Basic Structure Characterization

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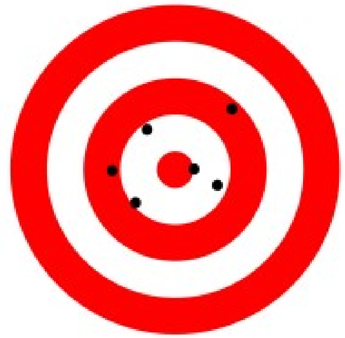
- We have studied crystal structure and microstructure
- Characterization is important to study structure
- Different techniques
- Input signal, output, noise, amplification
- Resolution, accuracy, precision
- Signal to noise ratio is the most important parameter

Resolution-Accuracy-Precision-Sensitivity

High precision-High accuracy



Low precision-High accuracy

High precision-Low accuracy

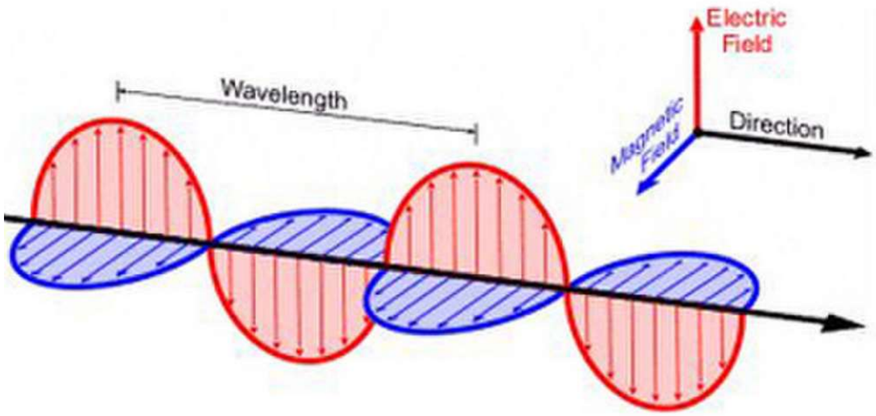
Low precision-Low accuracy

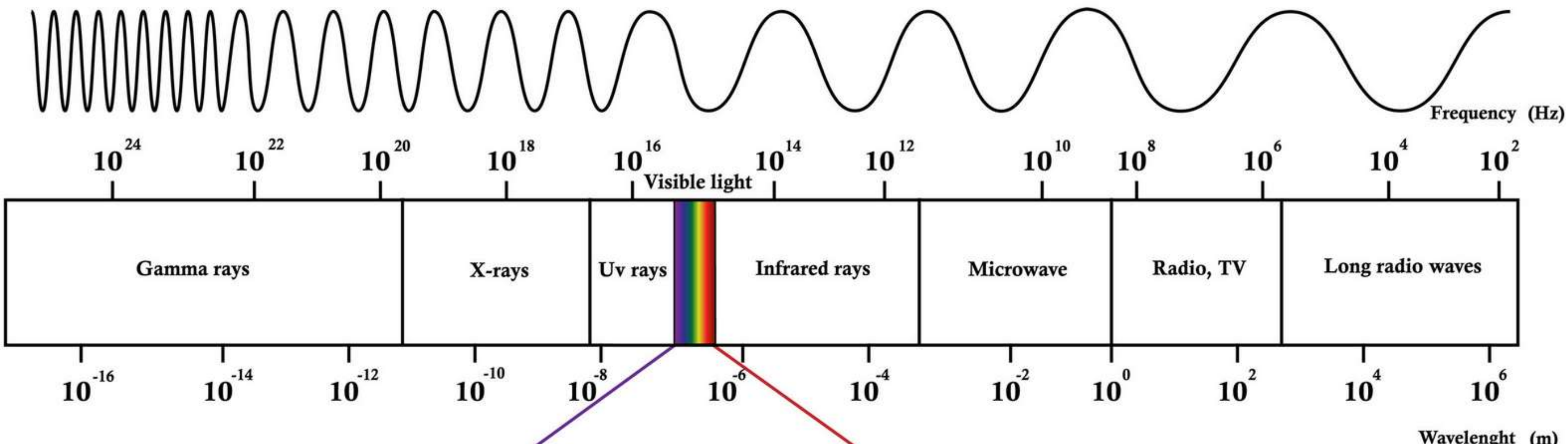
https://phidgets.wordpress.com/2014/05/20/accuracy-precision-and-resolution-theyre-not-the-same/

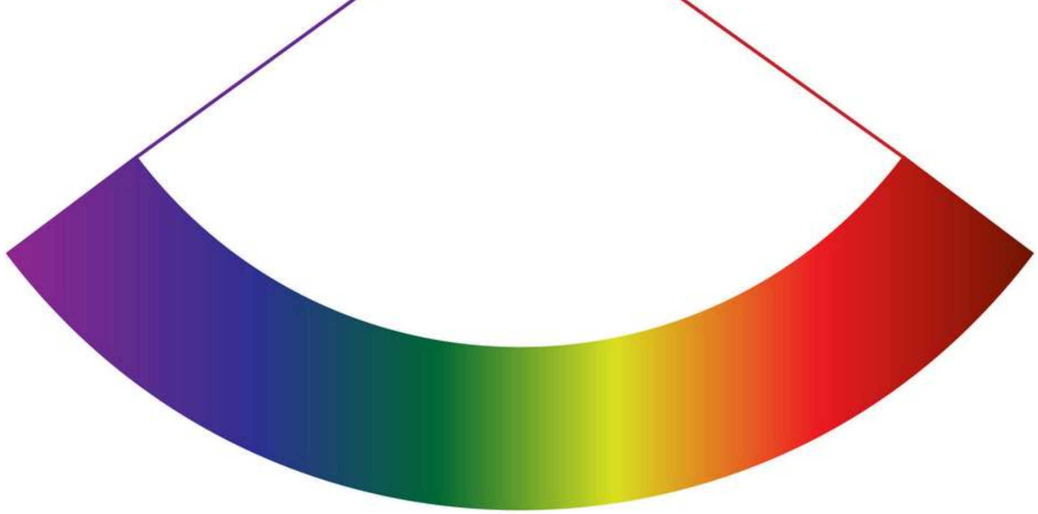
- **Accuracy** is a measure of “trueness”, while **precision** is a measure of variability
- One way that the resolution and precision are always related is that **resolution determines the upper limit of precision**. The precision in data cannot exceed resolution
- **Resolution** is the smallest unit of measurement that can be indicated by an instrument
- **Sensitivity** is the smallest amount of difference in quantity that will change an instrument's reading
- A measuring tape for example will have a resolution, but not sensitivity. An analytical balance will have both issues. An oscilloscope will have sensitivity but may not have resolution issues, depending on several variables
- Fidelity, reliability and error are also important
- Systematic and Random errors

Probes

- Visible light, electrons, X-rays
- Wave particle duality
- Basic physics
- Velocity of light 3 $\times 10^8$ m/s
- Quantized photon




Frequency (Hz)
10^{24} 10^{22} 10^{20} 10^{18} 10^{16} 10^{14} 10^{12} 10^{10} 10^{8} 10^{6} 10^{4} 10^{2}
Visible light
Gamma rays
X-rays
Uv rays
Infrared rays
Microwave
Radio, TV
Long radio waves
10^{-16} 10^{-14} 10^{-12} 10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{0} 10^{2} 10^{4} 10^{6}
Wavelenght (m)



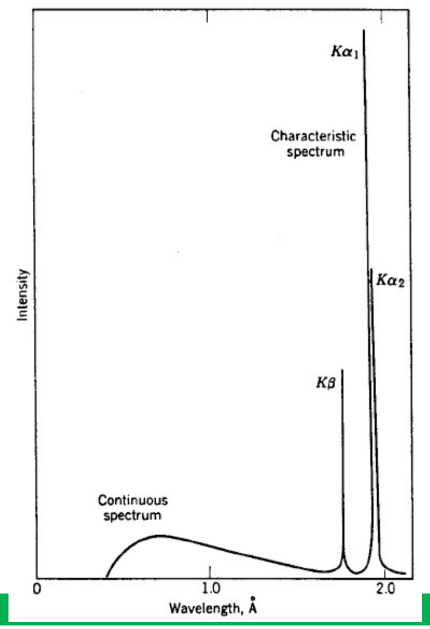

Magenta
Cyan
Yellow

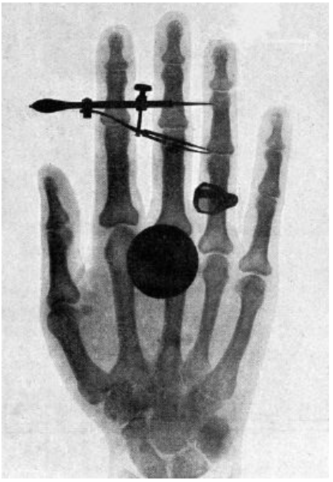
Interaction of EMR with matter

- Transmission
- Reflection
- Scattering
- Diffraction
- X-rays are EMR that interact with electrons
- Scattering of X-rays by electrons in a material

History

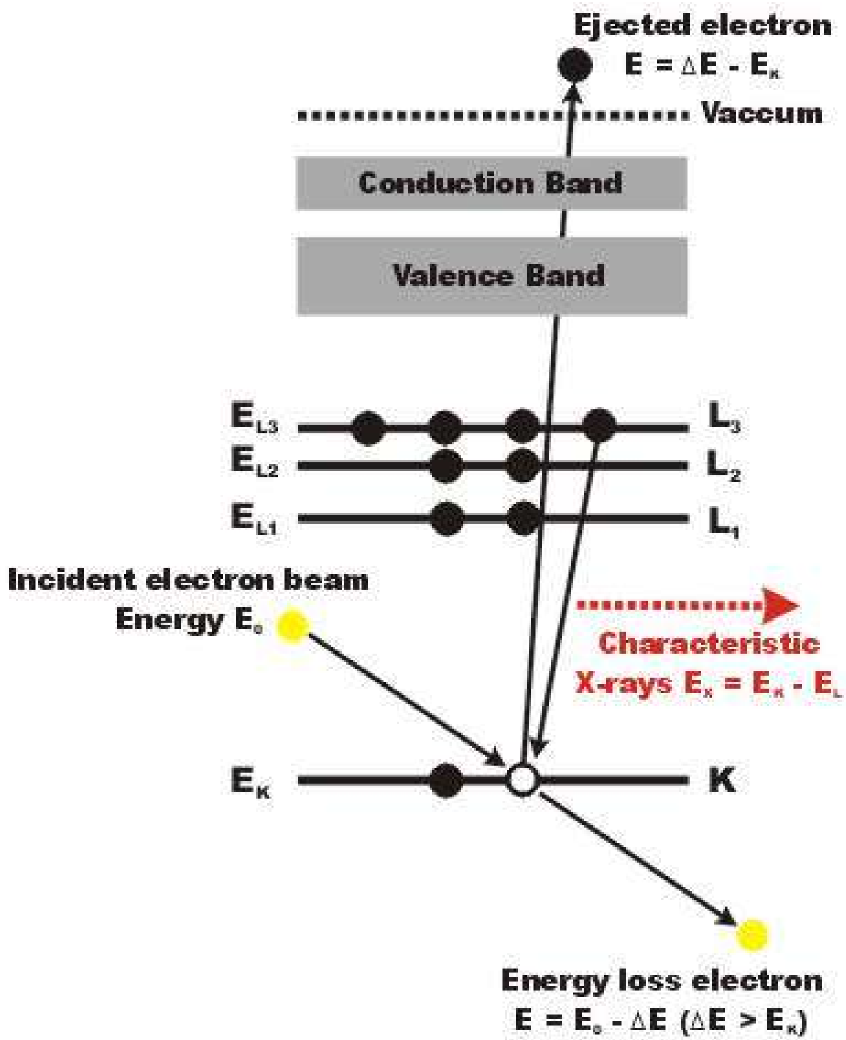
- 1665: Diffraction effects observed by Italian mathematician Francesco Maria Grimaldi
- 1868: X-rays Discovered by German Scientist Röntgen
- 1912: Discovery of X-ray Diffraction by Crystals: von Laue
- 1912: Bragg's Discovery

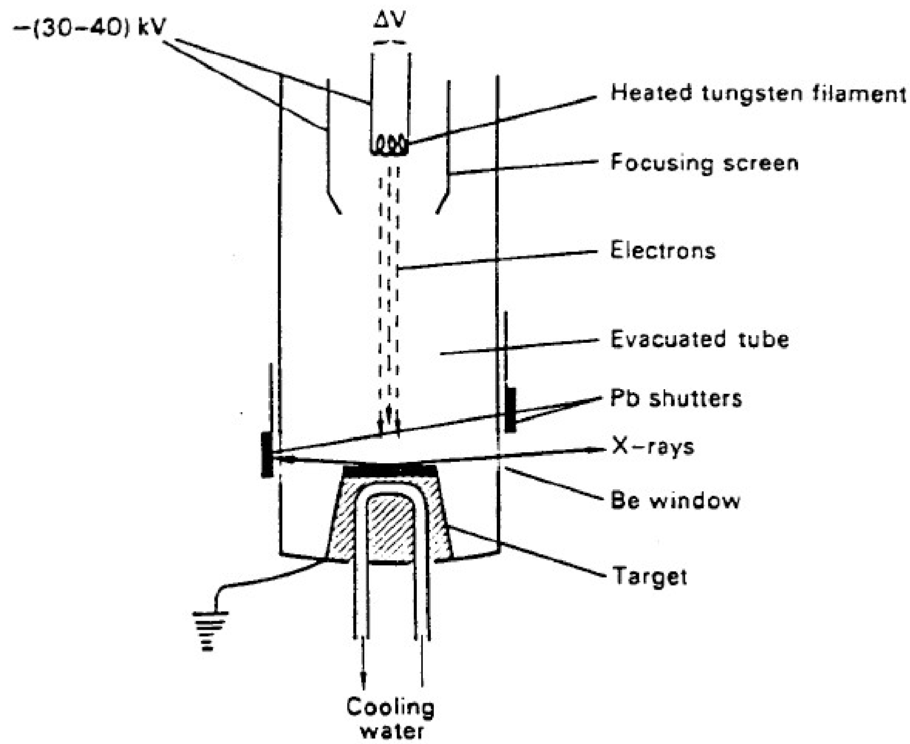




λ_{SWL}

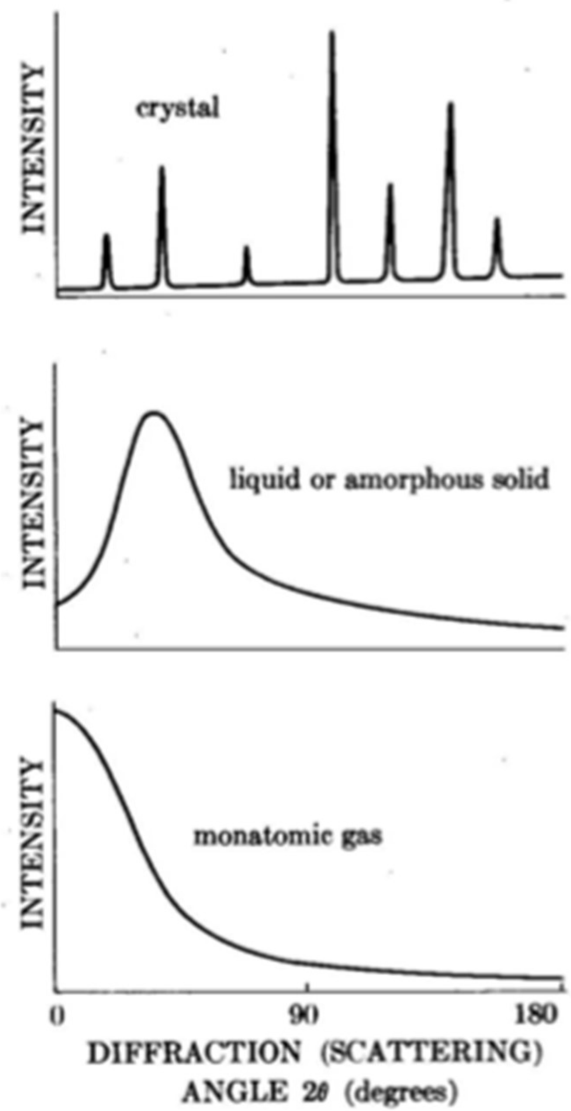
Generation of X-rays





- Random arrangement of atoms in space gives rise to scattering in all directions: weak effect and intensities add

- By atoms arranged periodically in space
  - In a few specific directions satisfying Bragg’s law: strong intensities of the scattered beam :Diffraction
  - No scattering along directions not satisfying Bragg’s law



"Elements of X-ray Diffraction",
B.D. Cullity & Stock

Scattering of X-rays by an unit cell

- Braggs equation

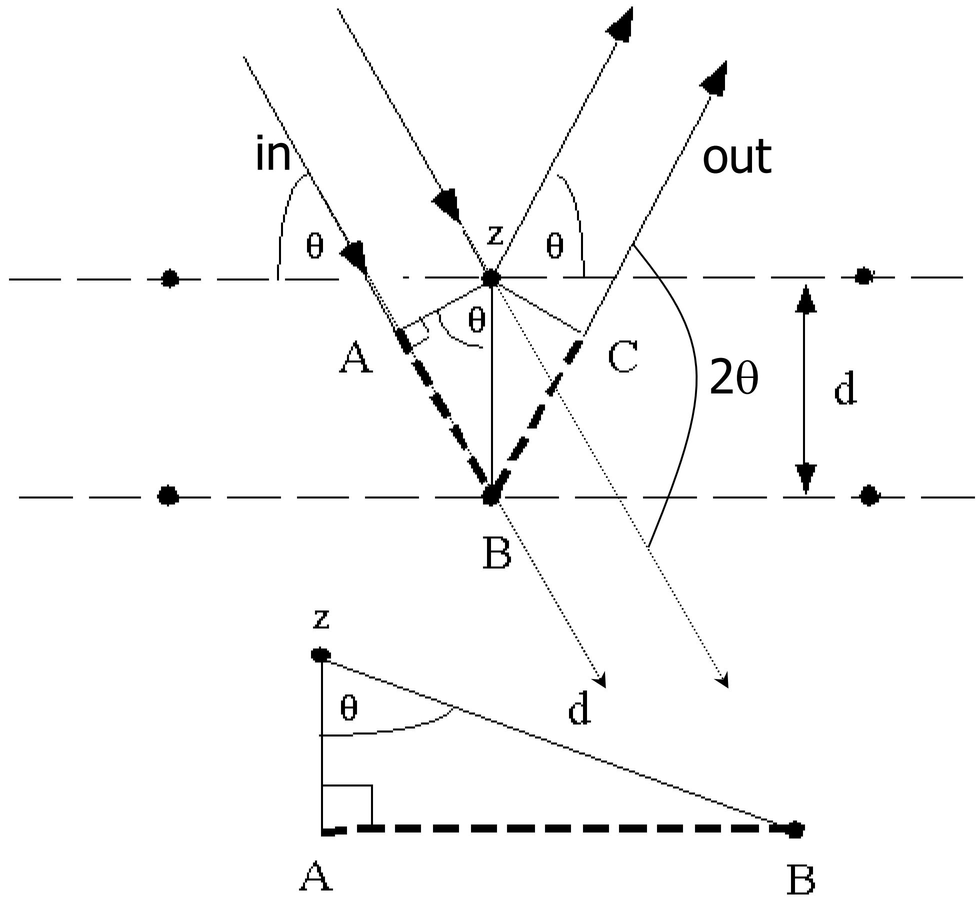
$n\lambda=2d.\sin\theta$

n: Order of reflection

d: Plane spacing

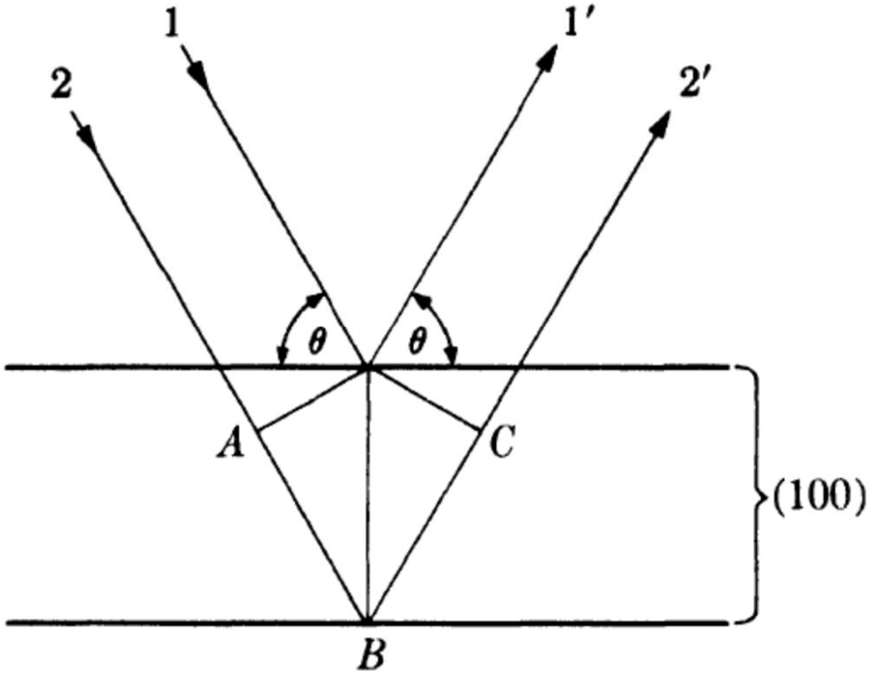
$$= \frac{a}{\sqrt{h^2+k^2+l^2}}$$

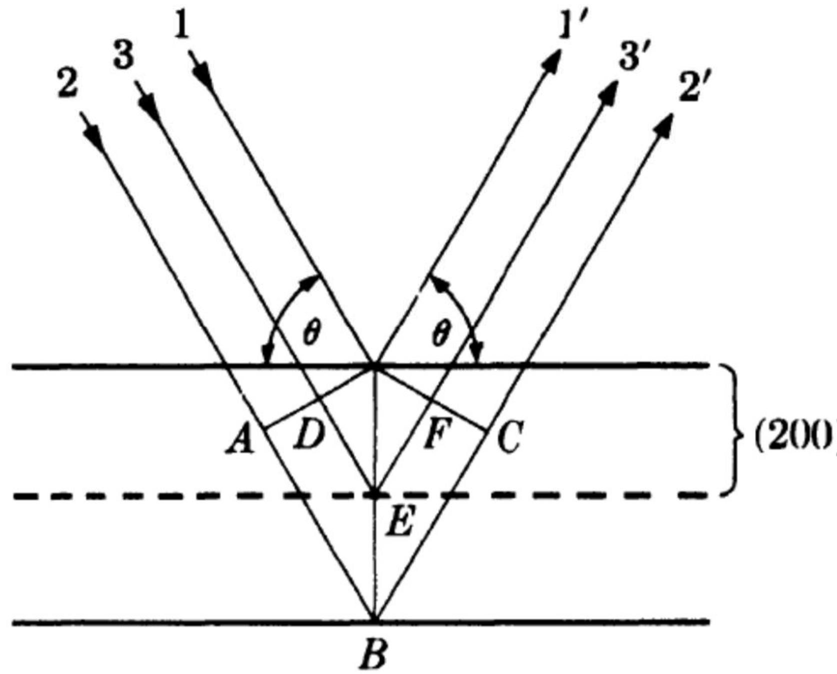
θ: Bragg Angle



Path difference must be integral multiples of the wavelength

$\theta_{in}=\theta_{out}$





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

$$\sin\theta = \frac{1/d}{2/\lambda}$$

Geometry of Bragg's law

- The incident beam, the normal to the reflection plane, and the diffracted beam are always co-planar.

- The angle between the diffracted beam and the transmitted beam is always 2θ (usually measured).

- Sin θ cannot be more than unity; this requires

  $n\lambda < 2d$, for $n=1$, $\lambda < 2d$

λ should be less than twice the d spacing we want to study

Order of reflection

- Rewrite Bragg's law $\lambda=2\sin\theta\, d/n$

- A reflection of any order as a first order reflection from planes, real or fictitious, spaced at a distance 1/n of the previous spacing

- Set $d' = d/n$

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

- An n^{th} order reflection from (hkl) planes of spacing d may be considered as a first order reflection from the (nh nk nl) plane of spacing $d' = d/n$

*The term reflection is only notional due to symmetry between incoming and outgoing beam w.r.t. plane normal, otherwise we are only talking of diffraction.

Reciprocal lattice vectors

- Used to describe Fourier analysis of electron concentration of the diffracted pattern

- Every crystal has associated with it a crystal lattice and a reciprocal lattice

- A diffraction pattern of a crystal is the map of reciprocal lattice of the crystal.

Real space | **Reciprocal space**

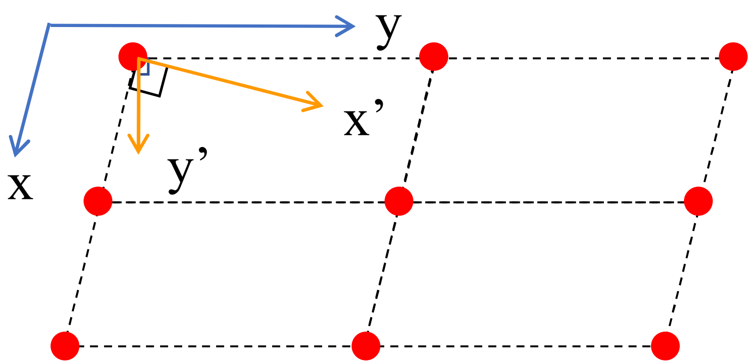
Crystal Lattice

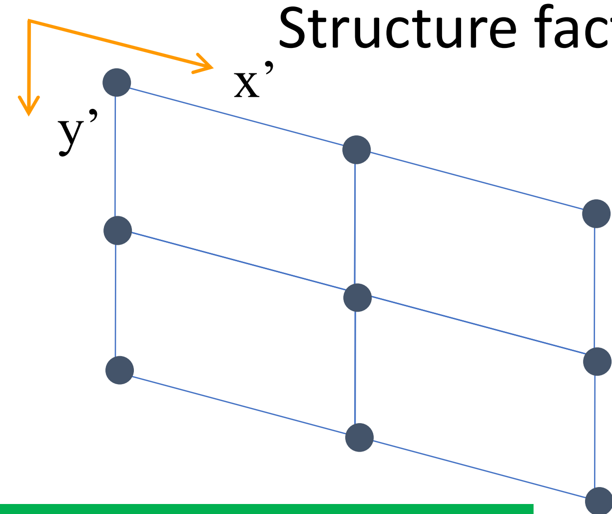
Reciprocal Lattice

Crystal structure → Diffraction pattern

Unit cell content

Structure factor





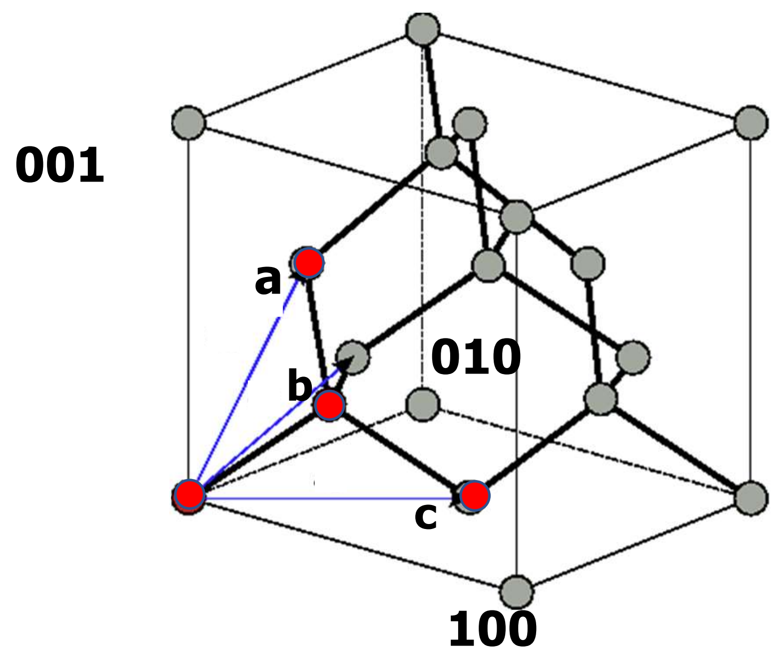
Reciprocal space

$$a^* = \frac{b \times c}{a \bullet (b \times c)}$$

$$b^* = \frac{c \times a}{a \bullet (b \times c)}$$

$$c^* = \frac{a \times b}{a \bullet (b \times c)}$$

Reciprocal lattice of FCC is BCC and vice versa



Scattering of X-rays by an electron

- Thompson effect
- Coherent scattering
- Very small intensity

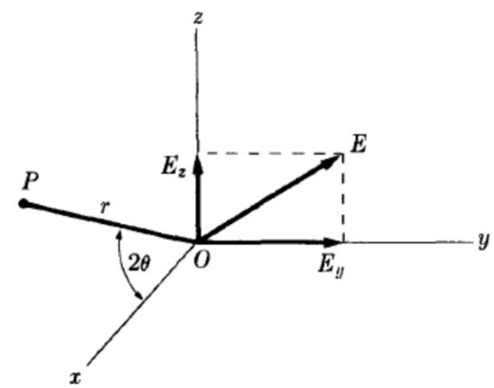


Fig. 4-3 Coherent scattering of x-rays by a single electron.

$$I_P = I_{Py} + I_{Pz} \quad = I_0 \frac{K}{r^2}\left(\frac{1 + \cos^2 2\theta}{2}\right).$$

Scattering of X-rays by an atom

- Directly proportional to number of electrons
- Intensity reduces with angle

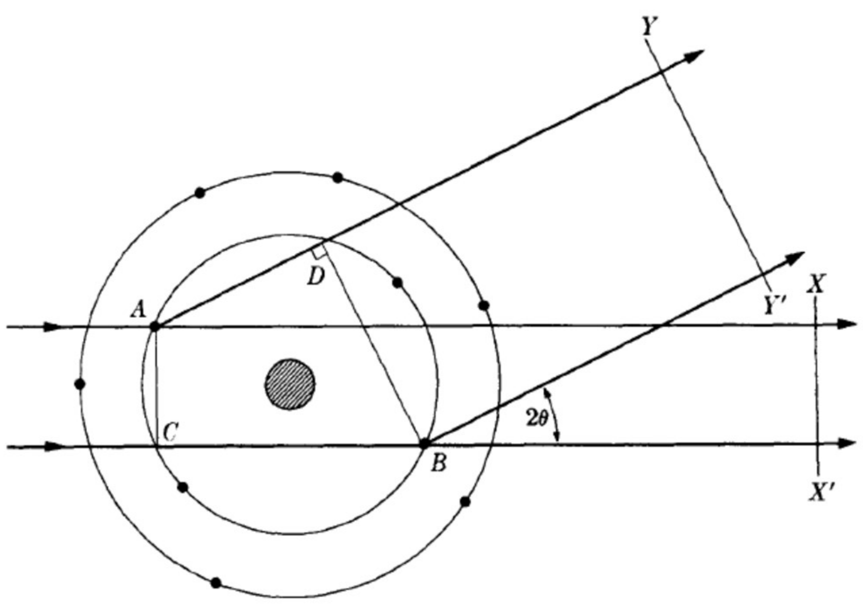


Fig. 4-5 X-ray scattering by an atom.

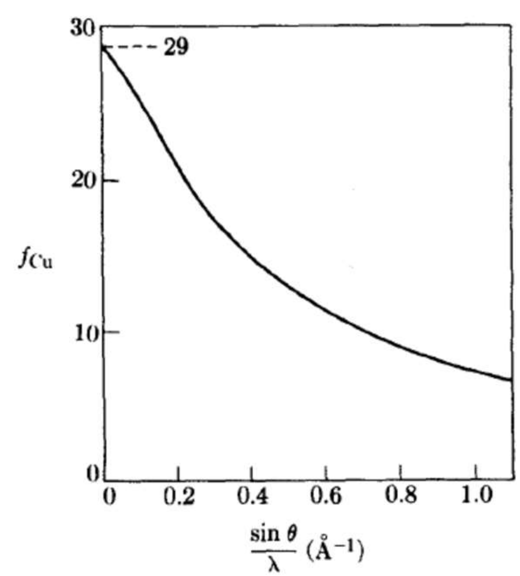


Fig. 4-6 The atomic scattering factor of copper.

Scattering of X-rays by an unit cell

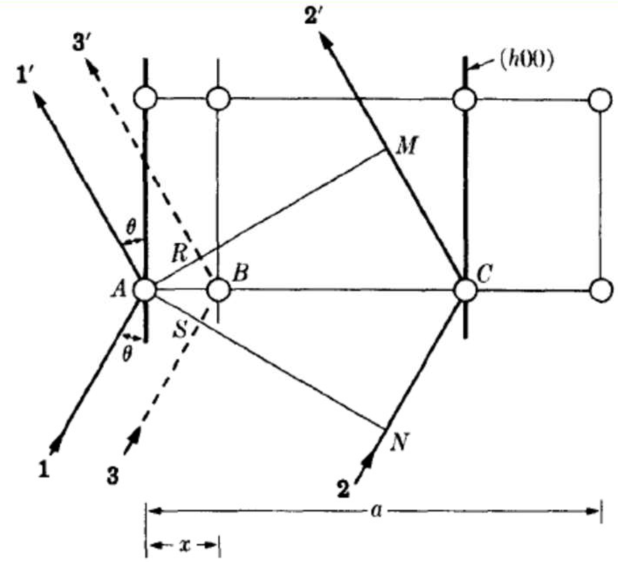


Fig. 4-8 The effect of atom position on the phase difference between diffracted rays.

$$\delta_{3'1'} = RBS = \frac{AB}{AC}(\lambda) = \frac{x}{a/h}(\lambda).$$

$$\phi = \frac{\delta}{\lambda}(2\pi).$$

$$Ae^{i\phi} = fe^{2\pi i(hu+kv+lw)}.$$

$$\phi = 2\pi(hu + kv + lw).$$

$$\boxed{F_{hkl} = \sum_{1}^{N} f_n e^{2\pi i(hu_n+kv_n+lw_n)}},$$

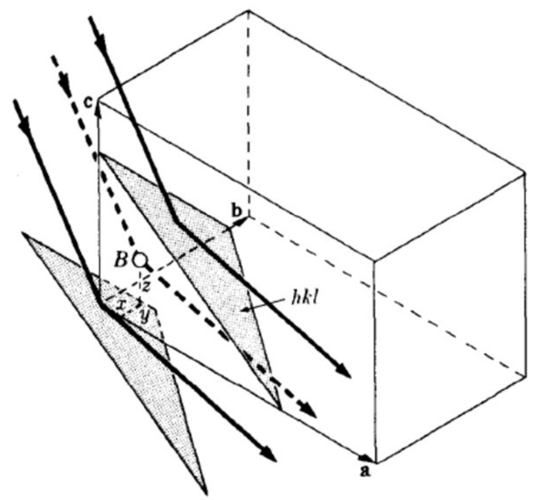


Fig. 4-9 The three-dimensional analogue of Fig. 4-8.

Structure factor

- Link crystal structure with diffraction pattern
- Position and intensity of peaks $$F_{hkl} = \sum_{1}^{N} f_n e^{2\pi i (hu_n + kv_n + lw_n)}$$
- Atomic positions decide presence of hkl peak
- SC: (0, 0, 0), so all peaks possible
- BCC: (0, 0, 0) and (0.5, 0.5, 0.5) so only h+k+l = even peaks possible
- Remember $e^{2n\pi i} = 1$, where n is an integer
- $e^{p\pi i} = -1$, if p is odd

Bravais Lattice	Reflections possibly present	Reflections necessarily absent
Simple	All	None
Body Centered	(h+k+l): Even	(h+k+l): Odd
Face Centered	h, k, and l unmixed i.e. all odd or all even	h, k, and l: mixed

Permitted Reflections

Simple Cubic	(100), (110), (111), (200), (210), (211), (220), (300), (221) ………
BCC	(110), (200), (211), (220), (310), (222)….
FCC	(111), (200), (220), (311)…..

- From hkl to theta
- We can measure 1/10th of a nanometer
- In fact we can get a precision of 1/1000th of a nanometer
- s = 1, 2, 3…6, 8 for SC (no 7)
- s = 2, 4, 6, 8 for BCC
- s = 3, 4, 8, 11, 12, 16….

$$\lambda = 2dSin\theta$$

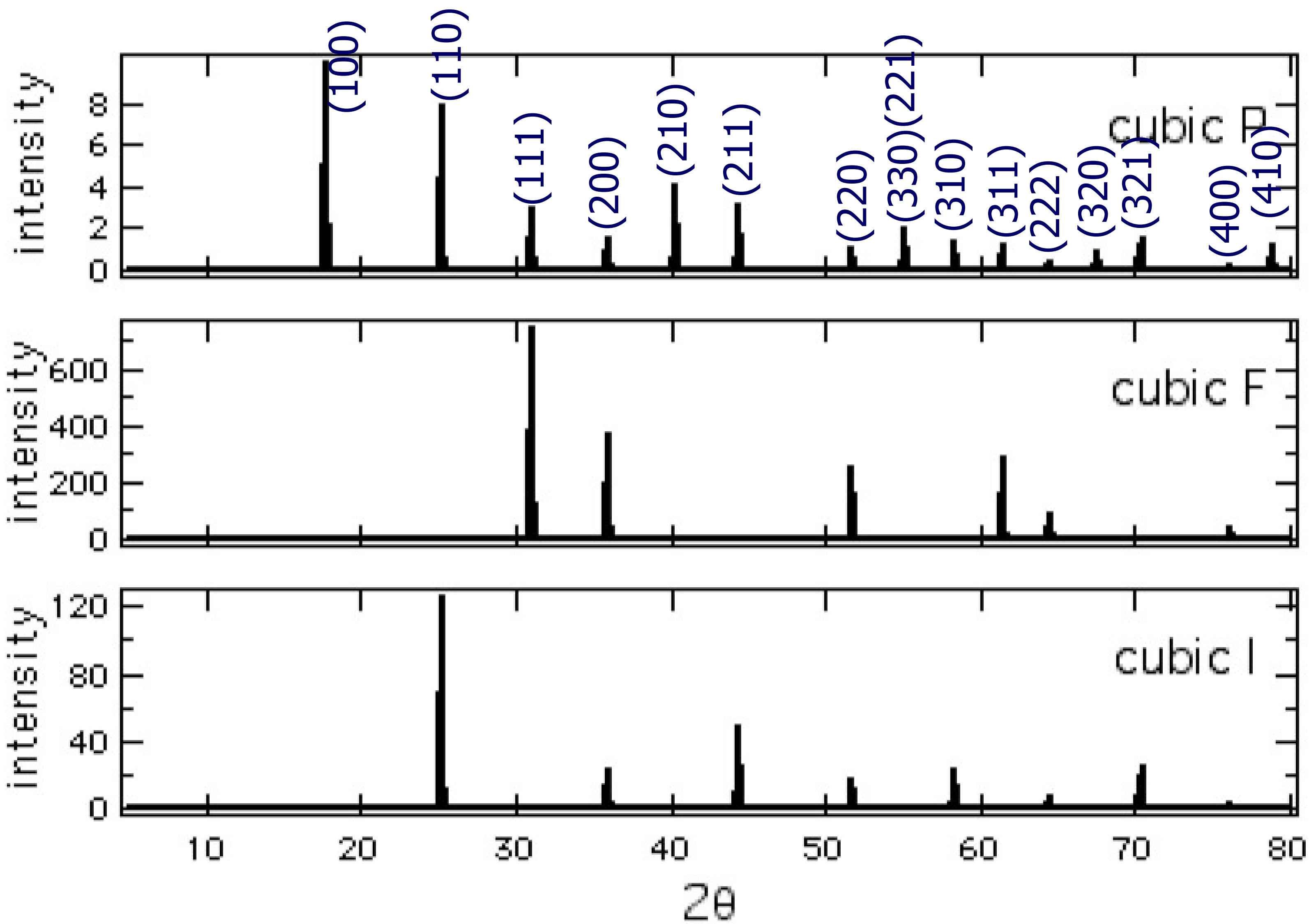
$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

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

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

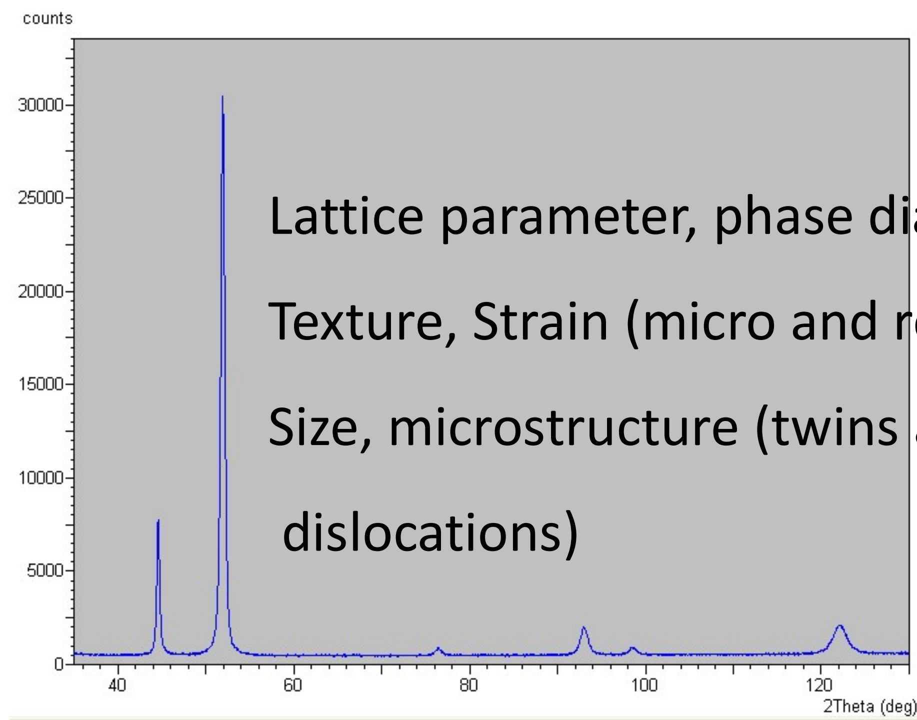
$$s = (h^2 + k^2 + l^2) \propto \sin^2 \theta$$

XRD pattern for Cubic Crystals



Intensity of X-ray pattern

- structure factor (F^2)
- polarization factor
- multiplicity factor
- Lorentz factor
- absorption factor
- temperature factor



Lattice parameter, phase diagrams

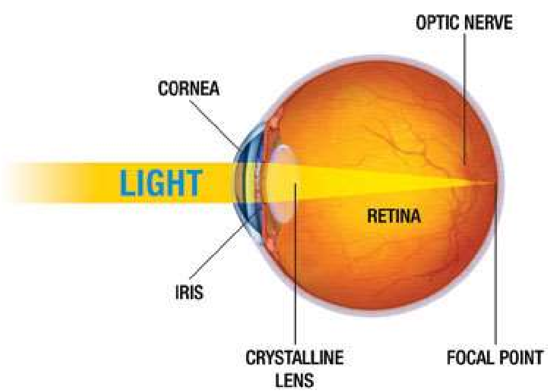
Texture, Strain (micro and residual)

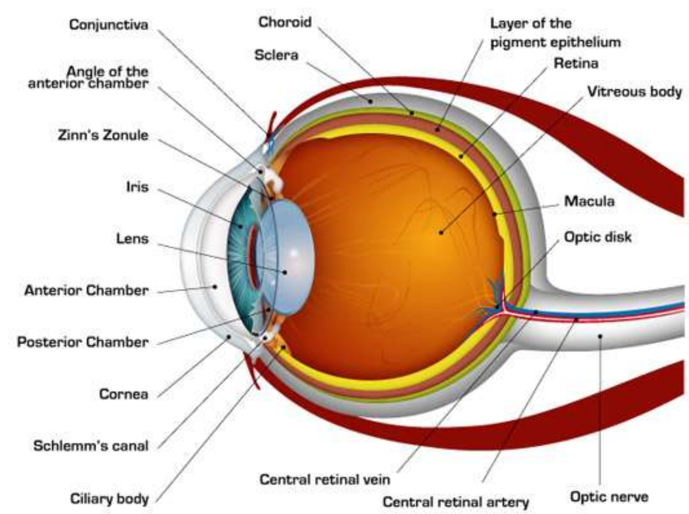
Size, microstructure (twins and

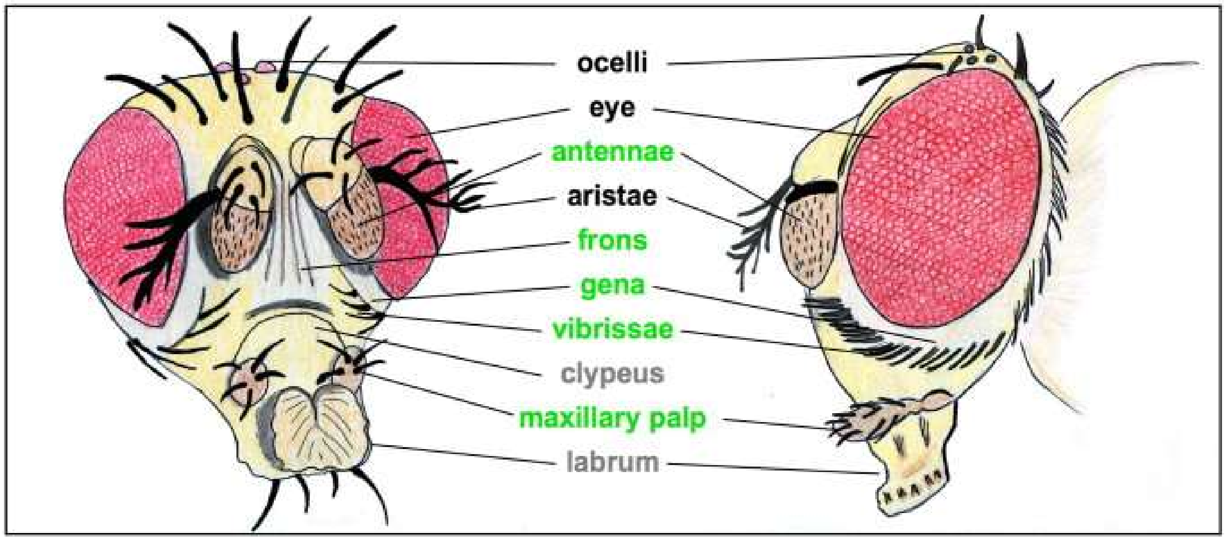
dislocations)

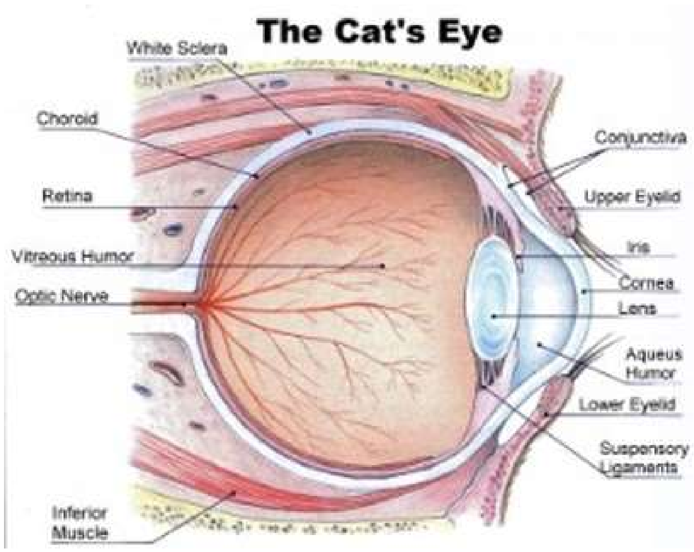
Seeing is Believing

- A picture is worth a thousand words
- Imaging of microstructure
- Human eye 0.1 mm resolution






ocelli
eye
antennae
aristae
frons
gena
vibrissae
clypeus
maxillary palp
labrum


The Cat's Eye
White Sclera
Choroid
Retina
Vitraous Humor
Optic Nerve
Inferior Muscle
Conjunctiva
Upper Eyelid
Iris
Cornea
Lens
Aqueus Humor
Lower Eyelid
Suspensory Ligaments

Interaction of visible light with matter

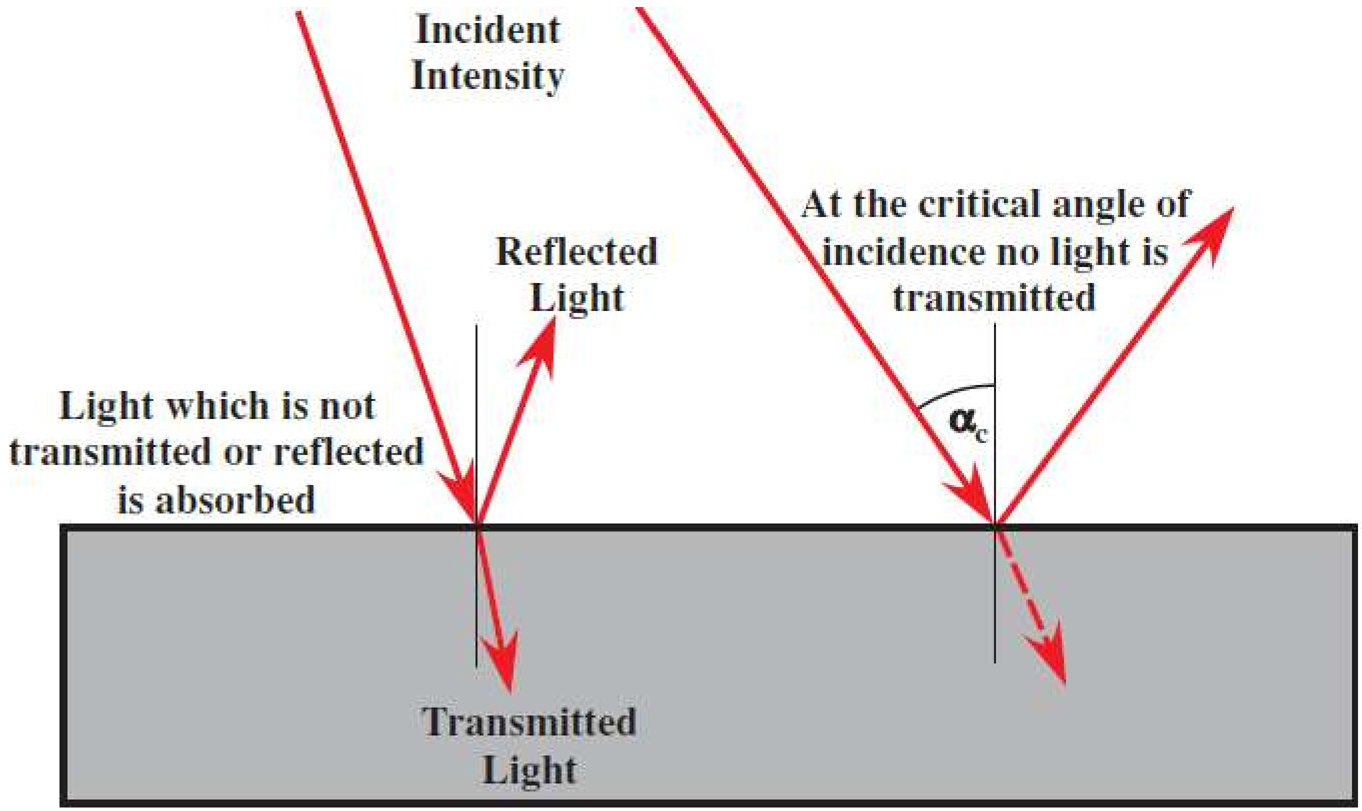
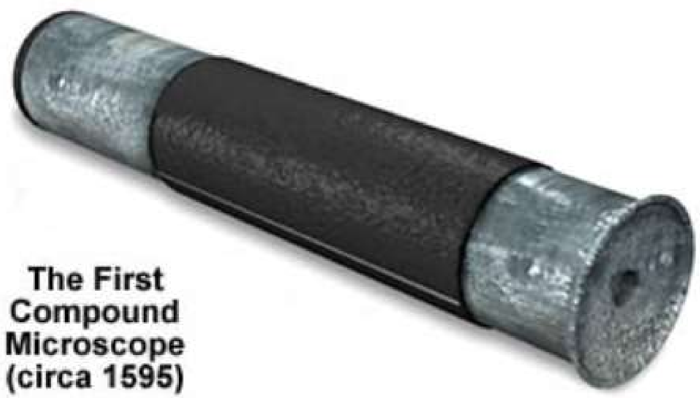


Figure 3.21 *The relation between the intensity reflected, transmitted and absorbed, and the 'critical' Brewster angle for a specularly reflecting surface.*

Optical microscopes



- Zaccharias Janssen and his father Hans
- Englishman Robert Hooke is credited with the microscopic milestone of discovering the basic unit of all life, the cell in the mid 17th century

Resolution

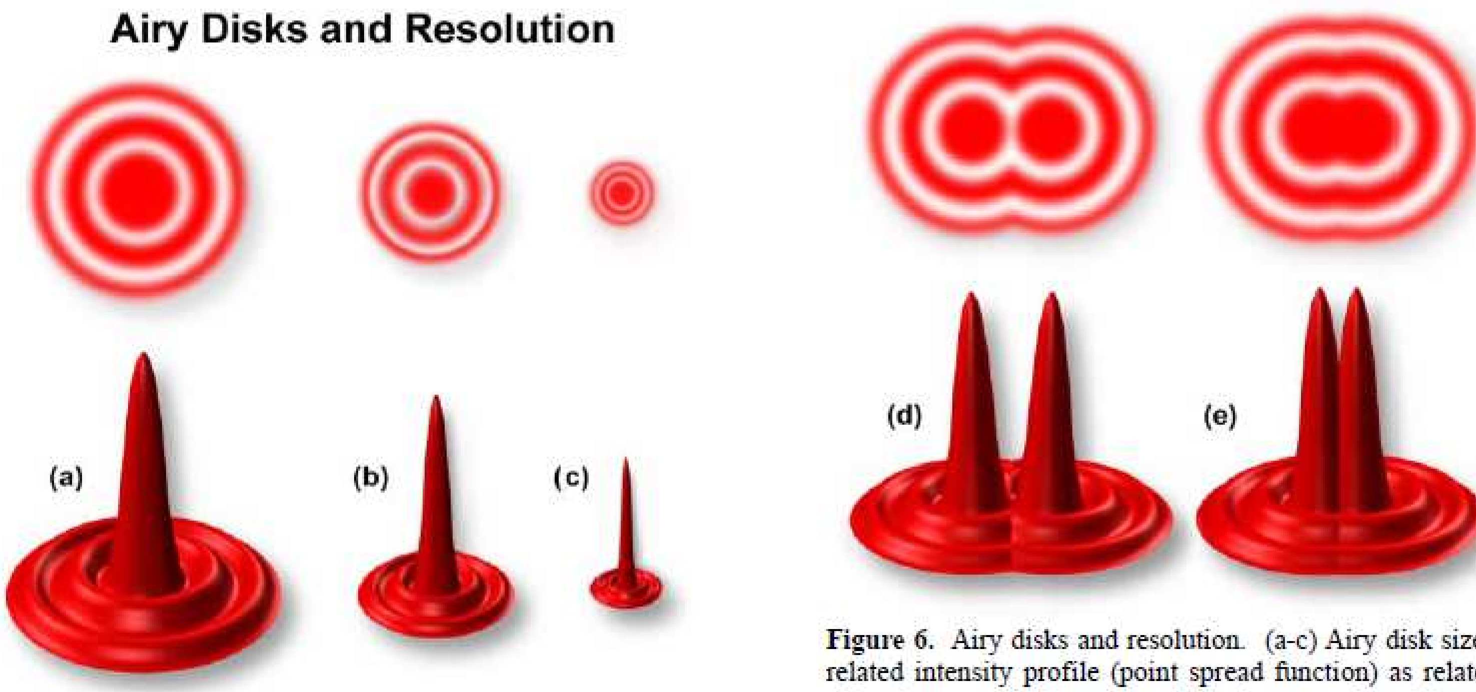


Figure 6. Airy disks and resolution. (a-c) Airy disk size and related intensity profile (point spread function) as related to objective numerical aperture, which decreases from (a) to (c) as numerical aperture increases. (e) Two Airy disks so close together that their central spots overlap. (d) Airy disks at the limit of resolution.

$$d = 1.22\ \frac{\lambda}{2(Numerical\ aperture)}$$

Numerical aperture

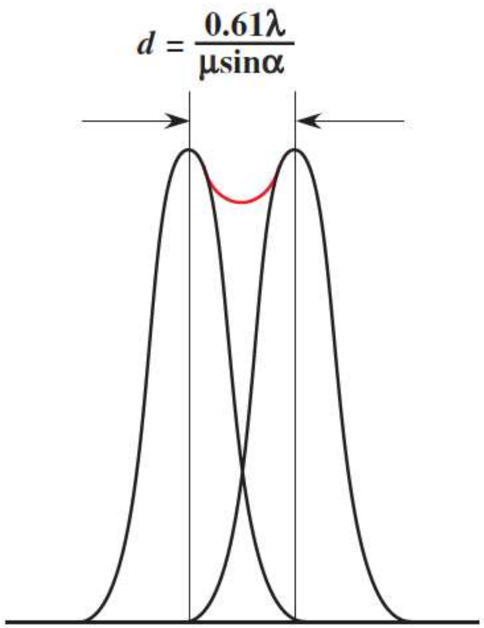
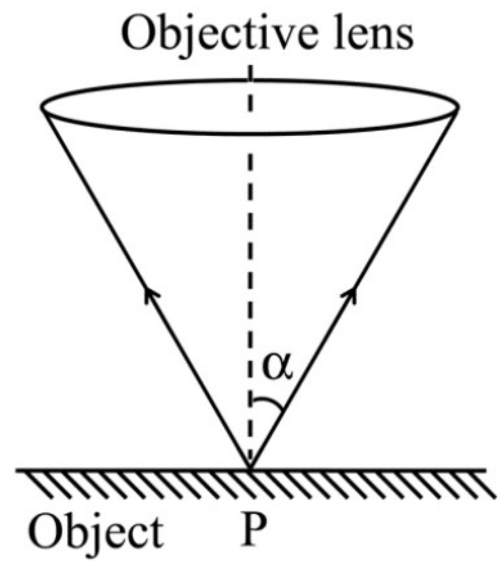
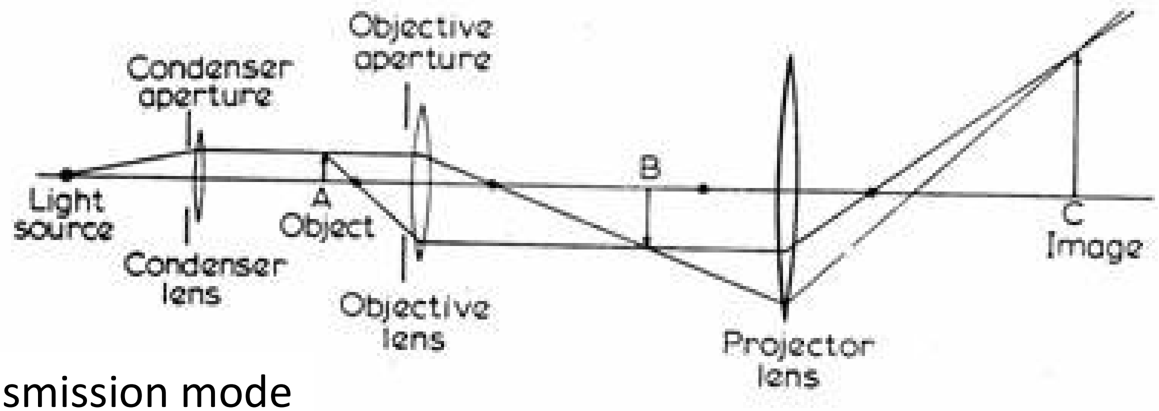


Figure 3.10 *The Raleigh resolution criterion requires that two point sources at infinity have an angular separation sufficient to place the maximum intensity of the primary image peak of one source at the position of the first minimum of the second.*

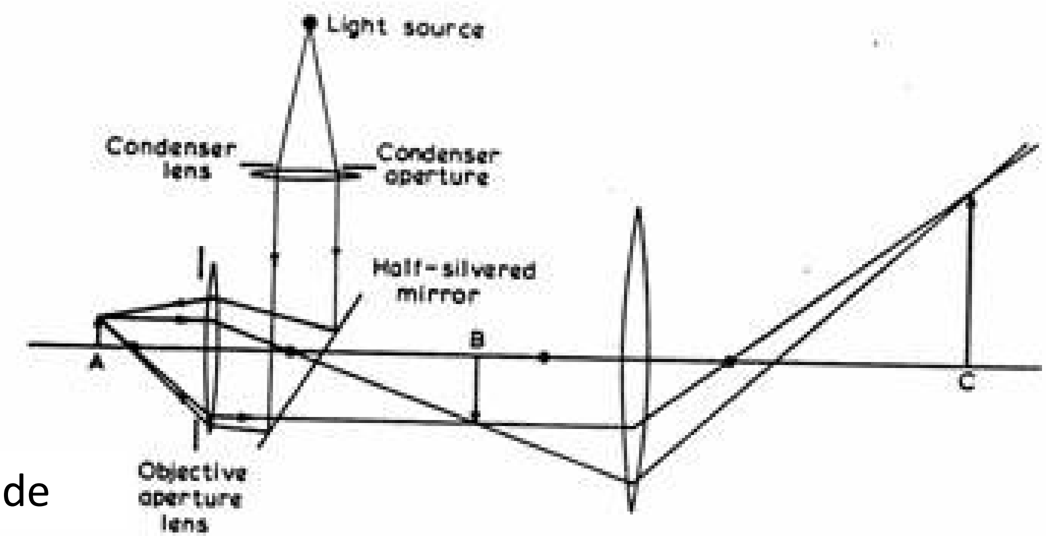


The numerical aperture is the collection angle of light that enters the objective

Block diagram of OM



Transmission mode



Reflection mode

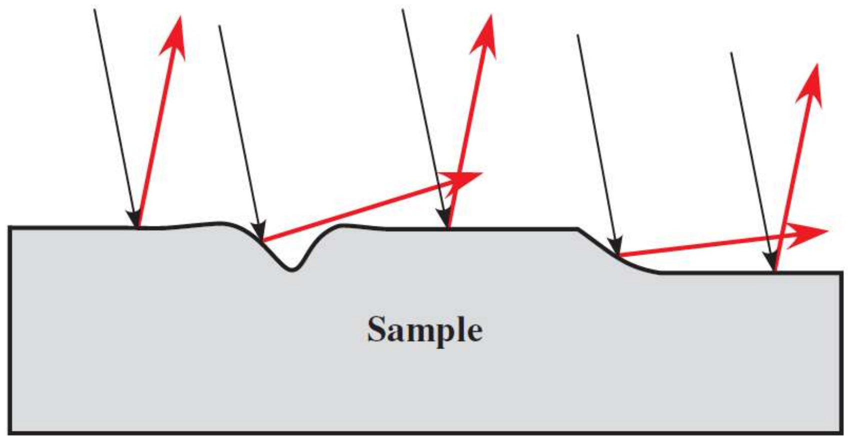


Figure 3.23 *In bright-field illumination topographical microstructural features are revealed by scattering of light outside the objective lens aperture.*

Type of image

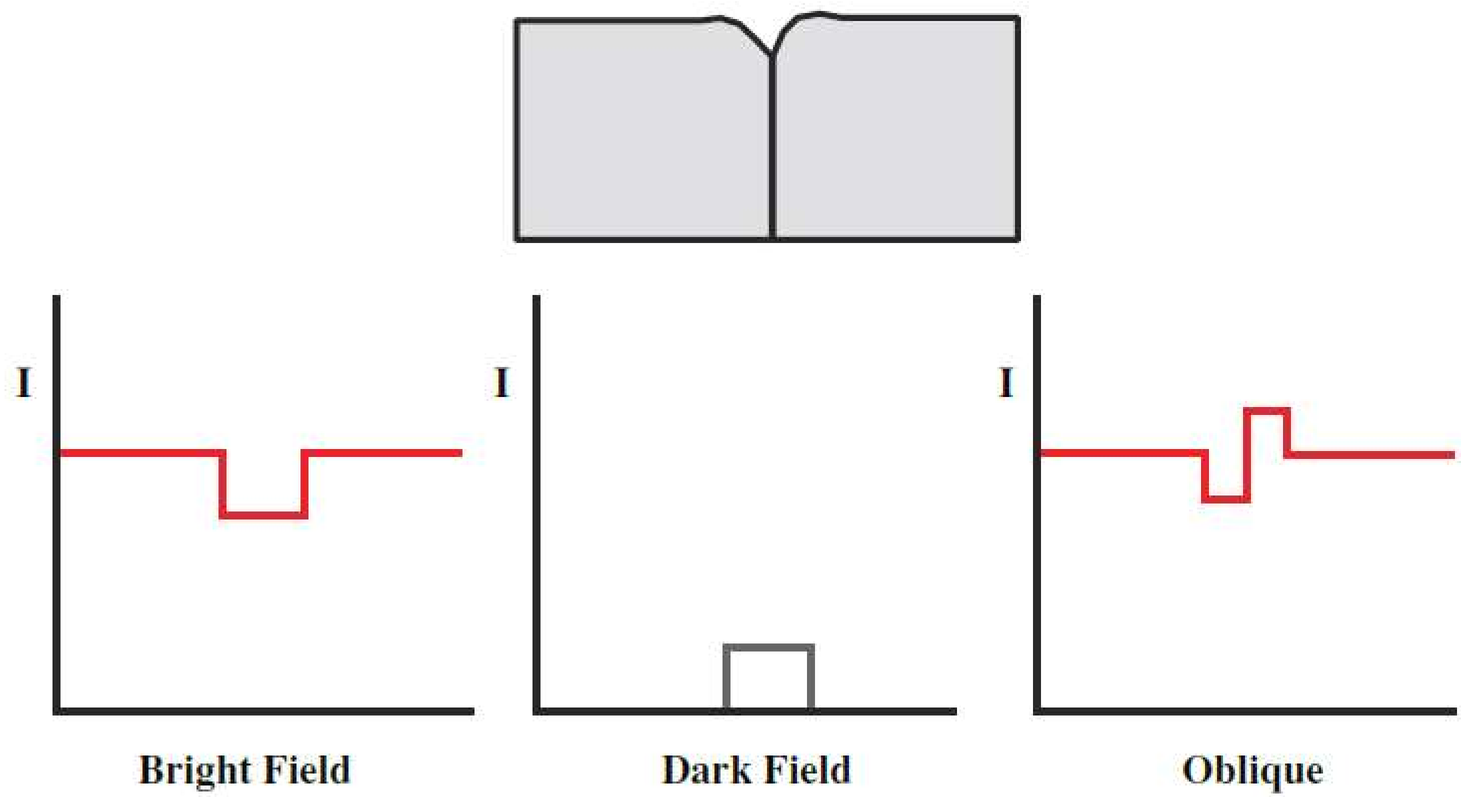
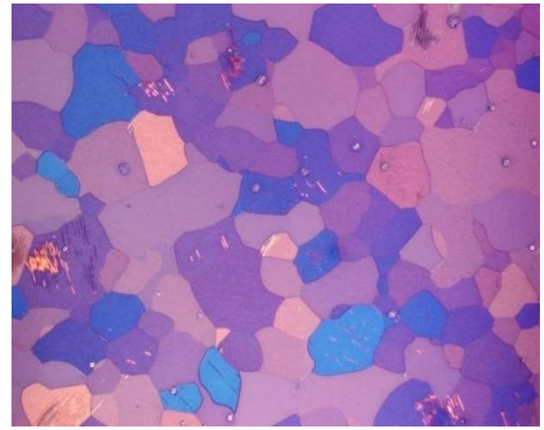


Figure 3.24 *A schematic comparison of contrast in bright-field, dark-field and oblique illumination.*

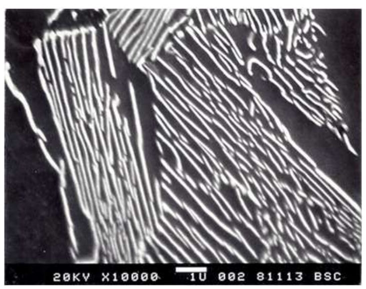
- Reflection and transmission mode
- Polarized light microscopy
- Limited resolution

Magnesium

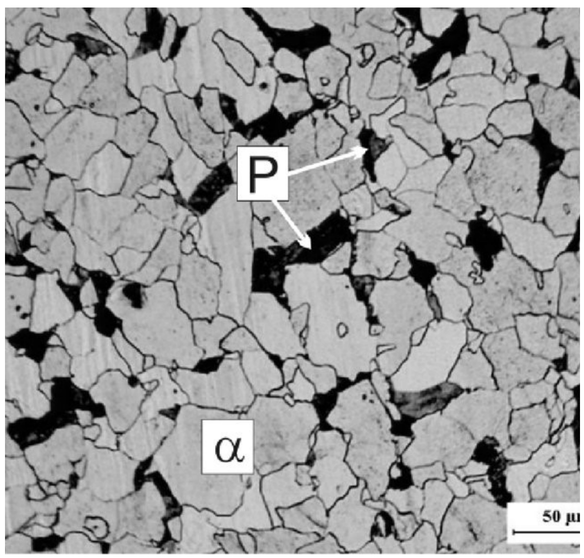


Pearlite

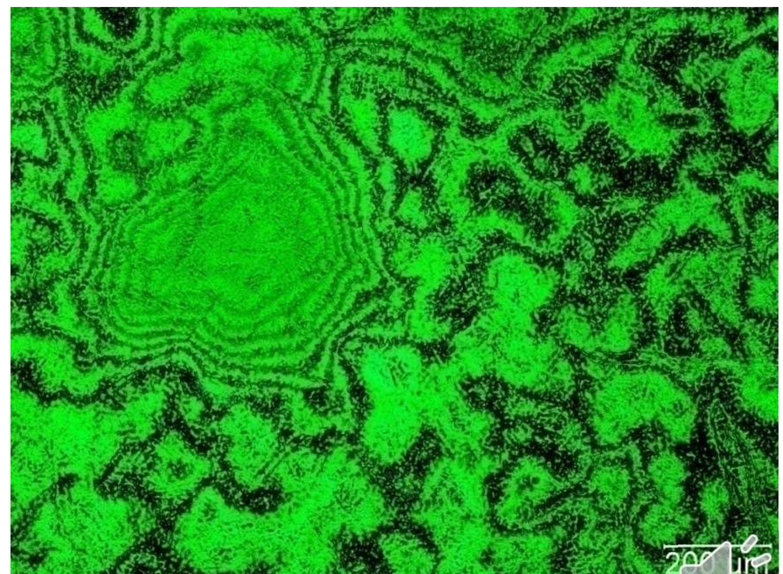
Alpha Ferrite and Cementite



Alpha Ferrite and Pearlite



Nano-cellulose



Scanning Electron Microscope SEM

- Limitation of optical microscope in terms of resolution and depth of field
- Lower wavelength better resolution
- X-rays not possible to focus so electrons
- Electromagnetic lens replace optical lens
- A new class scanning probe microscopes

Depth of field of optical vs SEM

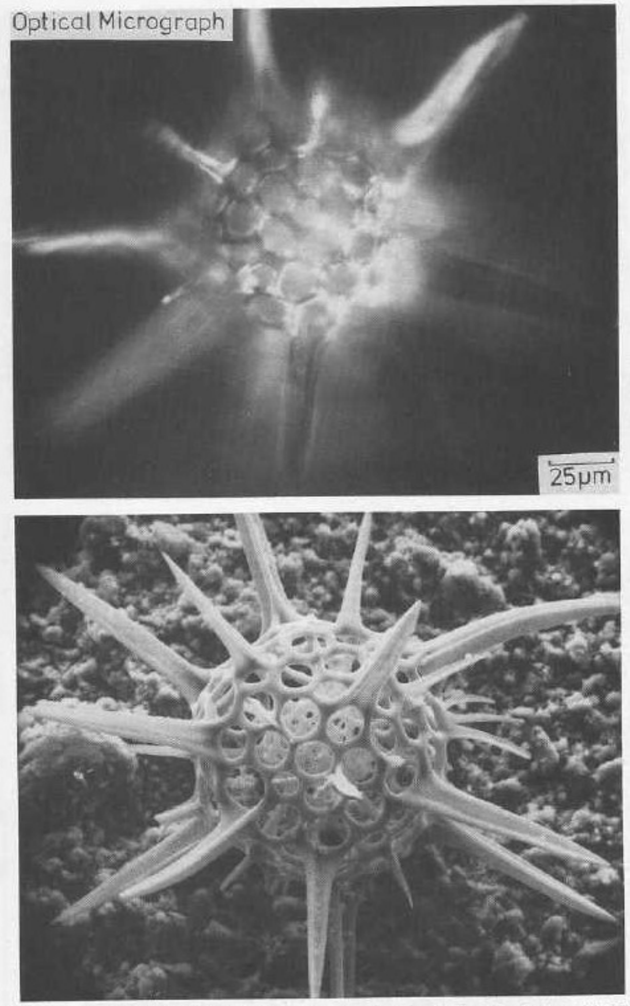
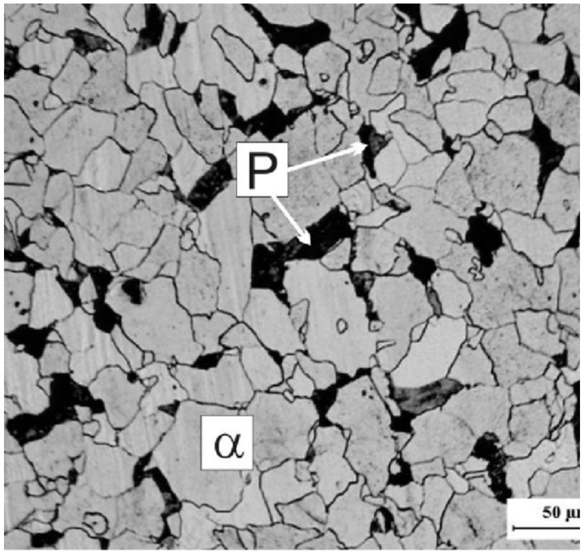
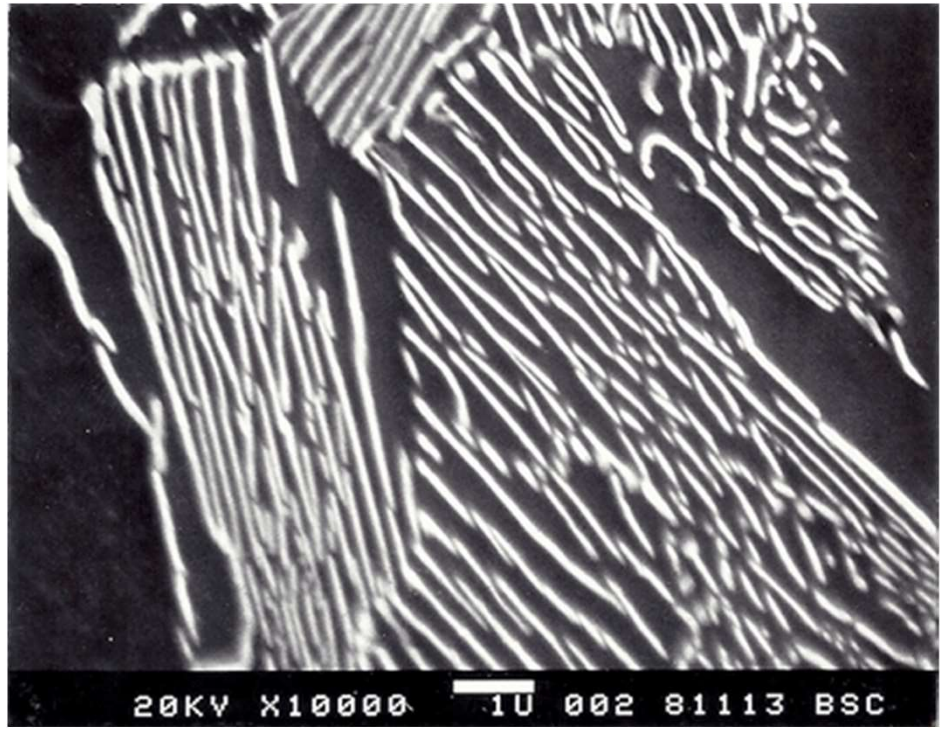
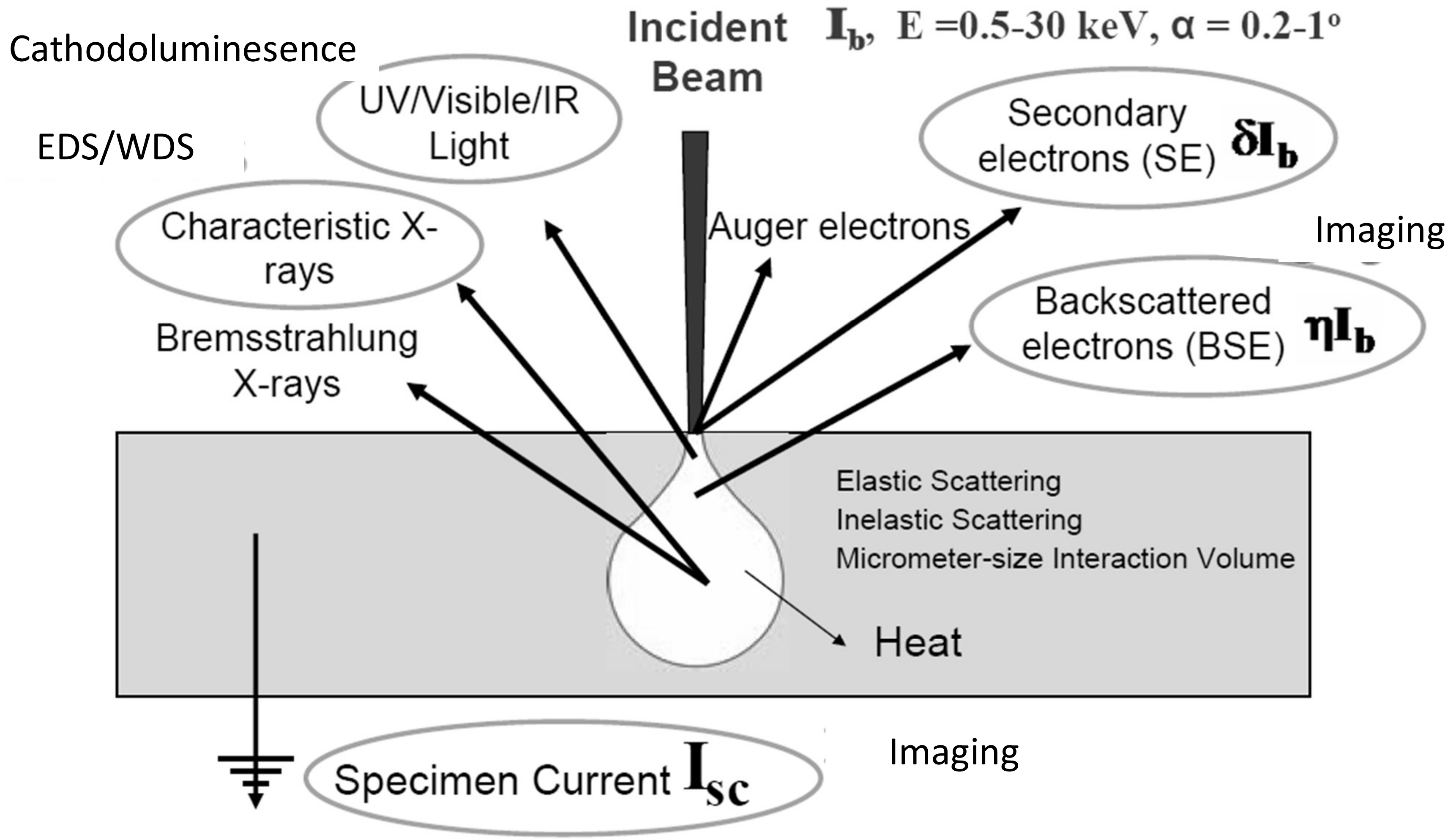


Figure 1.2. (a) Optical micrograph of the radiolarian *Trochodiscus longispinus.* (b) SEM micrograph of same radiolarian. The greater depth of focus and superior resolving capability are apparent.

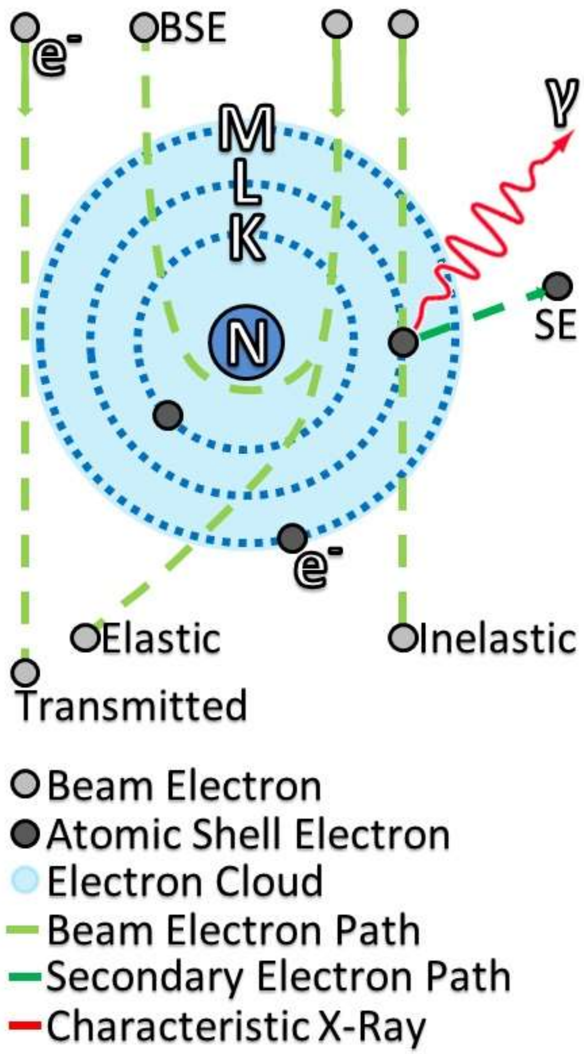

P
α
50 μm

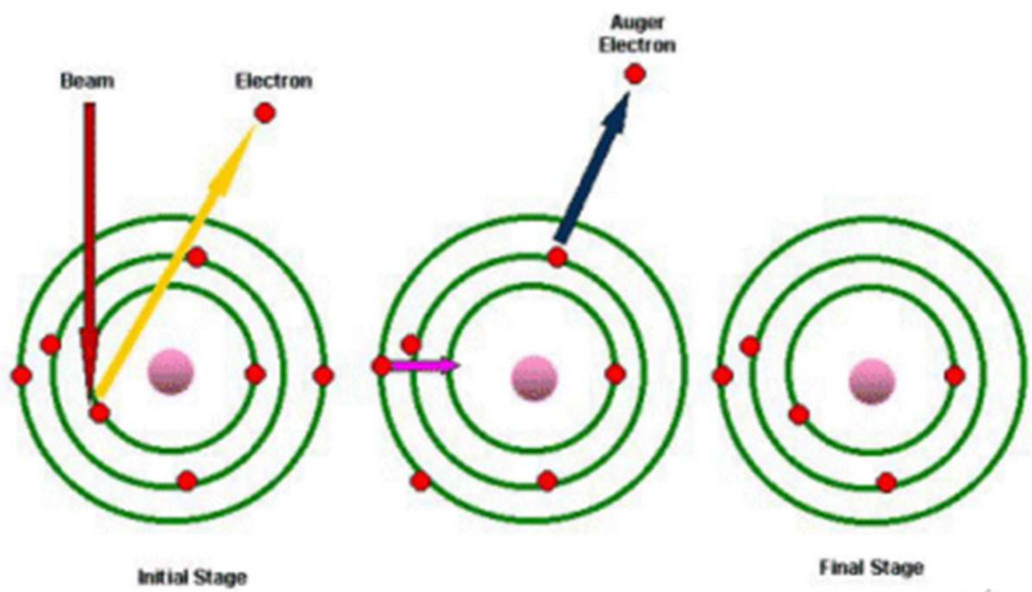

20KV X10000 1U 002 81113 BSC

Electron matter interaction

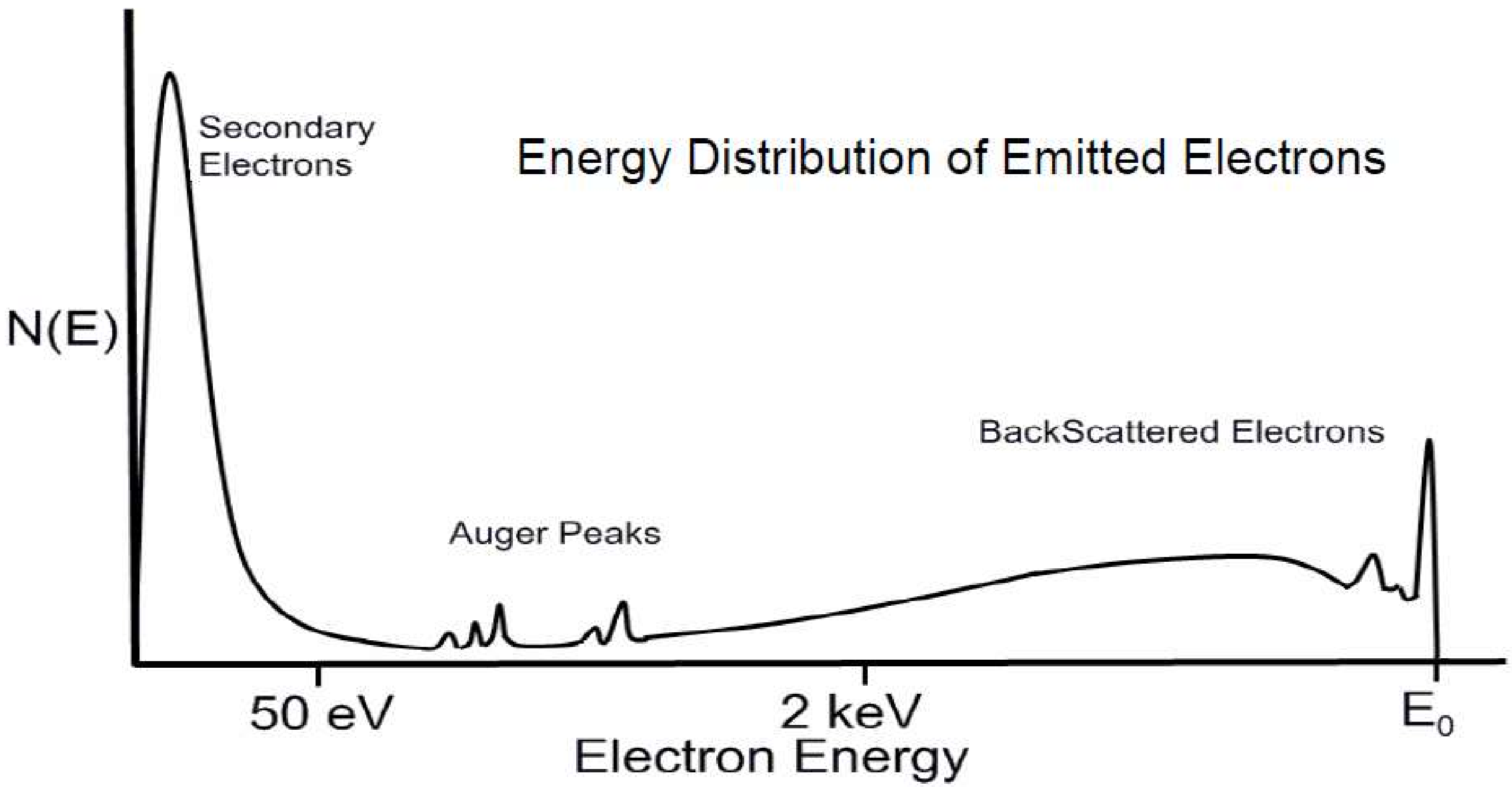


$$I_{sc} = I_b - \eta I_b - \delta I_b = I_b\,(1-(\eta+\delta))$$

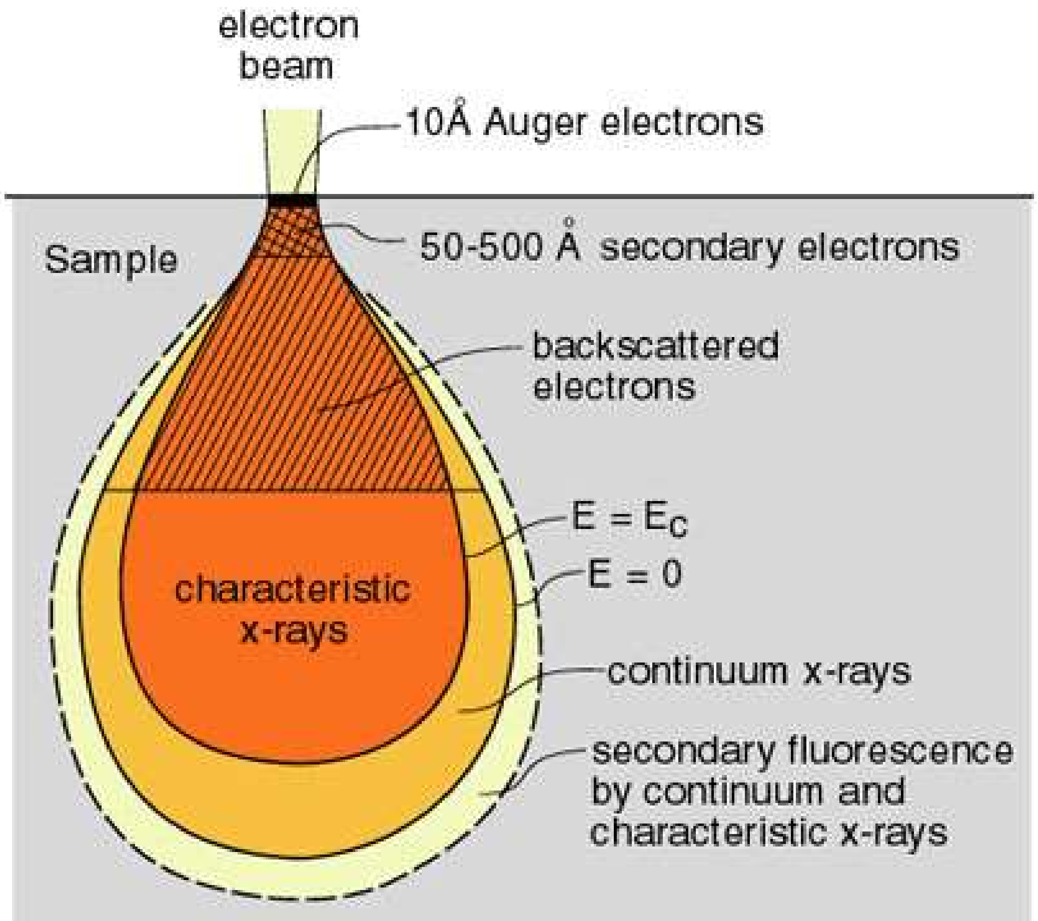

e-
BSE
γ
M
L
K
N
SE
e-
Elastic
Inelastic
Transmitted
Beam Electron
Atomic Shell Electron
Electron Cloud
Beam Electron Path
Secondary Electron Path
Characteristic X-Ray


Beam
Electron
Auger Electron
Initial Stage
Final Stage

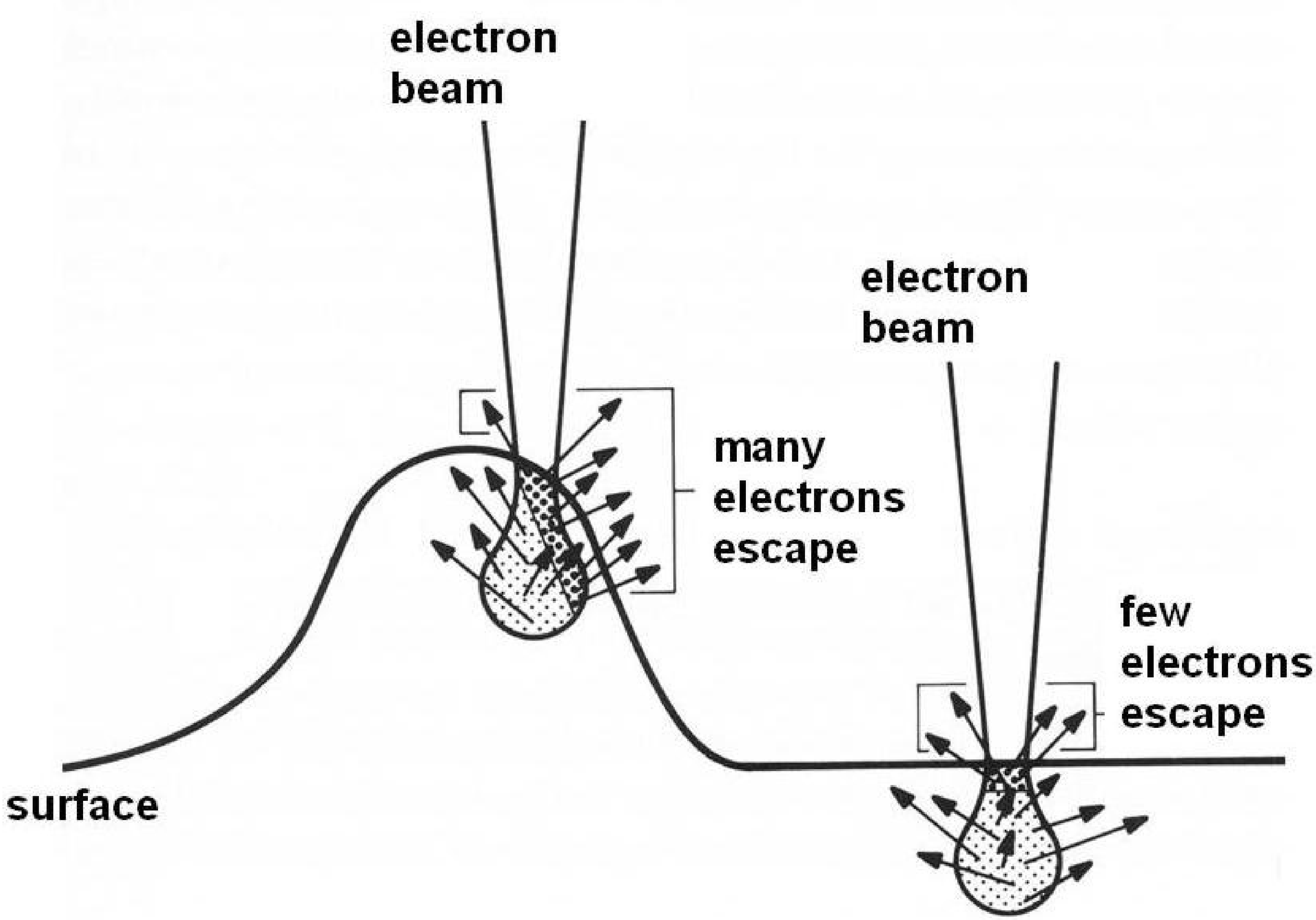
Electron matter signal



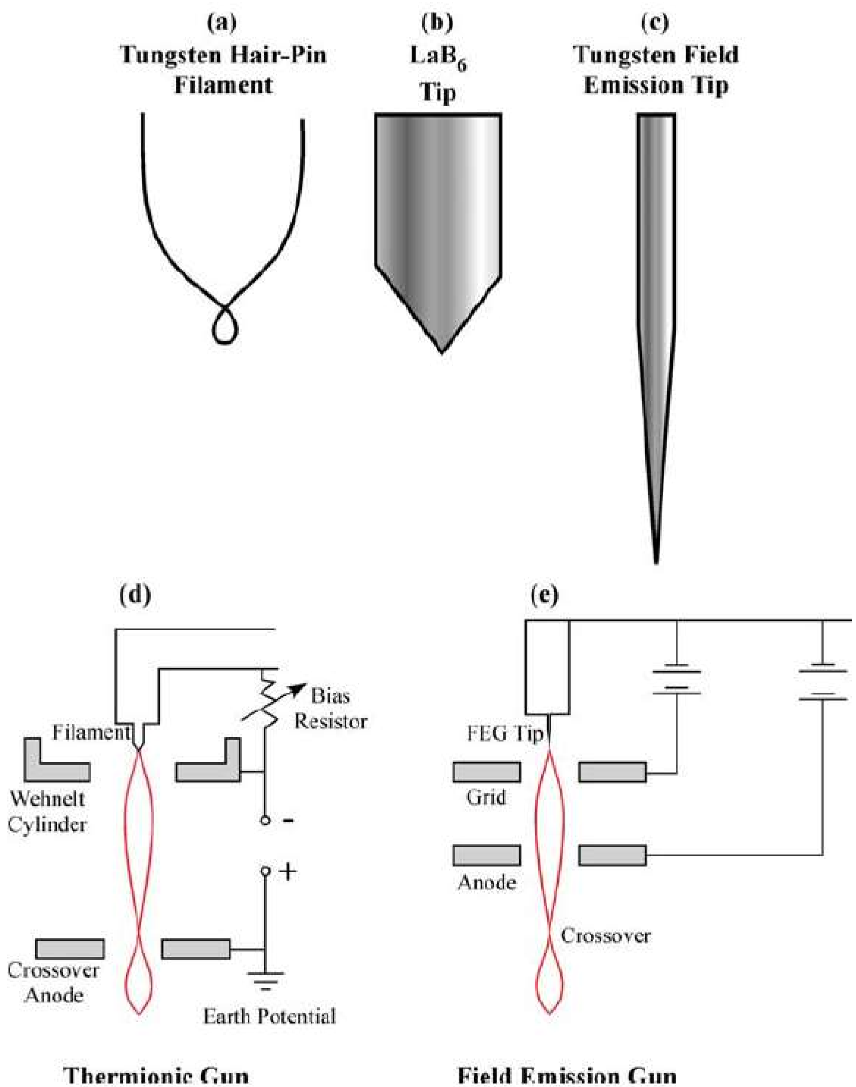
Interaction volume



Contrast in secondary electron imaging

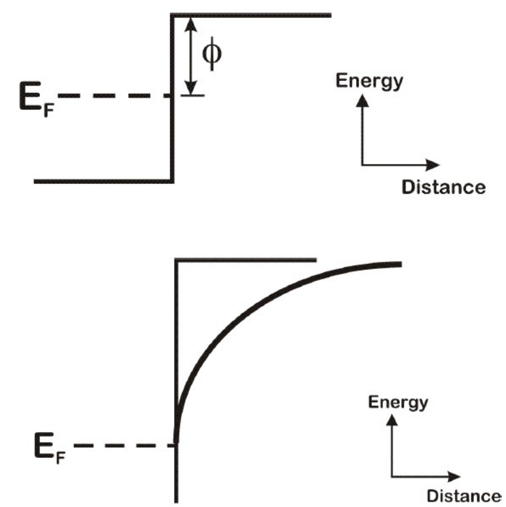


Electron source



Brightness (A/m²·sr)

Thermionic	10^9
Schottky	$5{\cdot}10^{10}$
Cold field emission	10^{13}



SEM cross section

- Scan coils above objective
- Used to raster image
- Magnification is area of screen by area scanned

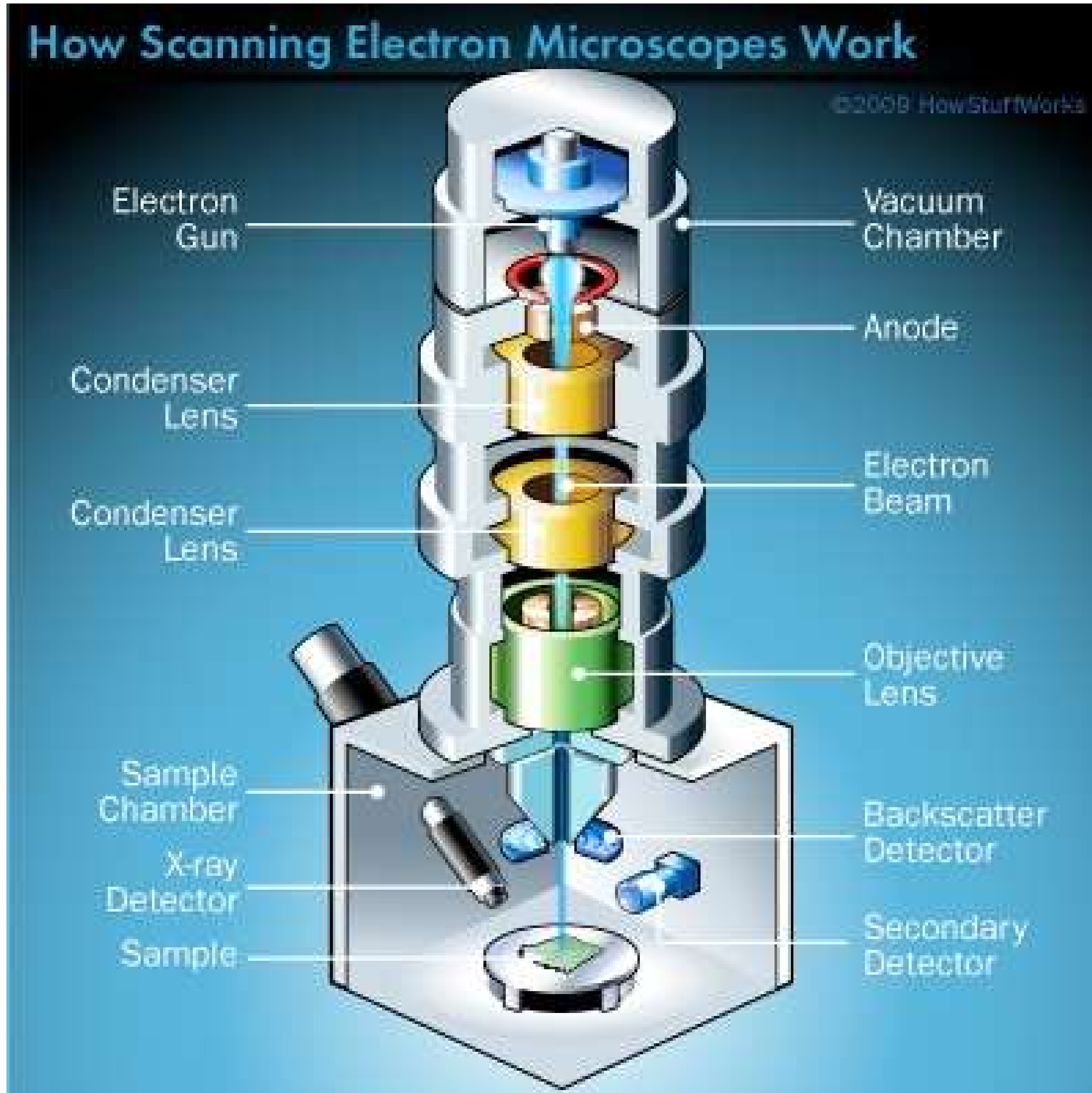
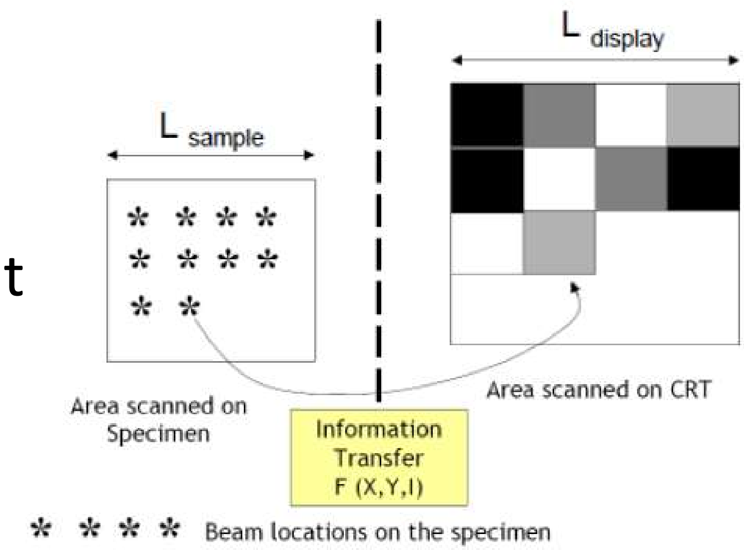


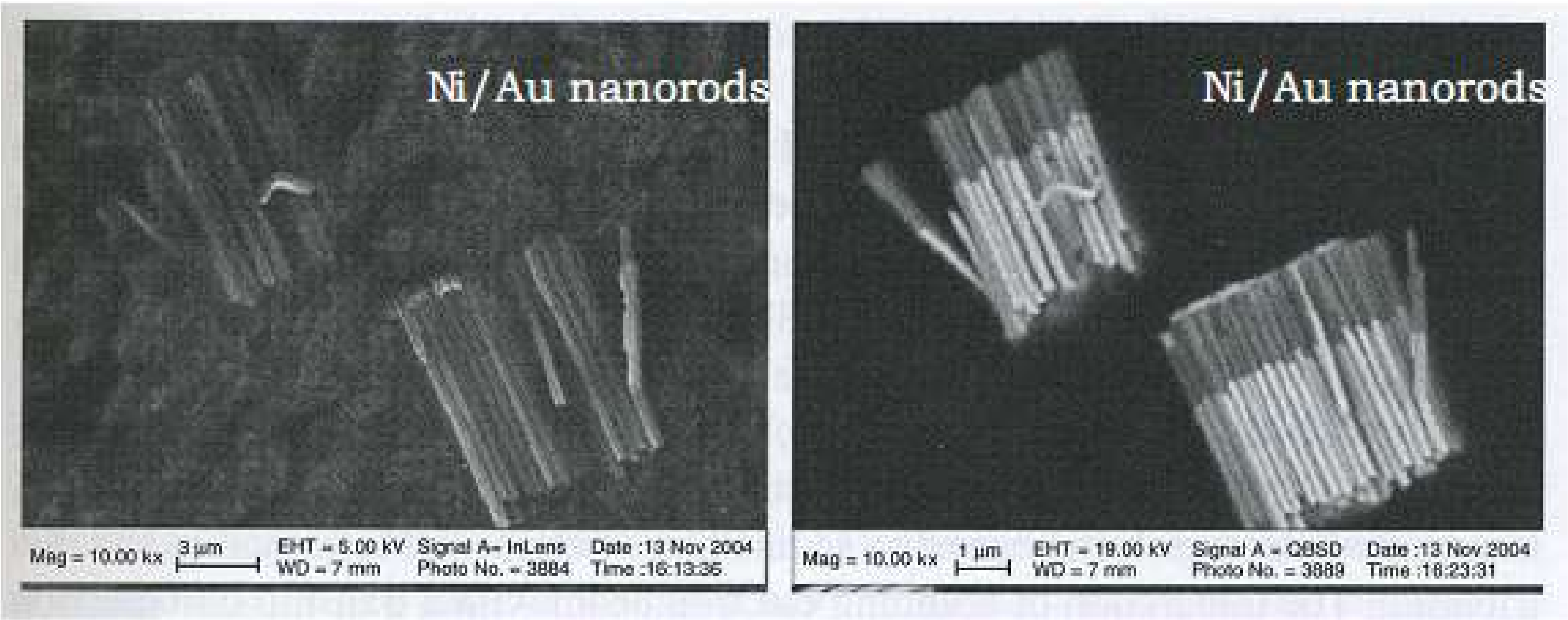
Image formation

- SEM image is 2D intensity map
- Continuous map in analog system
- Discrete map in digital
- Pixel size and scanning rate important
- Signal to Noise ratio
- Fast scan and slow scan; Frame averaging
- Beam drift



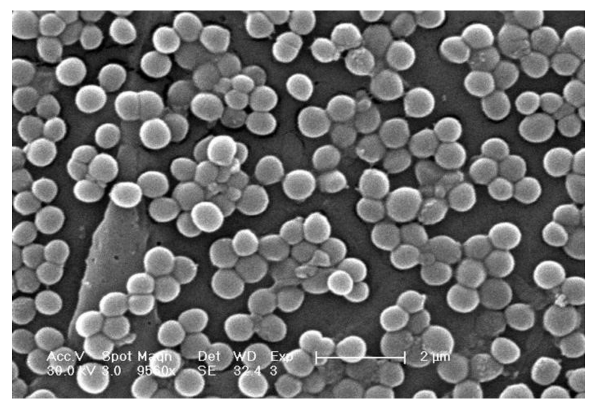
Secondary electron image

Backscattered electron image

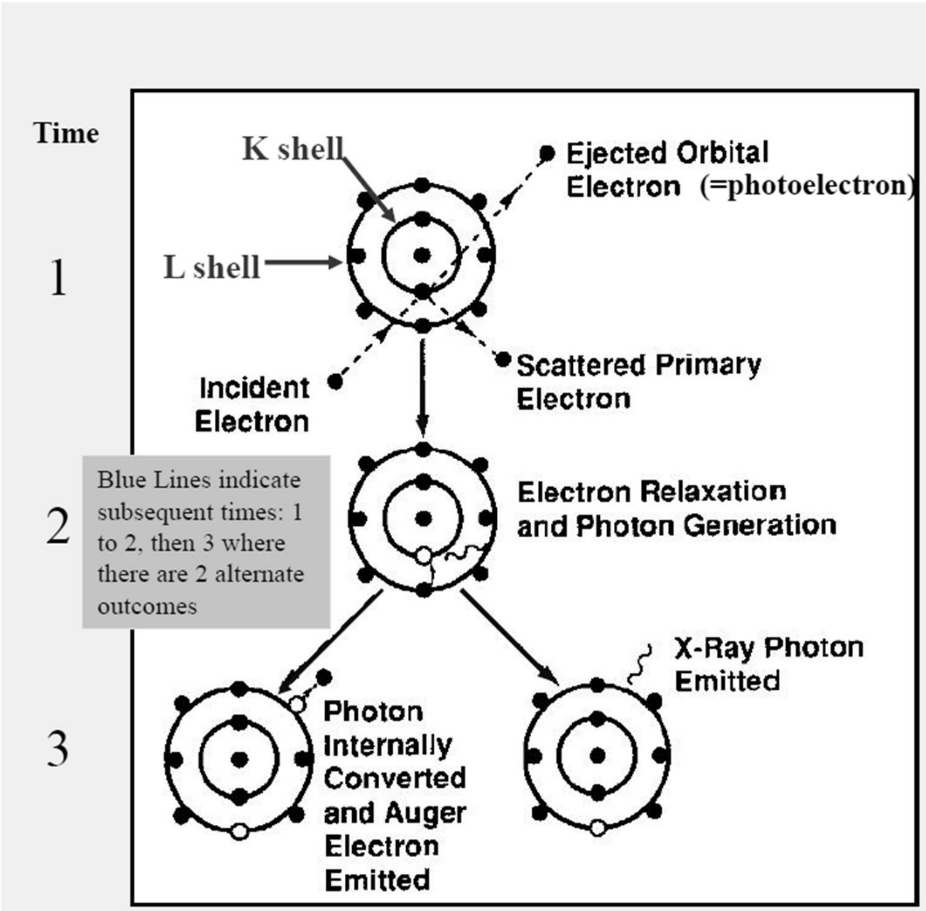


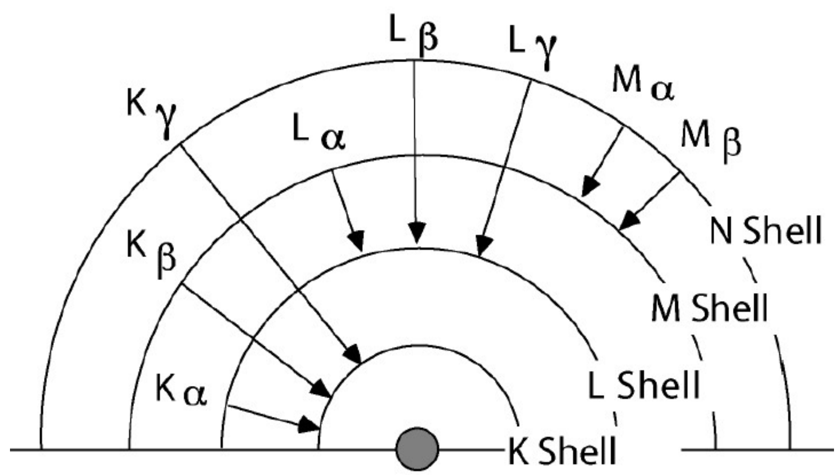
Resolution

- Secondary electron imaging of surface topography: 10 nm
- Backscattered electron imaging of atomic number contrast: 1 µm
- X-ray characterization of elemental chemistry: 2 µm using typical beam voltages of 20 kV (much better resolution, 100 nm, can be obtained using low voltage beams)
- Electron diffraction characterization of crystal structure and orientation: 1 µm



Microanalysis in SEM





Energy and Wavelength Dispersive Spectroscopy

- Energy Dispersive spectroscopy (EDS) records X-rays of all energies simultaneously
- Output is counts versus photon energy
- Wavelength Dispersive spectroscopy (WDS) uses Bragg crystal
- Operates in serial mode
- Spectrometer is tuned to one wavelength at a time
- Use several crystals for different elements
- Better spectral resolution that EDS

Principle of Electron Back Scatter Diffraction

- Electron beam incident on sample inclined at 70º
- BSE yield increases and path length decreases
- Some BSE satisfy Bragg condition

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

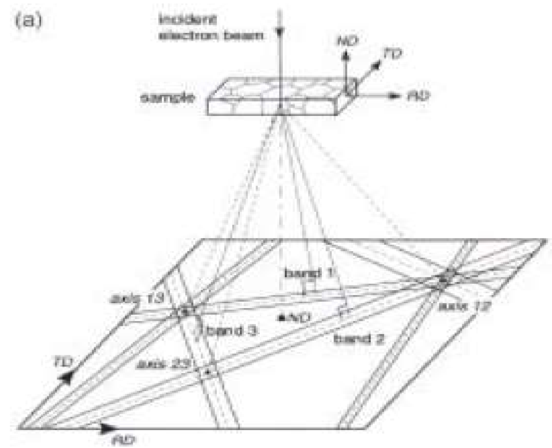
- Diffraction occurs from many planes in same unit cell
- θ_B very small, large radius of diffraction cones
- Kikuchi bands

- Intersections of the Kikuchi bands correspond to the intersection of zone axes in the crystal with the phosphor screen

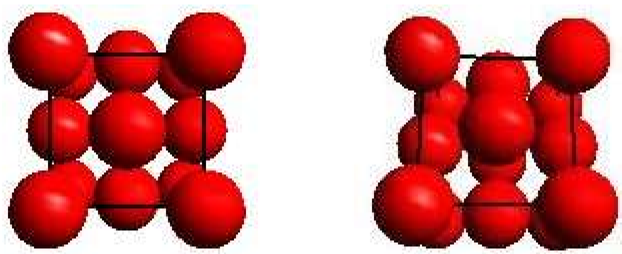
- w ≈ 2lθ ≈ nlλ/d; Low index plane high d, low w

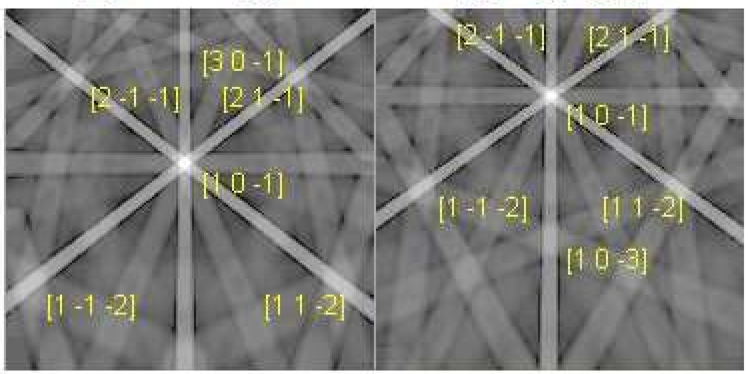
- Diffraction pattern bound to crystal structure of the sample

- Resultant diffraction pattern changes as crystal orientation changes



Kikuchi bands in TEM





Courtesy Old HKL website

Aged beta titanium alloy

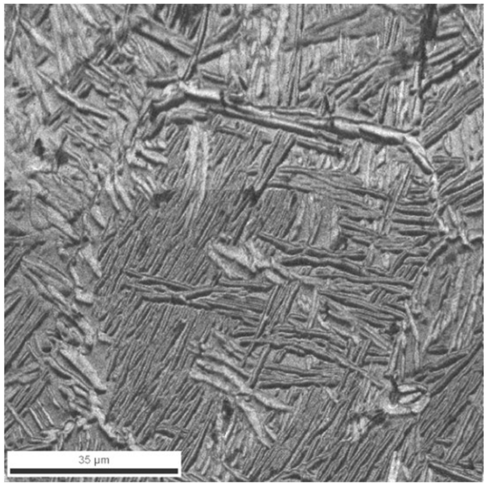
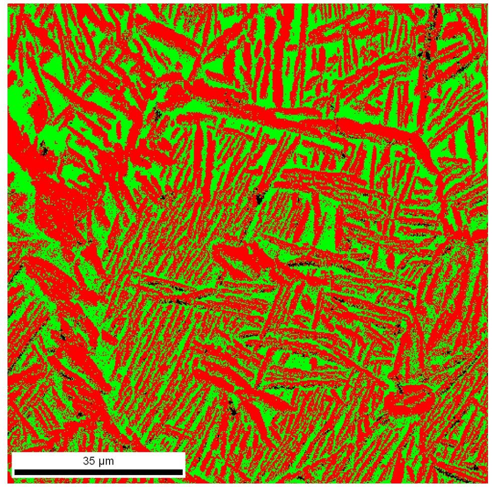
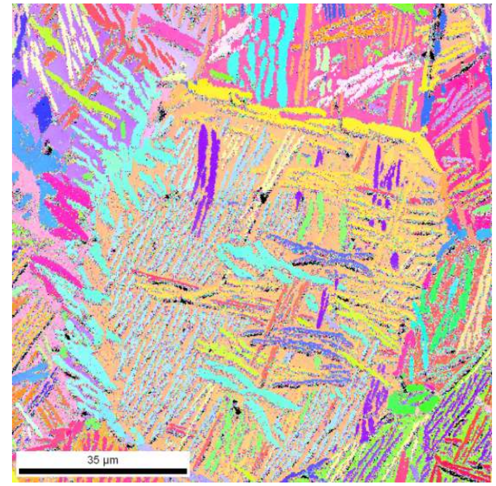


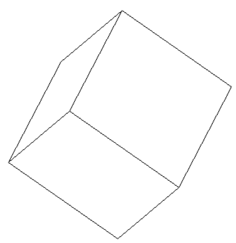
Image quality map

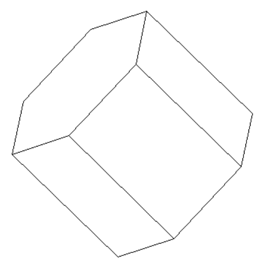


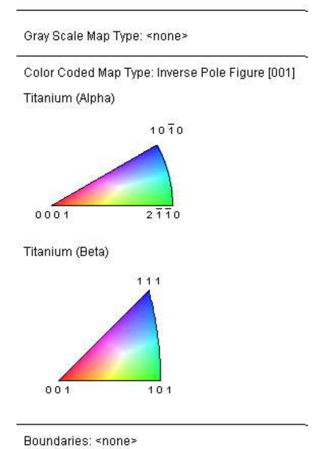
Phase map
red-alpha green-beta



Crystal orientation map



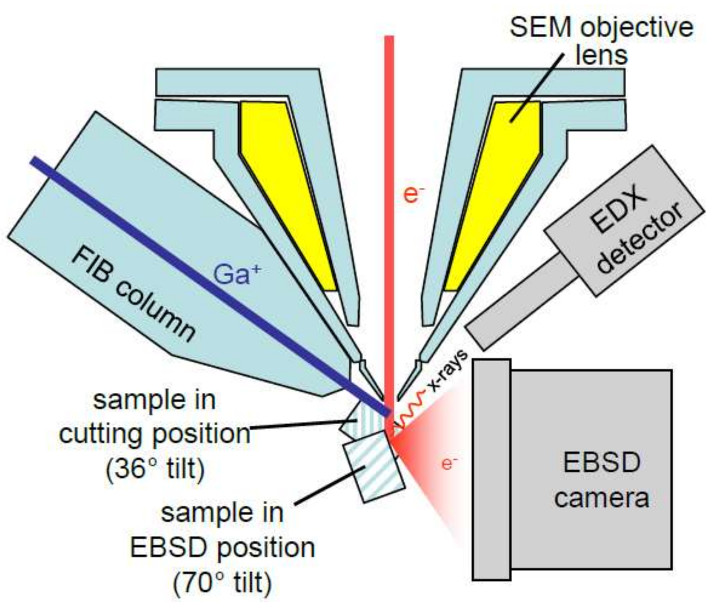


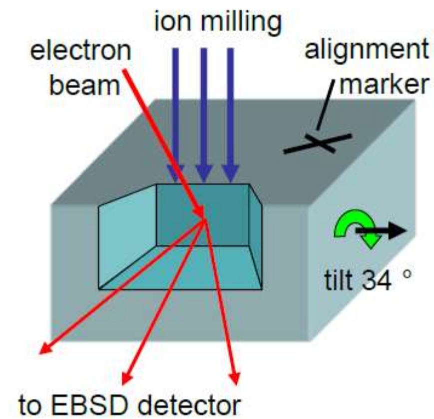


Gurao, Ali and Suwas, MSEA 2008

Dual beam Focused Ion Beam (FIB) SEM

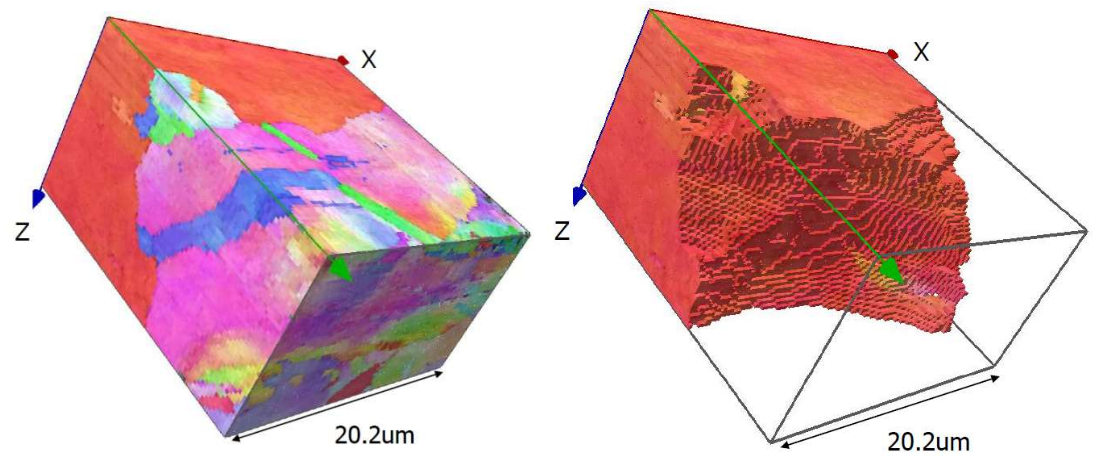
- FIB can make 'cuts' to remove precisely controlled amounts of material to expose a new surface for EBSD
- SEM can be used to acquire EBSD data in the normal manner
- Sample is 'serial sectioned' using FIB, and EBSD maps obtained after each cut
- Thus many 2D maps are acquired which can be 'stacked' and then be recompiled into a 3D view of the sample interior in a similar manner to tomography in medical imaging



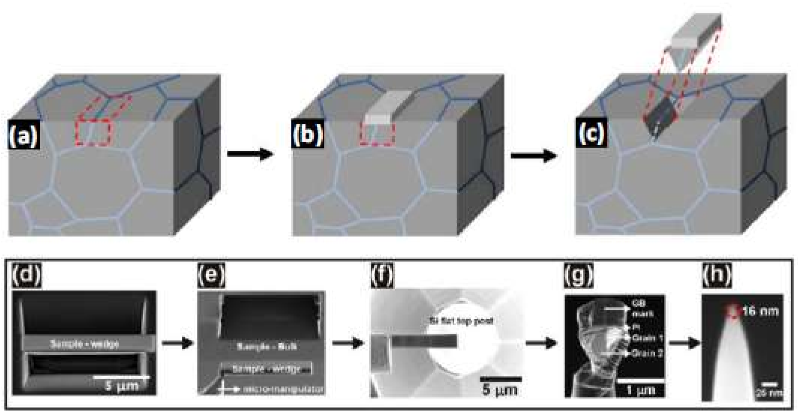


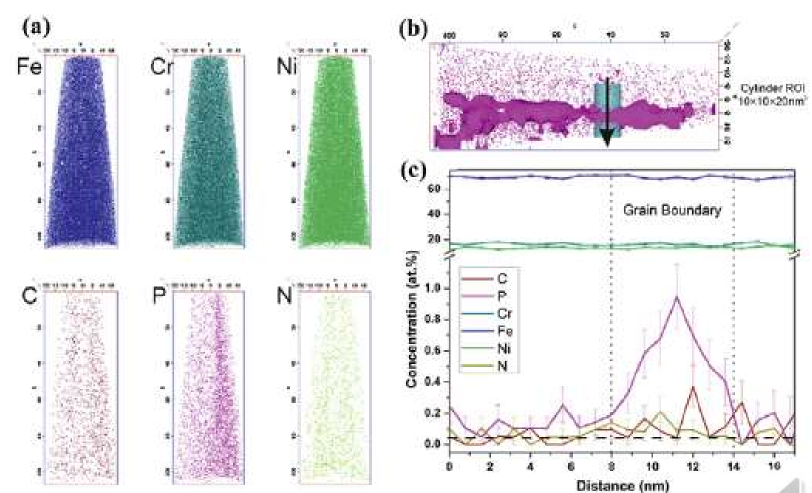
Visualization of grain boundaries

- Determination of precise grain boundary surface
- Grain boundary engineering in 3D
- Segregation and corrosion related issues
- Eg. Brittleness in 304L steel due to phosphorous segregation at ∑9 boundary



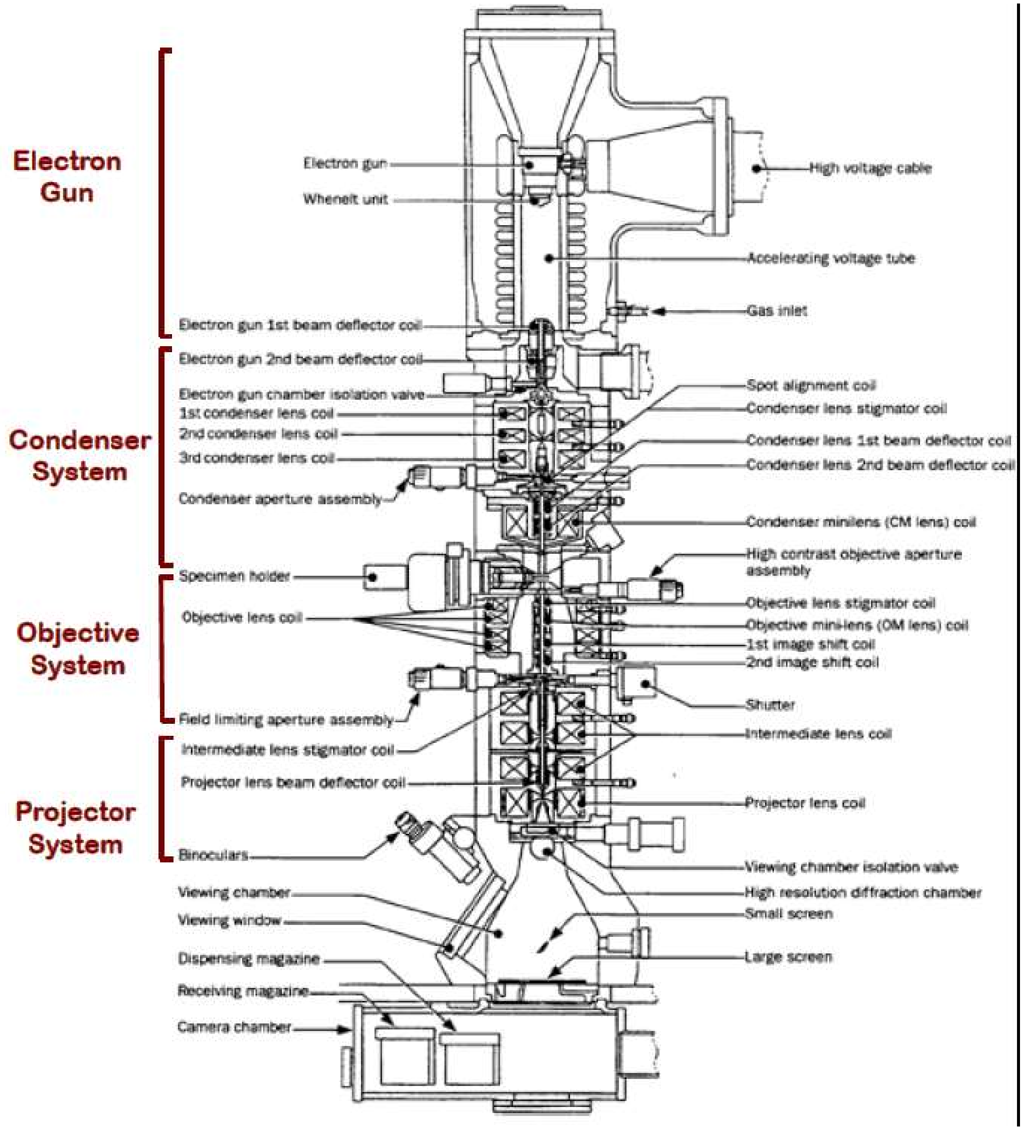
D Raabe 2011

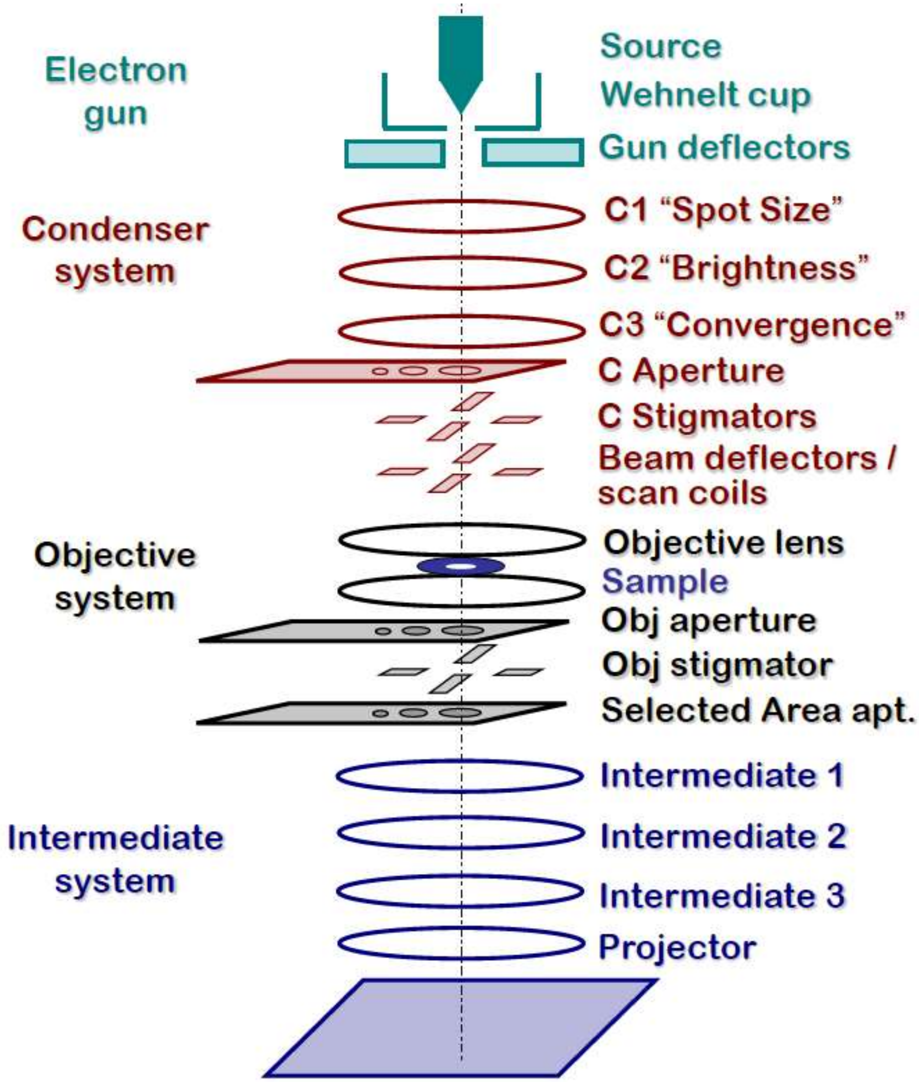


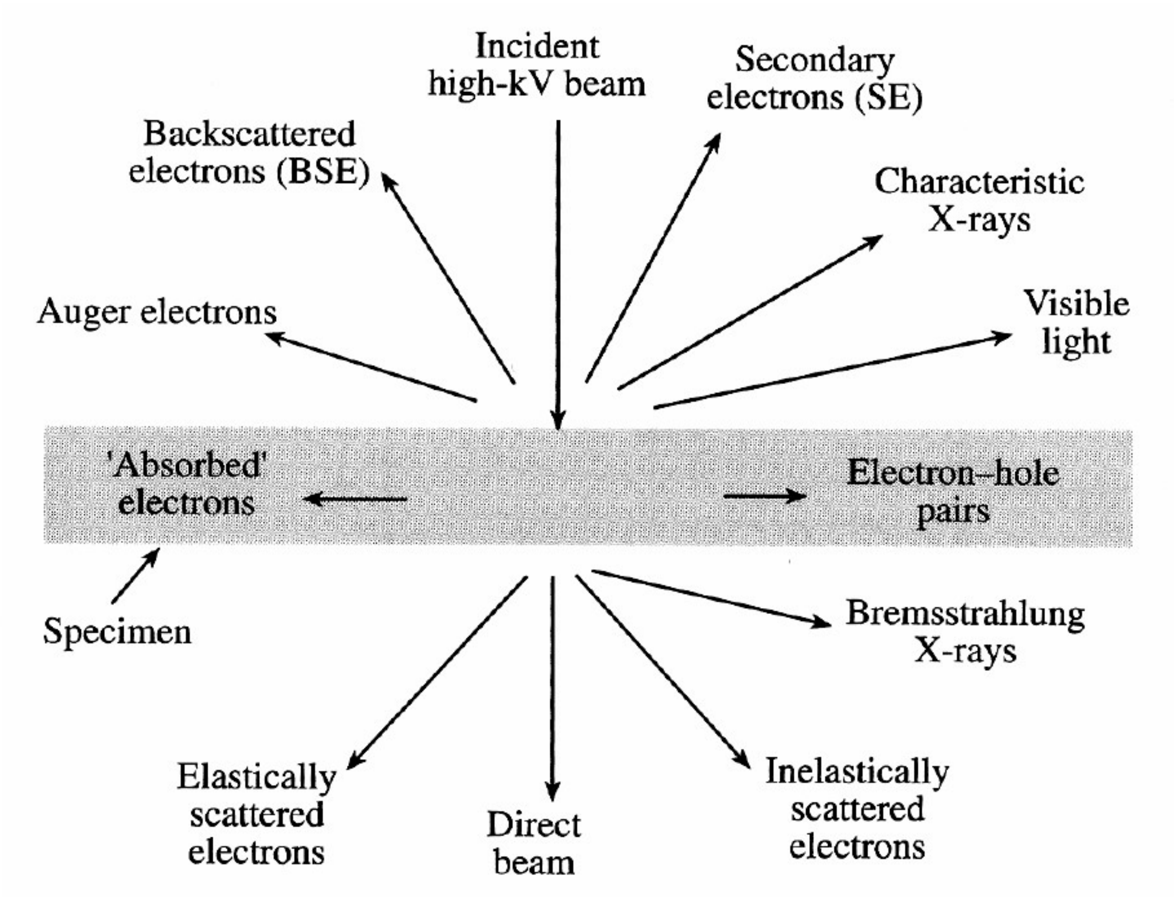


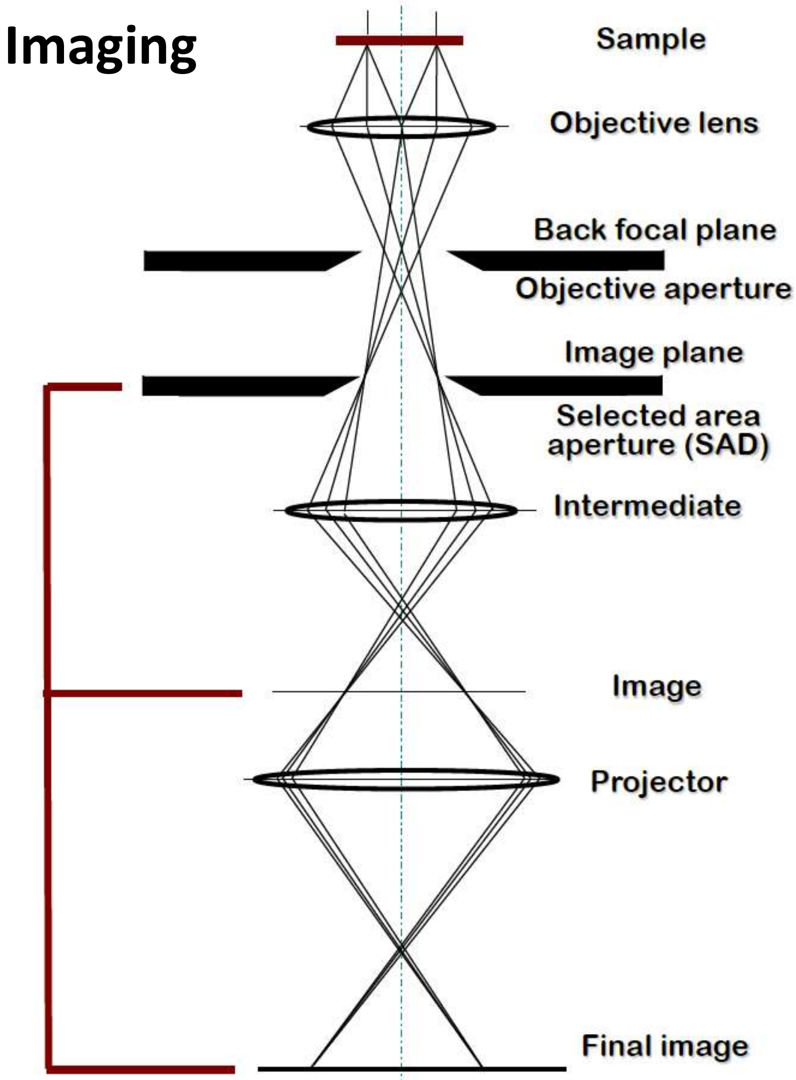
S. Mandal et al. Scripta Mater. 81 (2014) 16

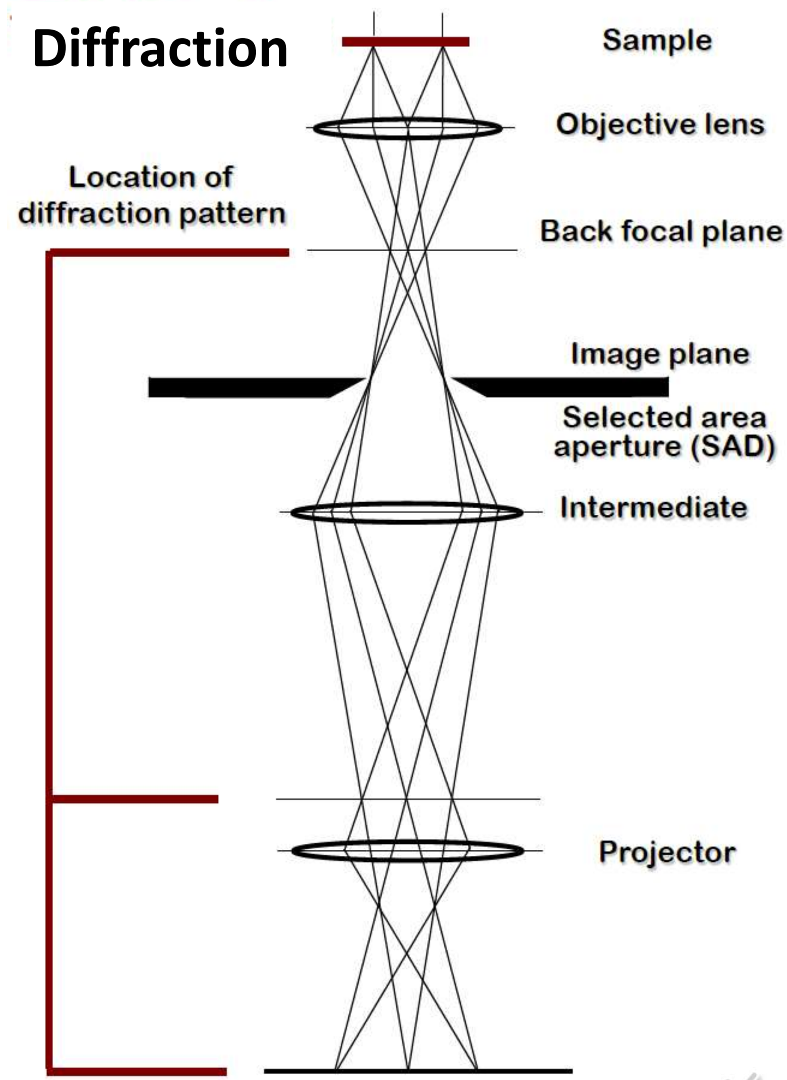
Transmission Electron Microscope

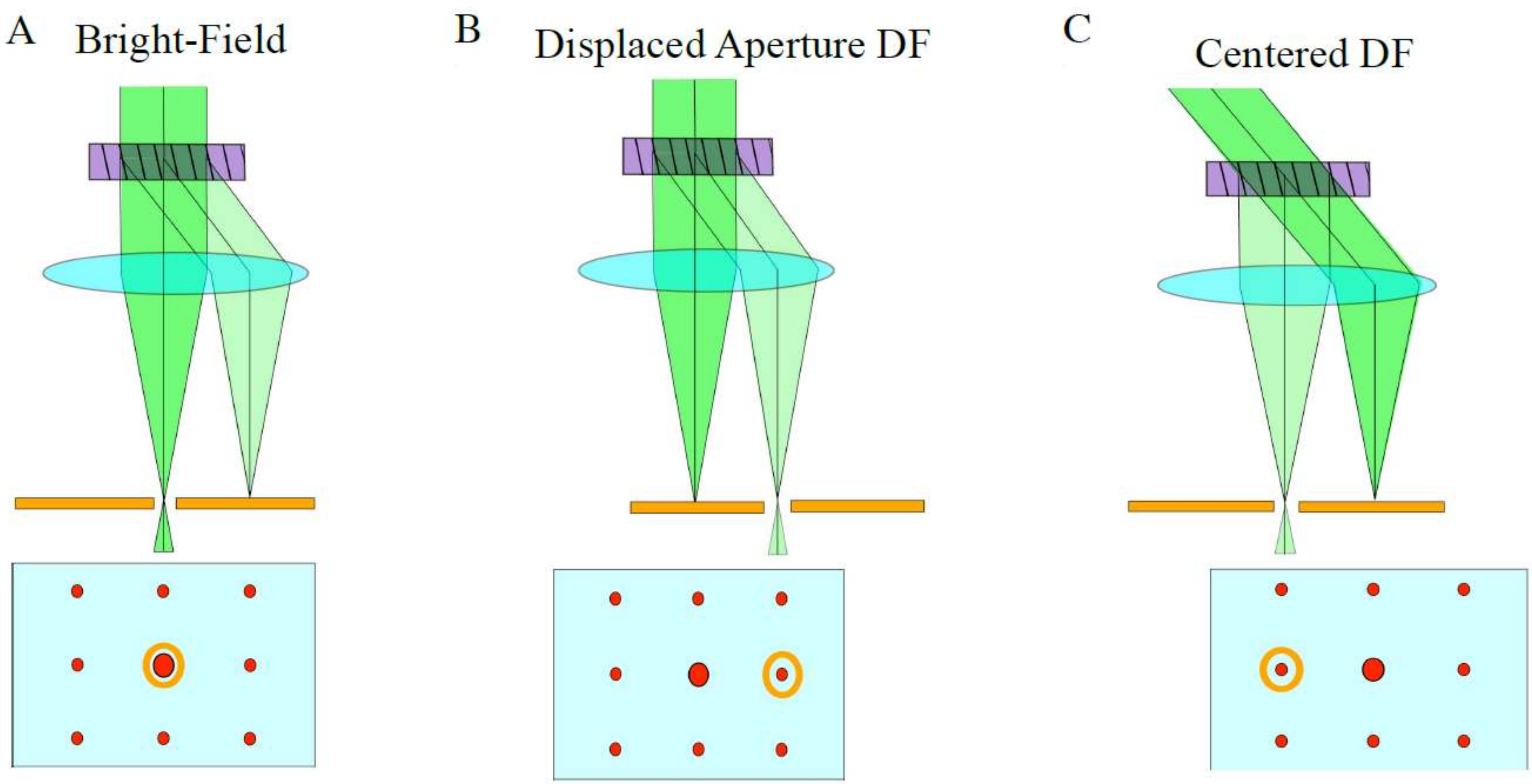



Electron gun
Source
Wehnelt cup
Gun deflectors
Condenser system
C1 "Spot Size"
C2 "Brightness"
C3 "Convergence"
C Aperture
C Stigmators
Beam deflectors / scan coils
Objective system
Objective lens
Sample
Obj aperture
Obj stigmator
Selected Area apt.
Intermediate system
Intermediate 1
Intermediate 2
Intermediate 3
Projector


Incident high-kV beam
Secondary electrons (SE)
Backscattered electrons (BSE)
Characteristic X-rays
Auger electrons
Visible light
'Absorbed' electrons
Electron–hole pairs
Specimen
Bremsstrahlung X-rays
Elastically scattered electrons
Direct beam
Inelastically scattered electrons

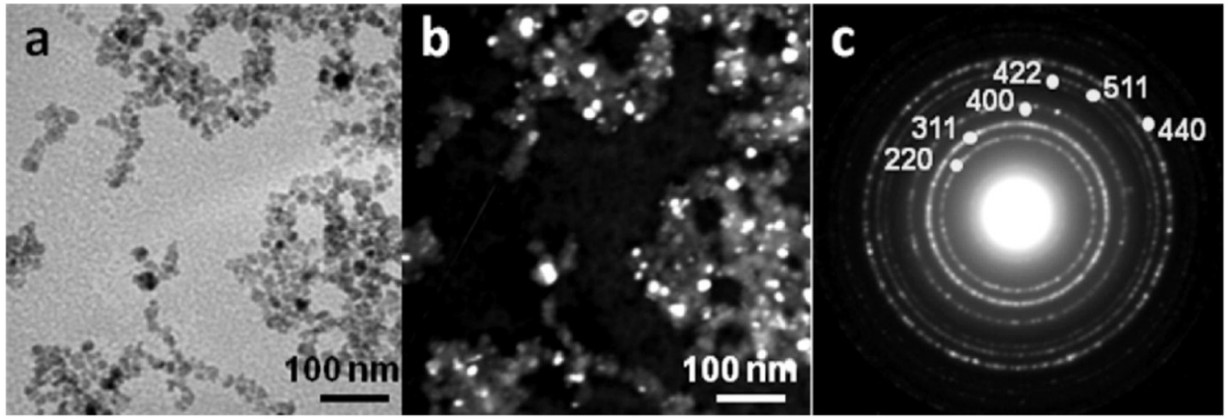

Imaging
Sample
Objective lens
Back focal plane
Objective aperture
Image plane
Selected area
aperture (SAD)
Intermediate
Image
Projector
Final image


Diffraction
Sample
Objective lens
Location of
diffraction pattern
Back focal plane
Image plane
Selected area
aperture (SAD)
Intermediate
Projector


A Bright-Field
B Displaced Aperture DF
C Centered DF

Bright field Dark field Diffraction pattern

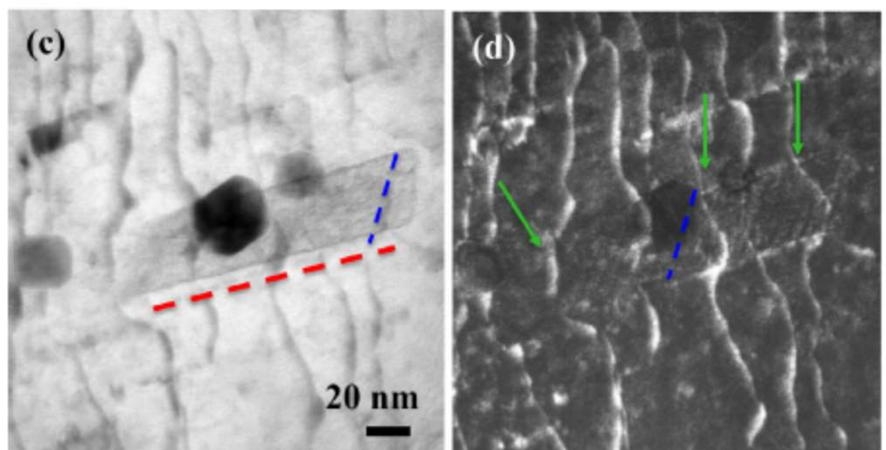
Magnetite nanoparticle



Castillo et al. Journal of Nanotechnology 2014

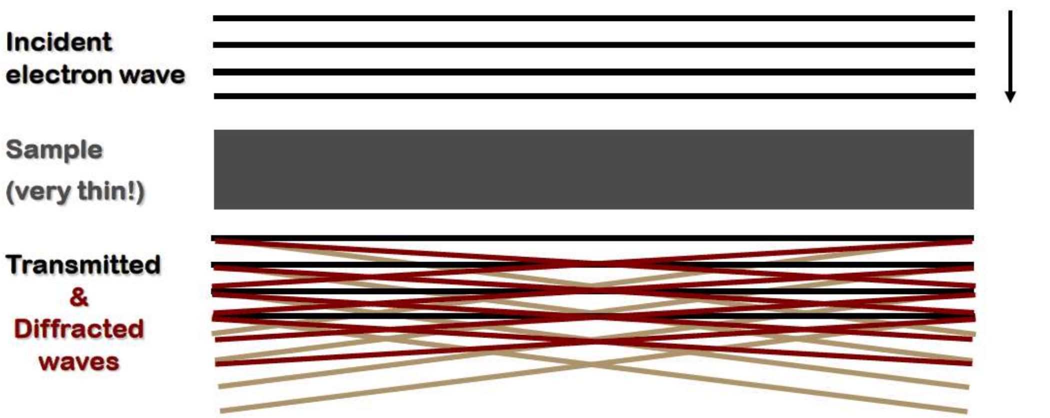
Bright field Dark field

Interaction of dislocations with precipitates in Mg alloy



Wang et al. Acta Mater. 2020

High Resolution TEM (HRTEM)



Transmitted & diffracted waves each have a different phase

Result is an interference pattern - our 'phase contrast' or HREM image

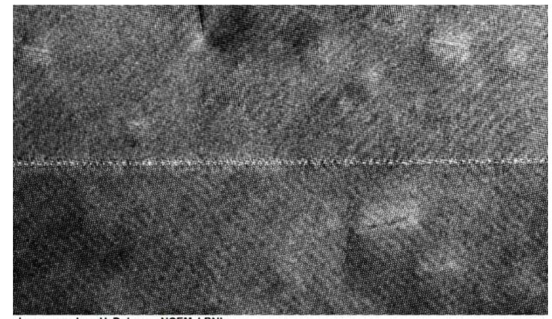


Image courtesy U. Dahmen, NCEM, LBNL

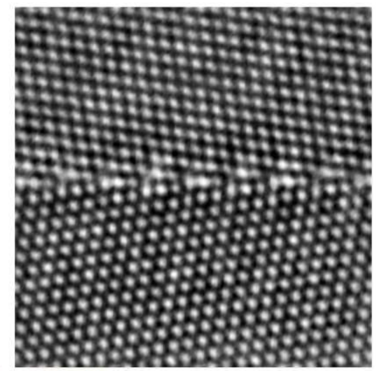
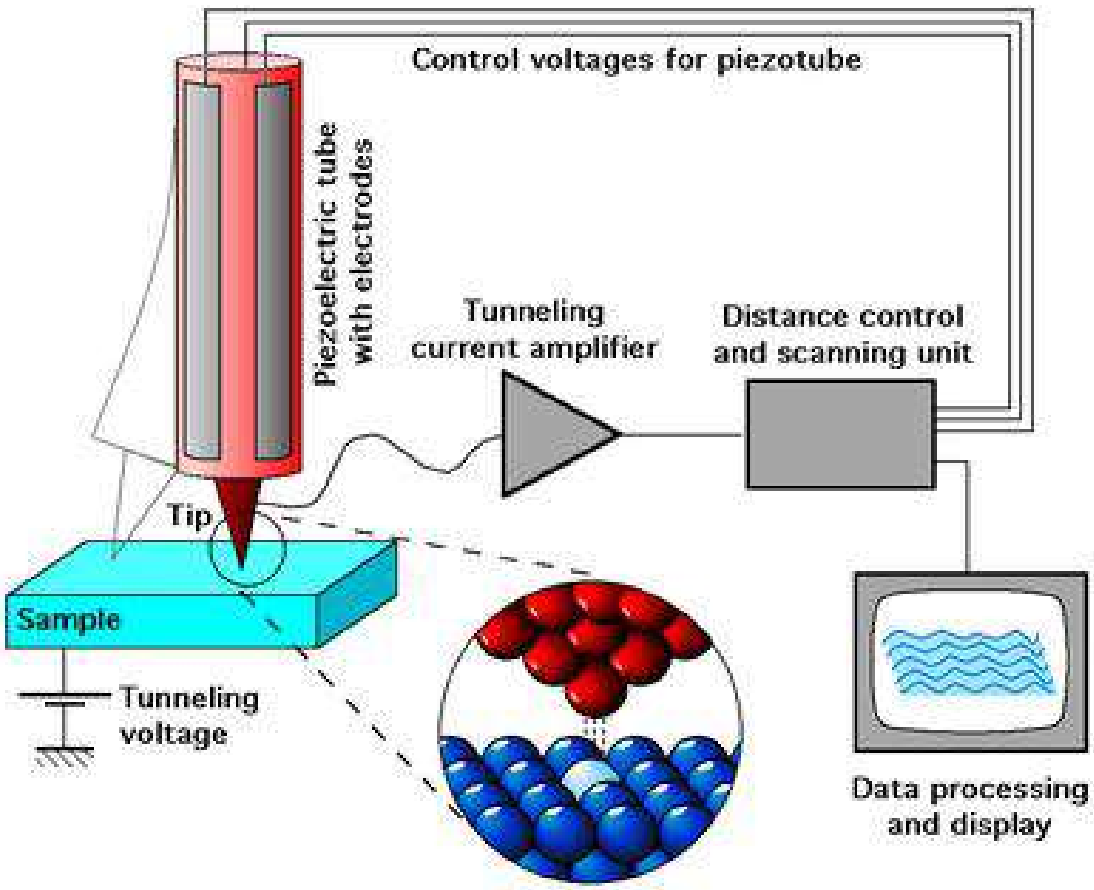
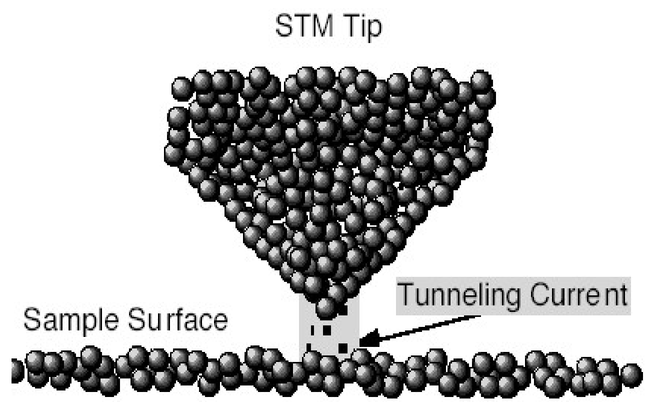


Image courtesy U. Dahmen, NCEM, LBNL

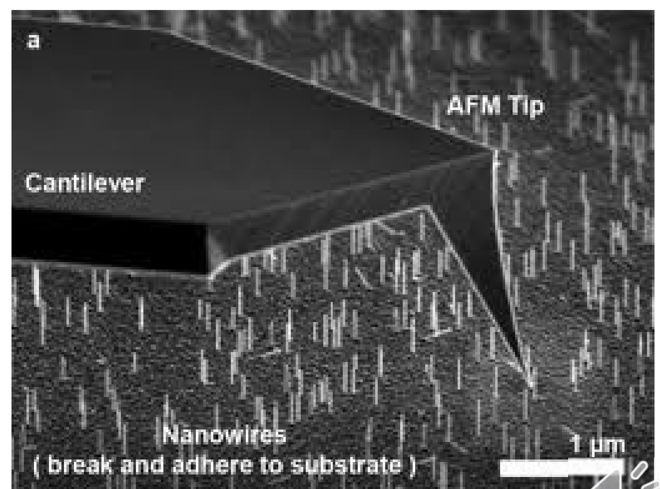
- Each diffracted wave presents a different solution to the Schrodinger equation
- Manifests periodic potential (strength and spacing) between the atoms in the sample

Scanning Probe Microscopy: Atomic Force Microscopy





g. 3: A good STM tip has only one atom at the tip. This restricts the tunneling current between the tip and the sample surface to just a few atoms.



Contact, non-contact mode

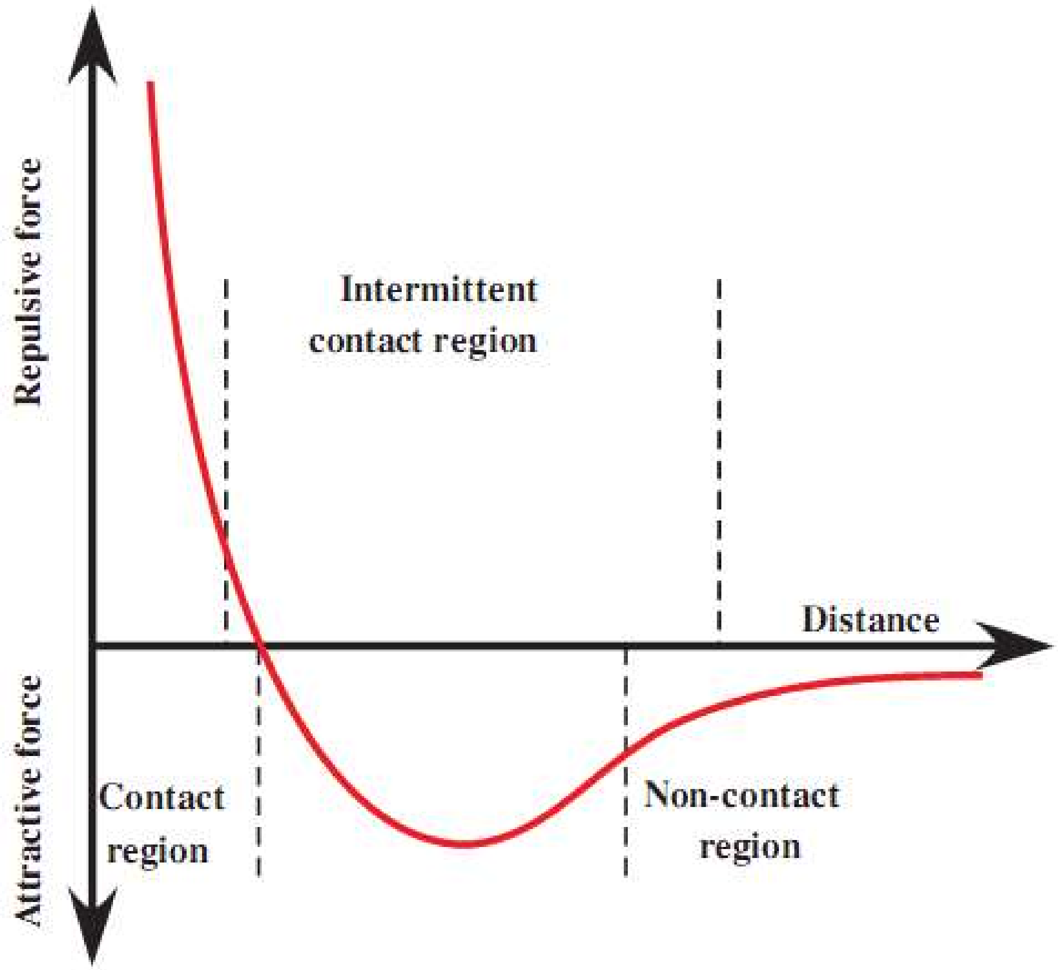
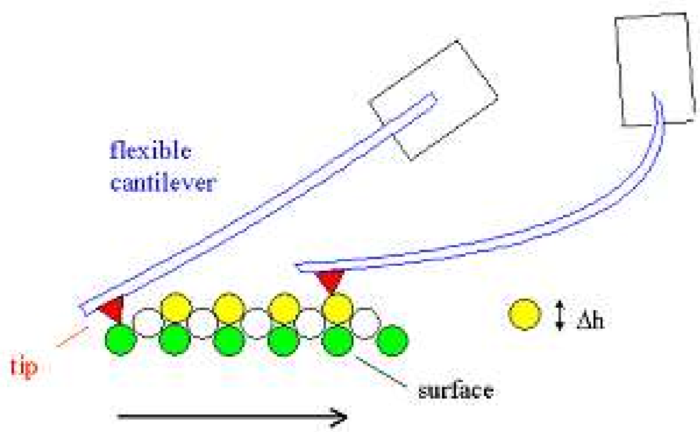


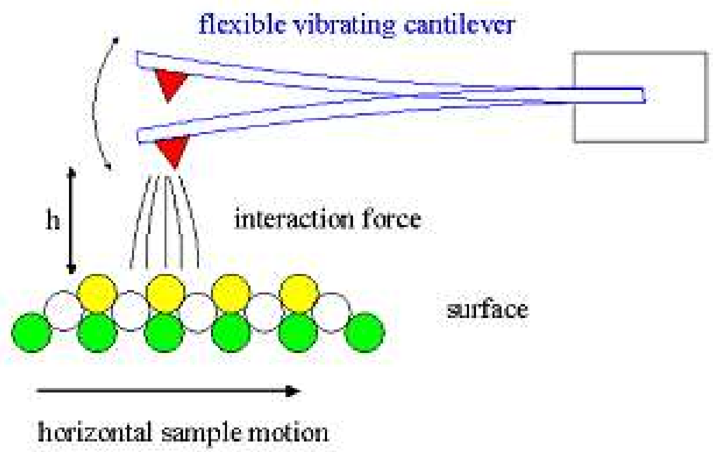
Figure 7.3 *Three regions can be distinguished on the potential energy curve for the interaction of two solid surfaces: a non-contact region dominated by attractive forces; a contact region dominated by the repulsive force; an intermediate, semi-contact region that includes the equilibrium separation and in which the attractive and repulsive forces are of similar magnitude.*

Operation Modes of AFM

I. Contact mode

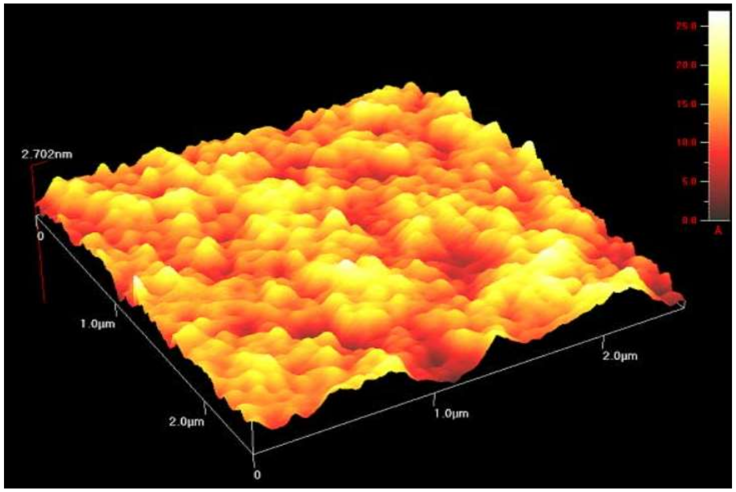


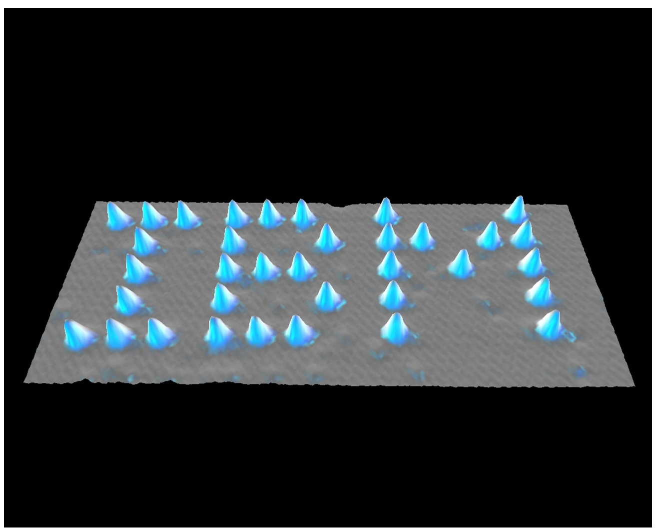
II. Tapping mode

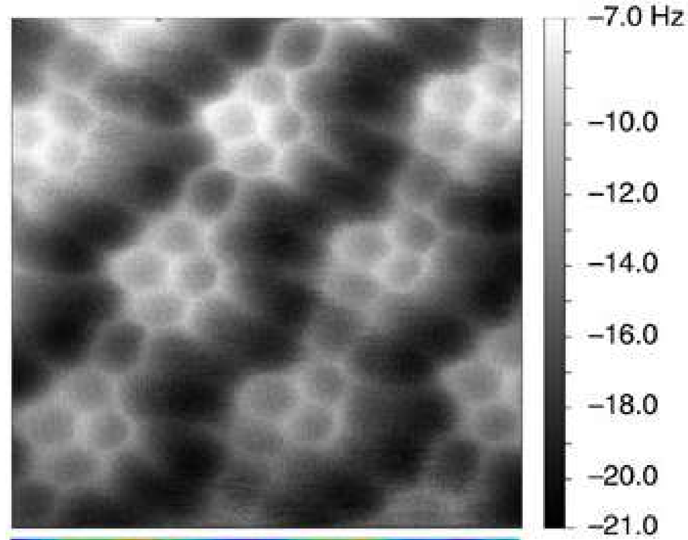


- Tip touching surface
- Interaction force is repulsive (10^{-8} - 10^{-6}N)

- >10nm above surface, no contact
- Cantilever set into vibration
- Detect changes in the resonant frequency of cantilever
- Feedback control of height


2.702nm
0
1.0µm
2.0µm
1.0µm
2.0µm
0




−7.0 Hz
−10.0
−12.0
−14.0
−16.0
−18.0
−20.0
−21.0