Transmission Electron Microscopy
I. Introduction

EMA 6518

- Instructors:

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- Time: Mon 2:00-4:00pm
- Location: MME conference room
- Office hours: by appointment
- Prerequisite: EMA 5507

- Reference:

  Transmission Electron Microscopy

  I: Basics

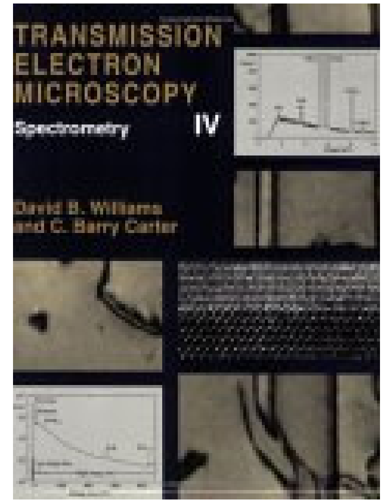
  II: Diffraction

  III: Imaging

  IV: Spectrometry

  by D.B.Williams and C.B.Carter

  Plenum Press, New York and London, 1996



- Grading:
  - ✓ 1 Written exam: 20%
  - ✓ Lab: 30%
  - ✓ Homework: 20%
  - ✓ Report & presentation: 30%

Extremely expensive equipment!

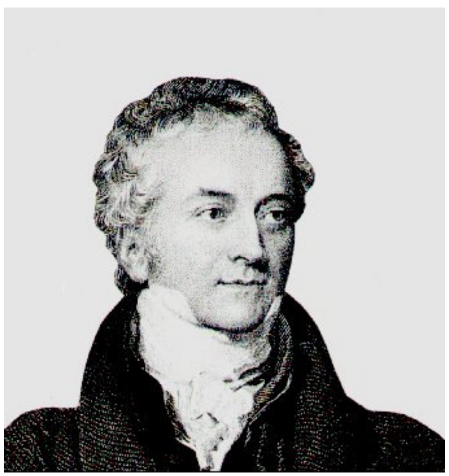
- A typical commercial TEM costs about $2 (up to $4-5) for each electron volt of energy in the beam.
- Beam energy of a TEM: 100,000-40,000 eV

?

- Why use electrons?
- Why you need TEM to characterize materials?
- Advantages and Drawbacks?

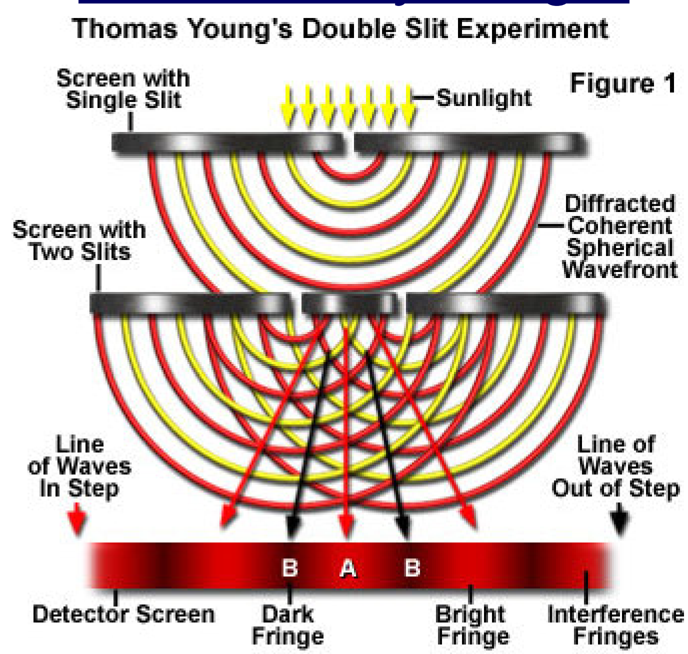
Brief History

- In 1801, Thomas Young passed a beam of light through two parallel slits in an opaque screen, forming a pattern of alternating light and dark bands on a white surface beyond. This led Young to reason that light was composed of waves.



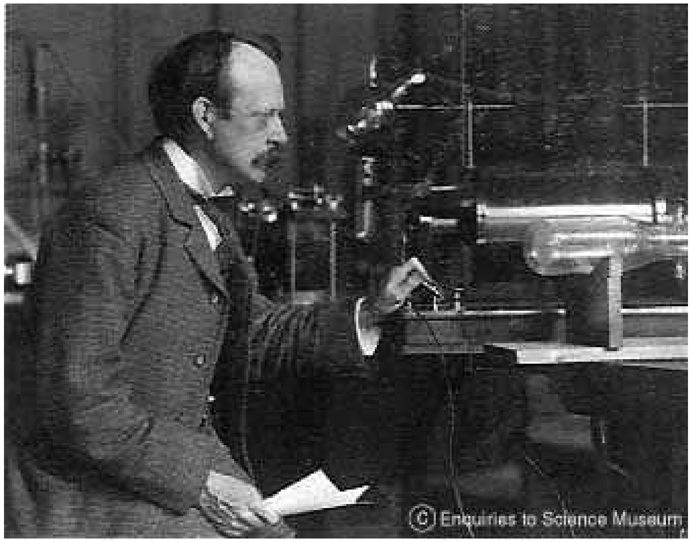
Thomas Young (1773-1829)

wave theory of light



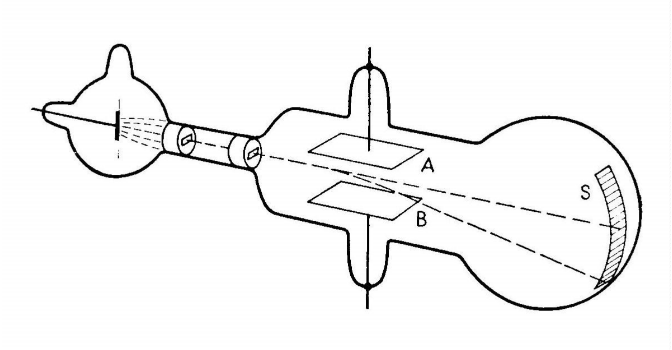
Brief History

- In 1897, J.J.Thomson discovered “corpuscles”, small particles with a charge/mass ratio more than 1000 times greater than that of protons, swarming in a see of positive charge (“plum pudding model”).



Sir Joseph John Thomson
(1856-1940)
Nobel prize 1906

Discovery of the ELECTRON



Thomson’s 2nd Cathode ray experiment

Brief History

- In 1924, Louis de Broglie first theorized that the electron had wave-like characteristics. Application of the idea of particle – wave dualism (only known for photons up to then) for any kind of matter. (first person to receive a Nobel Prize on a PhD thesis)

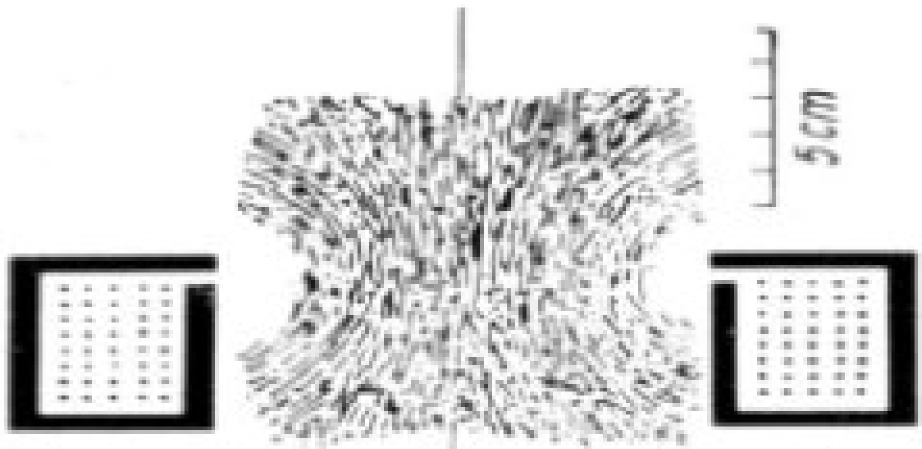
Louis Victor de Broglie (1892-1987)
Nobel prize 1929

Electron=Particle & Wave

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Brief History

- In 1926, Hans Busch discovered that magnetic fields could act as lenses by causing electron beams to converge to a focus (electron lens).



Electrons are focused by a short magnetic coil

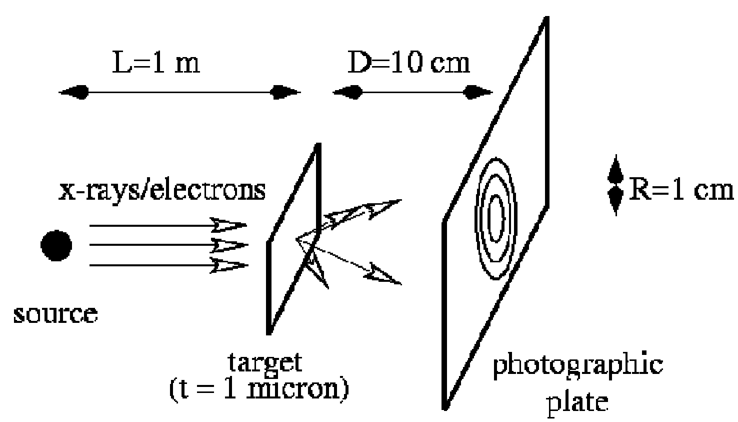
$$\frac{1}{d_{object}} + \frac{1}{d_{image}} = \frac{1}{f} \qquad M = \frac{d_{image}}{d_{object}}$$

Brief History

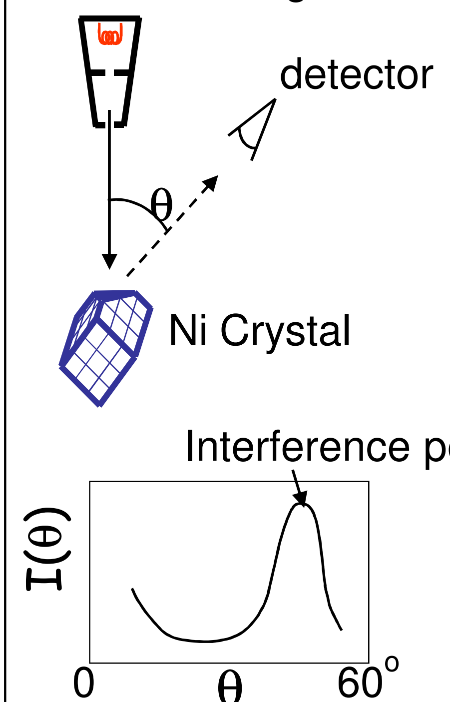
- In 1927, Davisson and Germer, Thomson and Reid, independently carried out their classic electron diffraction experiments (demonstration of wave nature of electrons)

Sir George Paget Thomson
(1892 – 1975)
Nobel Prize: 1937
(shared with C.J. Davison)

Electron=Wave



GP Thomson Experimental Apparatus and Results



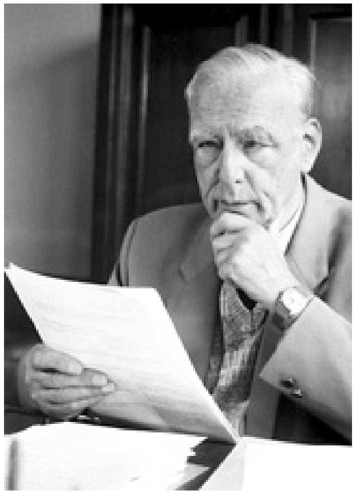
Davisson-Germer experiment

Brief History

- In 1931, Knoll (inventor of SEM, 1935) and Ruska co-invent electron microscope and demonstrated electron images.

Knoll and Ruska co-invent electron microscope

Max Knoll
(1897-1969)



Ernst Ruska
(1906-1988)
Nobel Prize 1986

Brief History

- 1938: M. von Ardenne: 1st STEM
- 1936: the Metropolitan Vickers EM1, first commerical TEM, UK
  - 1939z: regular production, Siemens and Halske, Germany
  - After World War II: Hitachi, JEOL, Philips, RCA, etc
- 1945: 1nm resolution
- 1949: Heidenreich first thinned metal foils to electron transparency
- Cambridge group developed the theory of electron diffraction contrast
- Thomas pioneered the practical applications of the TEM for the solution of materials problems (1962)
- ……

Microscope

- Bright-field microscope
- Dark-field microscope
- Phase-contrast microscope
- Fluorescence microscope

•≥2 optical lenses

•Resolution: wavelength of light

UV, violet, or blue light

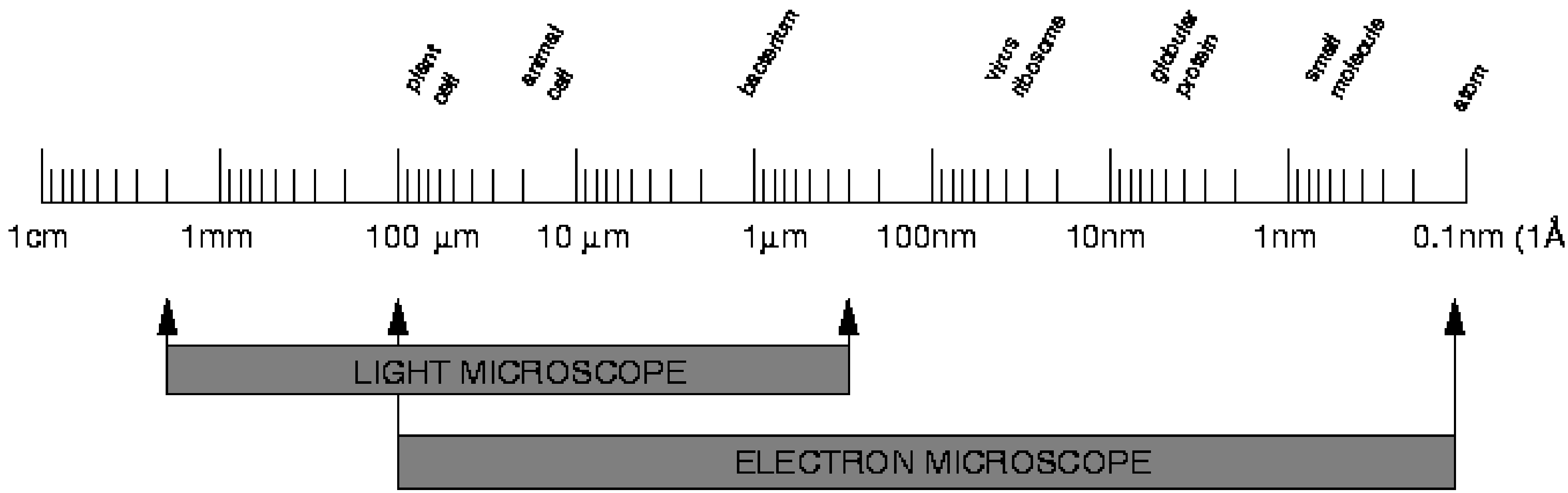
- Confocal microscope → laser

- Scanning Electron Microscope (SEM)
- Transmission Electron Microscope (TEM)

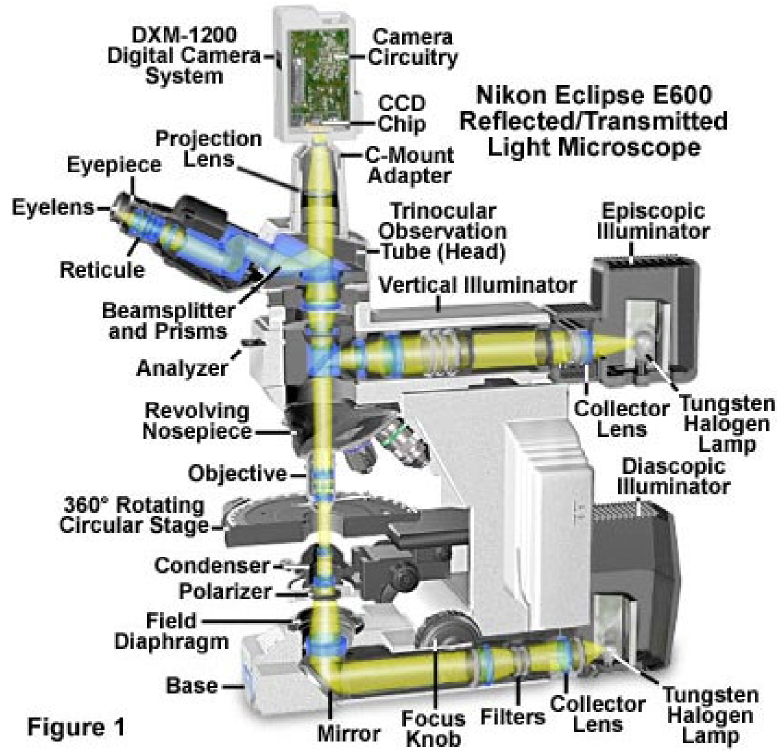
Electron beam

- Scanning Probe Microscope (SPM):
  - Atomic force microscope (AFM) → Constant distance
  - Scanning tunneling microscope (STM) → Constant current

Optical vs. Electron Microscopy



Optical vs. Electron Microscopy



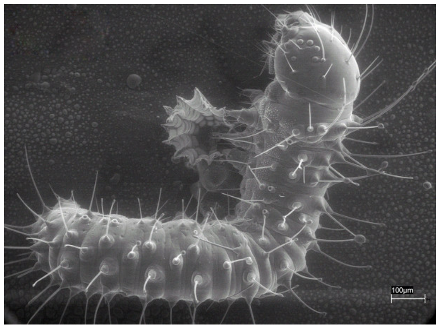
First Place, Nikon's Small World 1995 Competition, Christian Gautier, Larva of Pleuronectidae (20x), Rheinberg Illumination and Polarized Light

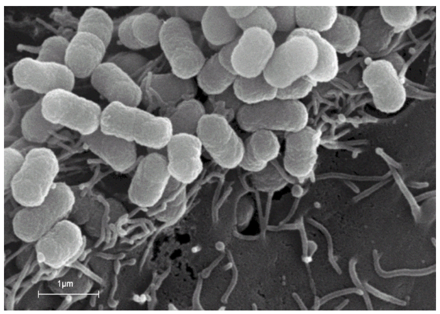
First Place Winner, Nikon's Small World 2005 Competition, Charles B. Krebs, Muscoid fly (house fly) (6.25x) Reflected light

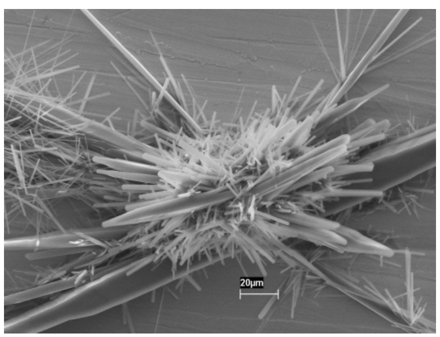
- Easy to use
- Samples in air or water
- Total magnification: ×100-1000
 product of the magnifications of the ocular lens and the objective lens
- Image processing by CCD

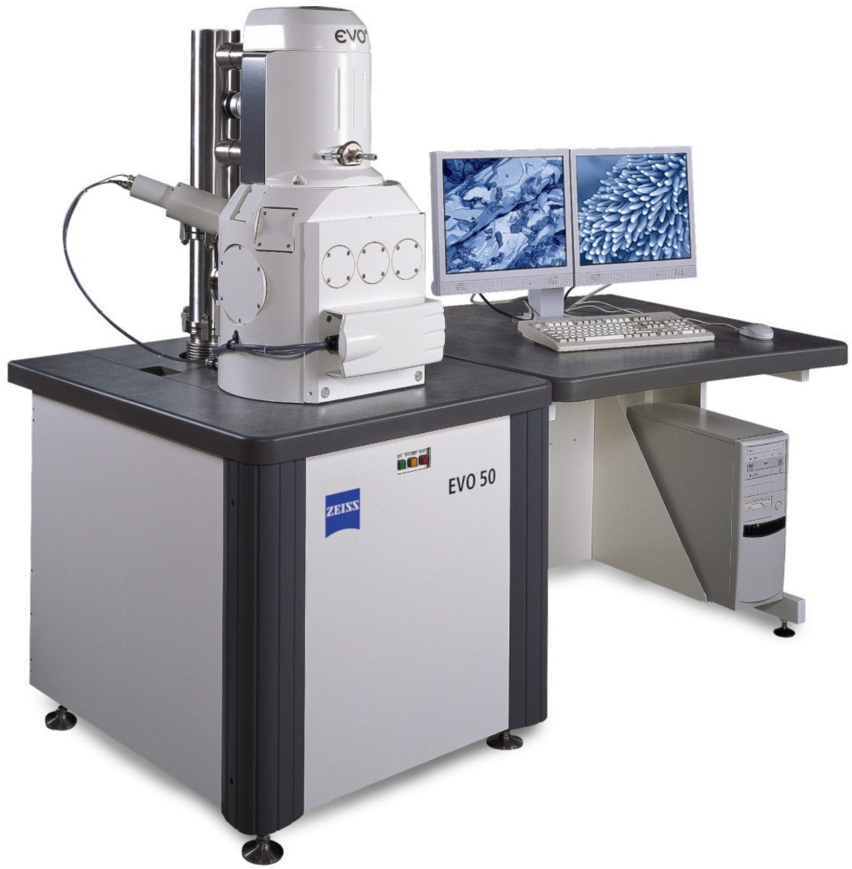
http://www.microscopyu.com/articles/optics/components.html

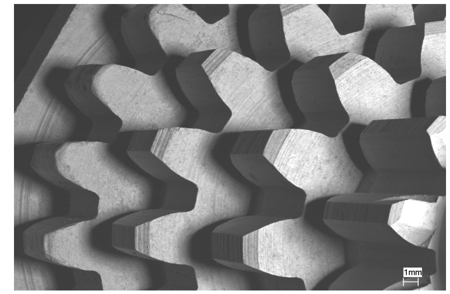
Optical vs. Electron Microscopy

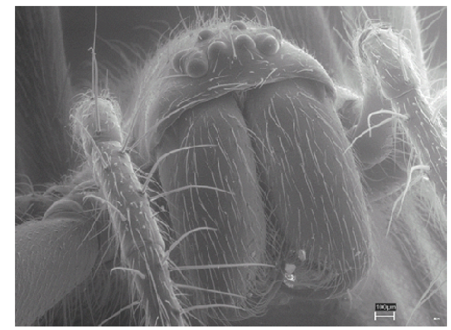


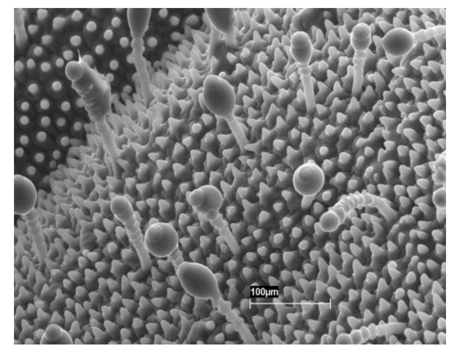




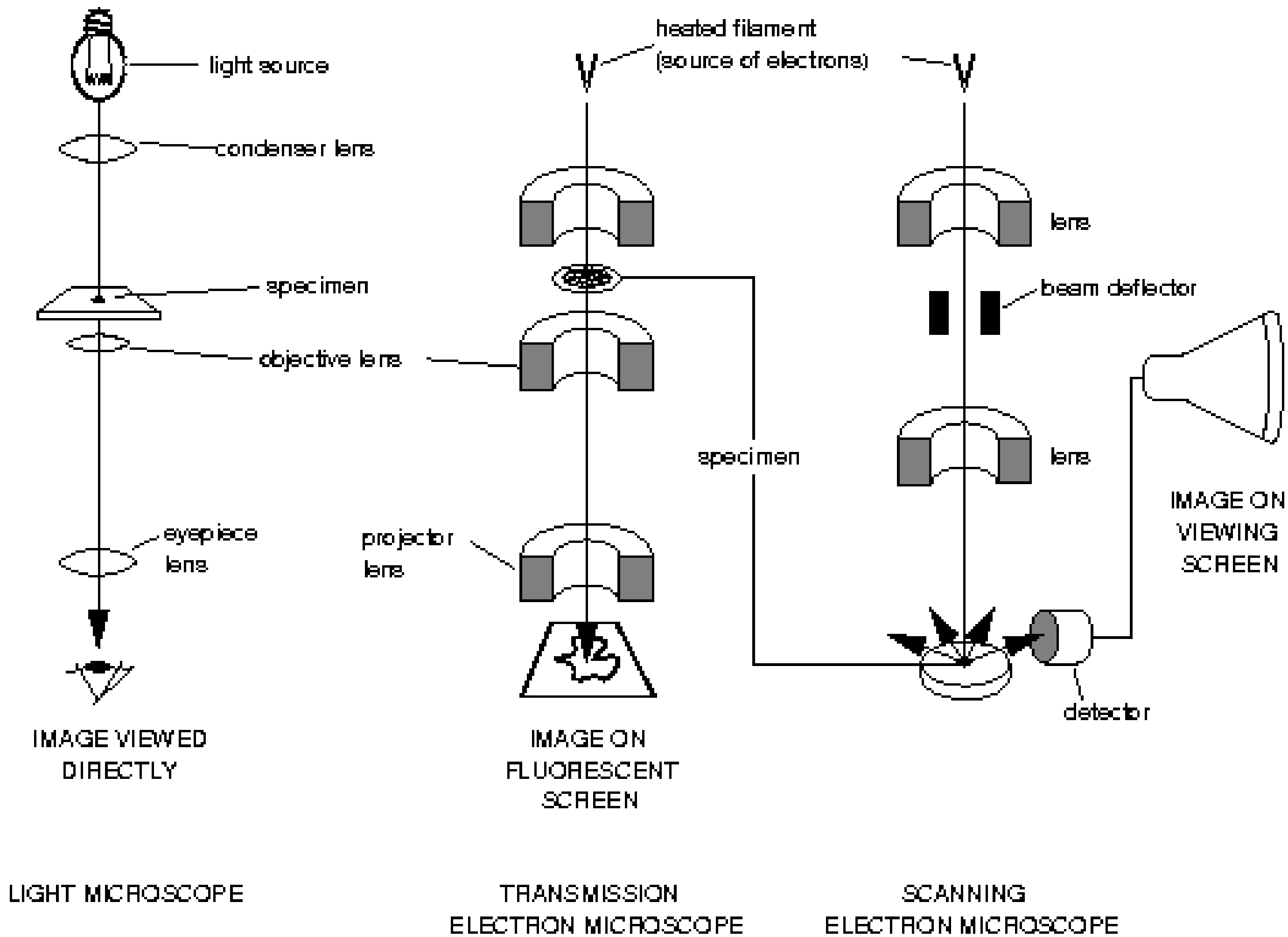




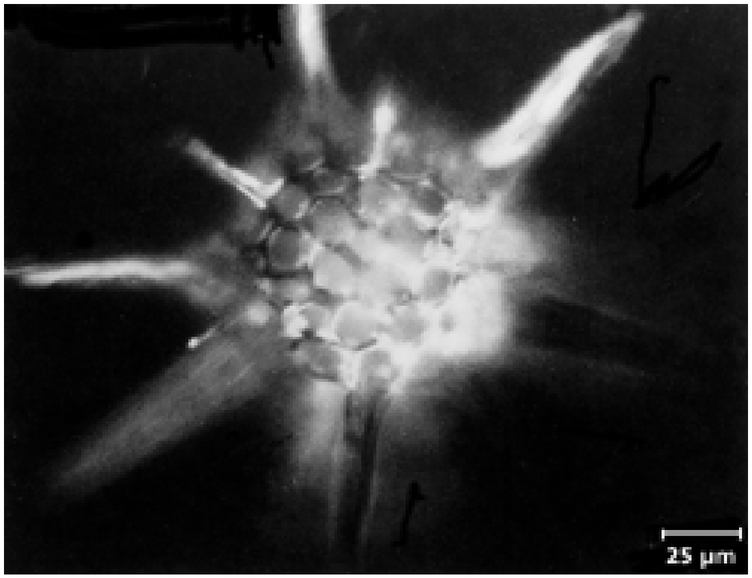




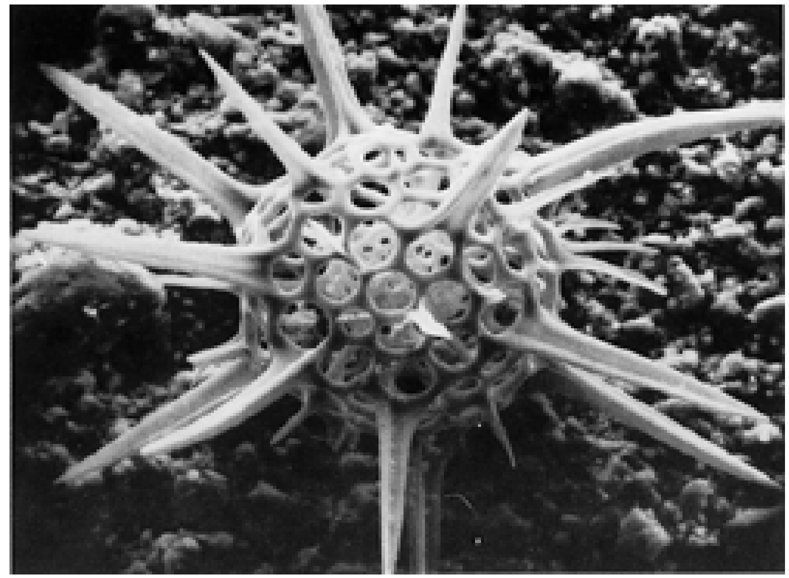
Optical vs. Electron Microscopy



Optical vs. Electron Microscopy



(a)



(b)

(a) Optical micrograph of the radiolarian *Trochodiscus longispinus (Skelton of a small marine orgnism)*. (b) SEM micrograph of same radiolarian. (Taken from J.I. Goldstein et al., eds., Scanning Electron Microscopy and X-Ray Microanalysis, (Plenum Press,NY,1980).)

Optical vs. Electron Microscopy

Why electrons?

- Resolution
- Depth of Focus

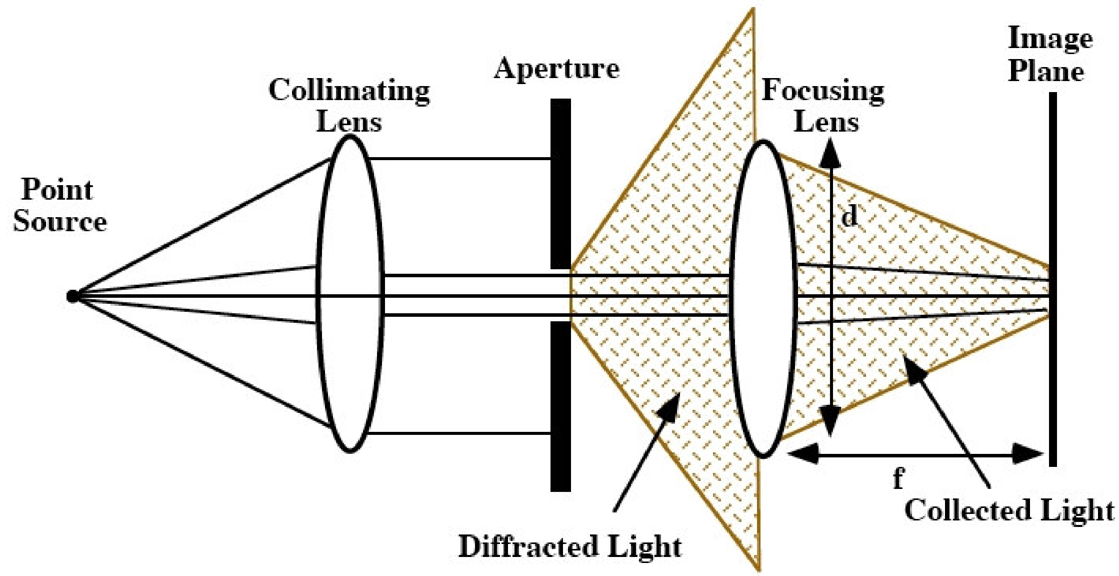
Resolution:

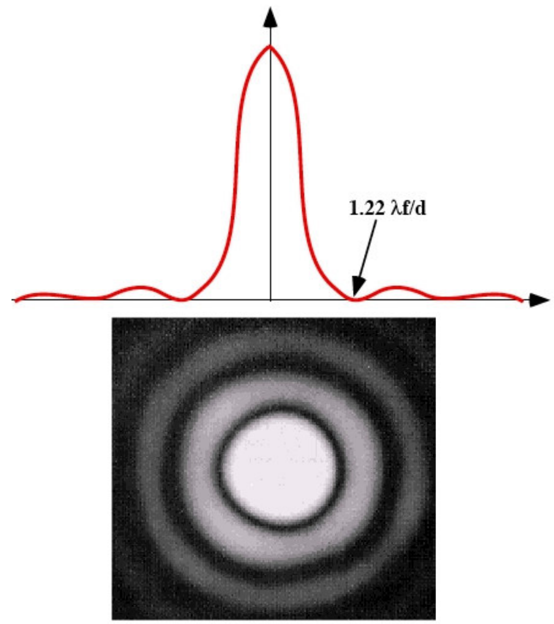
- ❑ Our eyes: 0.1-0.2 mm
- ❑ Optical microscope: 400-700nm, resolution?
- ❑ Electron microscope:100-1000 keV, resolution?

"The best possible resolution that can be resolved with a light microscope is about 2,000 Angstroms" --Slayter, Elizabeth. Microscope. *Grolier Multimedia Encyclopedia Online*. Grolier, 1998.

Diffraction

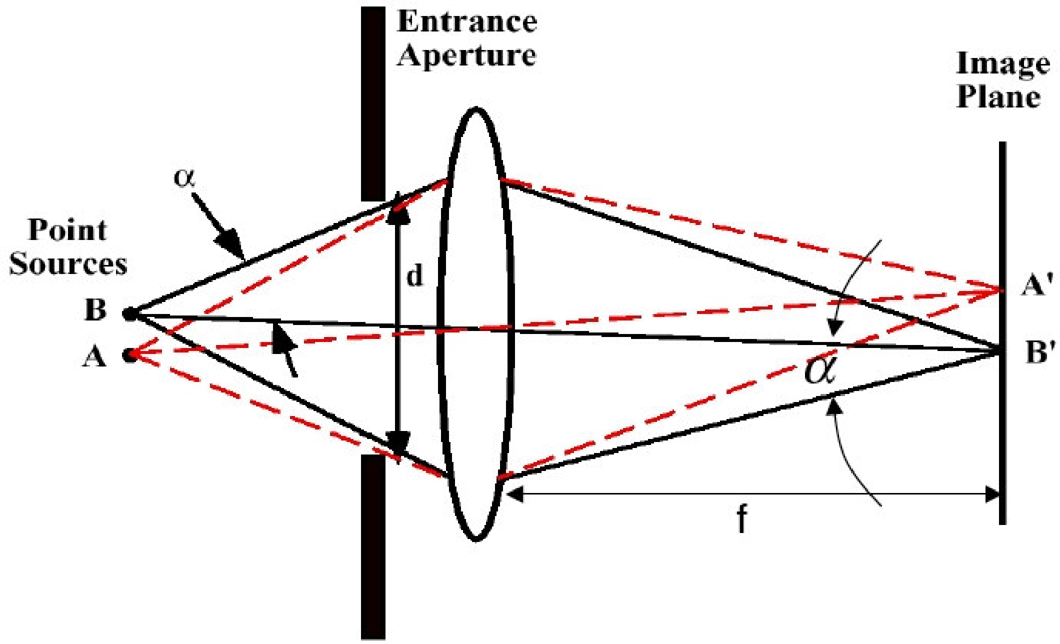
- Image formed by a small circular aperture (Airy disk) as an example
- Image by a point source forms a circle with diameter 1.22λf/d surrounded by diffraction rings (airy pattern)
- Diffraction is usually described in terms of two limiting cases:
  - ✓Fresnel diffraction - near field.
  - ✓Fraunhofer diffraction - far field.





Rayleigh resolution

- Rayleigh suggested that a reasonable criterion for resolution (R = distance between A and B) is that the central maximum of one point source lies at the first minimum of the Airy pattern of the other point (R = diameter of circle)



Rayleigh resolution

- The numerical aperture (NA) of a lens represents the ability of the lens to collect diffracted light and is given by NA = n sin α in this expression *n* is the index of refraction of the medium surrounding the lens and a is the acceptance angle of the lens (*n* = 1 for air)

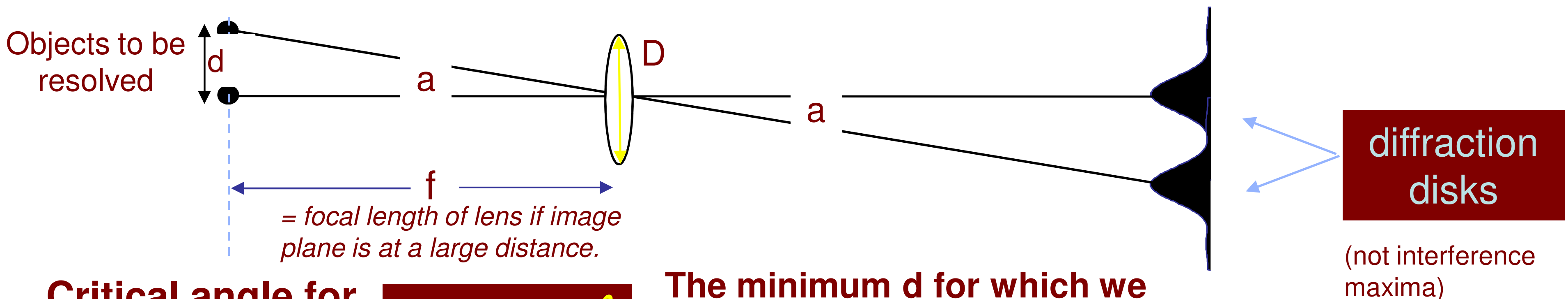
$$\mathbf{R=}\ \frac{1.22\,\lambda f}{d} = \frac{1.22\,\lambda f}{n(2f\sin\alpha)} = \frac{0.61\,\lambda}{n\sin\alpha} = \frac{0.61\,\lambda}{NA}$$

$$\text{Rayleigh resolution: } R = \frac{0.61\lambda}{NA}$$

$$\text{Practical resolution: } R = k_1\frac{\lambda}{NA} \quad \text{where } 0.6 < k_1 < 0.8$$

Why electrons?

- The ability to “resolve” tiny objects improves as the wavelength decreases. Consider the microscope objective:



Critical angle for resolution:

$$\alpha_c = 1.22\frac{\lambda}{D}$$

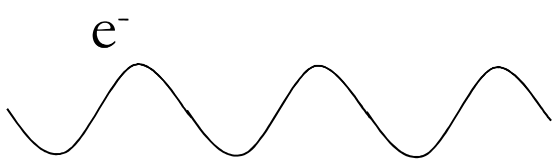
The minimum d for which we can still resolve two objects is a_c times the focal length:

$$d_{min} \approx f\alpha_c = 1.22\lambda\frac{f}{D}$$

A good microscope objective has f/D ≅ 2, so with λ~ 500 nm the optical microscope has a resolution of $d_{min} \cong$ 1 μm.

Why electrons?

❑Resolution of Electron microscope: ?



- Wave Behaviors
  - images and diffraction patterns
  - wavelength can be tuned by energies

- Charged Particle Behaviors
  - strong electron-specimen interactions
  - chemical analysis is possible

Light

- $p = h/\lambda$ (matter also)
- $p = E/c$
- $E = hf = hc/\lambda$

Matter

- $p = h/\lambda$ (light also)
- $p = \sqrt{2mE}$
- $E = h^2/2m\lambda^2$

h: planck's constant

$$h = 6.626\ 0693(11) \times 10^{-34}\ \mathrm{J \cdot s}$$

$$h = 4.135\ 667\ 43(35) \times 10^{-15}\ \mathrm{eV \cdot s.}$$

$h = 4.135\ 667\ 43(35) \times 10^{-}$ s.

Wavelength of an Electron

- The DeBroglie wavelength of an electron:

$$\lambda = h/p$$

- the relation between the electron's wavelength and its kinetic energy E.

p and E are related through the classical formula:

$$E = \frac{p^2}{2m} \qquad m_e = 9.11\times10^{-31}\,\text{kg}$$

$$E = \frac{h^2}{2m\lambda^2} \qquad h = 4.14\times10^{-15}\,\text{eV}\cdot\text{s}$$

For $m = m_e$:
(electrons)

$$E = \frac{1.505\, eV\cdot nm^2}{\lambda^2}$$

E in electron volts

λ in nanometers

Don't confuse with $E_{photon} = \frac{1240\, eV\cdot nm}{\lambda}$ for a photon !

Why electrons?

- For a 100 keV electron:

  λ ~0.004nm (4pm)

- BUT nowhere near building TEMs that approach this wavelength limit of resolution, because we can't make perfect electron lenses.
- HRTEM
- HVEM: 1-3 MV (1960s)

  300-400 kV (1980s), very high resolution close to that achieved at 1 MV

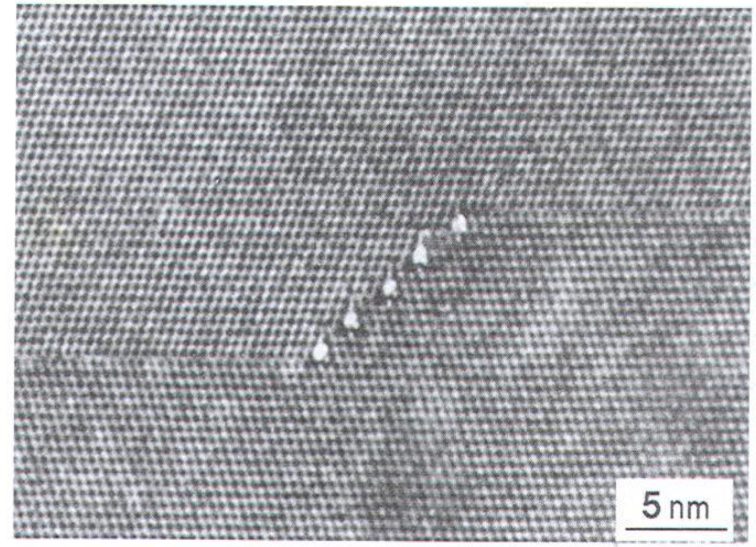
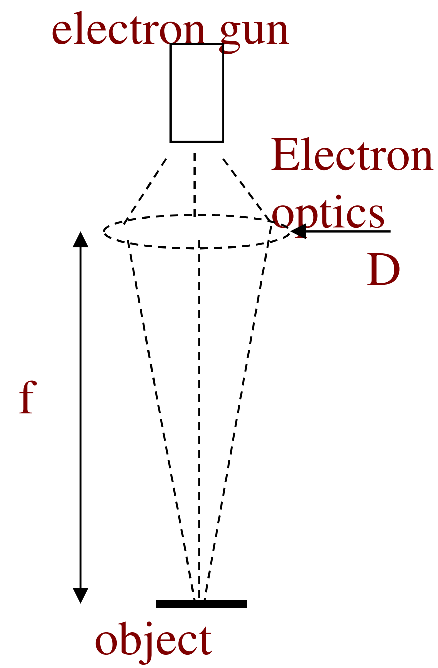


Figure 1.2. A twin boundary in spinel stepping from one {111} plane to another parallel plane. The white dots are columns of atoms. The change in atomic orientation across the twin boundary can be readily seen, even if we do not know what causes the white dots or why, indeed, they are white.

Imaging a Virus*

- You wish to observe a virus with a diameter of 20 nm, which is much too small to observe with an optical microscope. Calculate the voltage required to produce an electron DeBroglie wavelength suitable for studying this virus with a resolution of $d_{min} = 2$ nm. The "f-number" for an electron microscope is quite large: $f/D \approx 100$.



Solution

$$d_{min} \approx 1.22\lambda \frac{f}{D}$$

$$\lambda \approx d_{min}\left(\frac{D}{1.22f}\right) = 2nm\left(\frac{D}{1.22f}\right) = 0.0164\,nm$$

$$E = \frac{h^2}{2m\lambda^2} = \frac{1.505\,eV \cdot nm^2}{(0.0164\,nm)^2} = 5.6\,keV$$

To accelerate an electron to an energy of 5.6 keV requires 5.6 kilovolts .

Depth of Focus & Depth of Field

- Depth of Field of a microscope is a measure of how much of the *object* we are looking at remains "in focus" at the same time.
- Depth of field is governed by the lenses in the microscope.

Depth of Focus & Depth of Field

- Depth of focus is a lens optics concept that measures the tolerance of placement of the image plane (e.g. film plane in a camera) in relation to the lens.

At *f*/32, background is distracting

Shallow DOF at *f*/5 isolates flowers from the background.

$$\mathrm{DOF} = k_2\,\lambda\,/(\mathrm{NA})^2$$

- The very small angular aperture of the electron probe forming system permits a large depth of field all in focus at once.

Depth of Focus & Depth of Field

• We have to use very small limiting apertures in the lenses, narrowing the beam down to a thin "pencil" of electrons (few micronmeters across).

✓In SEM, to produce 3D-like images

✓In TEM, usually in focus at the same time, independent of the specimen topography (as long as it's electron transparent)

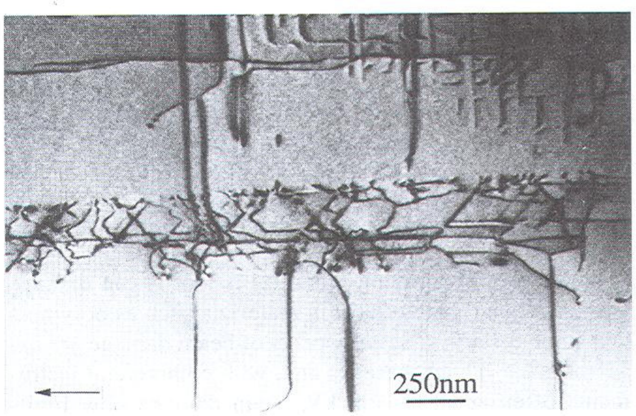


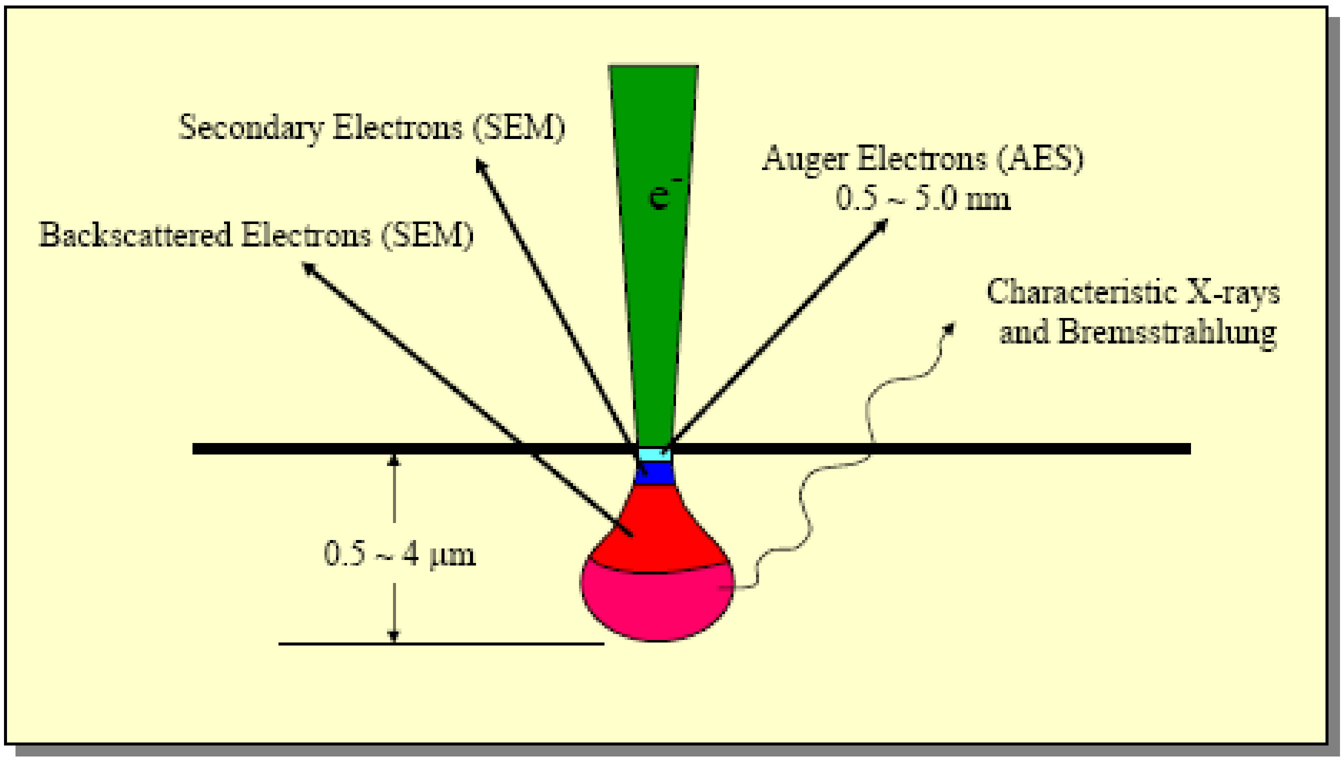
Figure 1.5. TEM image of dislocations in GaAs. A band of dislocations threads through the thin specimen from the top to the bottom but remains in focus through the foil thickness.

"depth of field" refers to the specimen

"depth of focus" refers to the image

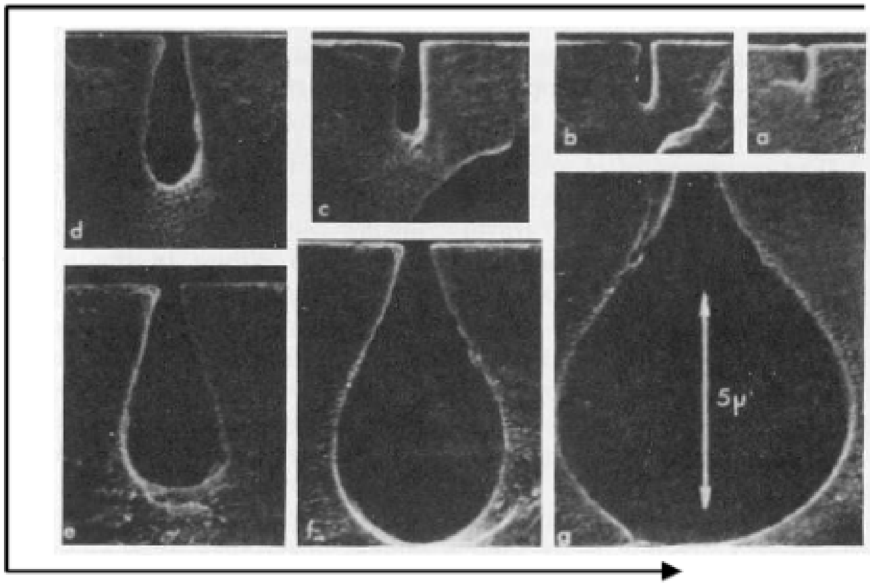
Interaction of high energy (~kV) electrons with (solid) materials

Interaction with a thick specimen (SEM)



Electron Beam-Specimen Interactions

----------------Visualizing the interaction volume



- Polymethylmethacrylate (PMMA)
- e-beam: 20 keV, ~ 0.5μm

•The interaction volume can be observed in certain plastic materials such as PMMA

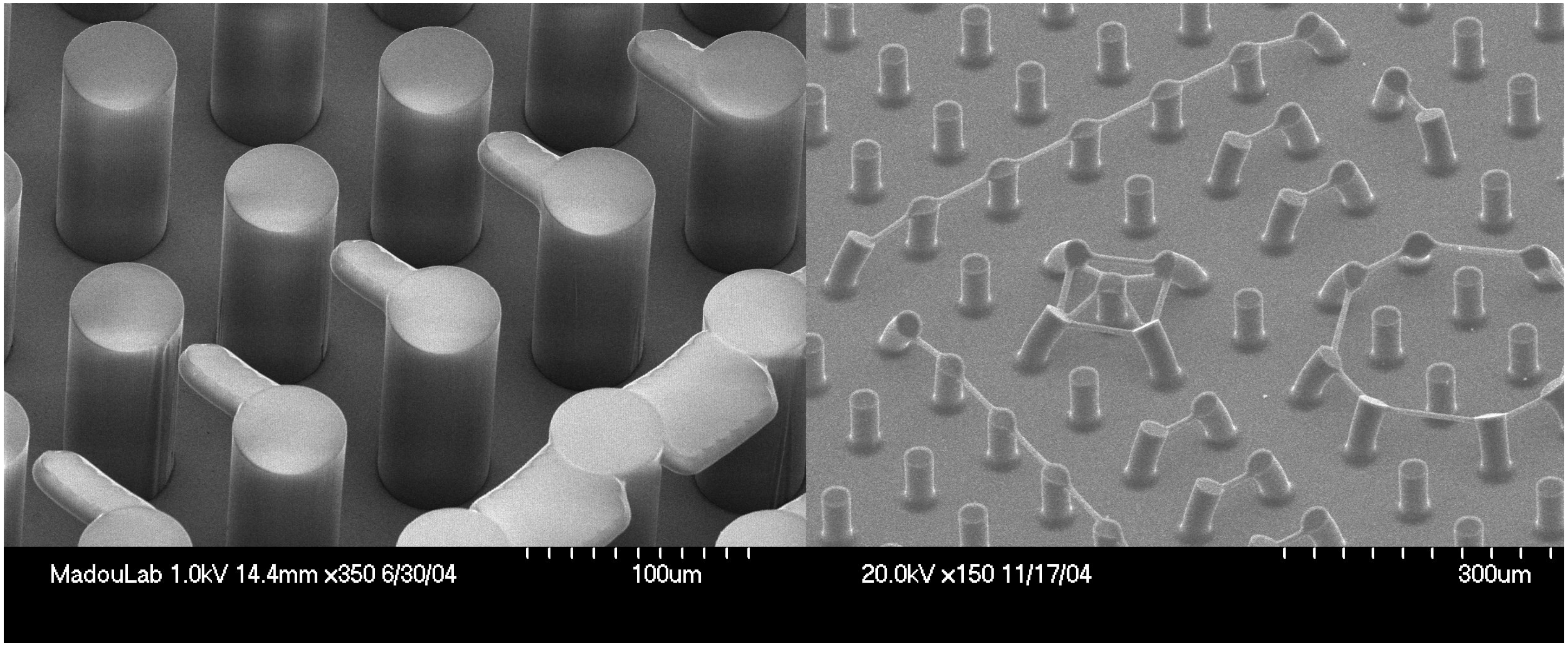
•Undergo Molecular bonding damage during electron bombardment that renders the material sensitive to etching in a suitable solvent

•This phenomenon is the basis for EB lithography

(Everhart et al., Proc. 6th Intl. Conf. on X-ray Optics and Microanalysis)

Electron Beam-Specimen Interactions

- EB lithography



Kartikeya Malladi, Chunlei Wang, and Marc Madou, “Microfabrication of Suspended C-MEMS structures by EB Writer and Pyrolysis”, Carbon, 44(13), (2006) 2602-2607

kV and keV

- With **kV** is meant the high voltage. If an electron was accelerated in this electrical field with e.g. 20 **kV**, the electron has finally an energy of 20 **keV**.

- for SEM, acceleration voltage is the high voltage applied to the filament. Acceleration voltage ranges from 100V to 70kV (up to 100kV). Low acceleration voltage means <1 kV.

Scanning Electron Microscope

- SEM permits the observation and characterization of heterogeneous organic and inorganic materials on a nm to µm scale.
    - » Imaging capabilities
    - » elemental analysis
- In the SEM, the area to be examined or the microvolume to be analyzed is irradiated with a fine focused electron beam, which may be swept in a raster across the surface of the specimen to form images or maybe static to obtain an analysis at one position.
- The types of signals produced from the interaction of electron beam with the sample include secondary electrons, backscattered electrons, characteristic x-rays, and other photons of various energies.

Interaction of high energy (~kV) electrons with (solid) materials

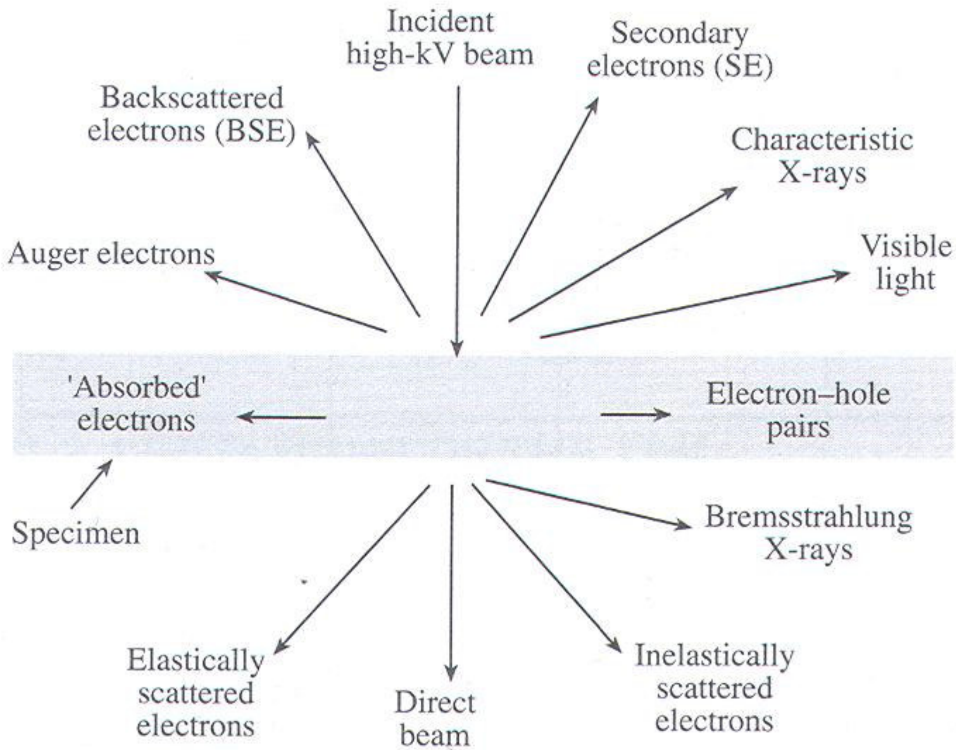


Figure 1.3. Signals generated when a high-energy beam of electrons interacts with a thin specimen. Most of these signals can be detected in different types of TEM. The directions shown for each signal do not always represent the physical direction of the signal but indicate, in a relative manner, where the signal is strongest or where it is detected.

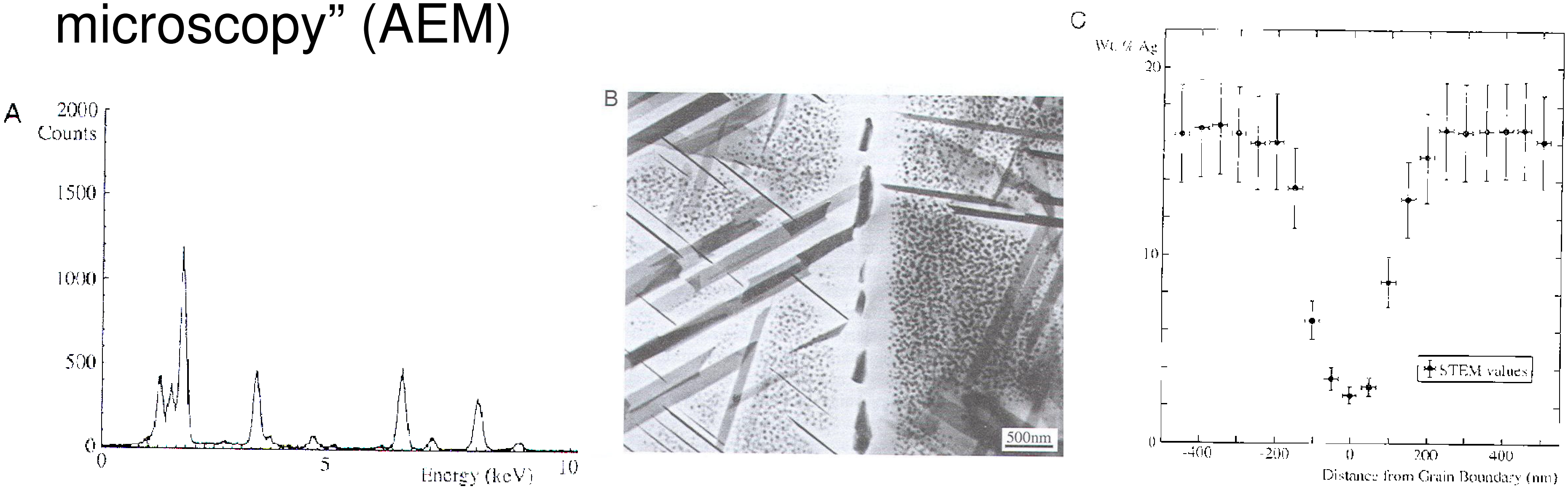
Cathodoluminescence

What is Cathodoluminescence?

- Cathodoluminescence is an optical and electrical phenomenon whereby a beam of electrons is generated by an electron gun and then impacts on a luminescent material such as a phosphor, causing the material to emit visible light. The most common example is the screen of a television.
- Cathodoluminescence occurs because the impingement of a high energy electron beam onto a semiconductor will result in the promotion of electrons from the valence band into the conduction band, leaving behind a hole. When an electron and a hole recombine, it is possible for a photon to be emitted. The energy (color) of the photon, and the probability that a photon and not a phonon will be emitted, depends on the material, its purity, and its defect state. In this case, the "semiconductor" examined can, in fact, be almost any non-metallic material. In terms of band structure, classical semiconductors, insulators, ceramics, gemstones, minerals, and glasses can be treated the same way.

Interaction of Electrons with Matter

- Electrons are one type of “ionizing radiation”---capable of removing one of the tightly bound inner-shell electrons from the attractive field of the nucleus.
- “Ionizing radiation” produces many of the secondary signals from the specimen are used in “analytical electron microscopy” (AEM)

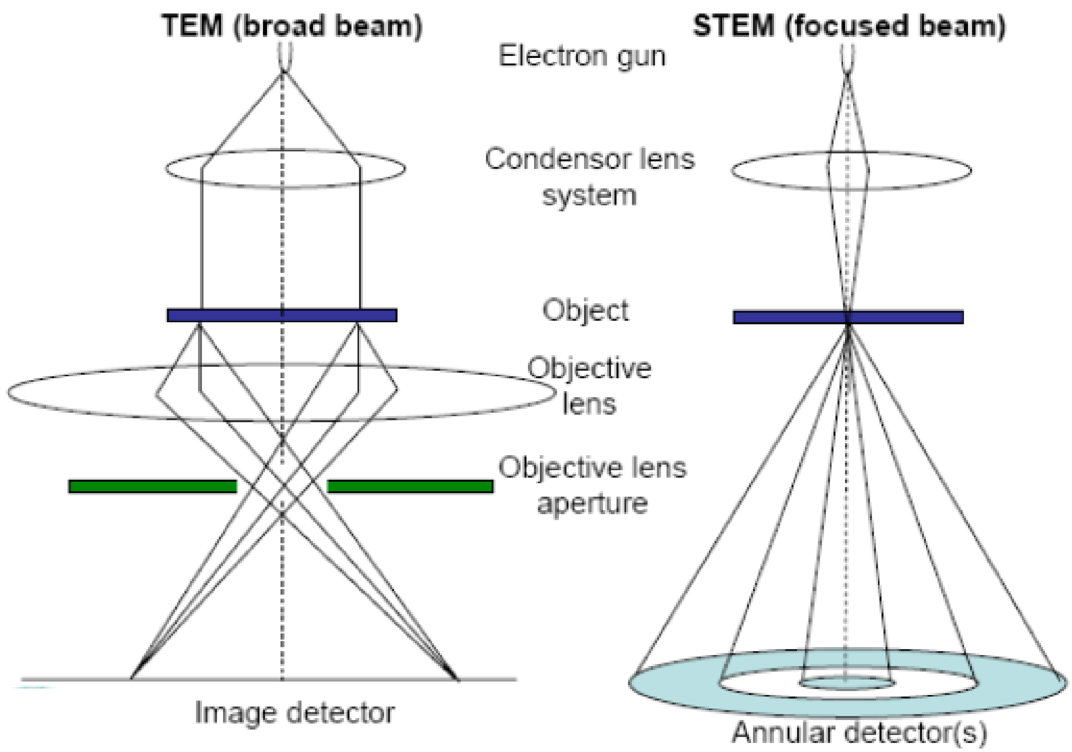


Abbreviations

- HEED: high energy electron diffraction
- LEEM: low energy electron microscope (many variations with special names)
- EELS: electron energy loss spectroscopy
- EDXS: energy dispersive X-ray spectroscopy
- SEM: scanning electron microscope (electrons do NOT normally transmit the sample)

Interaction of Electrons with Matter

- Modern TEMs are very good signal-generating instruments.
- Electron beam: typically <10 nm and at best <1nm
- Combining TEM and SEM ⟶ STEM



Diffraction

• Electron diffraction is an indispensable part of TEM and is the most useful aspect of TEM for materials scientists.

- Crystal structure, lattice repeat distance, specimen shape, point-group and space-group determination, etc.

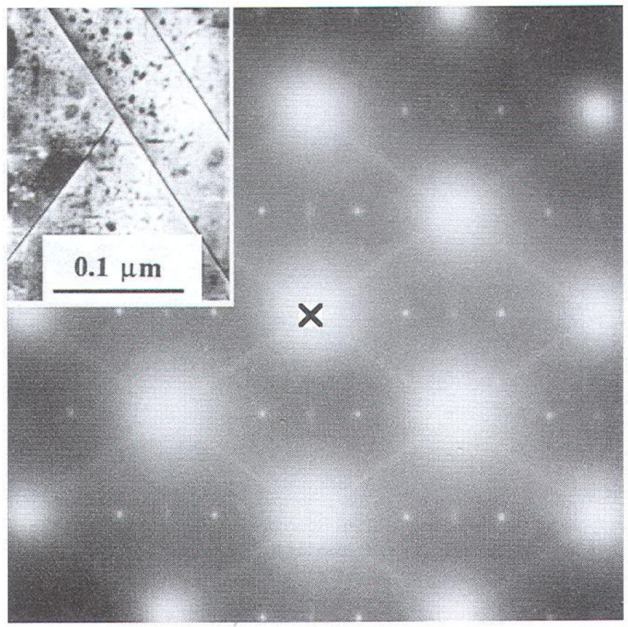
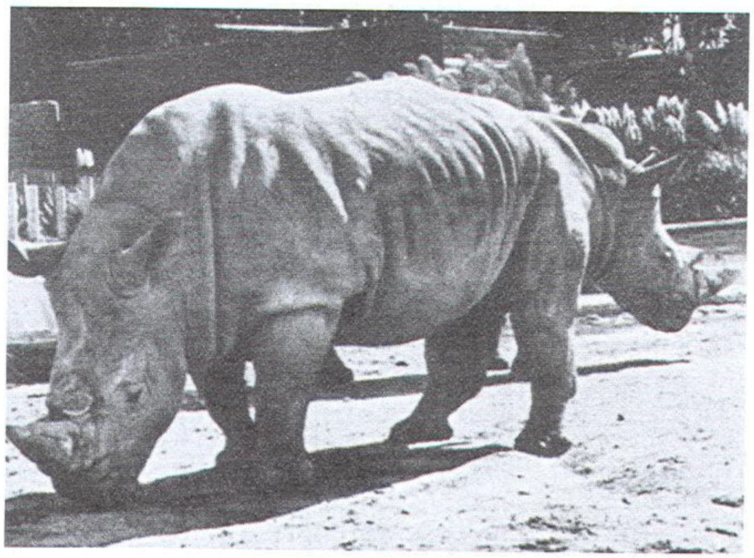
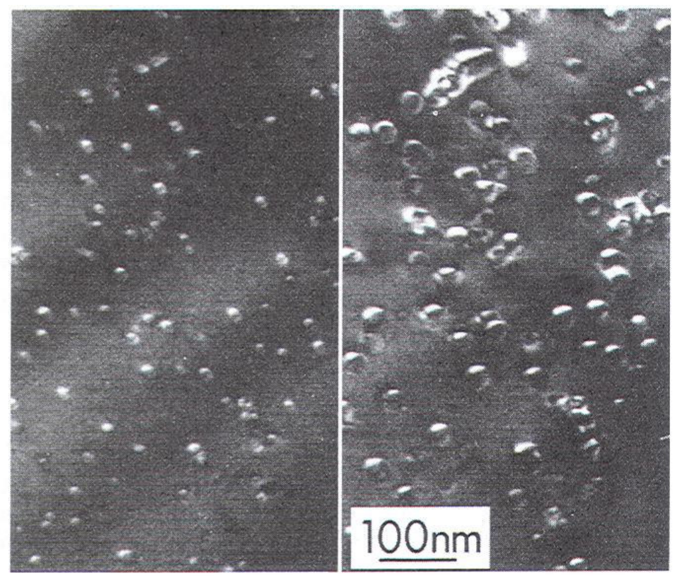


Figure 1.6. TEM diffraction pattern from a thin foil of Al-Li-Cu containing various precipitate phases, shown in the inset image. The central spot (X) contains electrons that come directly through the foil and the other spots and lines are diffracted electrons which are scattered from different crystal planes.

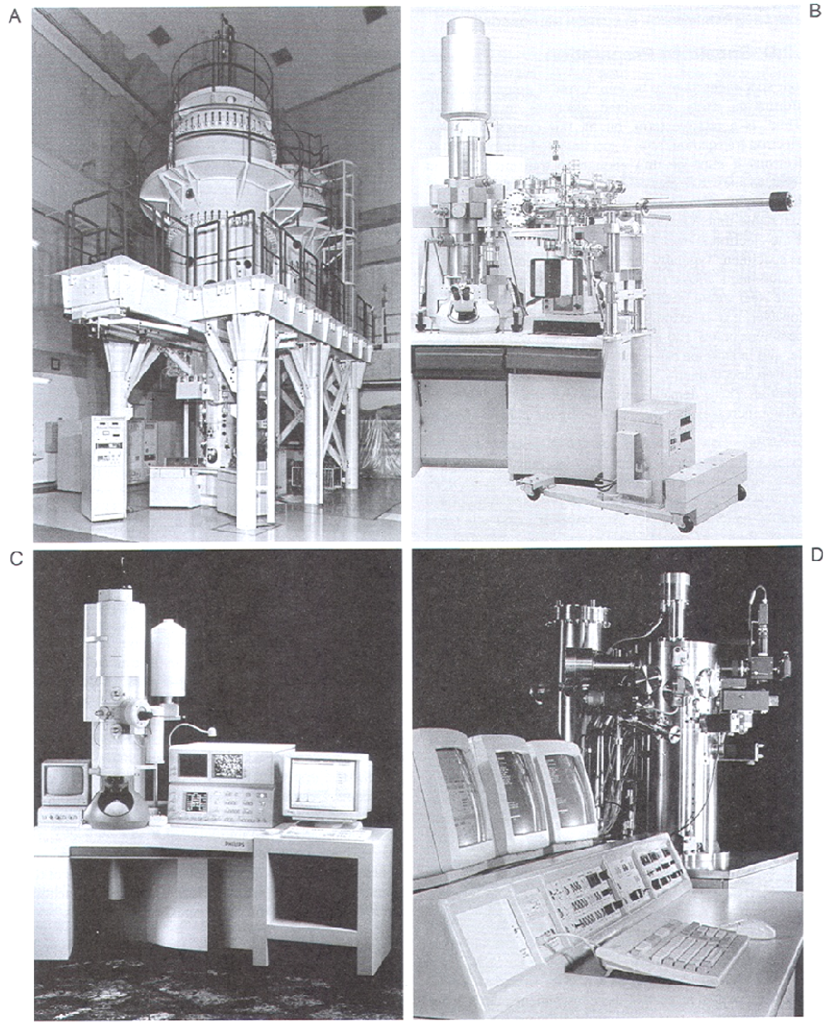
Limitations of the TEM

• Sampling---0.3mm^3 of materials
• Interpreting transmission images---2D images of 3D specimens, viewed in transmission, no depth-sensitivity.
• Electron beam damage and safety---particularly in polymer and ceramics
• Specimen preparation---"thin" below 100nm





Different Kinds of TEMs



A wide variety of types:

- HRTEMs
- HVEMs
- IVEMs (intermediate high voltage electron microscopes,400kV)
- STEMs
- AEMs

Some Fundamental Properties of Electrons

- Typical electron beam current in a TEM is 0.1-1μA, which corresponds to 10^{12} electrons passing through the specimen plane.

- With 100-keV engery, these electrons travel at about 0.5c (1.6×10^{8} m/s), so they are separated by 0.16 cm and this means that there is never more than one electron in the specimen at any one time.

- Electron diffraction and interference occur, both of which are wave phenomena, and imply interaction between the different electron beams.

Some Fundamental Properties of Electrons

Table 1.1. Fundamental Constants and Definitions

Charge (e)	(−) 1.602×10^{-19} C
1 eV	1.602×10^{-19} J
Rest mass (m_0)	9.109×10^{-31} kg
Rest energy (m_0c^2)	511 keV
Kinetic energy (charge × voltage)	1.602×10^{-19} N m (for 1 volt potential)
Planck's constant (h)	6.626×10^{-34} N m s
1 ampere	1 C/sec
Speed of light in vacuum (c)	2.998×10^{8} m/sec

Some Fundamental Properties of Electrons

Table 1.2. Electron Properties as a Function of Accelerating Voltage

Accelerating voltage (kV)	Nonrelativistic wavelength (nm)	Relativistic wavelength (nm)	Mass ($\times m_0$)	Velocity ($\times 10^8$ m/s)
100	0.00386	0.00370	1.196	1.644
120	0.00352	0.00335	1.235	1.759
200	0.00273	0.00251	1.391	2.086
300	0.00223	0.00197	1.587	2.330
400	0.00193	0.00164	1.783	2.484
1000	0.00122	0.00087	2.957	2.823

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