering
- Unit Cell (UC) is representative of the crystal structure
- Scattered waves from various atoms in the UC interfere to create the diffraction pattern





The wave scattered from the middle plane is out of phase with the ones scattered from top and bottom planes


Ray 1 = R_1
Ray 3 = R_3
Ray 2 = R_2
R_1'
R_3'
R_2'
θ_B
A
θ
R
S
B
M
N
C
a
x
$d_{(h00)}$
(h00) plane
Unit Cell



$$\boxed{AC = d_{h00} = \frac{a}{h}}$$

$$\boxed{MCN :: AC :: \lambda}$$

$$\boxed{RBS :: AB :: x}$$

$$\boxed{\frac{AB}{AC} = \frac{x}{\lambda} = \frac{x}{a/h}}$$

$$\boxed{\delta_{R_1R_2} = MCN = 2d_{h00}\,Sin(\theta) = \lambda}$$

$$\boxed{\varphi = \frac{2\pi}{\lambda}\delta}$$

$$\boxed{\varphi\frac{\lambda}{2\pi} = \delta}$$

$$\boxed{\delta_{R_1R_3} = RBS = \frac{AB}{AC}\lambda = \frac{x}{a/h}\lambda}$$

$$\boxed{\varphi_{R_1R_3} = \frac{2\pi}{\lambda}\frac{x}{a/h}\lambda = 2\pi h\frac{x}{a}}$$

$$\boxed{\frac{x}{a} \rightarrow fractional\,coordinate \rightarrow x'}$$

$$\boxed{\varphi_{R_1R_3} = 2\pi h x'}$$

Extending to 3D $\boxed{\varphi = 2\pi(h\,x' + k\,y' + l\,z')}$ → *Independent of the shape of UC*

Note: R_1 is from corner atoms and R_3 is from atoms in additional positions in UC

$$\boxed{\varphi = 2\pi(h\,x' + k\,y' + l\,z')} \xrightarrow{\text{In complex notation}} \boxed{E = Ae^{i\varphi} = fe^{i[2\pi(h\,x'+k\,y'+l\,z')]}}$$

- *If atom B is different from atom A → the amplitudes must be weighed by the respective atomic scattering factors (f)*
- *The resultant amplitude of all the waves scattered by all the atoms in the UC gives the scattering factor for the unit cell*
- *The unit cell scattering factor is called the* ***Structure Factor*** *(**F**)*

Scattering by an unit cell = f(position of the atoms, atomic scattering factors)

$$\mathrm{F} = \text{Structure Factor} = \frac{\text{Amplitude of wave scattered by all atoms in uc}}{\text{Amplitude of wave scattered by an electron}}$$

$$I \propto F^2$$

$$F_n^{hkl} = \sum_{j=1}^{n} f_j\; e^{i\varphi_j} = \sum_{j=1}^{n} f_j\; e^{i[2\pi(h\,x'_j + k\,y'_j + l\,z'_j)]}$$

For n atoms in the UC

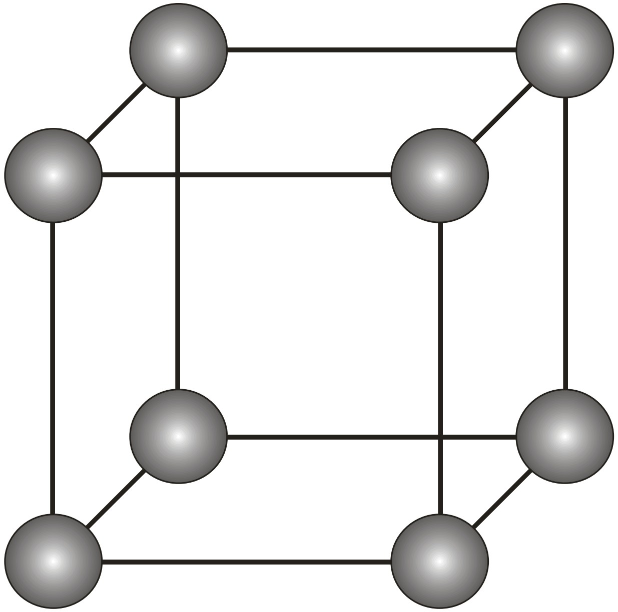
Structure factor is independent of the *shape* and *size* of the unit cell

If the UC distorts so do the planes in it!!

Structure factor calculations

Simple Cubic

A Atom at (0,0,0) and equivalent positions



$$e^{ni\pi} = (-1)^n$$

$$e^{(odd\ n)\,i\pi} = -1$$

$$e^{(even\ n)\,i\pi} = +1$$

$$e^{ni\pi} = e^{-ni\pi}$$

$$\frac{e^{i\theta} + e^{-i\theta}}{2} = Cos(\theta)$$

$$F = f_j \quad e^{i\varphi_j} = f_j \quad e^{i[2\pi(h\,x'_j + k\,y'_j + l\,z'_j)]}$$

$$F = f \quad e^{i[2\pi(h\cdot 0 + k\cdot 0 + l\cdot 0)]} = f\,e^0 = f$$

$$F^2 = f^2$$

$\Rightarrow$ *F is independent of the scattering plane (h k l)*

B

Atom at (0,0,0) & (½, ½, 0) and equivalent positions

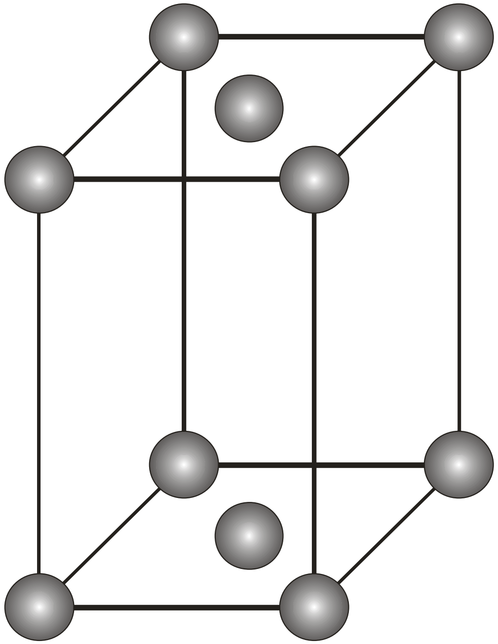
C- centred Orthorhombic

$$\boxed{F = f_j \; e^{i\varphi_j} = f_j \; e^{i[2\pi(h\,x'_j + k\,y'_j + l\,z'_j)]}}$$

$$F = f \; e^{i[2\pi(h\cdot 0 + k\cdot 0 + l\cdot 0)]} + f \; e^{i[2\pi(h\cdot\frac{1}{2} + k\cdot\frac{1}{2} + l\cdot 0)]}$$

$$= f\,e^{0} + f\,e^{i[\cancel{2}\pi(\frac{h+k}{\cancel{2}})]} = f[1 + e^{i\pi(h+k)}]$$

Real



$$\boxed{F = f[1 + e^{i\pi(h+k)}]}$$

(h + k) even

Both even or both odd

$$\boxed{F = 2f} \rightarrow \boxed{F^2 = 4f^2}$$

e.g. (001), (110), (112); (021), (022), (023)

Mixture of odd and even

(h + k) odd

$$\boxed{F = 0} \rightarrow \boxed{F^2 = 0}$$

e.g. (100), (101), (102); (031), (032), (033)

$\Rightarrow$ *F is independent of the ‘l’ index*

C

Atom at (0,0,0) & (½, ½, ½) and equivalent positions

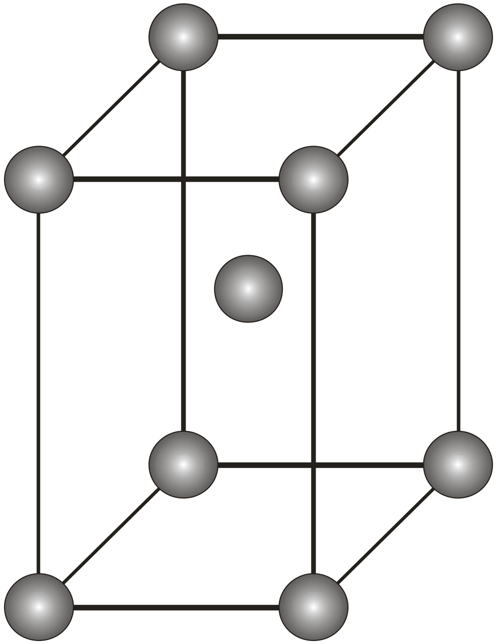
Body centred Orthorhombic

$$F = f_j \; e^{i\varphi_j} = f_j \; e^{i[2\pi(h\,x'_j + k\,y'_j + l\,z'_j)]}$$

$$F = f \; e^{i[2\pi(h\cdot 0 + k\cdot 0 + l\cdot 0)]} + f \; e^{i[2\pi(h\cdot\frac{1}{2} + k\cdot\frac{1}{2} + l\cdot\frac{1}{2})]}$$

$$= f\,e^{0} + f\,e^{i[\cancel{2}\pi(\frac{h+k+l}{\cancel{2}})]} = f[1 + e^{i\pi(h+k+l)}]$$

Real



$$F = f[1 + e^{i\pi(h+k+l)}]$$

(h + k + l) even

$$F = 2f \longrightarrow F^2 = 4f^2$$

e.g. (110), (200), (211); (220), (022), (310)

(h + k + l) odd

$$F = 0 \longrightarrow F^2 = 0$$

e.g. (100), (001), (111); (210), (032), (133) D

Atom at (0,0,0) & (½, ½, 0) and equivalent positions

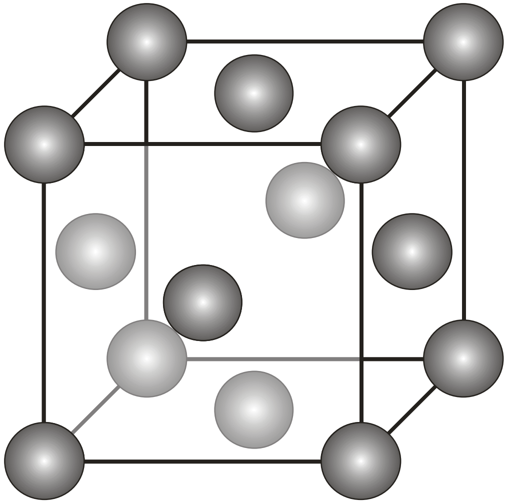
Face Centred Cubic

$$F = f_j \; e^{i\varphi_j} = f_j \; e^{i[2\pi(h\,x'_j + k\,y'_j + l\,z'_j)]}$$

$$F = f\left[e^{i[2\pi(0)]} + e^{i[2\pi(\frac{h+k}{2})]} + e^{i[2\pi(\frac{k+l}{2})]} + e^{i[2\pi(\frac{l+h}{2})]}\right]$$

$$= f[1 + \underbrace{e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}}_{\text{Real}}]$$

(½, ½, 0), (½, 0, ½), (0, ½, ½)



$$F = f[1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}]$$

(h, k, l) unmixed → $F = 4f$ → $F^2 = 16f^2$

e.g. (111), (200), (220), (333), (420)

(h, k, l) mixed → $F = 0$ → $F^2 = 0$

e.g. (100), (211); (210), (032), (033)

Two odd and one even (e.g. 112); two even and one odd (e.g. 122)

Mixed indices

Two odd and one even (e.g. 112); two even and one odd (e.g. 122)

Mixed indices	CASE	h	k	l
	A	o	o	e
	B	o	e	e

$$\text{CASE} \quad \text{A}: \; [1+e^{i\pi(e)}+e^{i\pi(o)}+e^{i\pi(o)}]=[1+1-1-1]=0$$

$$\text{CASE} \quad \text{B}: \; [1+e^{i\pi(o)}+e^{i\pi(e)}+e^{i\pi(o)}]=[1-1+1-1]=0$$

(h, k, l) mixed

$$F=0 \longrightarrow F^2=0$$

e.g. (100), (211); (210), (032), (033)

Unmixed indices

All odd (e.g. 111); all even (e.g. 222)

Unmixed indices	CASE	h	k	l
	A	o	o	o
	B	e	e	e

$$\text{CASE} \quad \text{A}: \; [1+e^{i\pi(e)}+e^{i\pi(e)}+e^{i\pi(e)}]=[1+1+1+1]=4$$

$$\text{CASE} \quad \text{B}: \; [1+e^{i\pi(e)}+e^{i\pi(e)}+e^{i\pi(e)}]=[1+1+1+1]=4$$

(h, k, l) unmixed

$$F=4f \longrightarrow F^2=16f^2$$

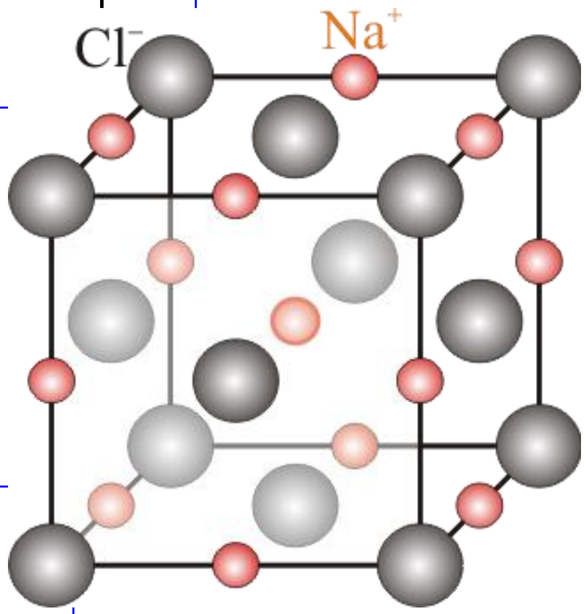
e.g. (111), (200), (220), (333), (420) E

Na$^+$ at (0,0,0) + Face Centering Translations → *(½, ½, 0), (½, 0, ½), (0, ½, ½)*
Cl$^-$ at (½, 0, 0) + FCT → *(0, ½, 0), (0, 0, ½), (½, ½, ½)*

NaCl:
Face Centred Cubic

$$F = f_{Na^+}\left[e^{i[2\pi(0)]} + e^{i[2\pi(\frac{h+k}{2})]} + e^{i[2\pi(\frac{k+l}{2})]} + e^{i[2\pi(\frac{l+h}{2})]}\right] + f_{Cl^-}\left[e^{i[2\pi(\frac{h}{2})]} + e^{i[2\pi(\frac{k}{2})]} + e^{i[2\pi(\frac{l}{2})]} + e^{i[2\pi(\frac{h+k+l}{2})]}\right]$$

$$F = f_{Na^+}[1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}] + f_{Cl^-}[e^{i\pi(h)} + e^{i\pi(k)} + e^{i\pi(l)} + e^{i\pi(h+k+l)}]$$



$$F = f_{Na^+}[1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}] + f_{Cl^-}\ e^{i\pi(h+k+l)}[e^{i\pi(-k-l)} + e^{i\pi(-l-h)} + e^{i\pi(-h-k)} + 1]$$

$$F = [f_{Na^+} + f_{Cl^-}\ e^{i\pi(h+k+l)}][1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}]$$

$$F = [f_{Na^+} + f_{Cl^-} e^{i\pi(h+k+l)}][1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}]$$

Zero for mixed indices

$$F = [Term-1][Term-2]$$

Mixed indices

Mixed indices	CASE	h	k	l
	A	o	o	e
	B	o	e	e

$$\text{CASE A}: Term-2 = [1 + e^{i\pi(e)} + e^{i\pi(o)} + e^{i\pi(o)}] = [1+1-1-1] = 0$$

$$\text{CASE B}: Term-2 = [1 + e^{i\pi(o)} + e^{i\pi(e)} + e^{i\pi(o)}] = [1-1+1-1] = 0$$

(h, k, l) mixed

$$F = 0 \longrightarrow F^2 = 0$$

e.g. (100), (211); (210), (032), (033) Unmixed indices

Unmixed indices	CASE	h	k	l
	A	o	o	o
	B	e	e	e

$$\text{CASE A}: Term - 2 = [1 + e^{i\pi(e)} + e^{i\pi(e)} + e^{i\pi(e)}] = [1+1+1+1] = 4$$

$$\text{CASE B}: Term - 2 = [1 + e^{i\pi(e)} + e^{i\pi(e)} + e^{i\pi(e)}] = [1+1+1+1] = 4$$

(h, k, l) unmixed →

$$F = 4[f_{Na^+} + f_{Cl^-}\ e^{i\pi(h+k+l)}]$$

e.g. (111), (222); (133), (244)

$$F = 4[f_{Na^+} + f_{Cl^-}] \longrightarrow \text{If } (h + k + l) \text{ is even} \longrightarrow F^2 = 16[f_{Na^+} + f_{Cl^-}]^2$$

e.g. (222),(244)

$$F = 4[f_{Na^+} - f_{Cl^-}] \longrightarrow \text{If } (h + k + l) \text{ is odd} \longrightarrow F^2 = 16[f_{Na^+} - f_{Cl^-}]^2$$

e.g. (111), (133)

⇒ *Presence of additional atoms/ions/molecules in the UC can alter the intensities of some of the reflections*

Selection / Extinction Rules

Bravais Lattice	**Reflections which *may be* present**	**Reflections necessarily absent**
Simple	all	None
Body centred	(h + k + l) even	(h + k + l) odd
Face centred	h, k and l unmixed	h, k and l mixed
End centred	h and k unmixed *C centred*	h and k mixed *C centred*

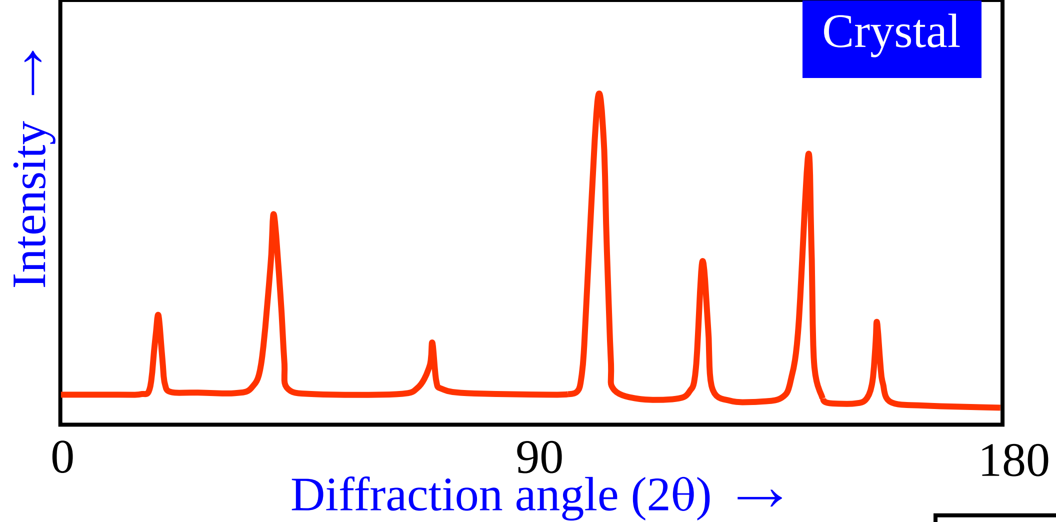
Bravais Lattice	***Allowed* Reflections**
SC	All
BCC	(h + k + l) even
FCC	h, k and l unmixed
DC	h, k and l are all odd Or all are even & (h + k + l) divisible by 4

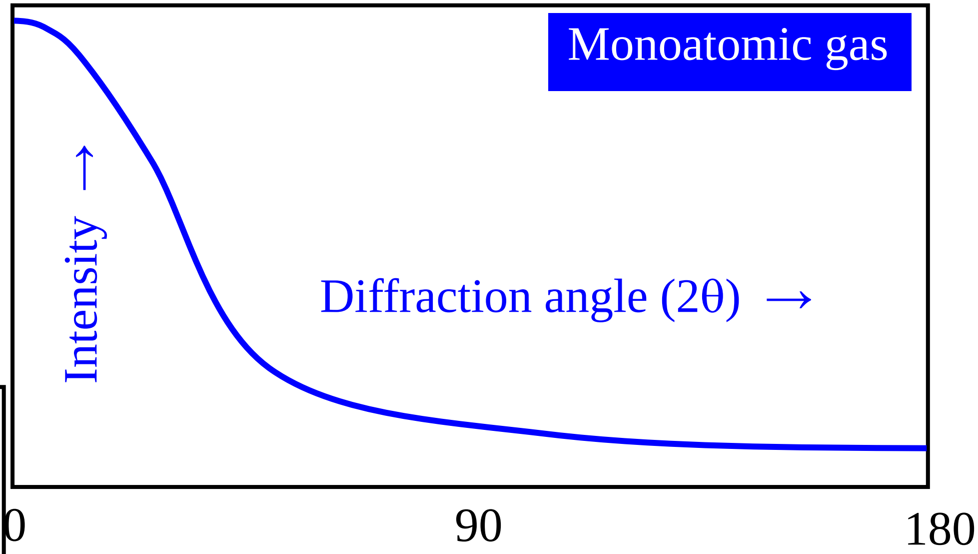
$h^2 + k^2 + l^2$	SC	FCC	BCC	DC
1	100			
2	110		110	
3	111	111		111
4	200	200	200	
5	210			
6	211		211	
7				
8	220	220	220	220
9	300, 221			
10	310		310	
11	311	311		311
12	222	222	222	
13	320			
14	321		321	
15				
16	400	400	400	400
17	410, 322			
18	411, 330		411, 330	
19	331	331		331

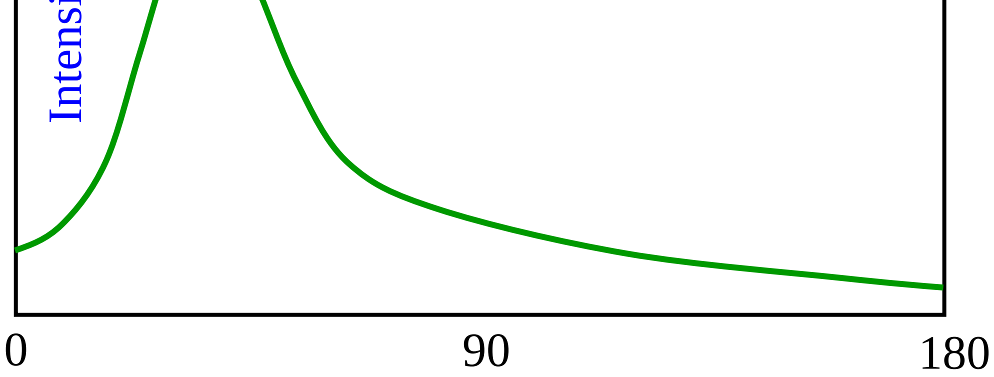
Applications of XRD

- Bravais lattice determination
- Lattice parameter determination
- Determination of solvus line in phase diagrams
- Long range order
- Crystallite size and Strain
- *More*

Schematic of difference between
the diffraction patterns of various phases







Crystallite size and Strain

- ❑ Bragg's equation assumes:
  - ➢ Crystal is perfect and infinite
  - ➢ Incident beam is perfectly parallel and monochromatic
- ❑ Actual experimental conditions are different from these leading various kinds of deviations from Bragg's condition
  - ➢ Peaks are not 'δ' curves → Peaks are broadened
- ❑ There are also deviations from the assumptions involved in the generating powder patterns
  - ➢ Crystals may not be randomly oriented *(textured sample)* → Peak intensities are altered

- ❑ In a powder sample if the crystallite size < 0.5 μm
  - ➢ there are insufficient number of planes to build up a sharp diffraction pattern

  ⇒ peaks are broadened

Crystal Structure Determination

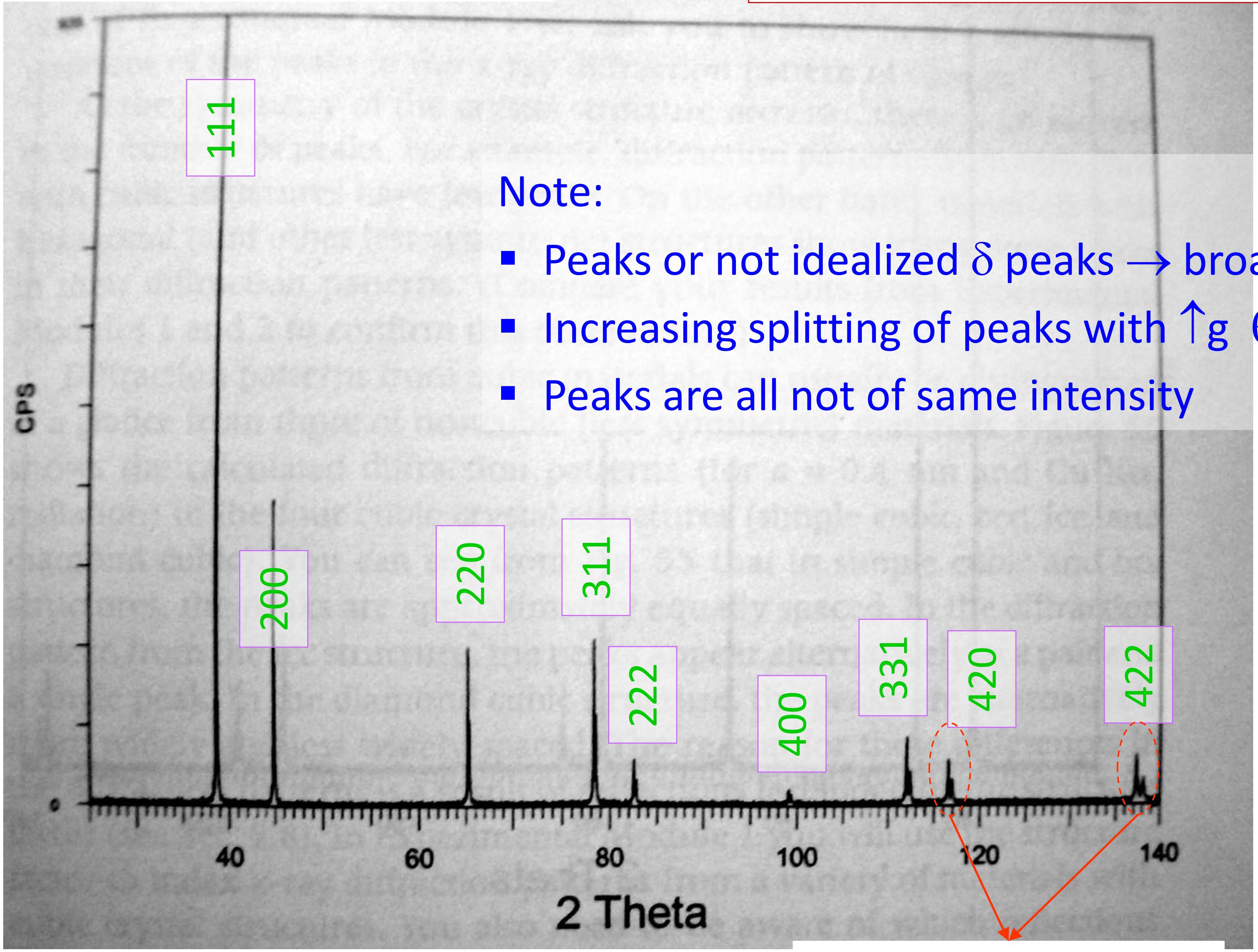
The ratio of $(h^2 + K^2 + l^2)$ derived from extinction rules

SC	1	2	3	4	5	6	8	…
BCC	1	2	3	4	5	6	7	…
FCC	3	4	8	11	12	…		
DC	3	8	11	16	…			

- In cubic systems, the **first XRD peak** in the XRD pattern will be due to diffraction from planes with the lowest Miller indices
- For the close packed planes *i.e.*:
  - simple cubic, (100), $h^2 + k^2 + l^2 = 1$
  - body-centered cubic, (110), $h^2 + k^2 + l^2 = 2$, and
  - face-centered, (111), $h^2 + k^2 + l^2 = 3$

Powder diffraction pattern from Al

Radiation: Cu Kα, λ = 1.54 Å



Note:

- Peaks or not idealized δ peaks $\rightarrow$ broadend
- Increasing splitting of peaks with ↑g θ
- Peaks are all not of same intensity

α_1 & α_2 peaks resolved

Determination of Crystal Structure from 2θ versus Intensity Data

n	**2θ**	**θ**	**Sinθ**	**Sin^2 θ**	**ratio**	**Index**
1	38.52	19.26	0.33	0.11	3	111
2	44.76	22.38	0.38	0.14	4	200
3	65.14	32.57	0.54	0.29	8	220
4	78.26	39.13	0.63	0.40	11	311
5	82.47	41.235	0.66	0.43	12	222
6	99.11	49.555	0.76	0.58	16	400
7	112.03	56.015	0.83	0.69	19	331
8	116.60	58.3	0.85	0.72	20	420
9	137.47	68.735	0.93	0.87	24	422

FCC

	$2\theta \rightarrow \theta$	Intensity	Sinθ	Sin$^2\theta$	ratio
1	21.5		0.366	0.134	3
2	25		0.422	0.178	4
3	37		0.60	0.362	8
4	45		0.707	0.500	11
5	47		0.731	0.535	12
6	58		0.848	0.719	16
7	68		0.927	0.859	19

→ FCC

Lattice parameter determination

For Cubic Materials:

- For cubic materials, interplanar spacing is given as: $$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$$
- Recall Bragg's law: $\lambda = 2d\sin\theta$

$$\lambda^2 = 4d^2\sin^2\theta \text{ OR } \sin^2\theta = \frac{\lambda^2}{4d^2}$$

- Combining above 2 equations:

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} = \frac{4\sin^2\theta}{\lambda^2}$$

$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)\left(h^2+k^2+l^2\right)$$

- λ, a are constants, hence $\frac{\lambda^2}{4a^2}$ is constant
- $\sin^2\theta$ is proportional to $h^2 + k^2 + l^2$ i.e. planes with higher Miller indices will diffract at higher values of θ.

- Allowed reflection for cubic lattices
  - Primitive $h^2 + k^2 + l^2 = 1,2,3,4,5,6,8,9,10,11,12,13,14,16\ldots$
  - Body-centered $h^2 + k^2 + l^2 = 2,4,6,8,10,12,14,16\ldots$
  - Face-centered $h^2 + k^2 + l^2 = 3,4,8,11,12,16,19,20,24,27,32\ldots$
  - Diamond cubic $h^2 + k^2 + l^2 = 3,8,11,16,19,24,27,32\ldots$

- After determining the hkl values for each reflection, put it in the equation given below:

$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)\left(h^2 + k^2 + l^2\right)$$

- Here the values of $\sin^2\theta$ and λ is known.
- So for each n, one value of 'a' can be calculated. Then the average of that will give the lattice parameter.

For Non-Cubic Materials:

- Many materials have crystal structures that are not cubic. In other words, they are based on noncubic Bravais lattices (e.g., hexagonal, tetragonal, orthorhombic, etc…).
- In fact, many intermetallic, semiconductors, ceramics, and minerals of interest have very complicated structures.
- Consider the plane spacing equations for the crystal structures of interest.

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

- Combining the above equations with bragg’s law:

Hexagonal	$\sin^2\theta=\left(\frac{\lambda^2}{4}\right)=\left[\frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\frac{l^2}{c^2}\right]$
Tetragonal	$\sin^2\theta=\left(\frac{\lambda^2}{4}\right)\left(\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}\right)$
Orthorhombic	$\sin^2\theta=\left(\frac{\lambda^2}{4}\right)\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)$

Thermal Analysis

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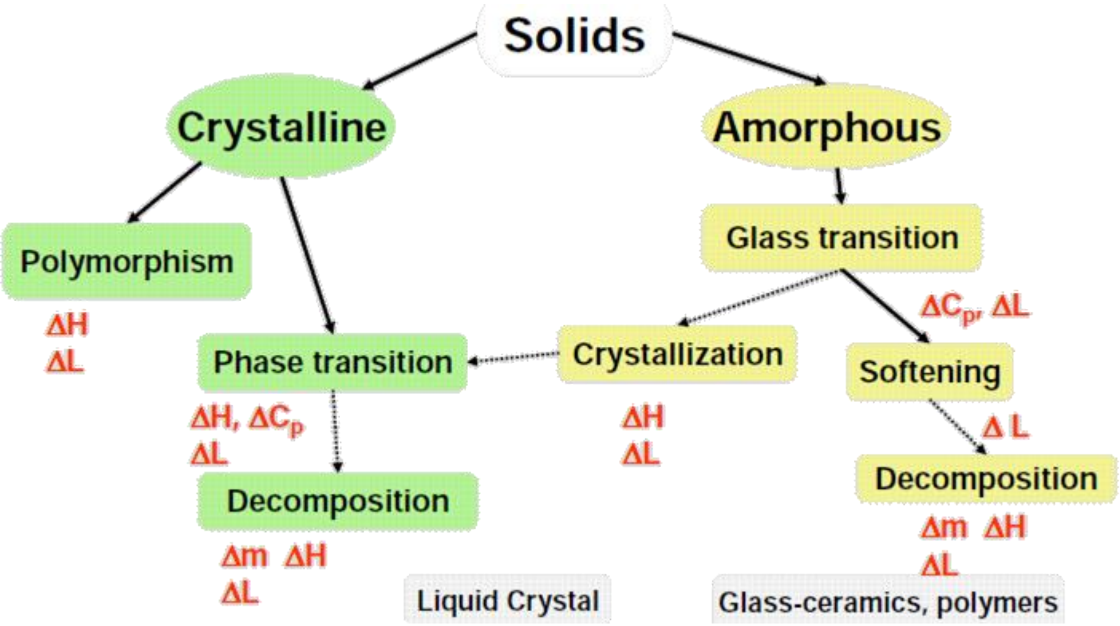
Thermal Analysis Techniques

- Thermal analysis (TA) is a group of techniques in which changes of physical or chemical properties of the sample are monitored against time or temperature, while the temperature of the sample is programmed.
- The temperature program may involve heating or cooling at a fixed rate, holding the temperature constant (isothermal), or any sequence of these.
- The sample is subjected to a predefined heating or cooling program.
- The sample is usually in the solid state and the changes that occur on heating include melting, phase transition, sublimation, and decomposition.

Application of thermal analysis in characterization of solids



Solids

Crystalline

Amorphous

Polymorphism

ΔH

ΔL

Phase transition

ΔH, ΔC_p

ΔL

Decomposition

Δm ΔH

ΔL

Liquid Crystal

Glass transition

ΔC_p, ΔL

Crystallization

ΔH

ΔL

Softening

ΔL

Decomposition

Δm ΔH

ΔL

Glass-ceramics, polymers

Types of Thermal Analysis Techniques

- ✓ Differential Thermal Analysis (DTA): The temperature difference between a sample and an inert reference material, ΔT = TS - TR, is measured as both are subjected to identical heat treatments.
- ✓ Differential Scanning Calorimetry (DSC): The sample and reference are maintained at the same temperature, even during a thermal event (in the sample). The energy required to maintain zero temperature differential between the sample and the reference, d Δq/dt, is measured.
- ✓ Thermogravimetric Analysis (TGA): The change in mass of a sample on heating is measured

- ✓ Dynamic Mechanical Analysis: Viscoelastic Properties
- ✓ Thermo mechanical Analysis: Thermal Expansion Coefficient
- ✓ Dielectric Thermal Analysis
- ✓ Evolved Gas Analysis
- ✓ Thermo-Optical Analysis
- ✓ Dilatometry

Differential Thermal Analysis (DTA)

- **PRINCIPLE:** A Technique in which the temperature difference between a substance and reference material is measured as a function of temperature, while the substance and reference are subjected to a controlled temperature programme.
- The record is the differential thermal or DTA curve; the temperature difference (ΔT) should be plotted on the ordinate (with endothermic reactions downwards and exothermic reactions upwards) and temperature or time on the abscissa increasing from left to right.
- Endothermic reaction (absorption of energy) includes vaporization, sublimation, and absorption & gives downward peak.
- Exothermic reaction (liberation of energy) includes oxidation, polymerization, and catalytic reaction & gives upward peak.

Specimens

- ✓ Sample
- ✓ Reference (Known substance, thermally inert over the temp range of interest)

Sample holder

- ✓ Container for sample and reference

Sensors

- ✓ Pt/Rh or chromel/alumel thermocouples one for the sample and one for the reference joined to differential temperature controller

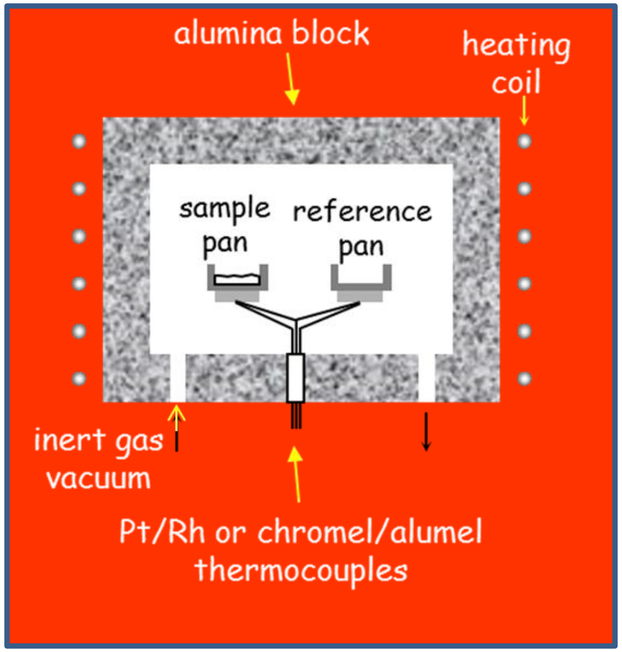
Furnace

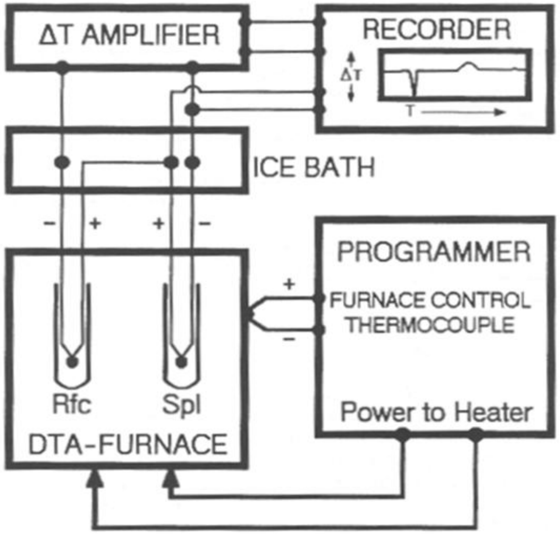
- ✓ alumina block containing sample and reference cells

Temperature controller/ Programmer

- ✓ controls for temperature program and furnace atmosphere
- ✓ Uniform heating rate: 10-20^{o}/min

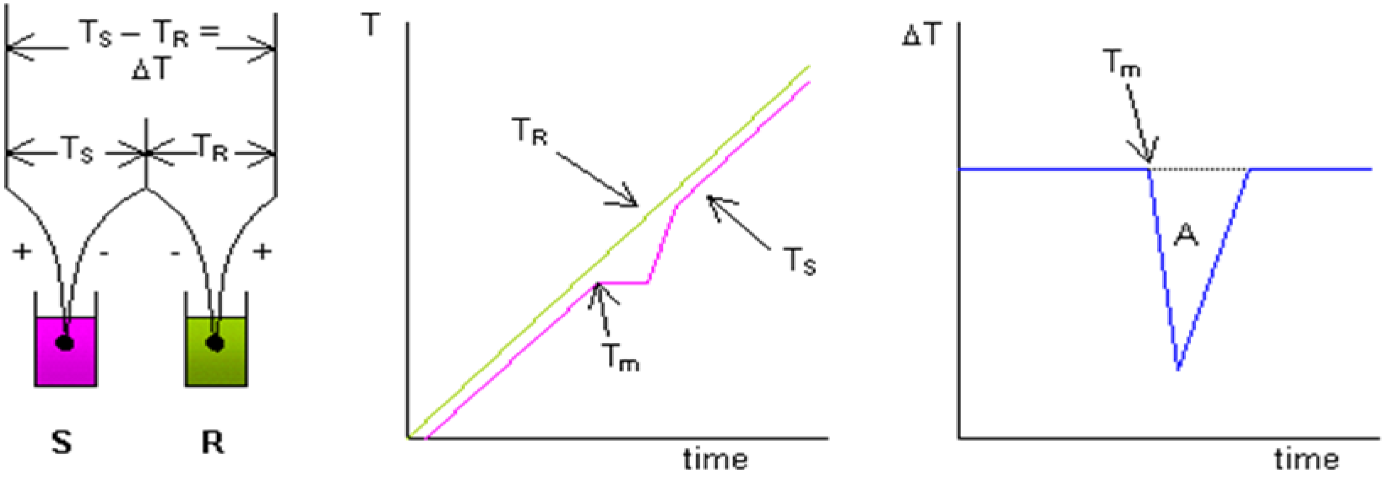
Recorder





SCHEMATIC OF A
DIFFERENTIAL THERMAL ANALYSIS
EXPERIMENT (DTA)

Differential Thermal Analysis Plot



- If S and R are heated at the same rate, by placing them in the same furnace, their temperatures will rise
- TR rises steadily, as the reference material is chosen to have no physical or chemical transitions
- TS also rises steadily in the absence of any transitions, but if for instance the sample melts, its temperature will lag behind TR as it absorbs the heat energy necessary for melting
- If an exothermic (heat-producing) event had occurred, the curve would show a peak in the opposite direction
- The area A on the curve is proportional to the heat of the reaction: $\Delta H = K.A = K \int \Delta T.dt$
- K: Proportionality constant and includes thermal properties of the substance

Applications of Differential thermal analysis

- ☐ Qualitative and Quantitative Identification of Minerals: detection of any minerals in a sample
- ☐ Measures:
  - ✓ T_g (Glass transition temperature), T_m (Melting temperature), T_d (decomposition)
  - ✓ Heat of fusion, vaporization, crystallization,
  - ✓ Heat of reaction, decomposition, solution, adsorption

Advantage & Disadvantage

Advantages:

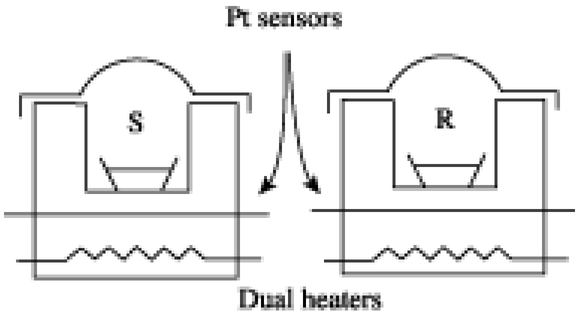
- ✓ Instruments can be used at very high temperatures
- ✓ Instruments are highly sensitive
- ✓ Flexibility in crucible volume/form
- ✓ Characteristic transition or reaction temperatures can be accurately determined
- ✓ Determination of transition temperatures are accurate in a DTA.

Disadvantages:

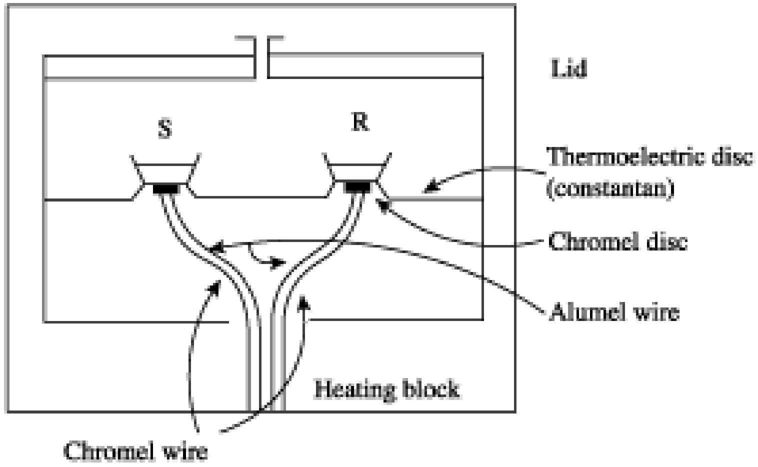
Estimates of enthalpies of transition are generally not accurate i.e. Uncertainty of heats of fusion, transition, or reaction ; estimations is 20-50%.

Differential Scanning Calorimetry

- **PRINCIPLE:** DSC differs fundamentally from DTA in that the sample and reference are both maintained at the temperature predetermined by the program (i.e. ΔT of reference/sample is maintained @ 0)
- During a thermal event in the sample, the system will transfer heat to or from the sample pan to maintain the same temperature in reference and sample pans.
- Current required to maintain isothermal conditions is recorded
- Endothermic processes will lower the sample temperature relative to that of reference, so the sample must be heated more in order to maintain equal T in both pans
- Two basic types of DSC instruments: power compensation and heat-flux



Power compensation DSC



Heat flux DSC

Power Compensation DSC

- ✓ Temperatures of the sample and reference are controlled independently using separate, identical furnaces.
- ✓ The temperatures of the sample and reference are made identical by varying the power input to the two furnaces; the energy required to do this is a measure of the enthalpy or heat capacity changes in the sample relative to the reference.

Sample holder: Al or Pt pans

Sensors

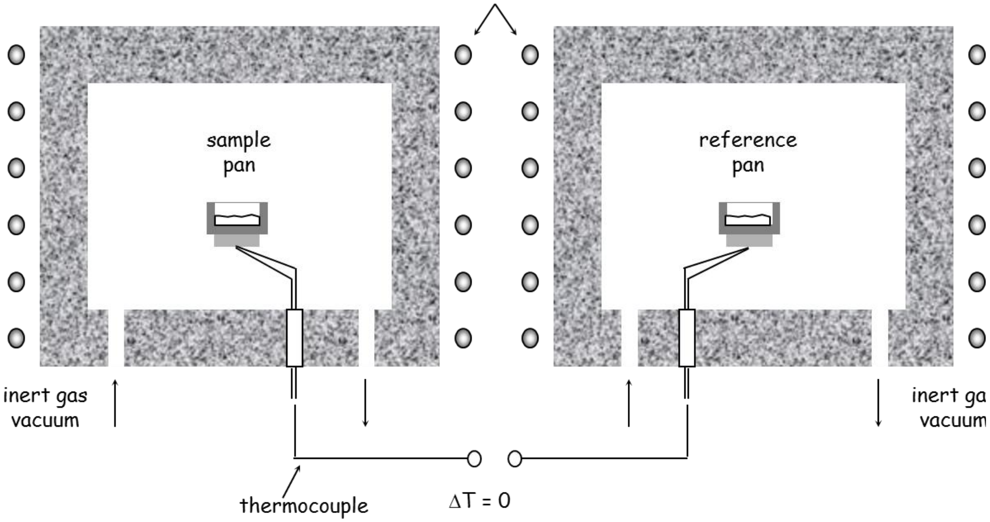
- ✓ Pt resistance thermocouples
- ✓ separate sensors and heaters for the sample and reference

Furnace

- ✓ separate blocks for sample and reference cells

Temperature controller

- ✓ differential thermal power is supplied to the heaters to maintain the temperature of the sample and reference at the program value



Heat flux DSC

- ✓ Sample and reference are connected by a low resistance heat flow path (a metal disc). The assembly is enclosed in a single furnace.
- ✓ Enthalpy or heat capacity changes in the sample cause a difference in its temperature relative to the reference; the resulting heat flow is small compared with that in differential thermal analysis (DTA) because the sample and reference are in good thermal contact.
- ✓ The temperature difference is recorded and related to enthalpy change in the sample using calibration experiments

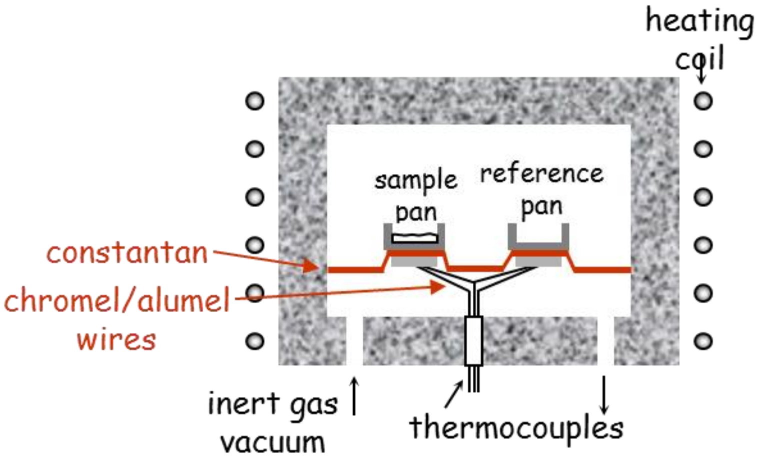
Sample holder

- ✓ sample and reference are connected by a low-resistance heat flow path
- ✓ Al or Pt pans placed on constantan disc

Sensors: Chromel®-alumel thermocouples

Furnace

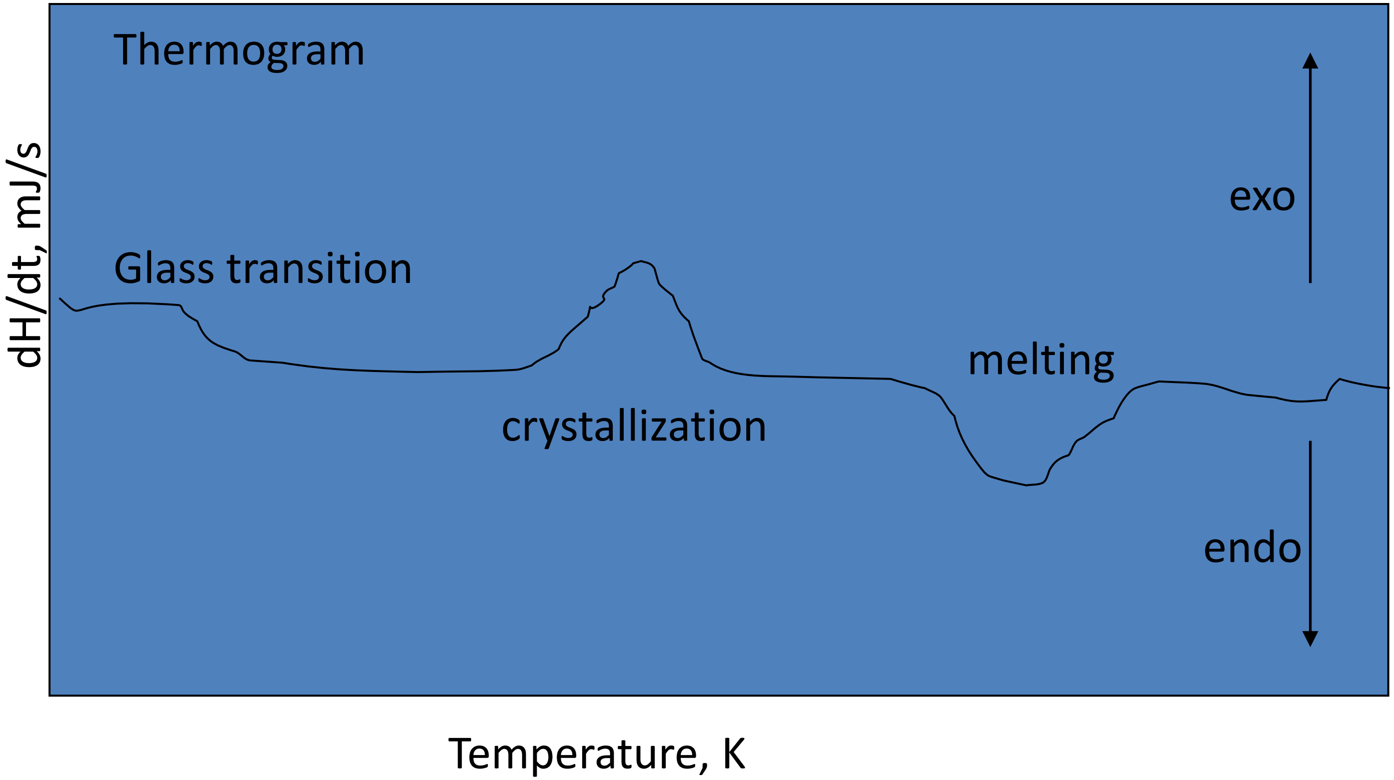
- ✓ One block for both sample and reference cells
- ✓ Heating block dissipates heat to the sample and reference via the constantan disc



Temperature controller

- ✓ The temperature difference between the sample and reference is converted to differential thermal power, dΔq/dt, which is supplied to the heaters to maintain the temperature of the sample and reference at the program value

Output of DSC



Application of DSC

- ☐ To observe fusion and crystallization events as well glass transition temperature
- ☐ To study oxidation, as well as other chemical reactions
- ☐ Glass transition may occur as the temperature of an amorphous solid is increased. These transition appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity.
- ☐ As the temperature increases, an amorphous solid will become less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature. This transition from amorphous to crystalline is an exothermic process, and results in a peak in the DSC signal.
- ☐ As the temperature increases the sample eventfully reaches its melting point. The melting process results in an endothermic peak in the DSC curve.
- ☐ The ability to determine transition temperature and enthalpies makes DSC an invaluable toll in producing phase diagram for various chemical systems.

Calibration for DTA & DSC

Parameters to be calibrated are as follows:

- ✓ Energy calibration may be carried out by using either known heats of fusion for metals, commonly indium, or known heat capacities
- ✓ Temperature calibration is carried out by running standard materials, usually very pure metals with accurately known melting points

Thermogravimetry

PRINCIPLE

- ✓ Changes in the mass/weight of a sample are studied while the sample is subjected to a programme.
- ✓ The temperature programme is most often a linear increase in temperature, but, also be carried out, when the changes in sample mass with time are followed.
- ✓ TGA is inherently quantitative, and therefore an extremely powerful thermal technique, but gives no direct chemical information.

Thermo balance/microbalance:

- ✓ Balance sensitivity is usually around one microgram, with a total capacity of a few hundred milligrams

Furnace

- ✓ A typical operating range for the furnace is ambient to 1500°C, with heating rates up to 200°C/min

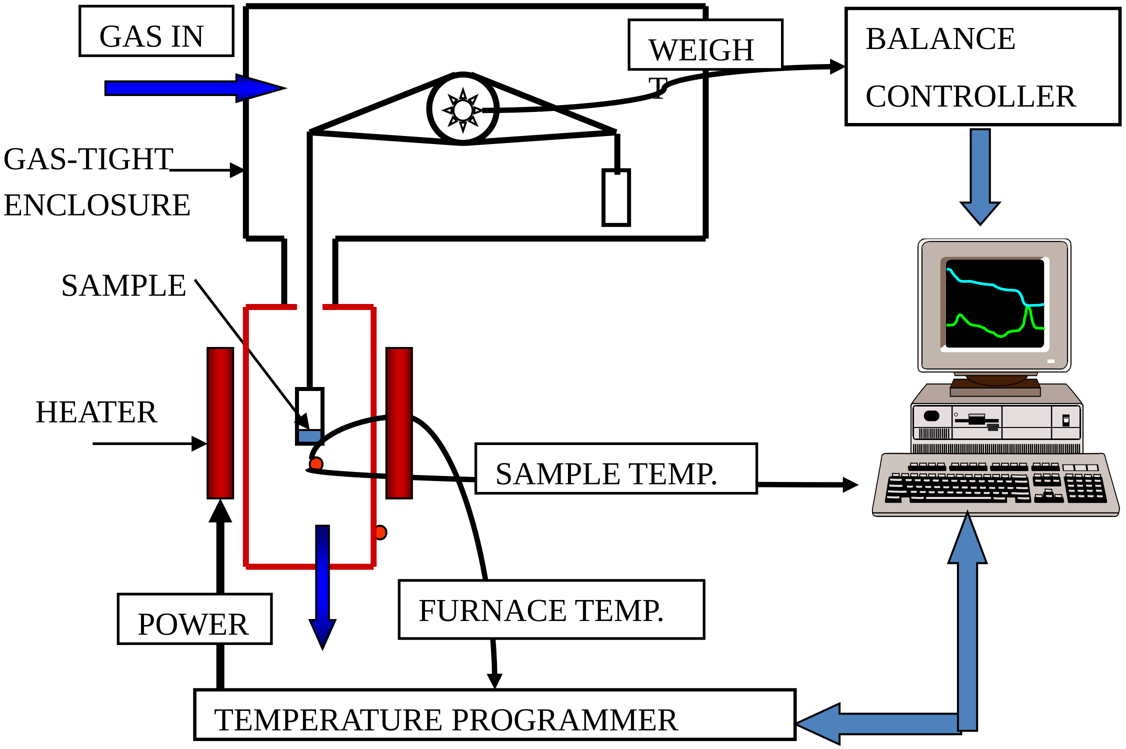
Temperature sensor: Thermocouple placed close to the sample

Sample holder/pan

- ✓ An enclosure for establishing the required atmosphere: Reactive or inert

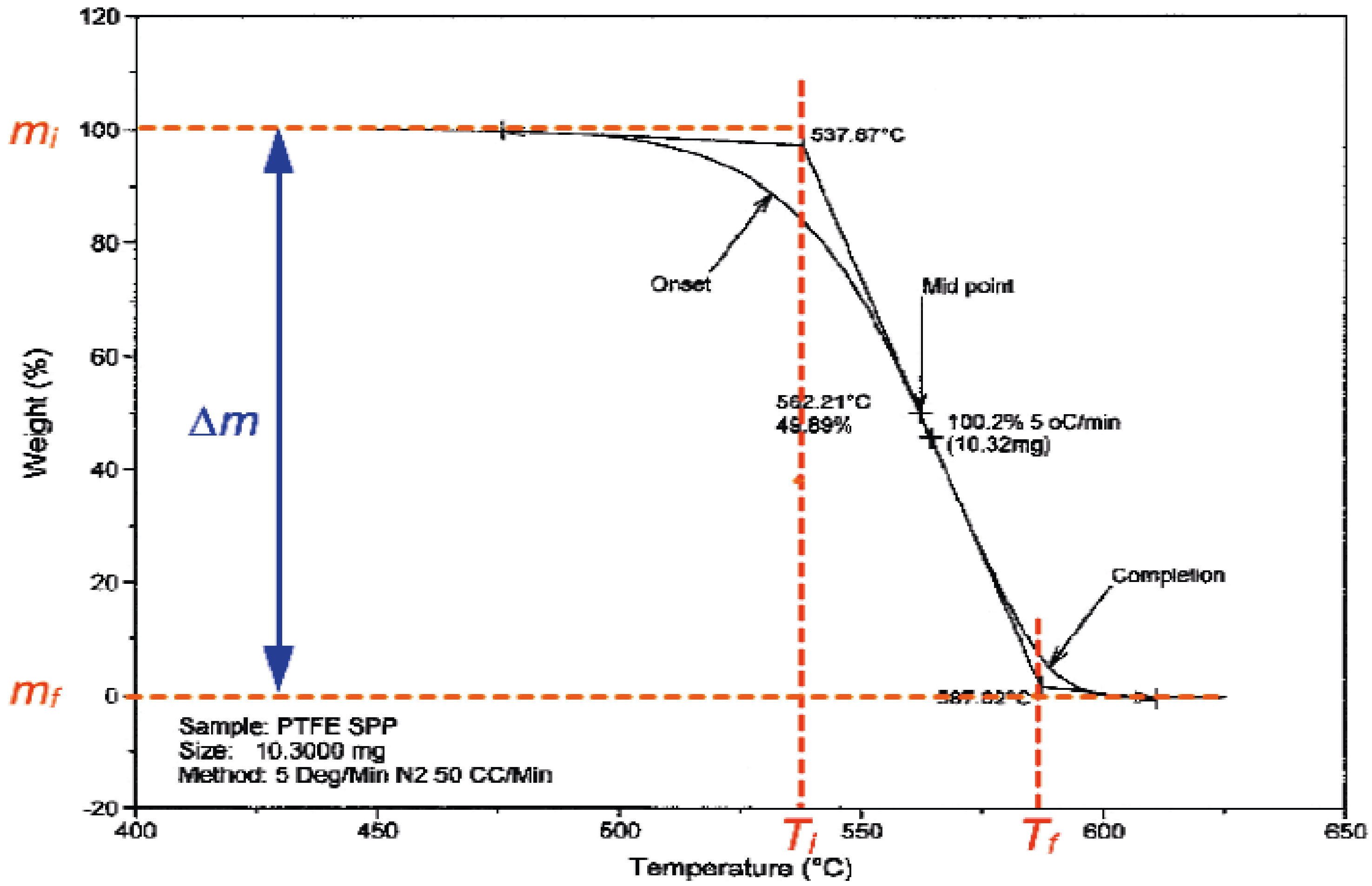
Microcomputer/microprocessor: Instrument control, Data acquisition and display

TGA Instrument



Process	Weight gain	Weight loss
Ad- or absorption	Yes	
Desorption, drying		Yes
Dehydration, desolvation		Yes
Sublimation		Yes
Vaporisation		Yes
Decomposition		Yes
Solid-solid reactions(some)		Yes
Solid-gas reactions	Yes	Yes
Magnetic transitions	Yes	Yes

TGA Plot



- ❑ Thermogram is graph of mass versus temperature. Sometimes given as % of original mass.
- ❑ Draw tangents of the curve to find the onset and the offset points

Application

- **Thermal Stability:** related materials can be compared at elevated temperatures under the required atmosphere. The TG curve can help to elucidate decomposition mechanisms.
- **Material characterization:** TG and DTG curves can be used to "fingerprint" materials for identification or quality control.
- **Compositional analysis:** by careful choice of temperature programming and gaseous environment, many complex materials or mixtures may be analyzed by selectively decomposing or removing their components. This approach is regularly used to analyze e.g. filler content in polymers; carbon black in oils; ash and carbon in coals, and the moisture content of many substances.
- **Simulation of industrial processes:** the thermo balance furnace may be thought of as a mini-reactor, with the ability to mimic the conditions in some types of industrial reactor.
- **Kinetic Studies:** a variety of methods exist for analyzing the kinetic features of all types of weight loss or gain, either with a view to predictive studies, or to understanding the controlling chemistry.
- **Corrosion studies:** TG provides an excellent means of studying oxidation, or reaction with other reactive gases or vapors.

Introduction to Advanced Microscopy Techniques

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Scanning transmission electron microscopy (STEM)

- An imaging mode that merges both SEM and TEM is also possible on most modern TEM instruments.
- Uses a LaB6 source that produces a focused electron beam with a high current density and extremely small diameter.
- Instead of monitoring the transmitted electrons from a static beam as performed in standard TEM imaging, the beam within a STEM is scanned across the sample – analogous to SEM.
- Due to a higher beam intensity, thicker samples may be analyzed in a STEM; furthermore, staining is generally not necessary for low-Z elements due to a higher sensitivity to sample density/composition.
- In particular, it is possible to overlay the image with the EDS data – a technique known as elemental dot-mapping, widely used for SEM/EDS analysis.

Electron energy-loss spectroscopy

- ❑ In order to increase the sensitivity toward the detection of light elements, this technique (EELS) may be utilized.

- ❑ This method may be carried out within a (S)TEM, and consists of monitoring the loss in energy (due to inelastic scattering) of the beam electrons as they pass through the sample.

- ❑ Since it is more difficult to focus X-rays relative to electrons with appropriate lenses, oscillation of many outer-shell (valence or conduction) electrons.

- ❑ The most useful application for this peak is the accurate determination of the sample thickness, of upto several thousand nanometers with a precision of a few percent.

- ❑ At higher energy losses, an EELS spectrum will exhibit a variety of sharp features known as “edges,” which are diagnostic for the presence of specific elements.

- ❑ The positions of the edges correspond to the binding energies of the core electrons in the sample.

- ❑ Once the background is subtracted, the area under each edge peak(s) is integrated in order to determine the elemental concentrations

Auger Spectroscopy

❑ Auger spectroscopy can be considered as involving three basic steps :

(1) Atomic ionization (by removal of a core electron): Typically carried out by exposing the sample to a beam of high energy electrons (typically having a primary energy in the range 2 - 10 keV). Such electrons have sufficient energy to ionise all levels of the lighter elements, and higher core levels of the heavier elements.

(2) Electron emission (the Auger process): The ionized atom that remains after the removal of the core hole electron is, of course, in a highly excited state and will rapidly relax back to a lower energy state by Auger emission

(3) Analysis of the emitted Auger electrons: Each element in a sample being studied will give rise to a characteristic spectrum of peaks at various kinetic energies.

❑ Auger Electron Spectroscopy (AES) is a surface-sensitive spectroscopic technique used for elemental analysis of surfaces; it offers high sensitivity (typically ca. 1% monolayer) for all elements except H and He.

❑ A means of monitoring surface cleanliness of samples

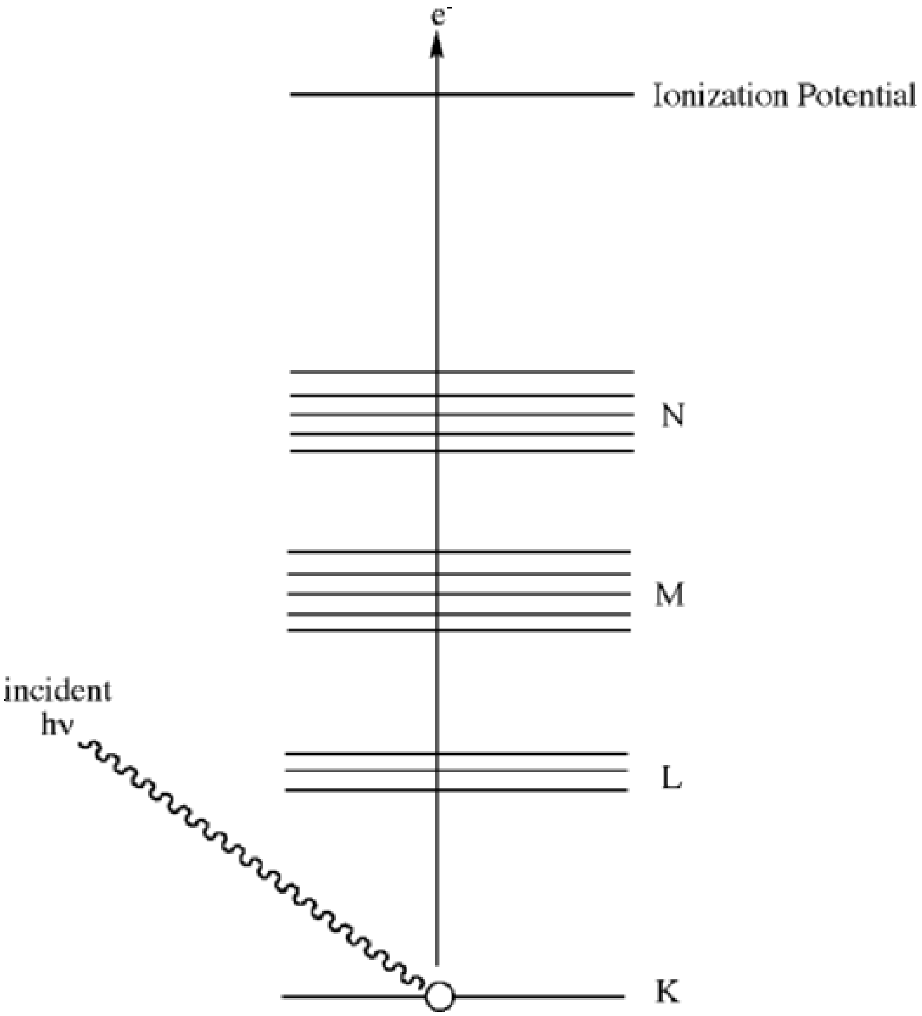
❑ Quantitative compositional analysis of the surface region of specimens, by comparison with standard samples of known composition.

Photoelectron Spectroscopy

- The photoelectric effect, first outlined by Einstein in the early 1900s, refers to the ejection of electrons from a surface due to photon impingement.

- However, it was not until the 1960s that this phenomenon was exploited for surface analysis – a technique referred to as X-ray photoelectron spectroscopy (XPS), or electron spectroscopy for chemical analysis (ESCA). This technique consists of the irradiation of a sample with monochromatic X-rays (e.g., Al Kα (1.487 keV), Mg Kα (1.254 keV), Ti Kα (2.040 keV)), which releases photoelectrons from the sample surface.

- Due to the short free mean path (FMP) of the photoelectrons in the solid, this technique provides compositional information from only the top 1–5 nm of a sample.



Surface Characterization Techniques Based on Ion Bombardment

These techniques employs the “collide and collect” principle, by using a number of ions.

Metastable impact electron spectroscopy (MIES):

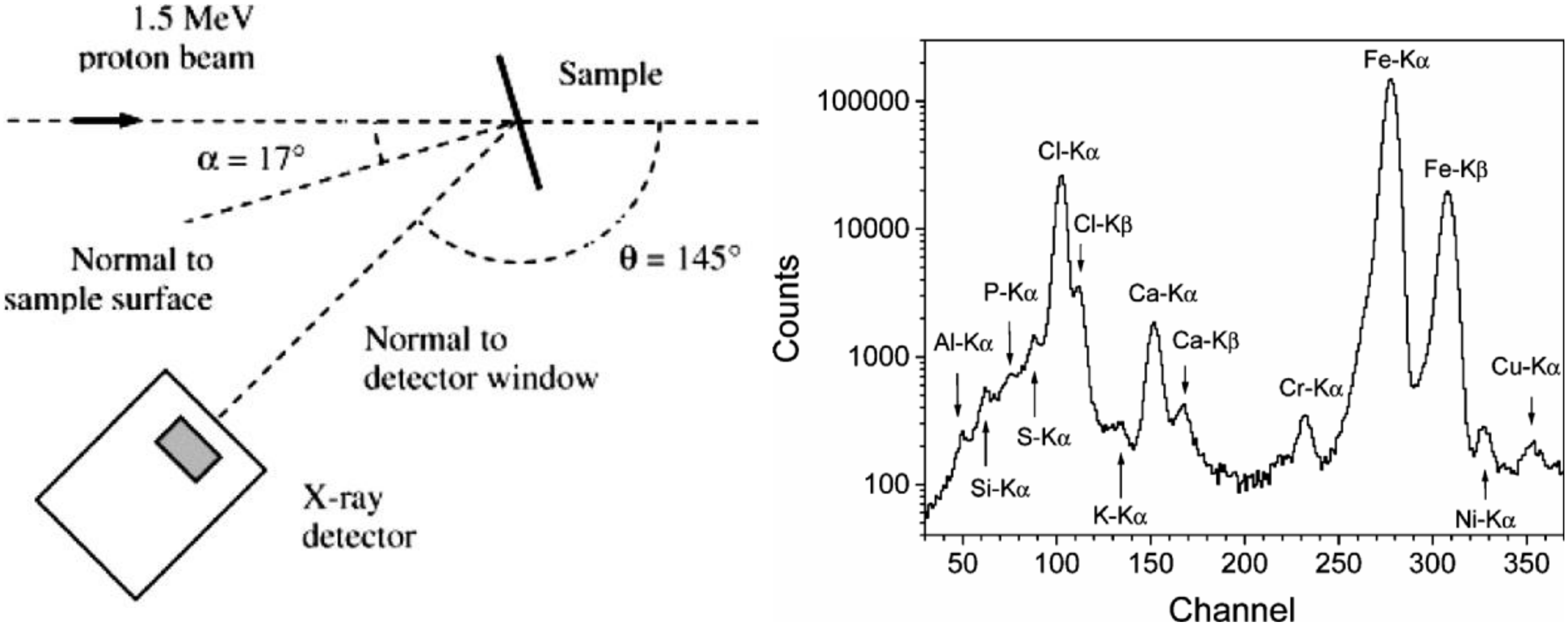
- Metastable He atoms (in an excited 2s1 state, with an energy of 19.8 eV and a lifetime of ca. 4,000 s) are directed toward a sample.
- As the atom collides with the sample, the 2s electron tunnels into an empty valence orbital in a sample atom, releasing an Auger electron.

Ion neutralization spectroscopy (INS):

- Carried out by incident He ions.
- Since the incident atoms/ions are not sufficiently energetic, the beam does not penetrate through the sample surface.
- Hence, the spectra resulting from these techniques provide information regarding the density of states for the topmost surface monolayer of the sample.

Particle-induced X-ray emission (PIXE):

- Uses high-energy H+ or He+ ions (at >2 MeV) as the incident beam which dislodge inner-shell electrons, releasing characteristic X-rays.
- This technique offers a nondestructive quantitative analysis of a sample (for elements with $Z \geq 13$).



Experimental setup and X-ray spectrum resulting from PIXE analysis of single-walled carbon nanotubes.

Rutherford backscattering (RBS):

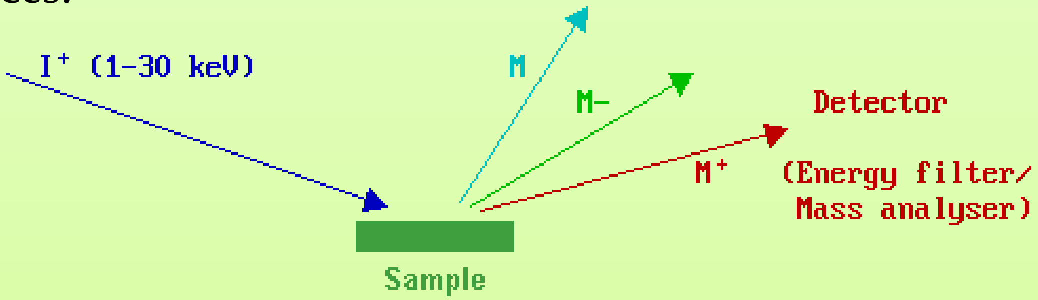
- ☐ If a high-energy beam (2–4 MeV) of He (α-particles) or H ions collides with a surface, information may be gained regarding the composition and thickness of a surface coating.
- ☐ As the energetic ion penetrates the material, it loses energy through collisions with electrons, and (less frequently) with nuclei.
- ☐ When the positively charged He+ ion approaches the nucleus of a sample atom, it will be electrostatically repelled.
- ☐ As you would expect, the energy of the backscattered ions will depend on their incident energy, as well as the mass of the surface atom that causes the scattering.
- ☐ For instance, contact with high-Z atoms such as gold, will result in the energy of the backscattered ions being almost equivalent as the incident beam.
- ☐ By measuring the energy spectrum of the backscattered ions, information on the composition of the elements, and their origination depth from the sample may be obtained.
- ☐ Hence, RBS provides facile compositional information regarding a sample, without the need for a reference sample.
- ☐ This technique is most often applied to determine the chemical composition versus depth for heavy elements in a low-Z matrix, amenable for thicknesses of up to 0.5 μm (for He ions) and 10 μm (for H ions).

Elastic recoil detection analysis (ERDA):

- This technique uses a high-energy ion beam (e.g., He, Au, Cl, C, or O ions), which causes light elements to be elastically ejected from the surface (i.e., “recoiled”) due to interactions between the incident beam and their atomic nuclei.
- By choice of the correct angle between the sample surface and detector, the incident beam is blocked by “stopper foil” to increase the signal/noise ratio for the measurement.
- Nondestructively quantifies light elements such as hydrogen or deuterium.

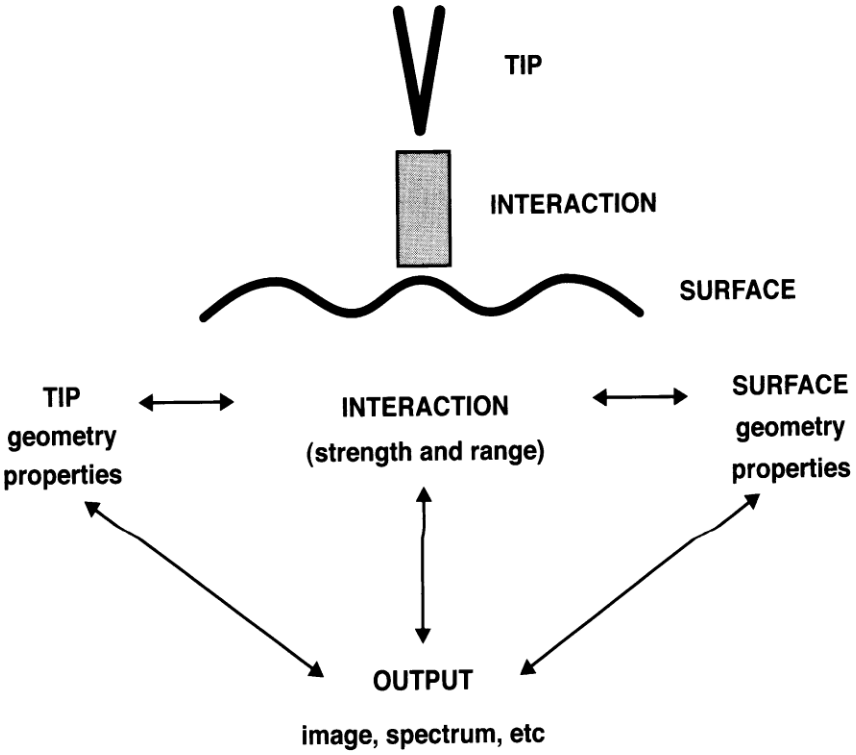
Secondary-ion mass spectrometry (SIMS):

- A high-energy (1–30 keV) ion source is directed onto a sample surface. The absorption of this energy by the top 50 ˚A of the sample results in the sputtering of neutral and charged (+/−) species from the surface.
- SIMS analyzes these secondary ions based on their relative mass/charge (m/z) ratios.
- It is the most sensitive surface characterization technique developed to date, with detection limits of 1010–1015 atoms cm−3 (i.e., 0.1 ppb − 0.1 ppm) and ability to detect/quantify any element in the Periodic Table.
- SIMS analyzes samples in their native state without the need for a suitable matrix solution. As a result, SIMS is the best choice to characterize organic-based thin films and polymer surfaces.



Scanning Probe Microscopy

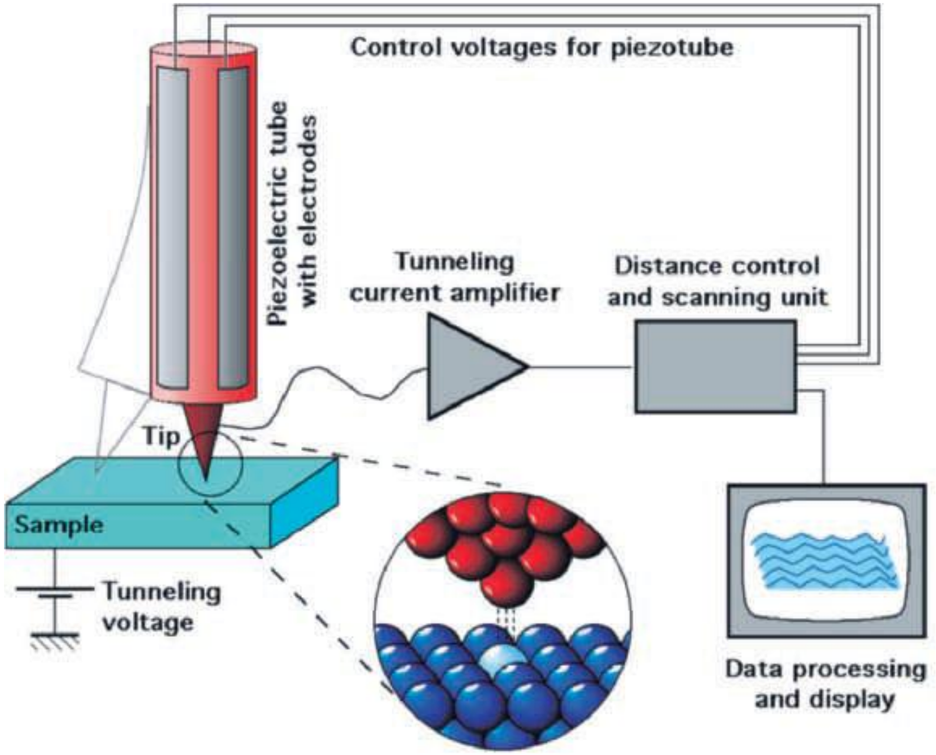
- ❑ This technique that does not involve irradiation, but rather features the scanning of a probe across a surface (hence, termed SPM).
- ❑ There are two primary forms of SPM:
  - ✓ Scanning tunneling microscopy (STM) – set the precedent for SPM in the early 1980s. The tip is held a few Angstroms from the sample surface during scans.
  - ✓ Atomic force microscopy (AFM) – the tip may interact with the sample surface through either contact or noncontact modes.
- ❑ Both types of SPM are most often used to provide an image of the surface topography.
- ❑ Though both techniques are frequently carried out under ambient temperatures/ pressures, or even in liquids, they may also be performed in an UHV chamber



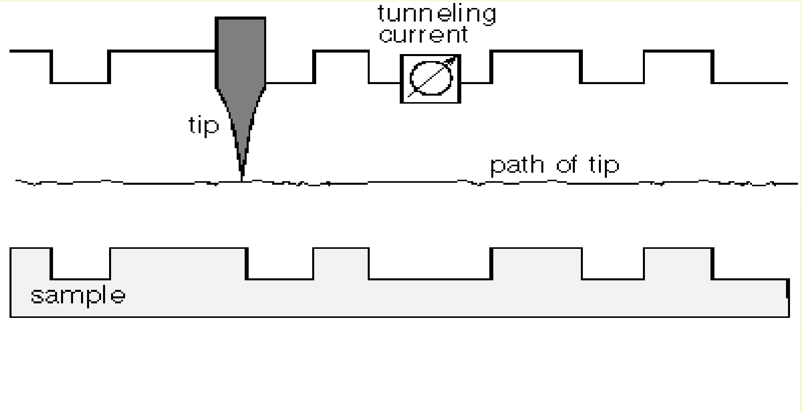
Basic Idea of SPM

Scanning tunneling microscopy (STM):

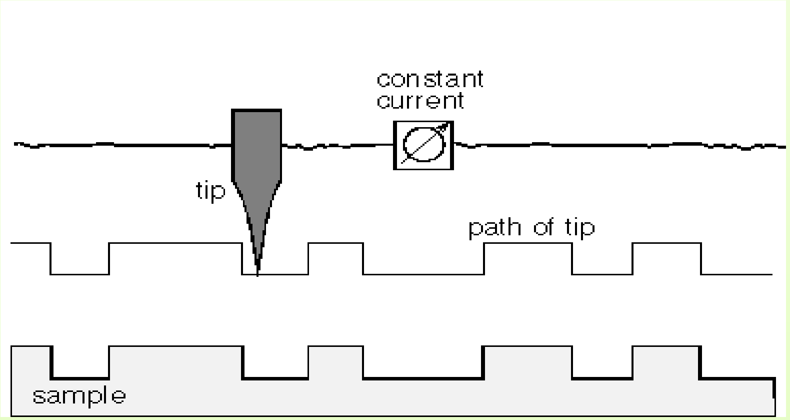
- ❑ As a STM tip is scanned across the sample, a quantum mechanical tunneling current is established between the sample surface and a sharpened W or Pt/Ir tip.
- ❑ The magnitude of the current is dependent on the distance between the tip and the surface (z), as well as the local density of states of the surface.
- ❑ Accordingly, STM is typically performed on conductive and semiconductive surfaces.
- ❑ During topographic imaging, a feedback loop is established to maintain a constant current through varying the distance between the tip and surface (“constant current mode”).
- ❑ In this respect, STM is able to provide real-time, three-dimensional images of the surface with atomic resolution.



- In constant-height mode, the tip travels in a horizontal plane above the sample and the tunneling current varies depending on topography and the local surface electronic properties of the sample. The tunneling current measured at each location on the sample surface constitute the data set, the topographic image.



constant-height mode

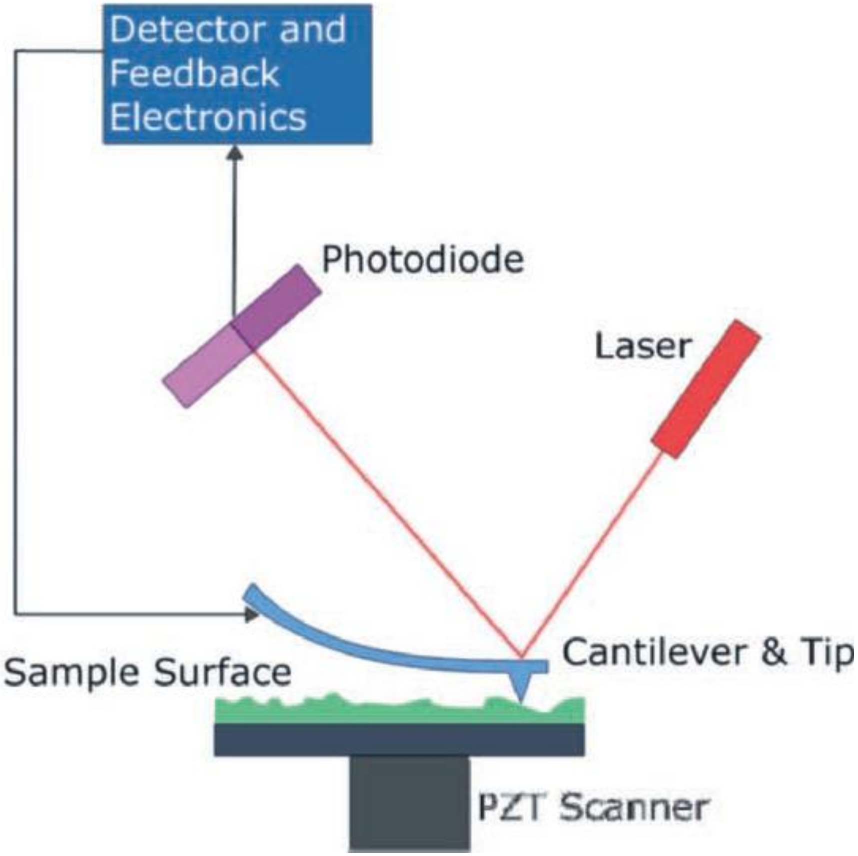


constant-current mode

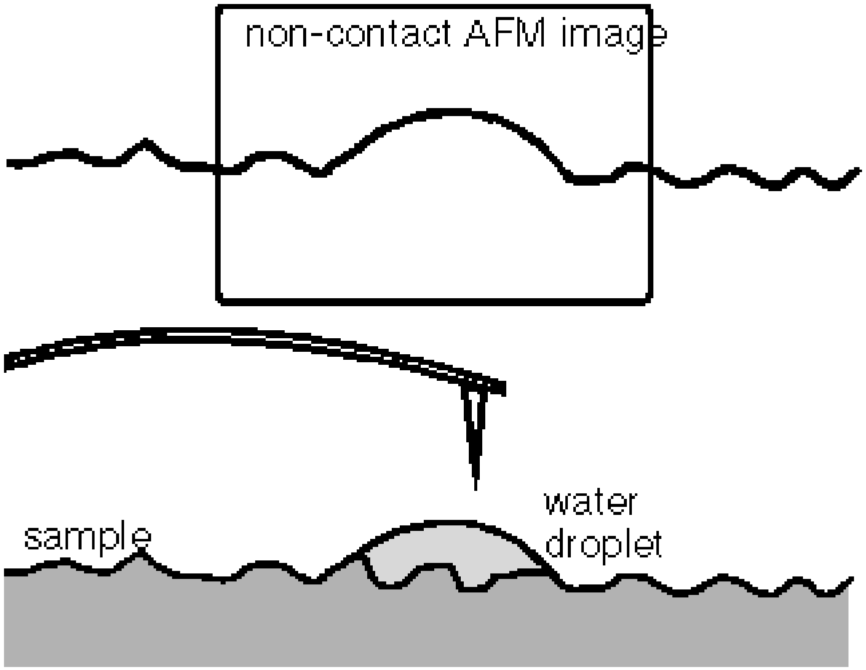
- In constant-current mode, STMs use feedback to keep the tunneling current constant by adjusting the height of the scanner at each measurement point. For example, when the system detects an increase in tunneling current, it adjusts the voltage applied to the piezoelectric scanner to increase the distance between the tip and the sample. In constant-current mode, the motion of the scanner constitutes the data set. If the system keeps the tunneling current constant to within a few percent, the tip-to-sample distance will be constant to within a few hundredths of an angstrom.

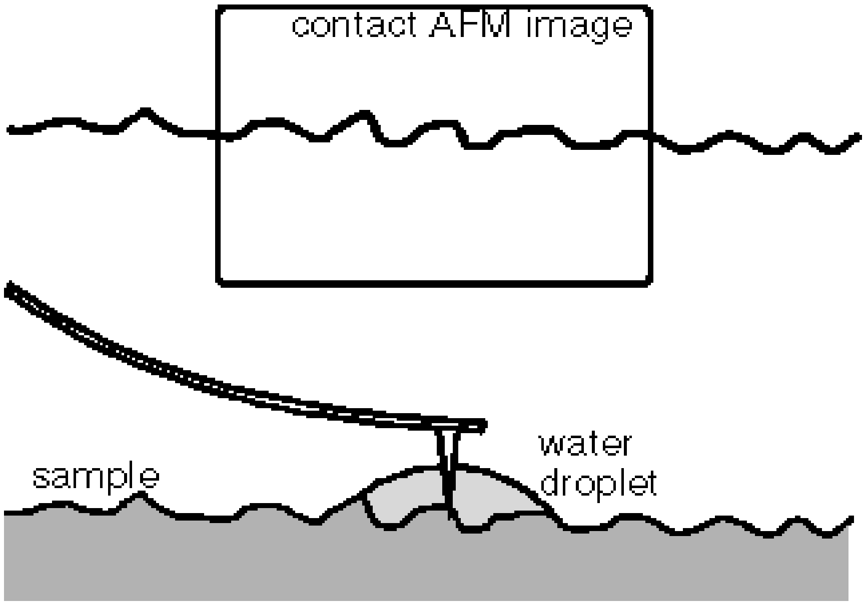
Atomic Force Microscopy (AFM):

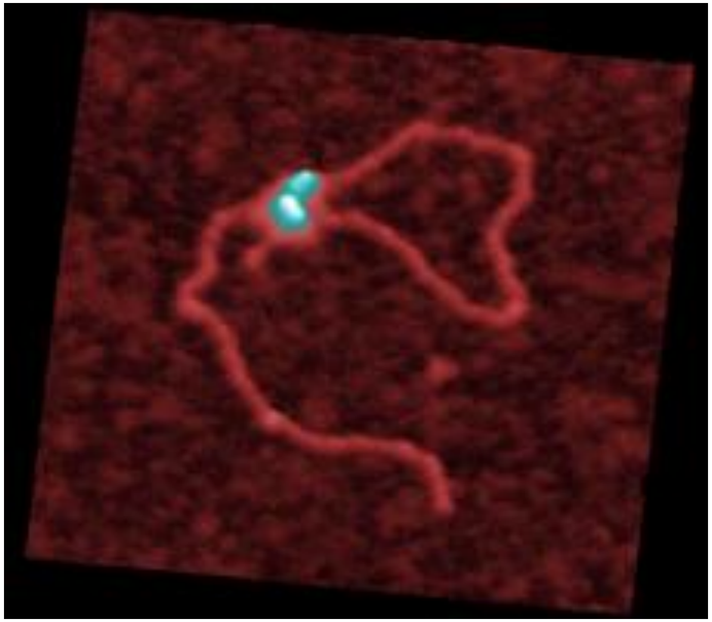
- Rather than monitoring electronic tunneling phenomena, AFM measures the forces between the tip and surface, which depends on the nature of the sample, the probe tip, and the distance between them.
- The deflection of the tip in response to surface–tip interfacial forces is recorded by using a laser focused on top of the Si or SiN cantilever, and reflected onto photodetectors.
- The signal emanating from the photodetector is used to generate a surface topographic map, or the direct measurement of surface intermolecular forces.
- A feedback loop is present in the system, which controls the distance between the tip and sample via an electrical current sent to piezoelectric transducers.



- Such "constant force" scanning is used most frequently, since "constant-height" scanning could result in collisional damage between the tip and surface.
- The most common operating modes of AFM are contact, noncontact, and tapping.
- In contact-mode AFM, there is a repulsive force between the sample and tip; the piezoelectric response of the cantilever either raises or lowers the tip to maintain a constant force. Similarly as STM, the best resolution will be obtained under UHV conditions.
- Noncontact AFM overcomes the frictional and adhesive forces between the tip and sample by hovering the tip a few Angstroms above the surface. In this mode, the attractive Vander Waal forces between the tip and surface are monitored.
- During tapping AFM, the cantilever oscillation amplitude remains constant when not in contact with the surface. The tip is then carefully moved downward until it gently taps the surface. As the tip passes over an elevated surface feature, the cantilever has less room to oscillate, and the amplitude of oscillation decreases (vice versa for a surface depression).







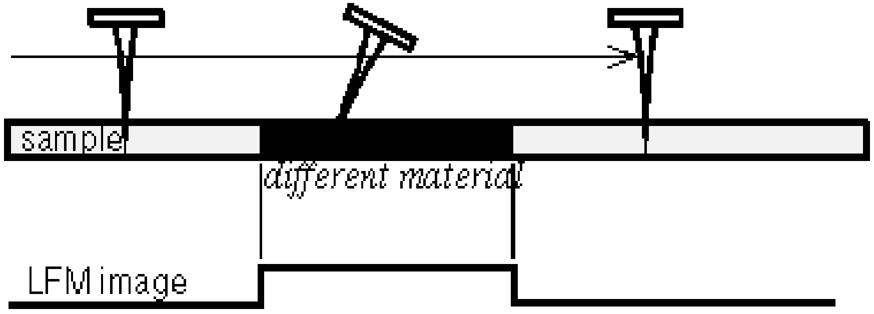
Tapping Mode

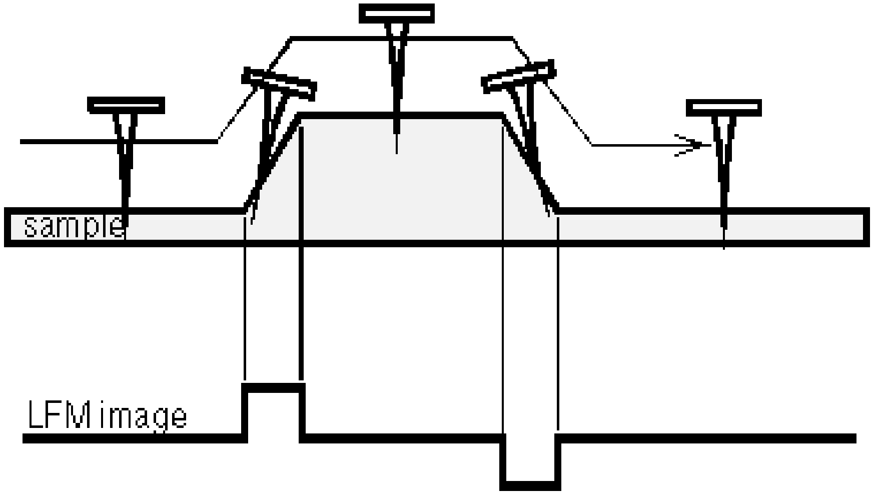
AFM exhibits a much greater versatility for surface analysis than STM. In particular, the following variations are possible, through altering the nature of the tip:

- Chemical force microscopy (CFM) – uses a chemically modified tip to examine interfacial behavior between the sample and functional groups on the tip surface.
- Magnetic force microscopy (MFM) – uses a noncontact magnetic-susceptible tip to map the magnetic properties of a surface, with spatial resolutions of <20 nm.
- Scanning thermal microscopy (SThM) – uses a resistive Wollaston wire instead of a conventional AFM probe, which acts as a localized heating source and microthermocouple, used to map the thermal conductivity of a surface.
- Scanning electrochemical microscopy (SECM) – based on the electrochemical interaction between a redox-active species produced at the tip, and the substrate

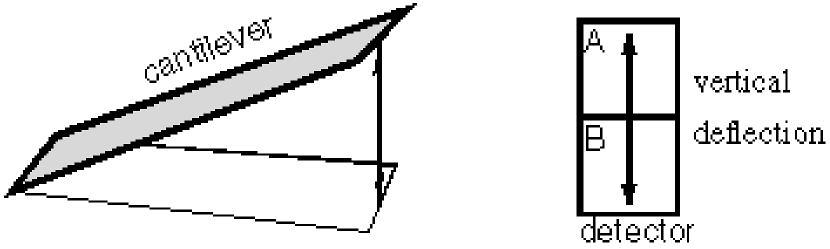
Lateral Force Microscopy

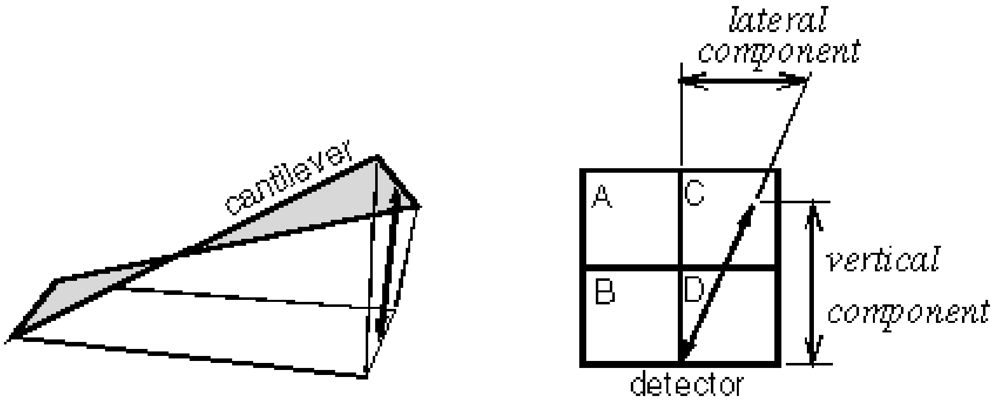
- Lateral force microscopy (LFM) measures lateral deflections (twisting) of the cantilever that arise from forces on the cantilever parallel to the plane of the sample surface.
- LFM studies are useful for imaging variations in surface friction that can arise from inhomogeneity in surface material, and also for obtaining edge-enhanced images of any surface.
- Lateral deflections of the cantilever usually arise from two sources: changes in surface friction and changes in slope. In the first case, the tip may experience greater friction as it traverses some areas, causing the cantilever to twist more strongly. In the second case, the cantilever may twist when it encounters a steep slope.
- To separate one effect from the other, LFM andAFM images should be collected simultaneously.





- LFM uses a position-sensitive photodetector to detect the deflection of the cantilever, just as for AFM. The difference is that for LFM, the PSPD also senses the cantilever's twist, or lateral deflection.
- AFM uses a "bi-cell" PSPD, divided into two halves, A and B.
- LFM requires a "quad-cell" PSPD, divided into four quadrants, A through D. By adding the signals from the A and C quadrants, and comparing the result to the sum fromthe B and D quadrants, the quad-cell can also sense the lateral component of the cantilever's deflection. A properly engineered system can generate both AFM and LFM data simultaneously.

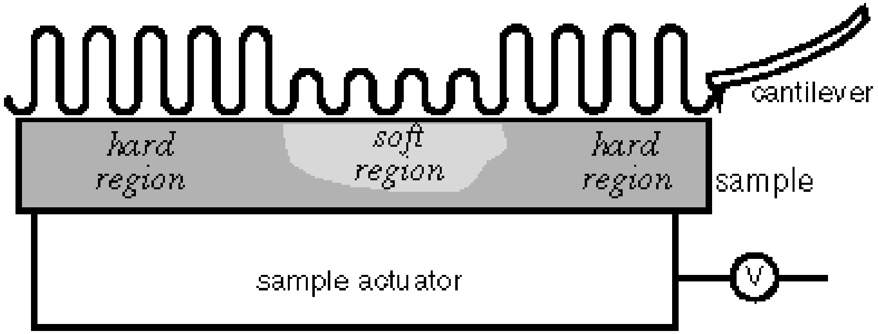


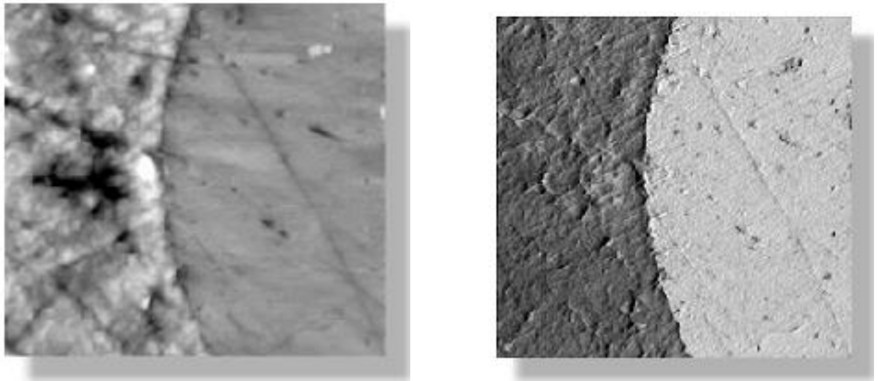


Force Modularion Microscopy

- In FMM mode, the AFM tip is scanned in contact with the sample, and the z feedback loop maintains a constant cantilever deflection (as for constant-force mode AFM).
- In addition, a periodic signal is applied to either the tip or the sample. The amplitude of cantilever modulation that results from this applied signal varies according to the elastic properties of the sample

- The system generates a force modulation image, which is a map of the sample's elastic properties, from the changes in the amplitude of cantilever modulation.
- The frequency of the applied signal is on the order of hundreds of kilohertz, which is faster than the z feedback loop is set up to track.
- Thus, topographic information can be separated from local variations in the sample's elastic properties, and the two types of images can be collected simultaneously.

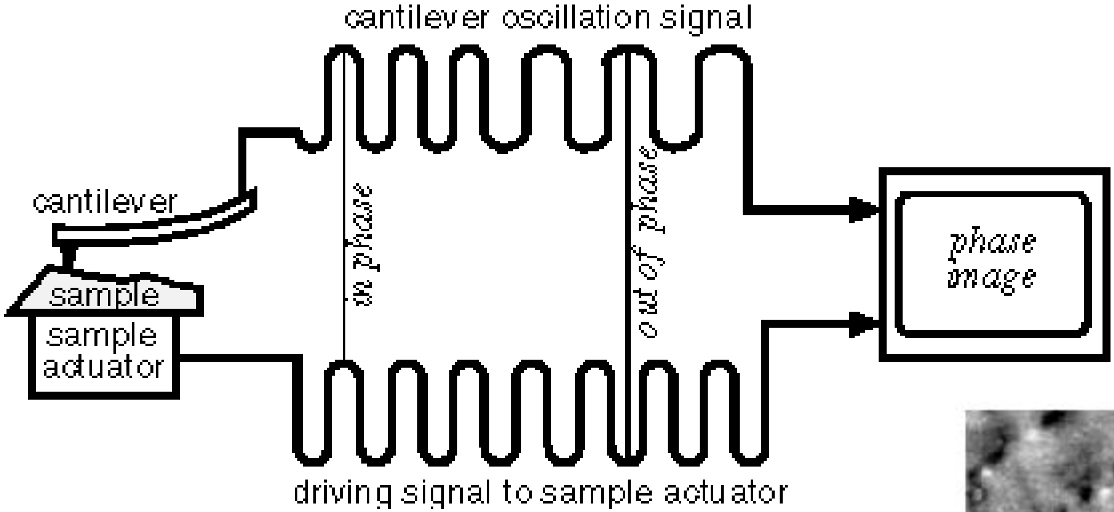


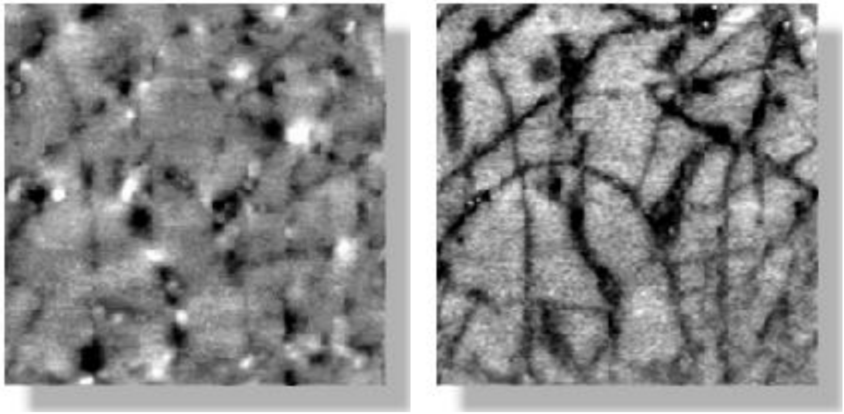


AFM image (left) and an FMM image (right) of a carbon fiber/polymer composite

Phase Detection Microscopy

- ❑ Phase detection refers to the monitoring of the phase lag between the signal that drives the cantilever to oscillate and the cantilever oscillation output signal.
- ❑ Changes in the phase lag reflect changes in the mechanical properties of the sample surface.



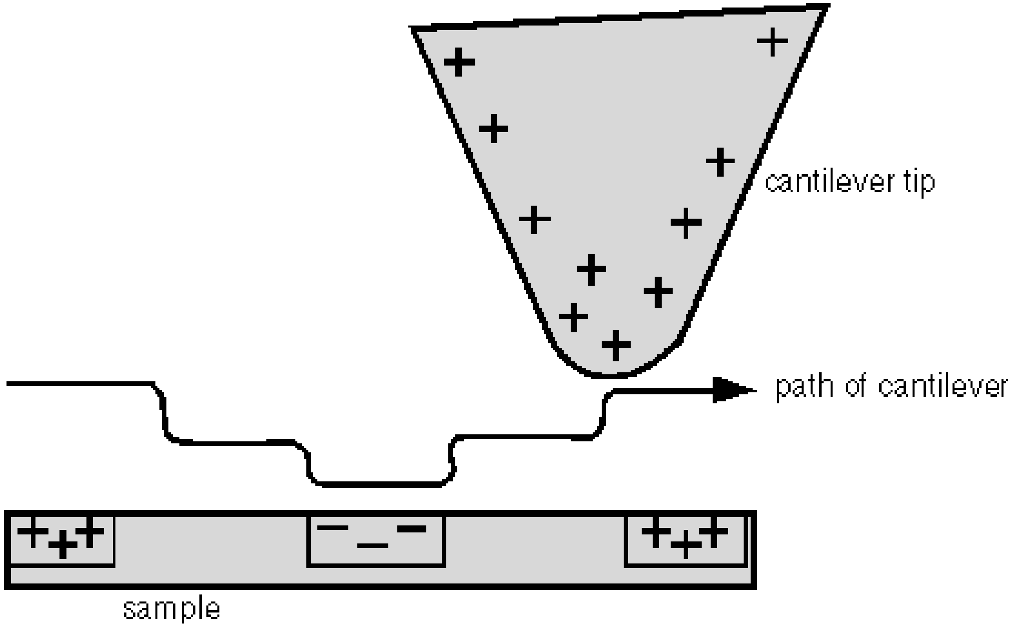


Non-contact AFM image (left) and PDM image (right) of an adhesive label, collected simultaneously. Field of view 3µm.

Electrostatic Force Microscopy

- ❑ Electrostatic force microscopy (EFM) applies a voltage between the tip and the sample while the cantilever hovers above the surface, not touching it.
- ❑ The cantilever deflects when it scans over static charges.

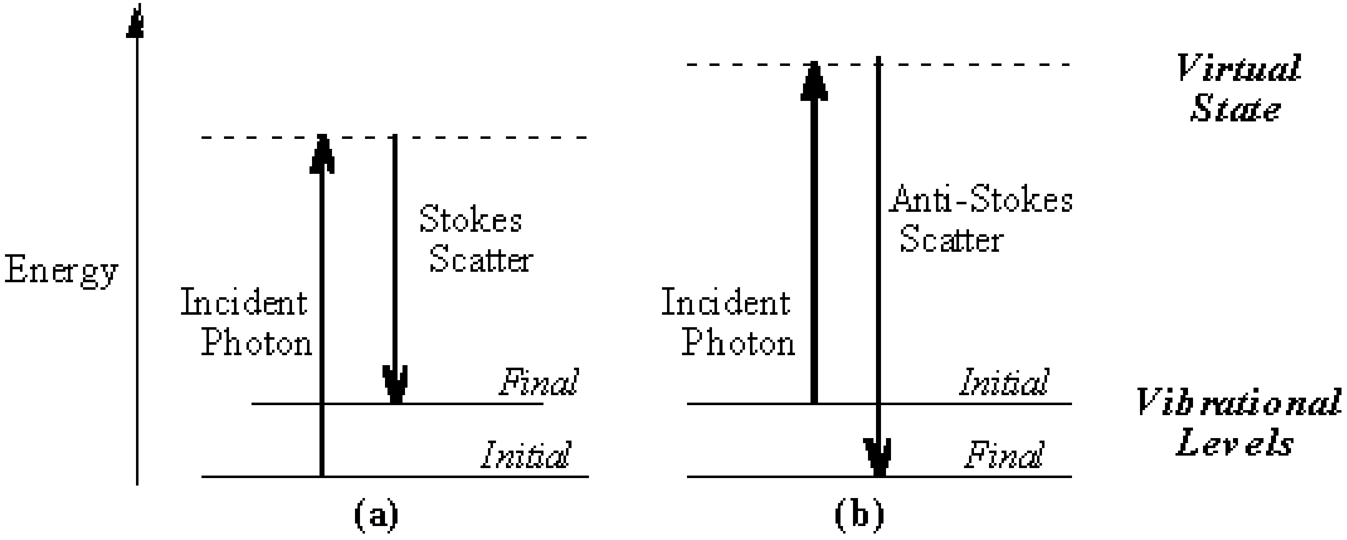
- ❑ EFM maps locally charged domains on the sample surface, similar to how MFM plots the magnetic domains of the sample surface.
- ❑ The magnitude of the deflection, proportional to the charge density, can be measured with the standard beam-bounce system. EFM is used to study the spatial variation of surface charge carrier density. For instance, EFM can map the electrostatic fields of a electronic circuit as the device is turned on and off.
- ❑ This technique is known as "voltage probing" and is a valuable tool for testing live microprocessor chips at the sub-micron scale.



Raman spectroscopy

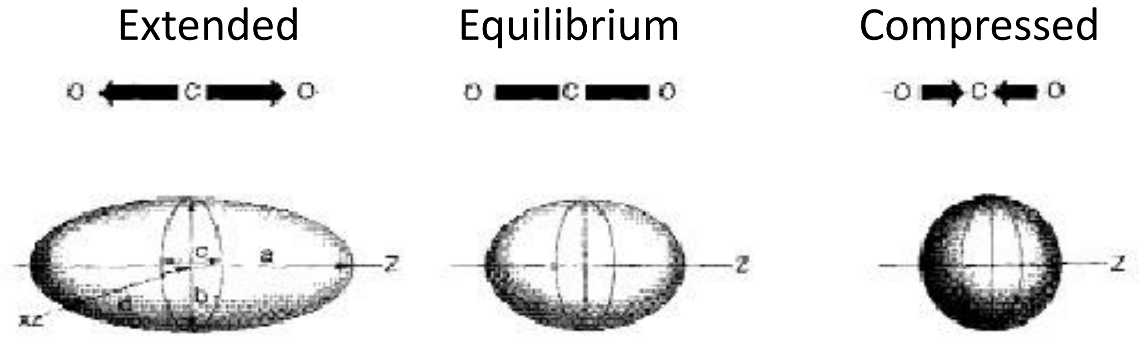
- The phenomenon behind this technique was first reported by Sir Chandrasekhara Venkata Raman (1888-1970) in 1928 – in 1930 he was awarded the Nobel Prize in physics for his findings.
- A small percentage of light scattered at a molecule is inelastically scattered (1 in 107 photons).
- At room temperature majority of molecules in initial (ground) state → anti-Stokes signal will be less pronounced: Ratio of anti-Stokes to Stokes can be used for temperature measurement.

Sir C.V. Raman



- The energy of a vibrational mode depends on molecular structure and environment. Atomic mass, bond order, molecular substituents, molecular geometry and hydrogen bonding all effect the vibrational force constant which, in turn dictates the vibrational energy.
- Vibrational Raman spectroscopy is not limited to intramolecular vibrations. Crystal lattice vibrations and other motions of extended solids are Raman-active
- Raman scattering occurs when it features a change in polarizability during the vibration
- This rule is analogous to the rule for an infrared-active vibration (that there must be a net change in permanent dipole moment during the vibration) - from group theory it is possible to show that if a molecule has a center of symmetry, vibrations which are Raman-active will be silent in the infrared, and vice versa

Raman = Polarizability of Molecules



- ❑ The frequency of the RBS mode is inversely proportional to the diameter of the nanotube.
- ❑ RBS mode and double peaked high energy modes are prove of the existence of single-wall nanotubes in a sample.
- ❑ In metallic carbon nanotubes the lower high-energy mode is strongly broadened and shifted to smaller energies (1540 cm^{-1}).