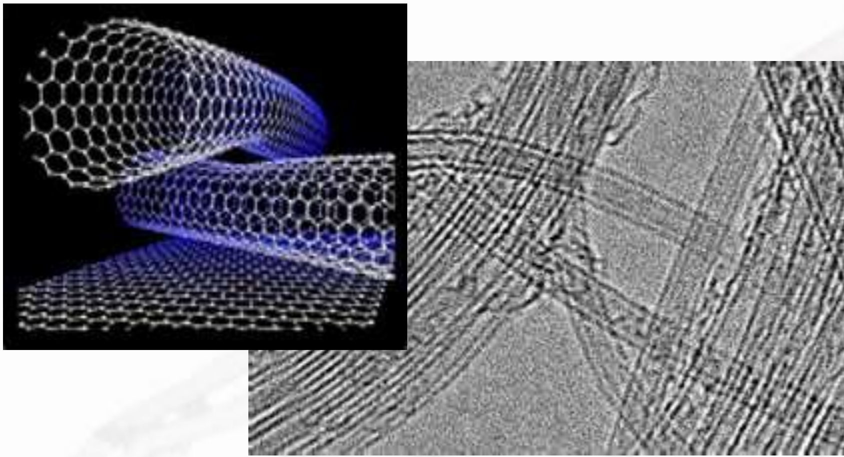
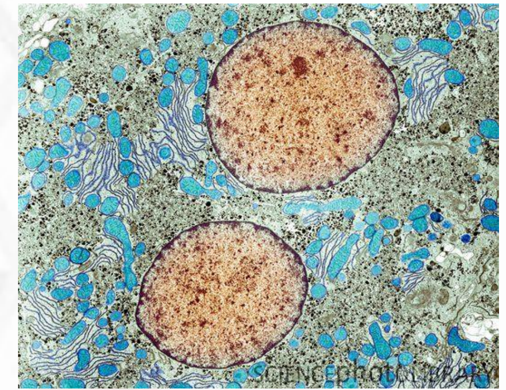
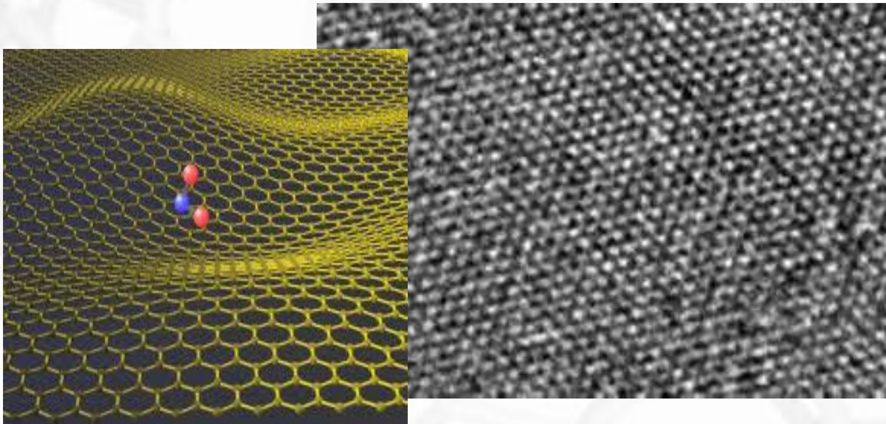


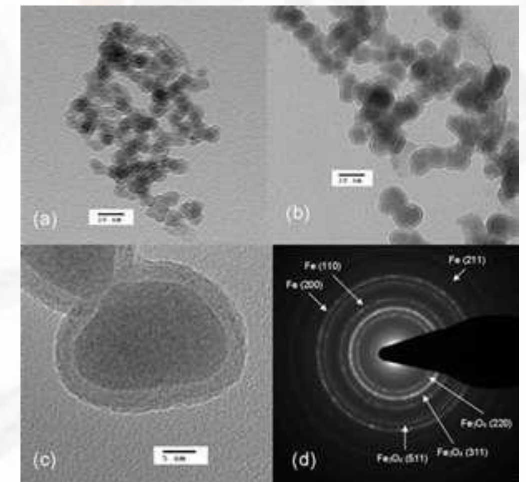


CBE 30361

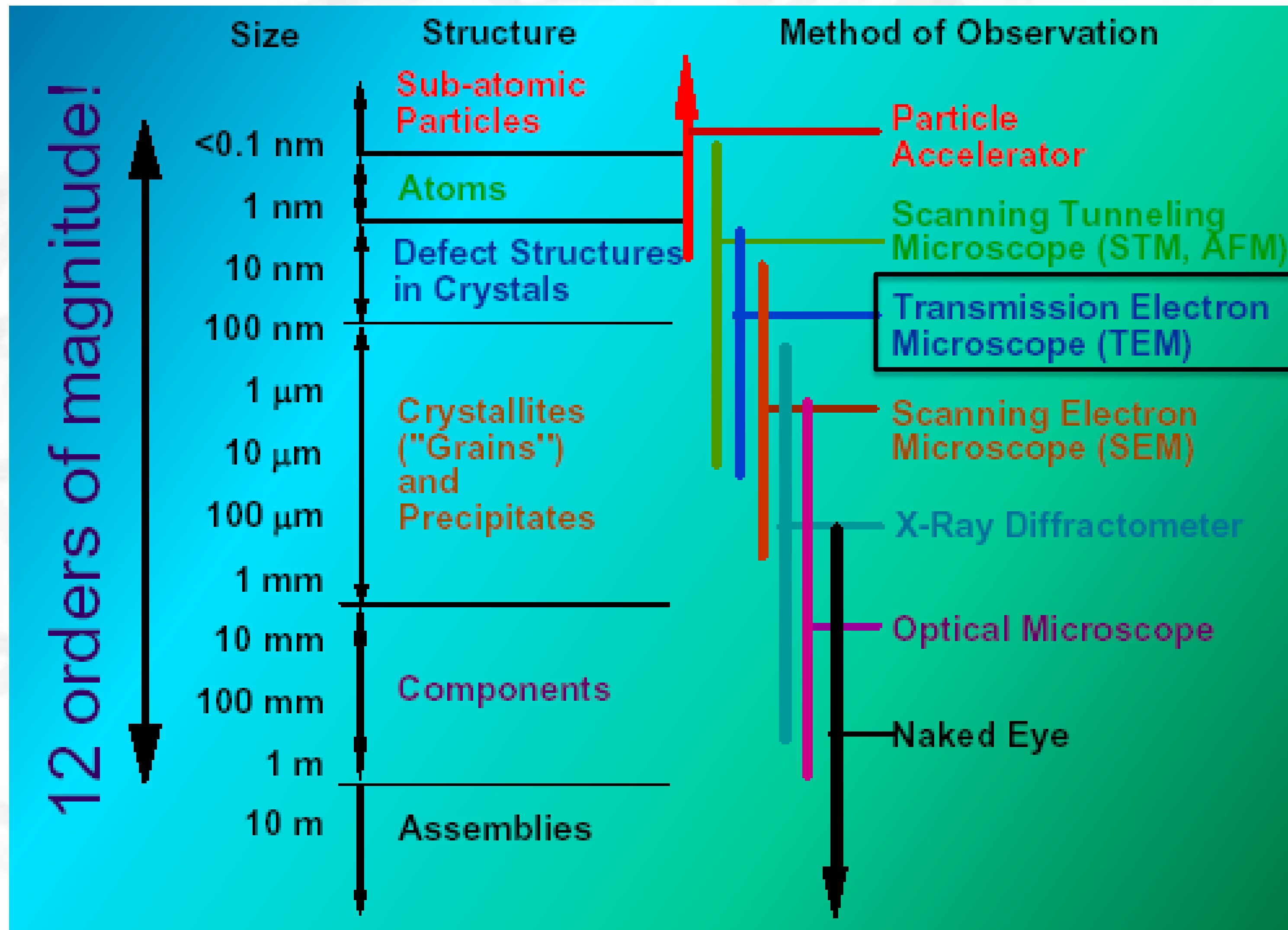
Science of Engineering Materials

Transmission Electron Microscopy (TEM)





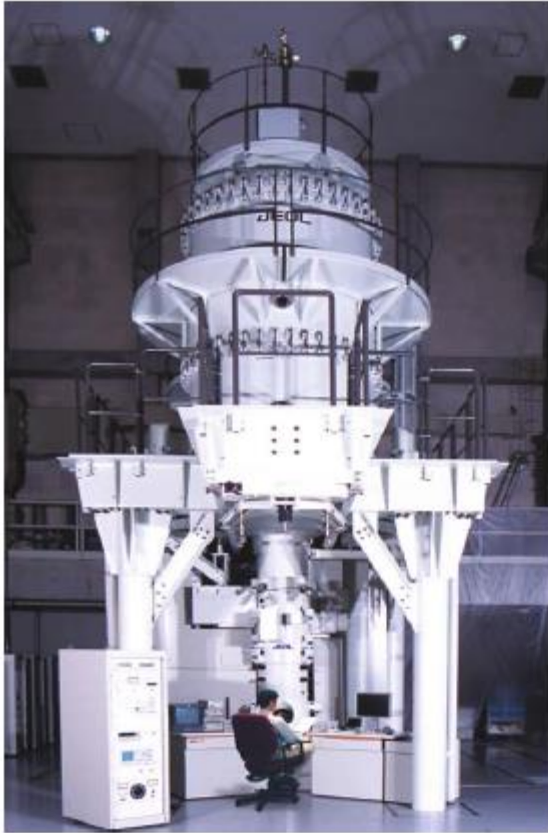
Scale of Structure Organization



Microscopes!

- **1931** **Max Knoll and Ernst Ruska** build first electron microscope
- **1933** Ruska developes an EM with higher resolution than an optical microscope
- **1937** The first scanning electron microscope is built
- **1939** Siemens brings the first commercial EM on the market
- **1965** First commercial SEM (Oatley)

Modern TEMs



- JEM 1.25 MeV HVEM. Note the size of the instrument; often the high-voltage tank is in another room above the column.

Zeiss HRTEM with a Cs corrector and an in-column energy filter. Note the large frame to provide high mechanical stability for the highest-resolution performance.

Why Use Electrons?

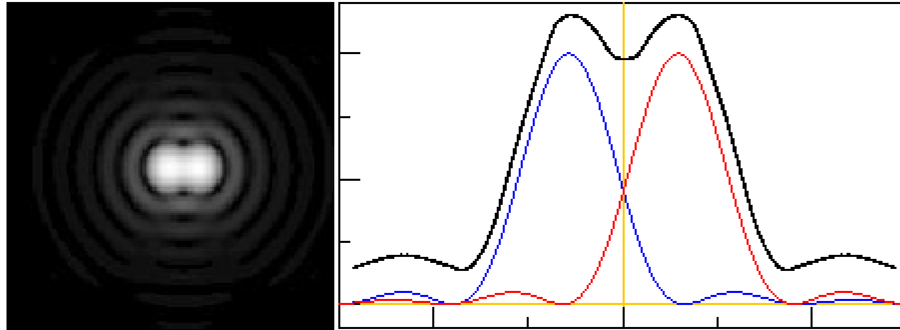
Electron Properties

Rest mass		m_0	$=$	9.1091×10^{-31} kg	
Charge		e	$=$	-1.602×10^{-19} C	
Kinetic energy		E	$=$	eU	
				$1\ \text{eV} = 1.602 \times 10^{-19}$ J	
Velocity of light		c	$=$	$2.9979 \times 10^{8}\ \text{m s}^{-1}$	
Rest energy		E_0	$=$	$m_0c^2 = 511$ keV	
Spin		s	$=$	$h/4\pi$	
Planck's constant		h	$=$	6.6256×10^{-34} J s	
Nonrelativistic	$(E \ll E_0)$			Relativistic $(E \sim E_0)$	
Newton's law	$\boldsymbol{F} = \frac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}\tau}$	$\boldsymbol{F}$	$=$	$\frac{\mathrm{d}}{\mathrm{d}\tau}(m\boldsymbol{v})$	(2.7)
Mass	$m = m_0$	m	$=$	$m_0/\sqrt{1 - v^2/c^2}$	(2.8a)
Energy	$E = eU = \frac{1}{2}m_0v^2$	mc^2	$=$	$m_0c^2 + eU = E_0 + E$	(2.9)
		m	$=$	$m_0(1 + E/E_0)$	(2.8b)
Velocity	$v = \sqrt{2E/m_0}$	v	$=$	$c\sqrt{1 - \frac{1}{(1 + E/E_0)^2}}$	(2.10)
Momentum	$p = m_0v = \sqrt{2m_0E}$	p	$=$	$\sqrt{2m_0E(1 + E/2E_0)}$	(2.11)
			$=$	$\frac{1}{c}\sqrt{2EE_0 + E^2}$	
Wavelength	$\lambda = \frac{h}{p} = h/\sqrt{2m_0E}$	λ	$=$	$h/\sqrt{2m_0E(1 + E/2E_0)}$	(2.12)
			$=$	$hc/\sqrt{2EE_0 + E^2}$	

Concept of Resolution

TABLE 1.2 Electron Properties as a Function of Accelerating Voltage

Accelerating voltage (kV)	Non-relativistic 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



Rayleigh criterion for visible-light Microscope states that **the smallest distance that can be resolved**, δ, is given approximately by:

$$\delta = \frac{0.61\lambda}{\mu \sin\beta}$$

λ is the wavelength of the radiation, μ the refractive index of the viewing medium, and β the semi-angle of collection of the magnifying lens. For the sake of simplicity we can approximate μ sin β to unity so the **resolution** is equal to about **half the wavelength of light.**

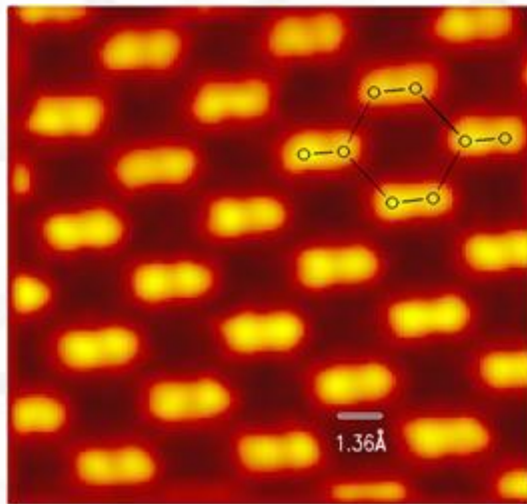
Visible light λ=400 nm R= 200nm
Electrons λ=4 pm **R= 2 pm << atom diameter**

Resolution: Limitations

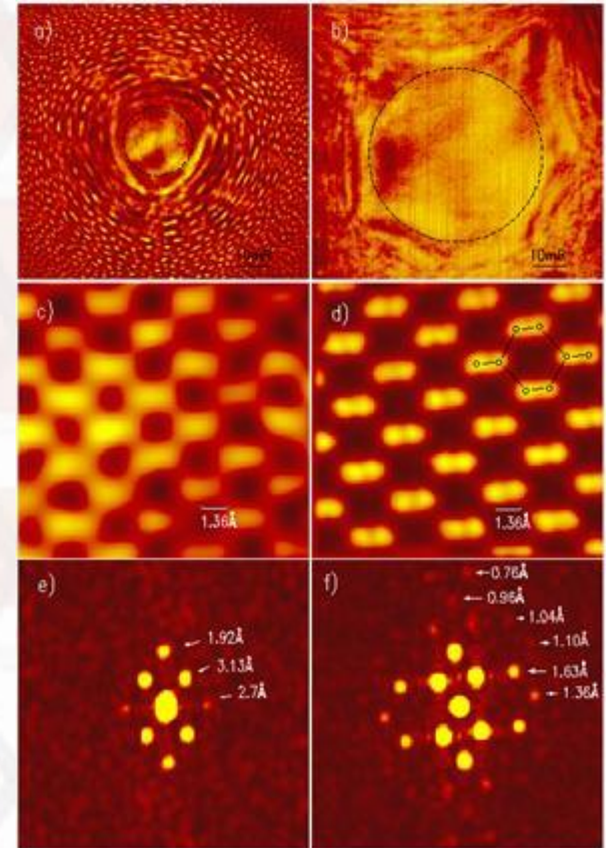
Perfect lenses: wave-length – limited limit of resolution

Real lenses: Despite of short λ, image resolution (minimum resolvable detail) is about 1.4 Å in most TEM's, and is limited by ***spherical aberration*** (C_s) and for thicker sample by ***chromatic aberration*** (C_c) of the objective lens.

Recent development of spherical aberration correctors (1998) improved resolution to < 1Å, and "corrected" commercial TEMS are now available. The FEI Titan TEM released in 2005 achieves 0.78Å TEM image resolution without a corrector.

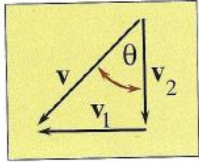


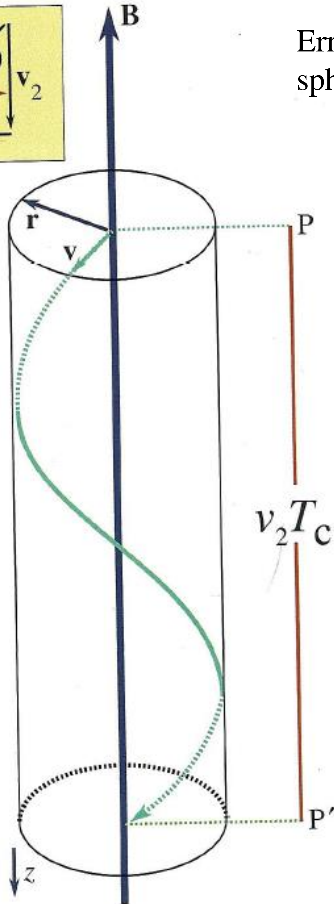
Si [110] projection using a 0.08nm probe at 120 keV



P.E. Batson, Niklas Dellby, and O.L. Krivanek,
Sub-Angstrom resolution using aberration corrected electron optics,
Nature 418, 617-620 (2002).

Real Lenses: Spherical Aberration





$v_2 T_c$

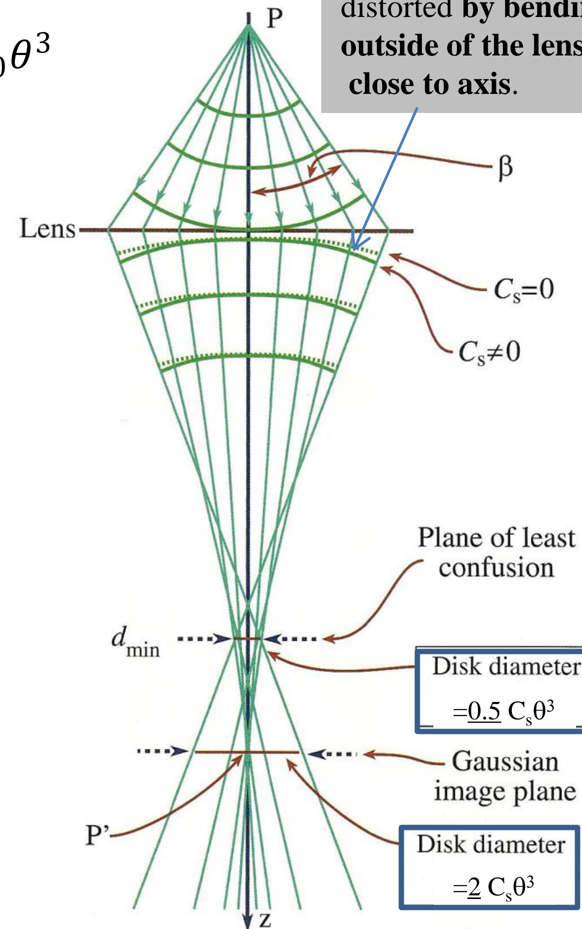
Error, δ, in the Gaussian image position due to spherical aberration:

$$\delta = \Delta z \tan\theta \sim \Delta z \cdot \theta = 0.5 L_0 \theta^3$$

$$\delta = C_s \theta^3$$

C_s – a constant (length) for each particular lens, the spherical aberration coefficient

Lens causes wave fronts from a point object P to be spherically distorted **by bending the rays at the outside of the lens more that those close to axis**.



Non-paraxial conditions

$$PP' = v_2 T_c = v T_c \cos\theta = 2\pi \frac{mv}{eB} \cdot \left(1 - \frac{\theta^2}{2} + \cdots\right) = L_0 \left(1 - \frac{\theta^2}{2} + \cdots\right)$$

$$PP' - PP'_0 = -\Delta z = 0.5 L_0 \theta^2$$

Real Lenses: Chromatic Aberration

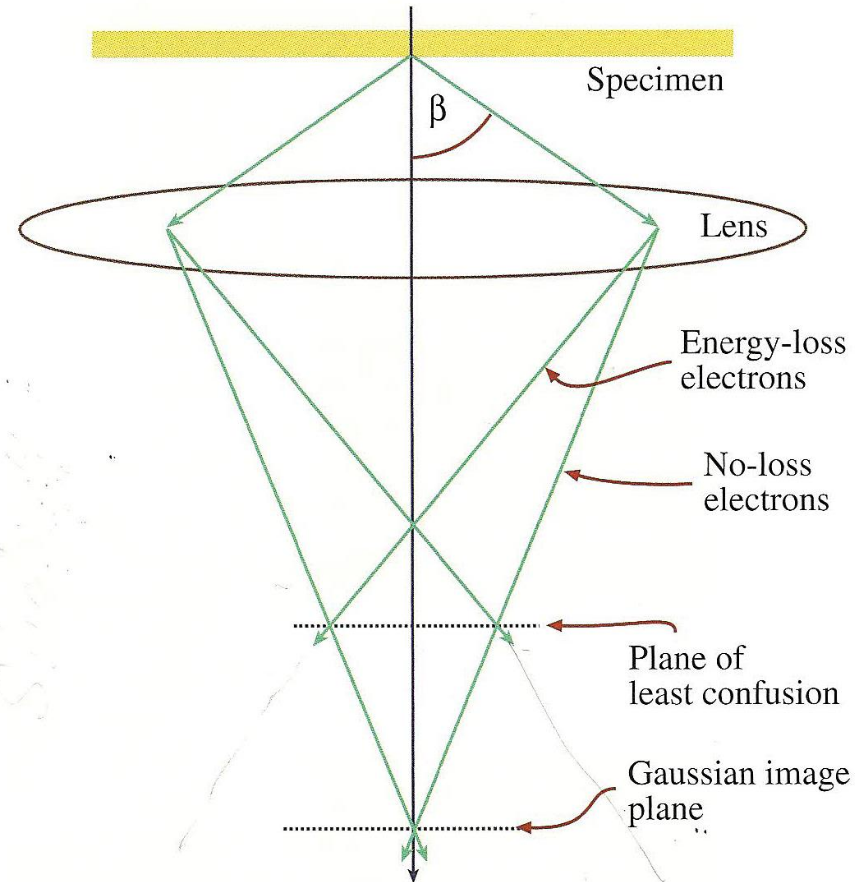
- Chromatic (**color**) aberration results in electrons **with a range of energies** being focused at different planes. The electrons with higher energy are less strong focused than those with lower energy.

- ΔE ~0.3 ev for FEG at E_0~100keV thus
  $\Delta E/E_0 \sim 10^6 << 1$ - important only if we suppressed C_s !!

The radius of the disk at the object plane:

$$r_{chr} = C_c \frac{\Delta E}{E_0} \beta$$

C_c – a chromatic aberration coefficient ,
for electrons coming through the 50-100 nm sample
ΔE~ 20eV and worse for **thicker sample.**

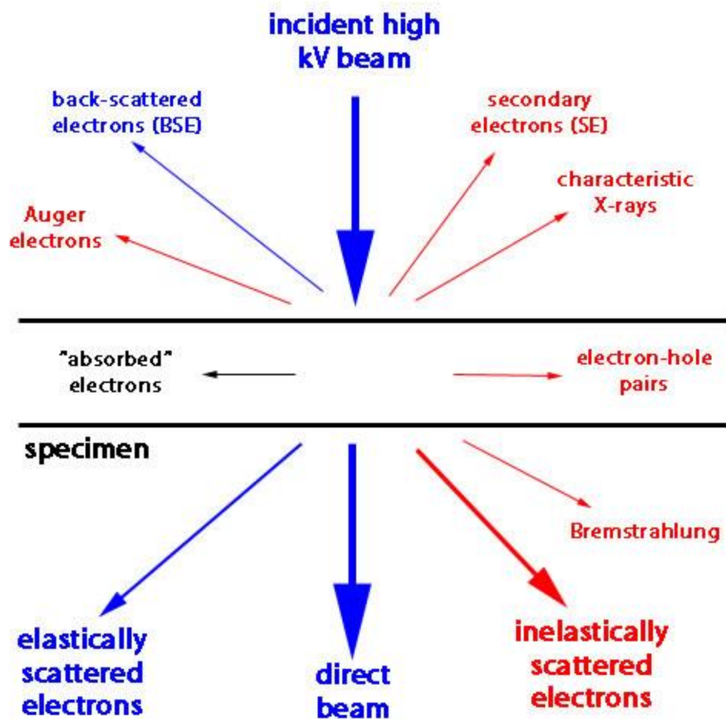


FEI Titan 80-300

- TEM Information limit (300kV) < 0.1 nm
- TEM point resolution (300kV) < 0.1 nm
- STEM resolution (300kV) 0.136 nm
- Energy resolution (300kV) 0.7 eV
- Lorentz mode resolution (300kV) 2 nm
- Pole piece gap 5.4 mm

- <u>Additional functions :</u>
- EELS Spectroscopy
- EFTEM
- Focus series reconstruction

Transmission Electron Microscopy: what can be done?



modified from Williams & Carter (1996) Fig. 1.3

1. TEM gives ***images of internal structure*** of a specimen sufficiently thin (~1000 Å) to allow transmission of electrons, typically 100-300 kV.

2. Electrons ***diffract.*** Electron diffraction patterns give detailed ***crystallographic information:***

Crystal orientation
Lattice parameters
Specimen thickness

3. Chemical analysis is also possible with available analytical attachments for x-ray or electron spectroscopy.

TEM Imagining

TEM Imagining

STANDARD TEM IMAGE MODES

BRIGHT FIELD (BF) IMAGE:

Only the transmitted beam is allowed to pass through the objective aperture. Image is ∴ bright where diffraction in specimen is weak.

DARK FIELD (DF) IMAGE:

Only one diffracted beam passes through objective aperture.
Image is dark where diffraction is weak, bright where diffraction is strong.

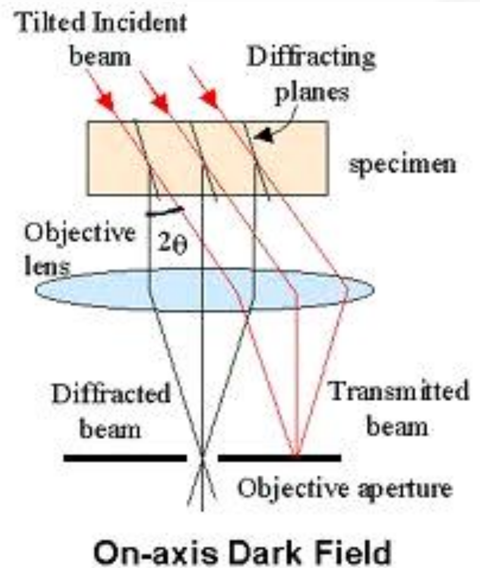
LATTICE IMAGE:

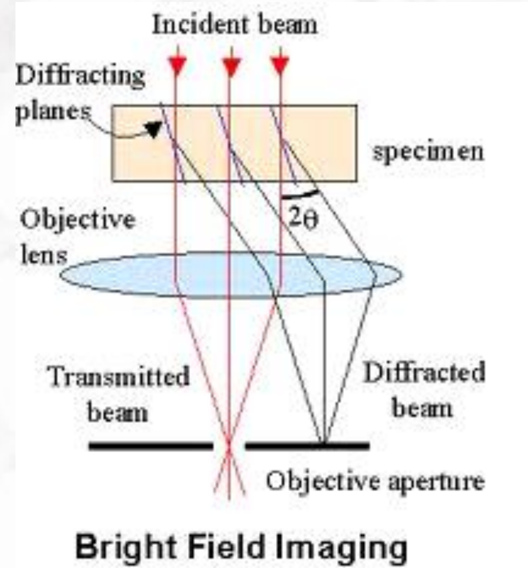
Interference of transmitted beam (TB) and diffracted beams (DBs) produces an image of the crystal lattice.

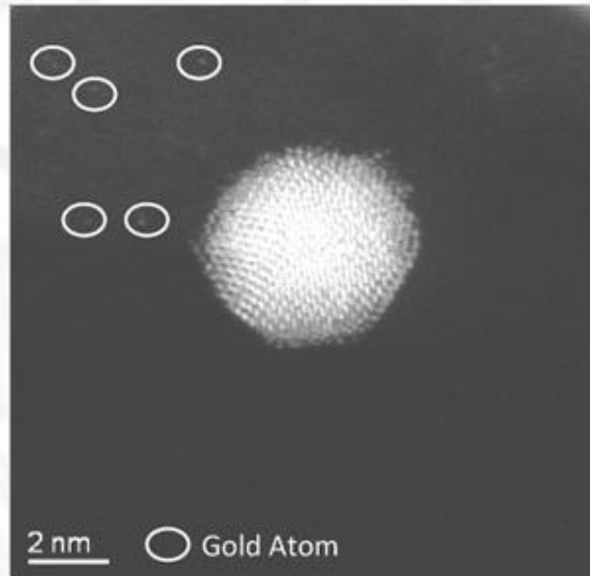
DIFFRACTION PATTERN:

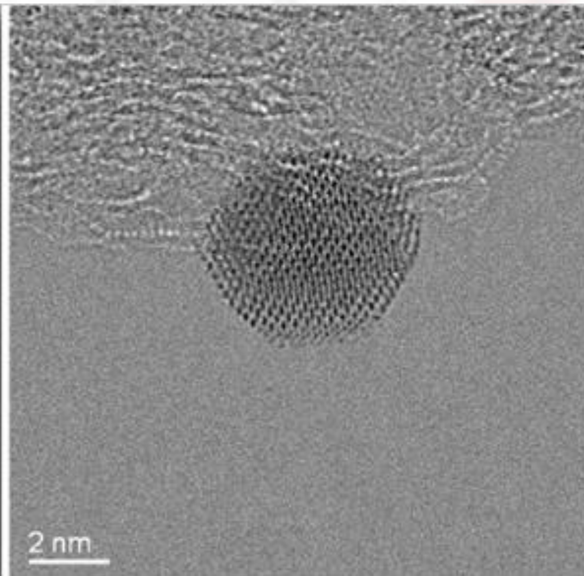
Intermediate lens adjusted to image the diffraction pattern formed in back focal plane (BFP) of objective lens.

BF & DF Imaging



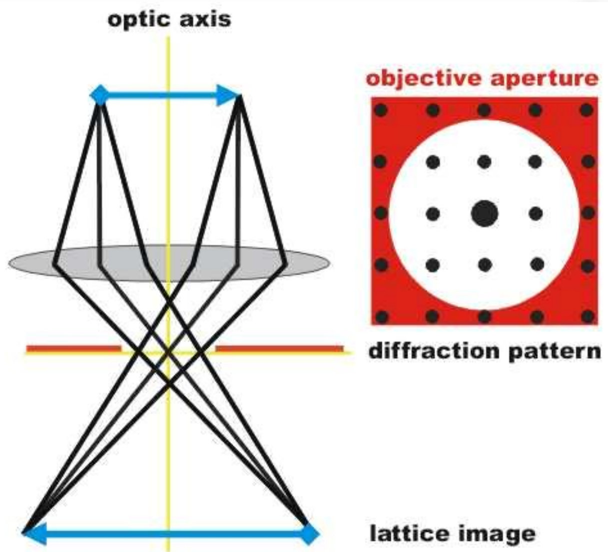


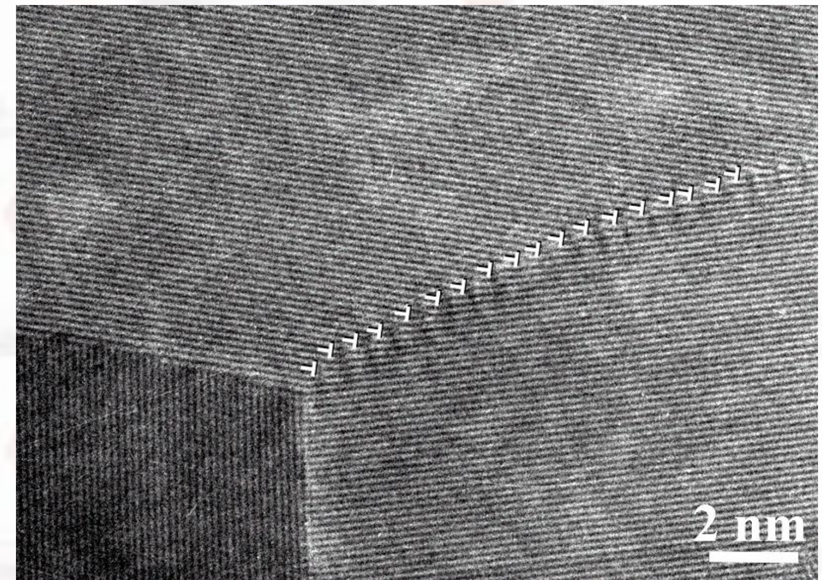




Isolated individual Gold Atoms around Gold Nanoparticles:
(left) dark field image,
(right) bright field image.

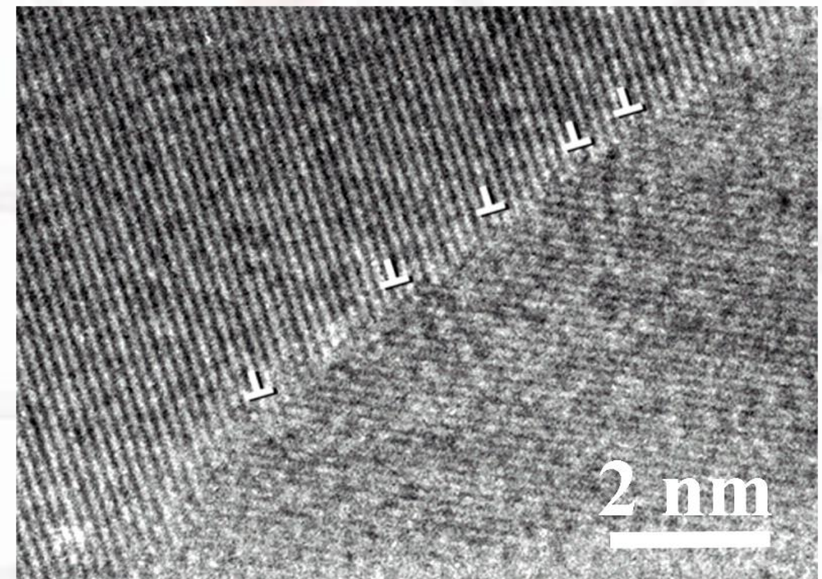
Lattice Imaging





Lattice-resolution imaging of Ni_3Al
The image shows three grains at a resolution where the lines are closely related to planes of atoms in the crystalline lattice. One grain boundary is being depicted as a series of edge dislocations.

HR-TEM image of Ni_3Al
High-resolution transmission electron microscopy is capable of resolving individual planes of atoms in the crystalline lattice. The lines in this image are closely related to planes of atoms in the crystalline lattice.



MAJOR IMAGE CONTRAST MECHANISMS

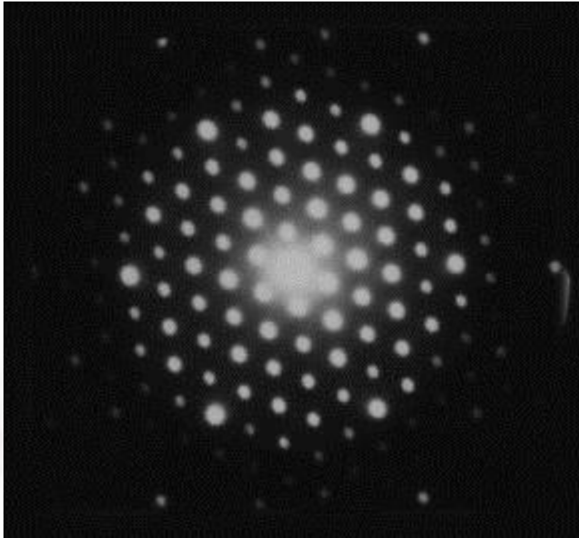
Mass-thickness contrast: scattering out of transmitted beam creates contrast due to difference of atomic number (Z) and/or thickness t; scattering is proportional to Z^2t. Higher-Z or thicker areas are darker in BF. Applicable to crystalline *or* amorphous materials.

Diffraction contrast: scattering out of transmitted beam creates contrast due to differences in diffracted intensity produces contrast for dislocations, grain boundaries, stacking faults, second phase particles etc. Strongly diffracting objects are darker in BF. Applicable *only* to crystalline materials.

Phase contrast: interference between transmitted and diffracted beam produces lattice fringes or atomic structure images (typically referred to as HRTEM (high-resolution TEM).

TEM Diffraction

Diffraction in TEM



An experimentally observed DP showing the central intense, direct beam ***and array of diffraction spots*** from different atomic planes.

- What is it?
- What can we learn from it?
- Why do we see it?
- What determines the scale?

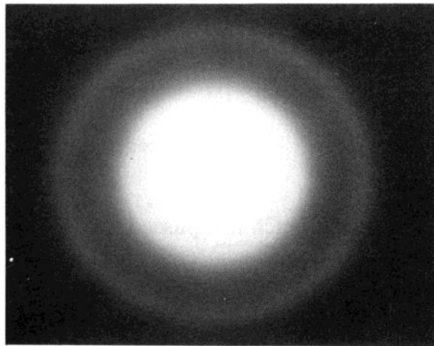
Comparison X-ray /Electrons:

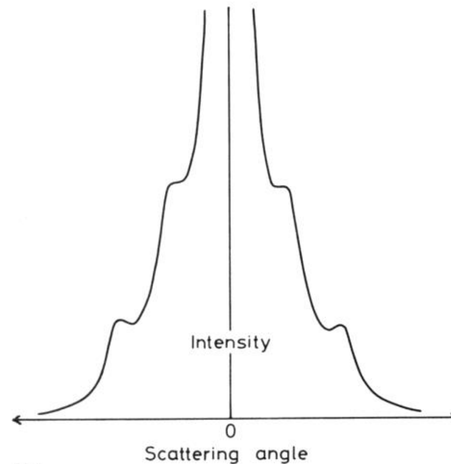
- Electrons have a much shorter wavelength than X-ray
- Electrons are scattered more strongly
-Electron beams are easily directed

However, much of electron **D** follows directly from X-ray **D**

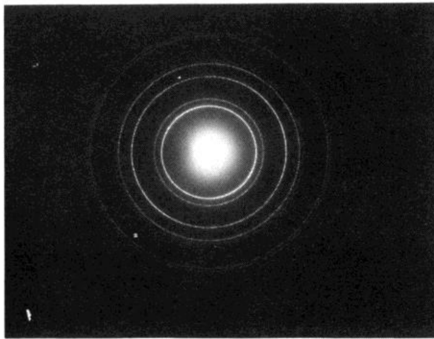
- Is the specimen crystalline or amorphous?
- If it is crystalline: what are crystallographic characteristics of the specimen?
- Is the specimen mono-crystalline?
- If not what is the grain morphology and grain size distribution?
- Is more than one phase presented, how are they oriented to each other?

Ring Patterns


(a)



(b)


(c)

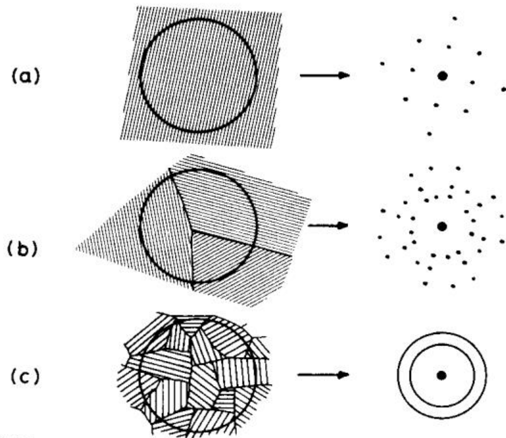
(d)

Goodhew and Humphreys
Figure 3.1 (*a*) Electron diffraction pattern from a thin film of amorphous carbon. (*b*) The variation of intensity with scattering angle obtained from Figure 3.1(*a*). (*c*) Diffraction pattern from a fine grained polycrystalline gold specimen. (*d*) Diffraction from a single crystal of aluminium.

- Amorphous (non-crystalline) materials give <u>diffuse</u> rings, as in (a) above, which is from a thin amorphous carbon support film. TEM grids with carbon support films are available from several microscopy suppliers. Crystalline materials give sharp rings, as in (c).

Ring Patterns

- The diffraction pattern from a polycrystalline specimen area contains overlapping spot patterns from all grains illuminated by the incident beam. If the number of grains is small, we see "spotty" rings. If the number is large (small grain size) we will see smooth continuous rings.



Goodhew & Humphreys

Figure 3.5 Types of diffraction pattern which arise from different specimen microstructures. (*a*) A single perfect crystal. (*b*) A small number of grains – notice that even with three grains the spots begin to form circles. (*c*) A large number of randomly oriented grains – the spots have now merged into rings.

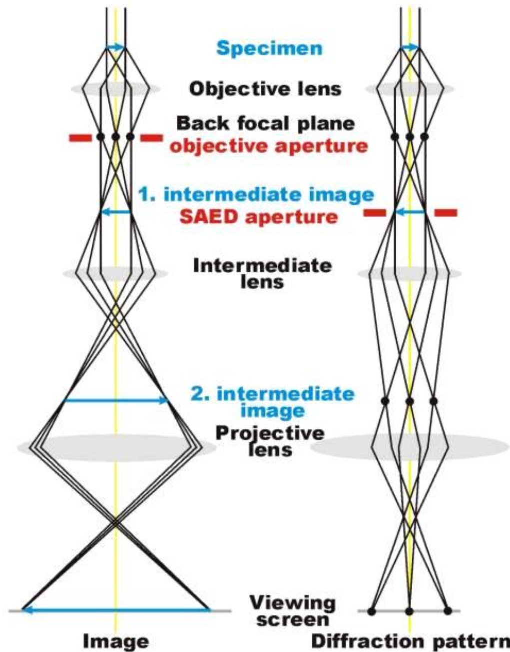
The ring radii are given by the camera formula:

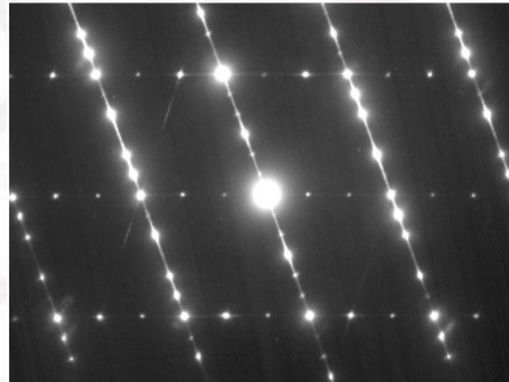
$$R = \frac{\lambda L}{d}$$

Where d is a crystal d-spacing; λ – wave length of the electron; L – constant of the TEM.

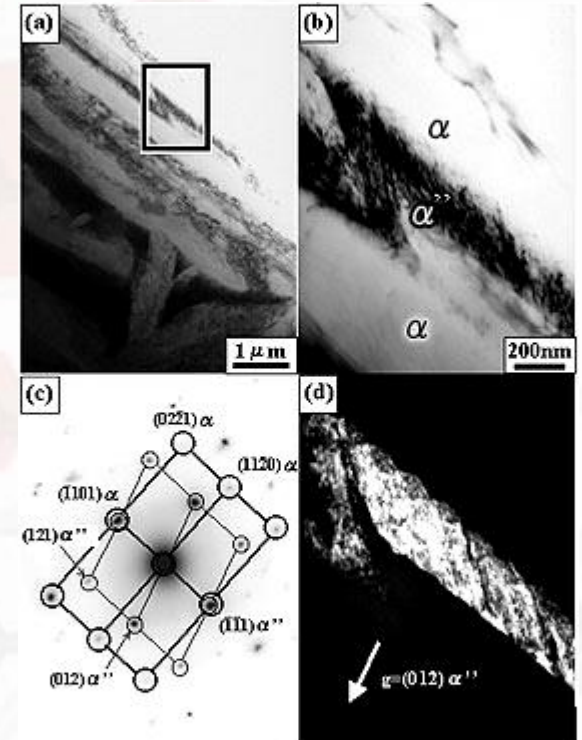
Selected Area Diffraction (SAD)

- Crystallographic structure from particular areas of a sample.
- Used to distinguish and identify ***crystalline (and amorphous) phases*** in a material.





SAD pattern:10-10 zone axis pattern of a hexagonal GaN/cubic GaN heterostructure



TEM micrographs taken from **Ti-15Zr-4Nb-4Ta Alloy** specimen :
(a) the bright field image,
(b) the magnified image of area,
(c) the selected area diffraction pattern
(d) the DF image taken with $(012)_{\alpha}$ reflection

The objective lens forms a diffraction pattern in the back focal plane with electrons scattered by the sample and combines them to generate an image in the image plane (1. intermediate image). Thus, diffraction pattern and image are simultaneously present in the TEM. It depends on the intermediate lens which of them appears in the plane of the second intermediate image and magnified by the projective lens on the viewing screen. Switching from real space (image) to reciprocal space (diffraction pattern) is easily achieved by changing the strength of the intermediate lens.

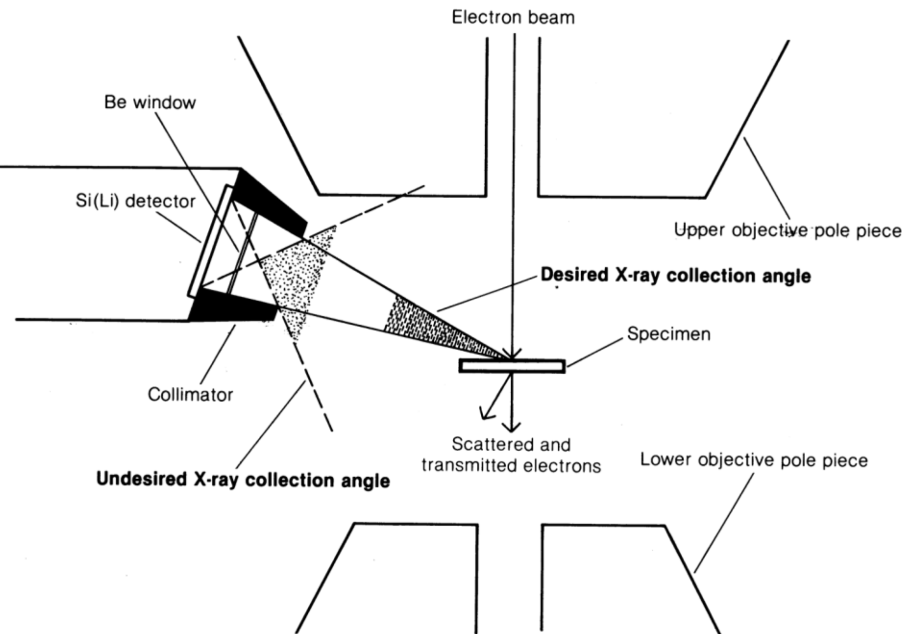
TEM Elemental Analysis

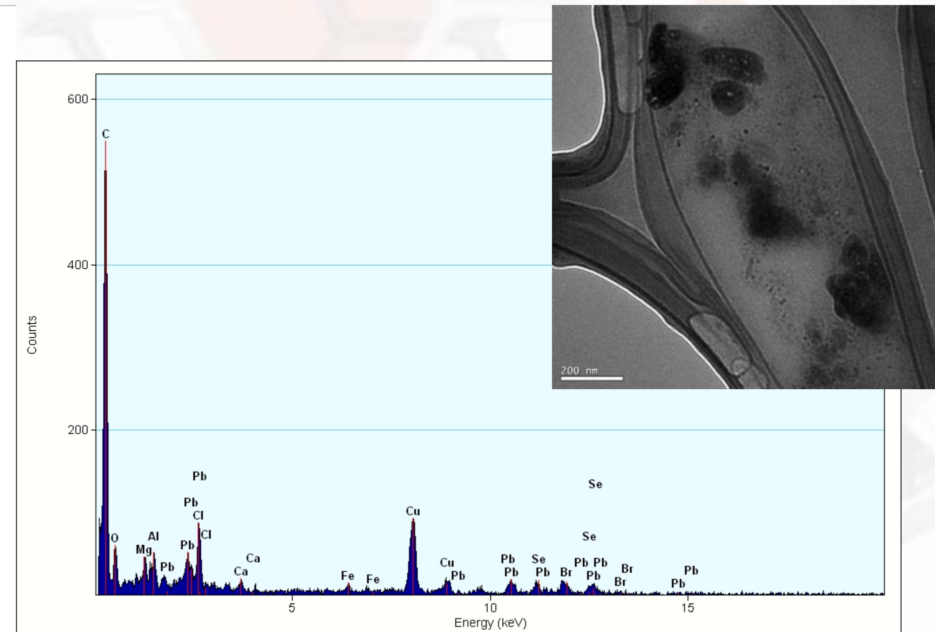
Chemical analysis: EDS

Energy Dispersive X-ray Spectroscopy (EDS)

– EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis..

– Spatial resolution on the order of probe size (can be as low as 2-3 Å)





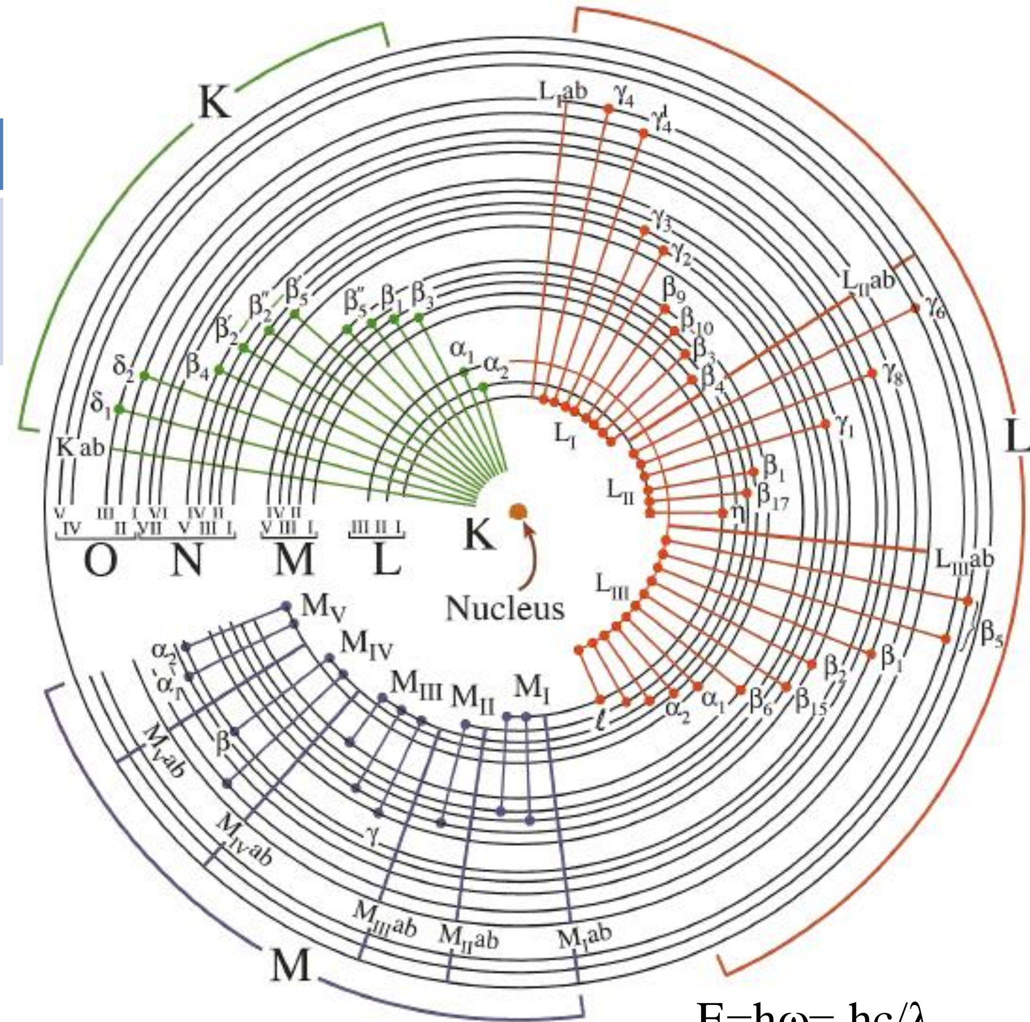
Representative example of ED spectrum obtained on a ~20 micron grain of titano maghemite from submarine basalt. EDAX Phoenix EDS system;15 kV.

Characteristic X-Ray Emission

The XEDS detectors can fill and resolve only ***K,L, and M and α and β lines.***

Relative Weights of X-ray Lines			
K_{α} (1) L_{α} (1) M_{α} (1)	K_{β} (1) $L_{\beta 1}$ (0.7) M_{β} (0.6)	$L_{\beta 2}$ (0.2) M_{ξ} (0.06)	$L_{\gamma 1}$ (0.08) M_{γ} (0.05)

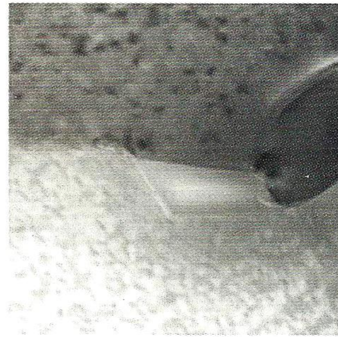
X-ray notation	Quantum numbers n	l	j	m	Maximum electron population
K	1	0	1/2	± 1/2	2
L_{I}	2	0	1/2	± 1/2	2
L_{II}	2	1	1/2	± 1/2	2
L_{III}	2	1	3/2	± 3/2 ± 1/2	4
M_{I}	3	0	1/2	± 1/2	2
M_{II}	3	1	1/2	± 1/2	2
M_{III}	3	1	3/2	± 3/2 ± 1/2	4
M_{IV}	3	2	3/2	± 3/2 ± 1/2	4
M_{V}	3	2	5/2	± 5/2 ± 3/2 ± 1/2	6
N_{I}	4	0	1/2	± 1/2	2
N_{II}	4	1	1/2	± 1/2	2
N_{III}	4	1	3/2	± 3/2 ± 1/2	4
N_{IV}	4	2	3/2	± 3/2 ± 1/2	4
N_{V}	4	2	5/2	± 5/2 ± 3/2 ± 1/2	6
N_{VI}	4	3	5/2	± 5/2 ± 3/2 ± 1/2	6
N_{VII}	4	3	7/2	± 7/2 ± 5/2 ± 3/2 ± 1/2	8

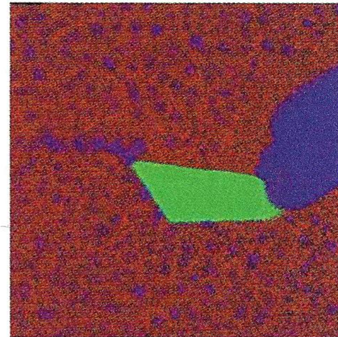


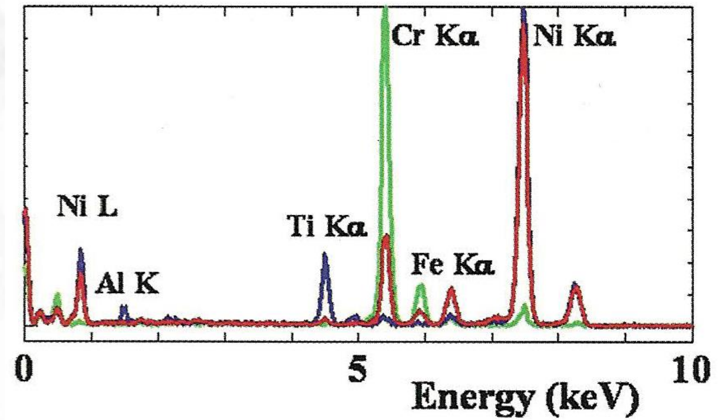
$E = h\omega = hc/\lambda$

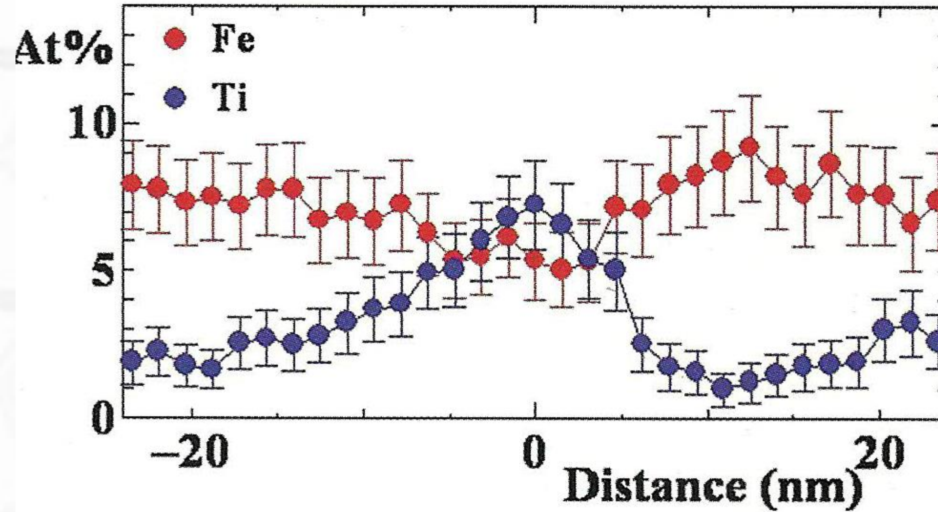
$\lambda = 1.24/E(keV)$

Chemical analysis: EDS







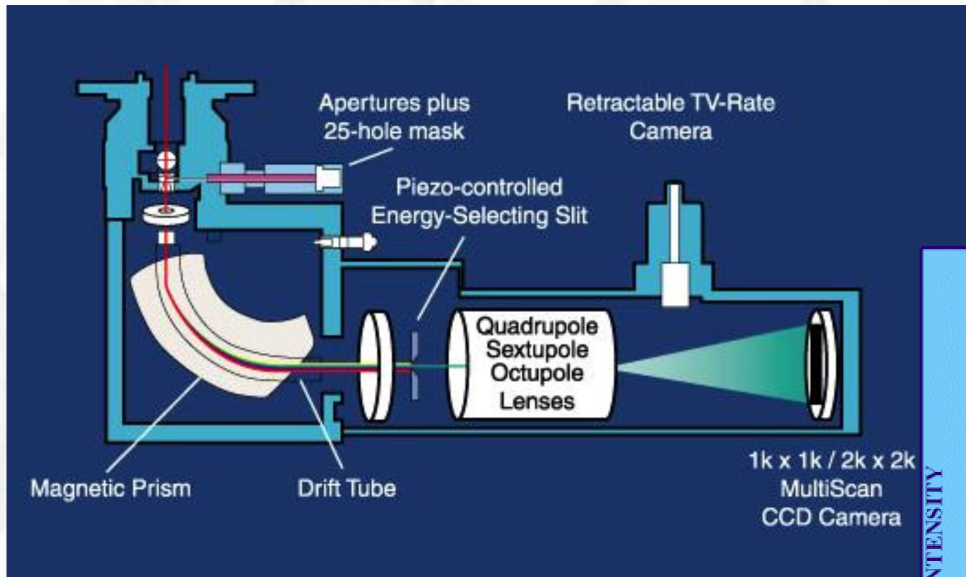


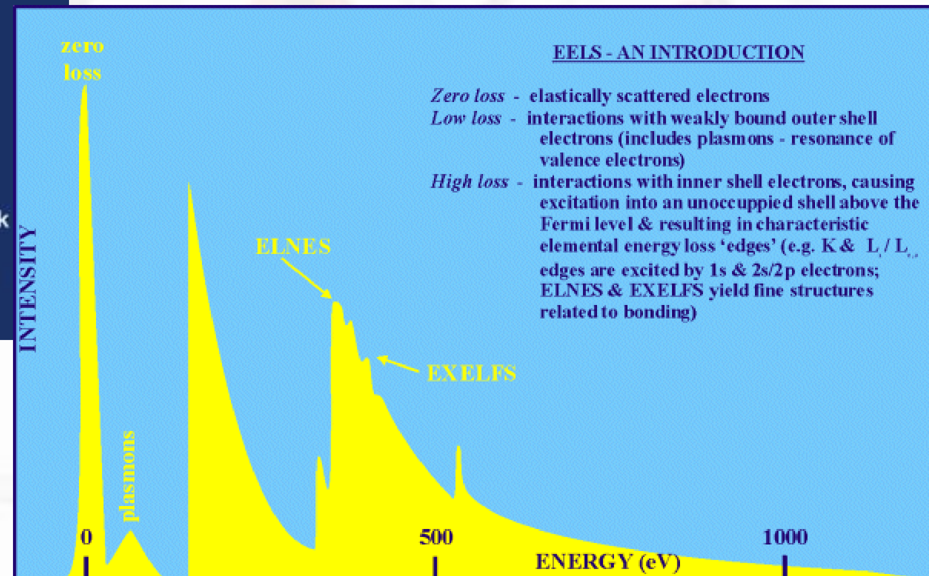
Nickel-based Supper Alloy

Chemical analysis: EELS

Electron energy loss spectroscopy (EELS)

Transmitted electrons lose energy due to plasmon excitation or excitation of atoms by ejecting inner-shell electrons. A bending magnet disperses electrons of different energies to different positions; a slit selects electrons of desired energy loss.

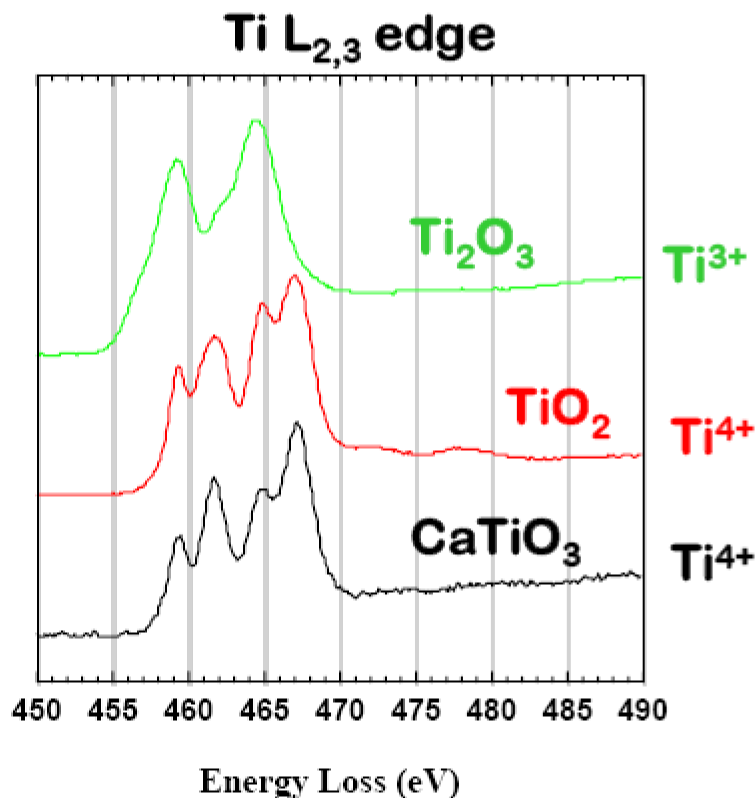




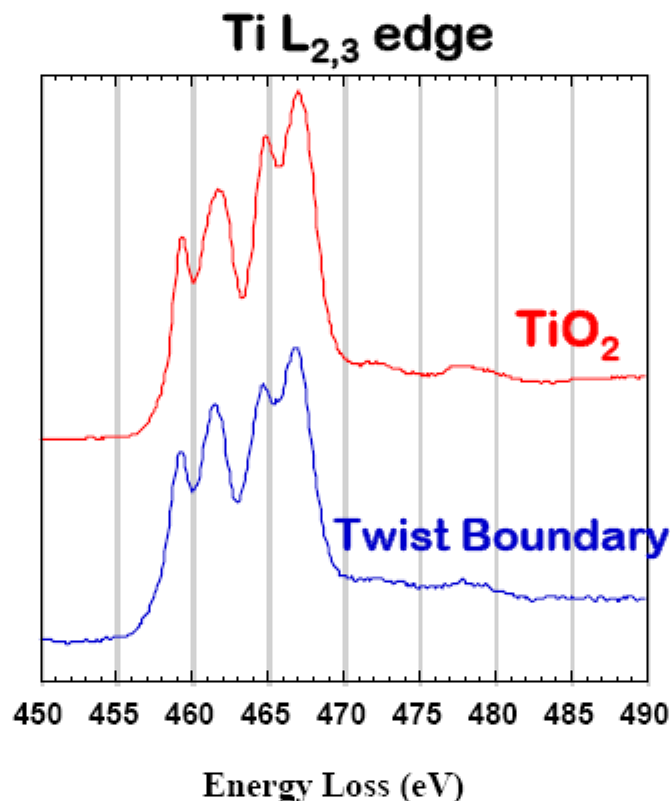
Allows for the determination of ***valence,*** bond length, nearest neighbor co-ordination and quantification of atomic species in minerals

Chemical analysis: EELS

Electron energy loss spectroscopy - Valence determination



Ti $L_{2,3}$ edge from trivalent Ti_2O_3 differs markedly from tetravalent compounds TiO_2 and $CaTiO_3$

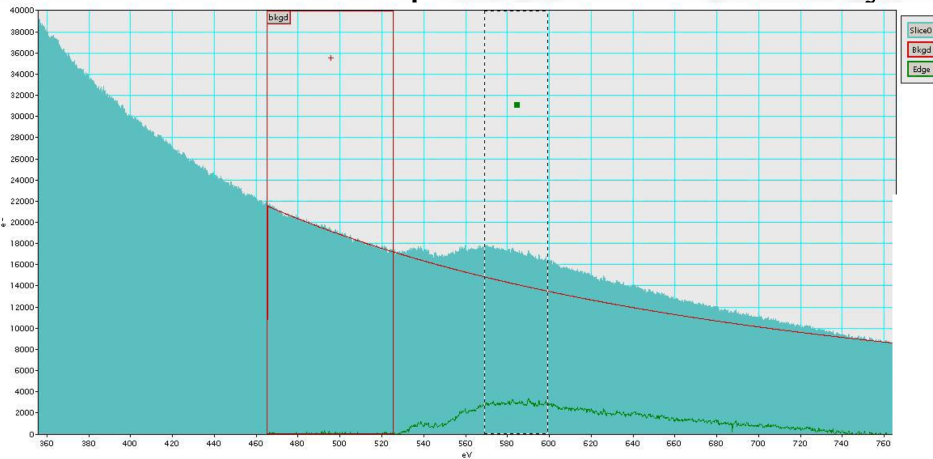


Ti $L_{2,3}$ edge from twist boundary closely matches edge structure of TiO_2 standard (Ti^{4+}).

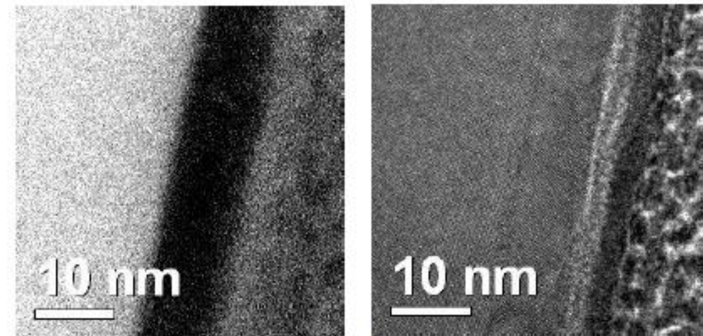
Data courtesy Seth Taylor

EFTEM Map Example

Sb map of Al0.45Ga0.55Sb layer in TFET wafer specimen 193C2

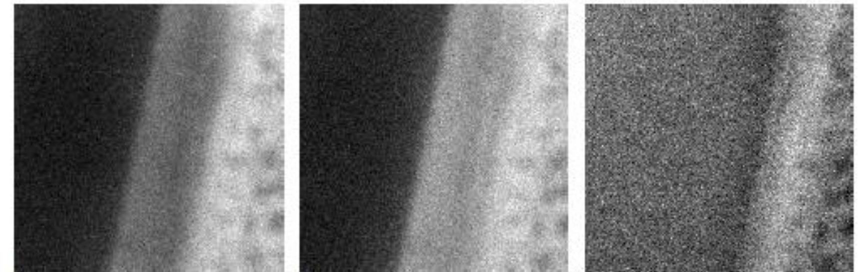


Spectrum showing Sb edge with background fit based on 2x30 = 60 eV range below L2,3 edge, and post-edge 30 eV window. Red curve = background; green = stripped edge



Sb map

Zero-loss image of map area



Pre-edge 1 image

Pre-edge 2 image

Post-edge image

TYPICAL STRUCTURAL FEATURES STUDIED by TEM

CRYSTAL STRUCTURE

Single crystal, polycrystalline or amorphous?
Determine exact orientation of crystal(s).
Identify crystal structure (diffraction).
Evaluate crystal quality (lattice imaging).

CRYSTAL DEFECTS

Presence or absence of dislocations, stacking faults, grain boundaries, twins
Dislocation Burgers vectors; nature of stacking faults

SECOND-PHASE PARTICLES

Size, shape, and distribution; crystallographic orientation relative to surrounding "matrix", chemical analysis via analytical attachments (EDXS, EELS)

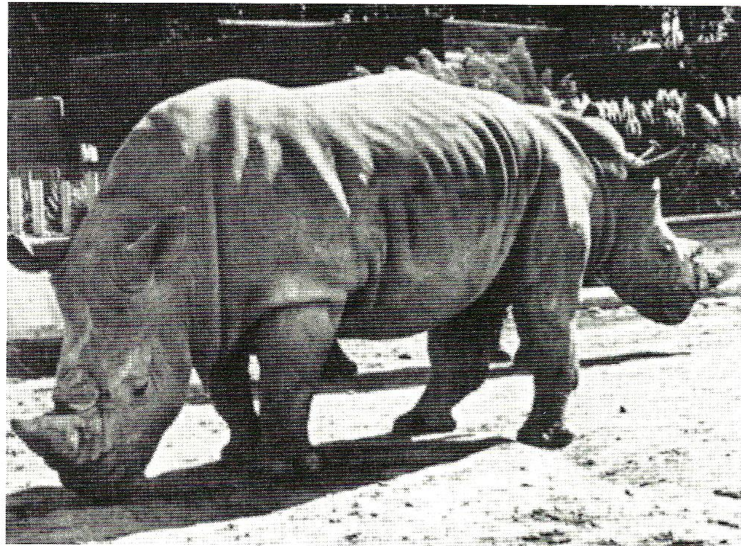
NANOPARTICLES, NANOWIRES, NANORODS etc.

Size distribution, crystal structure and orientation, crystal perfection

Limitation of the TEM

- ***Not a good sampling tool***: high-resolution technique allows to examine only small part of the specimen at one time!!
- ***Interpretation Transmission Images:*** 2D image of 3D specimen.

All images are averaged through the thickness of the specimen- no depth sensitivity!!

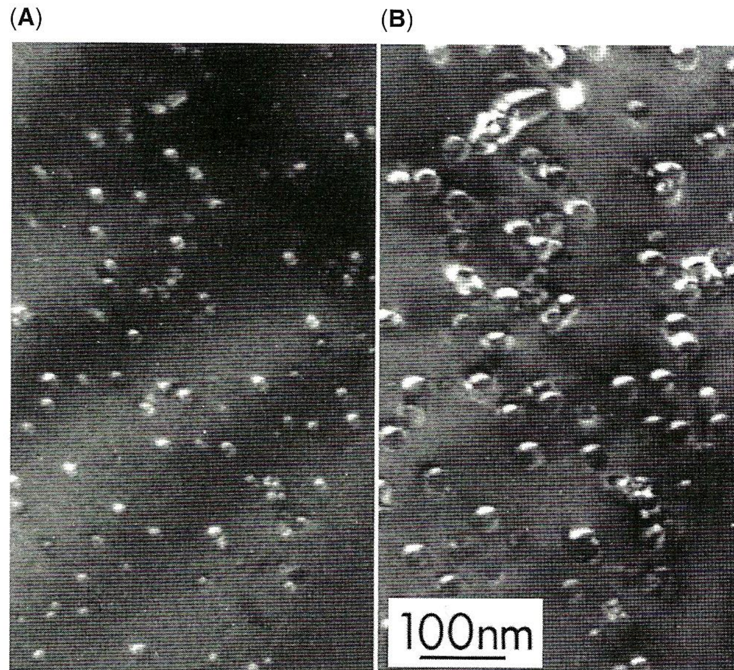


“when we see this image we laugh, but when we see equivalent images in the TEM we publish!!

Hayes

Limitation of the TEM

• ***Electron beam damage and safety:***



Beam damage (bright bubble-like region) in quartz after bombardment with 125 keV electrons
Time increases from (A) to (B)

• ***Specimen Preparation:***

TEM theorem (exemptions exist!!):

thinner is better < *100nm*

• Focused Ion Beam (FIB): drawbacks of FIB specimen preparation (e.g. Ga ions are incorporated to lattice structure)

Also never forget that you are dealing with a potentially dangerous instrument that generates radiation levels that will kill tissue.

Conclusions

- TEMs comprise a range of different instruments that make use of the properties of electrons, both as particles and as waves.
- The TEM generates a tremendous range of signals so we can obtain images, DPs, and several different kinds of spectra from the same small region of the specimen.
- If you count up the different imaging, diffraction, and spectroscopic operations that are available in a TEM there are almost 40 different modes of forming an image, DP, or spectrum, each of which produces different information about your specimen.
- No other characterization technique comes close to the combination of versatility and quantification that is produced by this remarkable instrument, particularly when you consider the enormous range of magnifications over which the information is obtainable.