Electron Microscopy

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Outline

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   including: Electron Diffraction
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1) Introduction

**Electron Microscopy (EM)**

- is a structural characterisation technique
- uses electrons as a "probe" of structure
- microscopy = image of something small
- also spectroscopy = measure the energy of an interaction

Two principle approaches:

(i) **SEM** = Scanning Electron Microscopy
(ii) **TEM** = Transmission Electron Microscopy
Structural characterisation techniques

- study the interaction of a "probe" with a sample
- knowledge of interaction $\rightarrow$ information about structure
- different types of probes $\rightarrow$ different types of interactions
• different types of probes
  – electromagnetic radiation
  – particles
  – physical contact

→ different energy
  – used for spectroscopy

different wavevector
  – used for scattering
Electrons

- electrons are elementary particles
  - charge (-1) or -1.6 $10^{-19}$ Coulomb, mass 9.1 $10^{-31}$ kg
  - most interactive and fastest moving of common particles
- $E = \text{kinetic energy in electron volts (eV) or kilo eV (keV)}$
  - where 1 eV = 1.6 $10^{-19}$ J, and valence electrons have $E \sim $ eV
- wave-particle duality from Quantum Mechanics
  - electrons are waves with wavelength $\lambda$
- e.g. 200 keV electron has $\lambda = 0.027\text{Å}$,
  - Note: velocity will be 20% of the speed of light!

\[
\lambda(\text{Å}) = \frac{0.39}{\sqrt{E(\text{keV})}}
\]

(1) wave property of electrons means they can be used for imaging
Sources of electrons

• current in wire is a flow of electrons, but they are not "free"
• natural sources of free electrons
  – radioactive materials: $\beta^-$ decay
  – UV light: photoelectric effect
• devices with free electrons, i.e. electron "beams"
  – "box" television
  – electron microscope
• based on "electron gun"
  – extraction of conduction electrons from metals using high voltage

(2) electron beams are strongly interacting, so must travel in vacuum
Interaction of electrons with atoms

- electrons interact with electrons in atoms
  (i) elastic scattering (no energy transfer)
    - used in electron diffraction
  (ii) inelastic scattering (some energy transfer)
    - called Electron energy loss spectroscopy
    - similar to Raman spectroscopy
  (iii) absorption
    - an electron cannot "disappear"
    - electron is "blocked" due to large amount of inelastic scattering
Results of electron interactions

- **transmission** - does not affect → **primary beam**
- **scattering** → **scattered electron**
  - elastic: electron undergoes diffraction → **electron diffraction**
  - inelastic: electron scattered by 180° → **backscattered electron**
  - inelastic: scattered electron loses energy → **electron energy loss**
- **secondary products**
  - second electron is knocked out of atom → **secondary electron**
  - core electron is knocked out of atom and replaced → **X-ray fluorescence** or **Auger electron**
- **Electron diffraction** used for **SEM image**.
- Escaping secondary electrons used for **SEM image**.
- Absorbed secondary electrons.
- **X-rays** used for **spectroscopy**.
- **TEM image**.
- Transmitted beam, scattered electrons, electron diffraction used for **TEM image**.
- Secondary electrons used for **TEM image**.
- Backscattered electrons used for **TEM image**.
- **X-rays** used for **spectroscopy**.
- Core electron, electron energy loss used for **spectroscopy**.
2) Background to Electron Microscopy

- Microscopy = image of a small object
- The image (x',y') is a "map" of the object (x,y)
- **Lens** is used to link the **object** to the **image**
  - quality of lens → quality of image
  - thin lens formula:
    \[
    \frac{1}{f} = \frac{1}{u} + \frac{1}{v}
    \]

- Magnification factor M
  - image is larger than object: i.e. x'=Mx, y'=My
  - thin lens formula:
    \[
    M = \frac{f}{u - f}
    \]
  - Note: in human eye the image is smaller than the object
Resolution of image

- resolution $\Delta r =$ smallest detail of object in image
- resolution is limited due to size of lens
  - some of the light from the object is "lost"
- size of lens = semi-angle of aperture $\alpha$
- Rayleigh formula: $\Delta r = \frac{0.61\lambda}{n\sin\alpha}$

(3) electron wavelength $\lambda$ much smaller than light
Lens aberrations

- focussing lens gives best resolution
- the focus is not sharp
  - called "disc of least confusion"
  (i) when wavelength $\lambda$ changes
    - called "chromatic" aberration
  (ii) when angle changes
    - called "spherical" aberration
  (iii) when orientation changes
    - called "astigmatism"

(4) electron lenses have more imperfections than glass lenses
Transmission approach to microscopy

recording: - whole image at once

illumination: - uniform illumination of whole image

magnification: - lens used to magnify
- lens after the sample

light in image: - transmitted through sample
- looks like a cross section

bacterium
Transmission Electron Microscope

- electrons pass through sample
  - sample must be very thin
  - little space for detectors before sample

- electrons must penetrate sample
  - large "high voltage" supply
  - very good vacuum required

- imaging lens is after the sample
  - column geometry
  - image at bottom of microscope
  - can be seen on screen

- image formed from
  - transmitted and scattered electrons
Scanning approach to microscopy

recording:  
- one point of image at a time
- image built by **scanning**

illumination:  
- focussed on one point using lens
- **lens before sample**

magnification:  
- obtained via **scanning**

light in image:  
- scattered from surface
- can look 3-dimensional

blood cell
Scanning Electron Microscope

- electrons do not pass through sample
  - sample can be large
  - sample must be conducting (coated)
  - space for detectors above sample

- electrons do not need to be penetrating
  - small "high voltage" supply
  - moderate vacuum required

- image formed by scanning
  - nothing to see "inside"
  - use a tv display of image

- image formed from
  - backscattered or secondary electrons
Not to be confused with

Other types of microscopy
• Scanning probe microscopy (SPM)
  or Scanning Tunnelling Microscopy (STM)
  or Atomic Force Microscopy (AFM)
  – uses electrons indirectly (not "free")

Other types of spectroscopy
• Electron Spectroscopy for Chemical Analysis (ESCA)
  or X-ray Photo-electron Spectroscopy (XPS)
  – uses X-rays directly to excite electrons
• Electron Probe Micro-Analysis (EPMA)
  – similar to SEM, but no imaging
3) TEM: Equipment

Source of electrons

- **thermionic emission (electron gun)**
  - heating wire helps electrons to escape
  - made from tungsten (W) or LaB$_6$
  - moderate brightness

- **field emission gun (FEG)**
  - very sharp metal point helps electrons to escape
  - high brightness, but requires ultra high vacuum
Accelerating electrons
- "high voltage" supply (V)
  - to extract and accelerate electrons
  - typically 200, 300 or 400 keV
- electron accelerated due to electric force

Moving electron beam
- deflectors coils
  - with two pairs of coils can tilt, shift or scan
- electron bends due to magnetic force
  - electron velocity $v$, magnetic field $B$

Force = $eV$
Force = $qv \otimes B$
Electron lens

- **Lens** is used to link the **object** to the **image**
  - (1) light spreads out from object
  - (2) lens causes light to bend more at high angles
  - (3) image formed when light converges on image

- optical lens (for light) is made of glass
  - light bends due to refractive index of glass

- electron lens is made of magnetic field
- electron bends due to magnetic force
  - non-uniform magnetic field \( \mathbf{B} \) causes electron velocity \( \mathbf{v} \) to bend more at high angles

- resolution \( \Delta r \) varies from \( \sim 3 \, \text{Å} \) to 1.7 Å
Recording image

Detecting electrons

- fluorescent screen (at bottom of microscope)
  - like the front of a "box" tv screen (CRT)
  - operator looks with their eyes!

- photographic camera
  - uses special photographic negatives
  - exposure time of ~1 sec

- CCD camera (like a digital camera)
  - semiconductor device
  - can be directly linked to a computer
Aligning TEM

- electron gun
  - obtain bright and symmetrical emission
- condensor lens and condensor aperture
  - choose intensity and coherence of illumination
- 2nd condensor lens and deflector coils
  - area of illumination
- insert sample into microscope
- objective lens
  - correct objective lens aberrations
  - focus lens
- intermediate lenses
  - magnification
- objective aperture for contrast
  - move diffraction pattern
- selected area aperture for microdiffraction
  - focus diffraction pattern
TEM: sample preparation

• sample must be thin very thin
  – TEM: thickness < 1 µm
  – HREM: thickness < 50 nm
  – biological samples must be frozen

• sample is supported on copper microscope grid

• sample preparation
  (1) grinding to make a powder
  (2) standard thinning:
    composite, diamond saw, grinder, dimpler, ion-beam
  (3) "focussed ion beam" (FIB) to cut the sample

• sample may become damaged
  – due to "high voltage" electron beam
TEM: image contrast

• transmission of electrons
  \[ I_T = I_0 \exp(-\mu t) \]
  – thickness contrast (t)
  – mass contrast (\( \mu \) depends on atomic no. \( Z \))

• scattering contrast
  – scattering deviates electrons

• **objective aperture** is used to block electrons
  – is located in the "focal plane"
  – **bright field**: only un-scattered electrons
  – **dark field**: only scattered electrons

• stronger effect for crystalline regions
  – diffraction deviates electrons more
thickness contrast
CaCO3 aragonite

scattering contrast
nanostructured Nb films

(a) bright field
(b) dark field

sample
objective lens
objective aperture
Diffraction contrast

- Electrons can be diffracted by crystals - principle is the same as X-ray diffraction
- 2 beams: primary beam & **diffracted beam**
  - Crystal oriented to satisfy Bragg condition
- Diffracted beam can be diffracted again
  - Goes back to primary beam
- Important tool to study crystal defects
  - Defect alters the orientation of diffracting planes

[Diagrams and images showing diffraction contrast of edge dislocations]
Electron diffraction

- in X-ray diffraction the angle is measured directly
- in electron diffraction the angle is ~0.5 degree

- objective lens bends the electrons to make a **diffraction pattern**
- **intermediate lens** magnifies the **diffraction pattern**
  - this is "**diffraction mode**"

- **selected area aperture** is used to choose region of sample
  - is called "**microdiffraction**"
  - e.g. $10^{-15}$ gram of sample
images of electron diffraction patterns = diffractograms

single crystal

diffractogram

polycrystalline

diffractogram

amorphous

diffractogram

\( n\lambda = 2d \sin \theta \) 

Bragg’s Law

for small angles

\( \lambda/d = 2\theta = r/L \)

\( L = \) camera length

\( r = \) distance on diffractogram

e.g. FCC (111) axis
High resolution electron microscopy

- scattering contrast has low resolution
  - because objective aperture limits size of objective lens
- highest resolution requires **no objective aperture**
  - both undiffracted and diffracted beams form image

- sample is oriented along crystal axis
  - electrons travel through crystal in Block waves
  - (or) electrons are diffracted by parallel planes
  - diffracted electrons have different phase

- **phase contrast** occurs due to phase difference between waves
  - e.g. destructive interference
    makes image darker

lens gives $\pi/2$ phase shift in diffracted beams w.r.t. main beam
HREM images of crystals

- image shows **planes** or **columns** of atoms
  - sample must be very thin so that diffracted electron remains in column
- **objective lens** alters the phase of diffracted electrons
  - determined by "**contrast transfer function**" (CTF) of the lens
  - best resolution obtained for "Scherzer" focus
  - image appearance varies strongly with focus

HREM image effect of lens focus on image of GaAs [110]
Energy dispersive X-ray spectroscopy (EDX)

- can be used in TEM or SEM
  - uses semiconductor detector
- detects X-ray fluorescence
  - electron knocks out core electron which is replaced
- shows elemental composition
  - spectra can be analysed quantitatively
- can be combined with "nanoprobe"
  - electron beam focused to ~nm sized spot
4) **STEM**

- **Scanning Transmission Electron Microscope**
  - combination of Scanning and Transmission approaches
- can be TEM with nanoprobe and scanning = TEM/STEM
- or "dedicated" STEM = STEM
  - SEM with a thin sample for transmission, and detectors after the sample
Scanning Transmission Electron Microscope

- electrons pass through sample
  - sample must be very thin
- electrons must penetrate sample
  - large "high voltage" supply
  - very good vacuum required
- image formed by **scanning**
  - nothing to see "inside"
  - use a tv display of image
- image formed from
  - **transmitted** and scattered electrons
STEM imaging

- Bright field image is the same in STEM and TEM
  - because "optical path" is the same
  - resolution limit is the same (best $\Delta r \approx 1.7\text{Å}$)
- Dark field image is different in STEM and TEM
  - dark field resolution is higher in STEM
- dedicated STEM has advantages
  - thin sample so small interaction volume
  - no lenses after sample so space for high angle detectors
High Angle Annular Dark Field Imaging

(HAADF)

• requires STEM
  – can use scintillator or semiconductor detector
• detects scattered electrons (similar to dark field imaging)
  – wide range of large scattering angles
• very sensitive to atomic number Z (called "Z-contrast")
  – inelastic scattering at large angle depends on $Z^2$

HAADF image of Au particles on TiO$_2$ support

HAADF image of grain boundary
Si pairs = 1.36Å
Electron energy loss spectroscopy (EELS)

- can be used in TEM or STEM
- detects energy lost when exciting core electrons
  - analogous to X-ray absorption spectroscopy
- gives quantitative elemental composition
- can be used with ~nm probe ("nanoprobe")

![Image of EELS spectrum with Fe and Co peaks]
EELS spectrometer

- transmitted electrons have energy $E' < E$
  - $E$ = energy of electron gun, e.g. 200 keV
- EELS spectrometer measures energy $E'$
  - energy loss is $\Delta E = E - E'$

- spectrometer uses a uniform magnetic field
  - electrons are deviated due to magnetic force
  - radius of circular path depends on velocity and $E'$
  - same principles as mass spectrometer

- electron detector
  - serial (diode): measure single point on spectrum
  - parallel (semiconductor): measure whole spectrum

\[ \text{Force} = qv \times B \]
EELS spectra

- **zero loss peak**
  - unscattered electrons with $\Delta E=0$
- **low-loss region**
  - $\Delta E$ up to 30eV
  - due to excitation of "plasmons"
- **high-loss region** (or "core" loss)
  - $\Delta E$ up to 2 keV
  - due to excitation of core electrons

- **edges** in EELS spectra
  - K-edges of light elements ($Z<15$)
  - L-edges of transition metals
  - same as X-ray absorption edges
Conclusions

- TEM is a versatile instrument but requires special training to operate.
- TEM with scattering contrast and electron diffraction can identify phases within microstructure.
- TEM /STEM or dedicated STEM can identify composition on nm-scale.
- TEM is an essential instrument for structural characterisation.
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