Chapter 2. Analytical Methods

- Materials parameters that affect properties: crystal structure, microstructure, phase, defects, topography, compositions, etc.
  => methods for getting these information
- Typical excitation source:
  photons (X-ray), electrons, ions (He$$^{++}$$),…
- Typical detection particles:
  photons (X-ray), electrons, ions
  => different combination => different methods
How x-ray interacts with samples?

- X-rays are scattered by the electrons in a material through an interaction between the negatively charged electrons and the electromagnetic field of the incoming X-rays.
Three major interactions

1. **photoelectric effect** (photoionization)

2. **inelastic scattering**
3. elastic scattering (the Thomson/Rayleigh scattering).
Mie scattering:

Tyndall scattering:
How x-ray interacts with samples?

(no energy loss)

Rayleigh Scatter

(energy loss)

Compton Scatter

3. elastic scattering (the Thomson/Rayleigh scattering).

- The scattered x-rays undergo interferences
  => constructive interference: when the angle of the incidence equals the angle of reflection
  => others, destructive interference.

**FIG. 2.1** An X-ray beam is reflected with constructive interference when the angle of incidence equals the angle of reflection.
• Knowledge about the interaction between the source particles and materials is the key to obtain valuable information about the materials.

• Crystal structure:

• Compositions:

• Topographic information:

• Microstructure information: Transmission electron microscope (TEM), X-ray topography, etc.
X-ray topography

- There are no efficient lenses for X-rays, no X-ray microscopes.
- Difficult to focus, and interact too strongly with matter.
- Like imaging with electron beams in the transmission electron microscope.

This intensity mapping reflects the distribution of scattering power inside the crystal ⇒ reveal the irregularities in a non-ideal crystal lattice.
2.1 Bragg Law

• Bragg diffraction of X-rays is primarily due to the scattering of X-ray from electrons bound to the atoms of the crystal structure.
• Constructive Interference: path differences \((2d\sin\theta)\) = Integer \(\times\) wavelength \((n\lambda)\)

\[ \rightarrow \text{Bragg Law} \quad 2d\sin\theta = n\lambda \]
\[ \left( \frac{h}{a} \right)^2 d_{hkl}^2 + \left( \frac{k}{b} \right)^2 d_{hkl}^2 + \left( \frac{l}{c} \right)^2 d_{hkl}^2 = 1 \rightarrow \left( \frac{h}{a} \right)^2 + \left( \frac{k}{b} \right)^2 + \left( \frac{l}{c} \right)^2 = \frac{1}{d_{hkl}^2} \]

Remember, the above equation is good for orthogonal axes.

For cubic crystal: \( a = b = c \)

\[ \rightarrow \frac{1}{a^2} \left[ (h)^2 + (k)^2 + (l)^2 \right] = \frac{1}{d_{hkl}^2} \rightarrow d_{hkl} = \frac{a}{\sqrt{(h)^2 + (k)^2 + (l)^2}} \]

For tetragonal crystal: \( a = b \neq c \) \( \alpha = \beta = \gamma = 90^\circ \)

\[ \rightarrow \frac{1}{a^2} \left[ (h)^2 + (k)^2 \right] + \left( \frac{l}{c} \right)^2 = \frac{1}{d_{hkl}^2} \]

For orthorhombic crystal: \( a \neq b \neq c \) \( \alpha = \beta = \gamma = 90^\circ \)

\[ \rightarrow \left( \frac{h}{a} \right)^2 + \left( \frac{k}{b} \right)^2 + \left( \frac{l}{c} \right)^2 = \frac{1}{d_{hkl}^2} \]
Monochromatic X-ray to see family planes

\[ d_{110} = 0.1181 \text{ nm} \]

**FIG. 2.3** Four of the eleven angles at which Bragg reflections occur using a crystal with an interplanar spacing of 0.1181 nm and X-rays of wavelength 0.02090 nm \((W K_\alpha 1)\)

**Cu, \( K_\alpha 1 = 0.1541 \text{ nm} \)**

\[
n \lambda = 2 \ d \ \sin \theta \\
1 \times 0.1541 = 2 \times 0.1181 \times \sin \theta \\
\Rightarrow \ \theta = 40.7^\circ
\]

**W, \( K_\alpha 1 = 0.0209 \text{ nm} \)**

\[
1 \times 0.0209 = 2 \times 0.1181 \times \sin \theta \\
\Rightarrow \ \theta = 5.08^\circ
\]
Although there are eleven angles at which a beam of wavelength \((W, K_{\alpha_1} = 0.0209 \text{ nm})\) will be reflected with

\[
\lambda = 2 \frac{d_{110}}{n} \sin \theta
\]

<table>
<thead>
<tr>
<th>(\lambda)</th>
<th>(\frac{d_{110}}{n})</th>
<th>(\theta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0209</td>
<td>(\frac{0.1181}{1})</td>
<td>(d_{110}) 5.08°</td>
</tr>
<tr>
<td>0.0209</td>
<td>(\frac{0.1181}{2})</td>
<td>(d_{220}) 10.19°</td>
</tr>
<tr>
<td>0.0209</td>
<td>(\frac{0.1181}{3})</td>
<td>(d_{330}) 15.39°</td>
</tr>
</tbody>
</table>
• Suppose x-ray is not monochromatic (containing all \( \lambda > \lambda_0 \), white x-ray), sample is in a fixed orientation with respect to the x ray beam:

\[ 2d \sin \theta = n \lambda \]

• Assume \( \theta = 60^\circ \) with the surface of the crystal (100) d for (100) = 0.1 nm; \( \lambda \), & d changing

\[ \Rightarrow \lambda = 2(d/n) \sin \theta = 2(0.1/n) \sin(60^\circ) \]
The reflecting planes are not necessarily parallel to the surface.

- Suppose x-ray is monochromatic (single $\lambda$)
  Normal to the surface (001)

*Fig. 2.4* X-ray reflections from planes not parallel to the surface of the specimen
Continuous X-ray

\[ \lambda = 2 \frac{d_{100}}{n} \sin \theta \]

\[ \begin{array}{c|c|c}
\lambda & \frac{d_{100}}{n} & \theta \\
0.1732 & 0.1 \left(\frac{1}{1}\right) & (d_{110}) 60^\circ \\
0.0866 & 0.1 \left(\frac{1}{2}\right) & (d_{220}) 60^\circ \\
0.0577 & 0.1 \left(\frac{1}{3}\right) & (d_{330}) 60^\circ \\
\end{array} \]
Four diffraction techniques mentioned in the textbook

2.2 The Laue method *(the first diffraction method ever used)*

- Laue photographs are the easiest kind of diffraction pattern to make and require only the simplest kind of apparatus.
The best source is a tube with a heavy-metal target, such as tungsten, since the intensity of the continuous spectrum is proportional to the atomic number of the target metal.
1. Transmission Laue Technique (samples cannot be too thick, ≤ 1 mm)

\[ \tan 2\theta = \frac{r_1}{D} \]

Transmission Laue camera

A: collimator tube; F: film; C: crystal; S: beam stop; D: specimen-to-film distance; \( r_1 \): distance of spot from center of film.
- The X-ray beam is mainly divergent, then a focusing action takes place on diffraction.
2. Back-reflection Laue Technique

FIG. 2.5 Laue back-reflection camera
2. Back-Reflection Laue Method

- The diffracted beams form arrays of spots, that lie on curves on the photographic film.
- No focusing occurs and a divergent incident beam continues to diverge in all direction after diffraction.
• Beam perpendicular to (0001): sixfold symmetry.

**Fig. 2.6** Laue back-reflection photographs. (A) Photograph with X-ray beam perpendicular to the basal plane (0001). (B) Photograph with X-ray beam perpendicular to a prism plane (1120). Dashed lines on the photograph are drawn to show that the back-reflection spots lie on hyperbolas.
• Both back-reflection and transmission Laue Techniques can be used to study a phenomenon: asterism.

**FIG. 2.8** Asterism in a Laue back-reflection photograph. The reflections from distorted- or curved-crystal planes form elongated spots.
2.3 The Rotating crystal method

- fixed $\lambda$ (monochromatic), rotating a crystal (variable $\theta$).
  $\Rightarrow$ typically used with single crystal, rotating to bring different diffraction plane into play.

**FIG. 2.9 (A)** Schematic diagram of a rotating single-crystal camera. **(B)** Schematic representation of the diffraction pattern obtained with a rotating crystal camera. Reflected beams make spots lying in horizontal rows.
2.4 The Debye Scherrer or powder method

- The specimen may be: a small polycrystalline or powder
- fixed $\lambda$, variable $\theta$ (not by rotation of the samples, but due to many small crystals).

**Fig. 2.10** Simple cubic lattice. Relative interplanar spacing for \{100\} and \{110\} planes. Note the unit cell of this lattice is a cube with atoms at its eight corners
• The specimen contains hundreds of randomly oriented crystals in the region illuminated.

\[ n\lambda = 2dsin \theta \]
- $S = 2\theta R$ (S, R known)
- To measure Bragg angle

**FIG. 2.12** Schematic representation of the Debye or powder camera. Specimen is assumed to be simple cubic. Not all reflections are shown.

**FIG. 2.13** Powder camera photograph. Diffraction lines correspond to the reflections shown in Fig. 2.12
2.5 X-ray Diffractometer

\[ n\lambda = 2dsin \theta \]  

**FIG. 2.14** X-ray diffractometer

**FIG. 2.15** The X-ray diffractometer records on a chart the reflected intensity as a function of Bragg angle. Each intensity peak corresponds to a crystallographic plane in a reflecting position.
• The intensity of the x-ray reflections is measured using an electronic device, such as Geiger counter tube or ionization chamber, instead of a photographic film.
2.7 Interactions between Electrons and Materials

- Any decelerated charge emits energy
- Some stop in one impact and release all their energy at once.

![Diagram of electron interactions in a thin specimen](image-url)
• Electrons are scattered by both the electrons and the nuclei in a material.

• The incoming negatively charged electrons interact with the local electromagnetic fields of the specimen.
Kanaya-Okayama Range (1972)

- **Electron range**: a measure of the distance traveled by the electron in the solid

\[
R = \frac{0.0276 \times A \times E^{1.67}}{(Z^{0.89} \times \rho)} \text{ } \mu m
\]

- Depth Penetration
- A = Atomic Weight (g/mole)
- E = Beam Energy (KV)
- Z = Atomic number
- \( \rho = \) density (g/cm³)

![Table 3.2: Comparison of Various Electron Ranges (in Micrometers)](image)
2.7 Interactions between Electrons and Materials

- Elastic scattering: the path (trajectory) of electrons is changed, but their energies are not altered significantly.

- Energy loss mechanisms:
  1. creating phonons (vibrations):
  2. creating oscillations in electron gas of the sample:
  3. continuous X-ray radiation (Bremsstrahlung):
4. secondary electrons:
5. Eject the electrons from the inner shells

![Diagram](image)
Interaction profile between Electrons and Materials
2.6 Transmission electron microscope (TEM):

- Penetration depth: several hundred of nm for typical electron energy used in TEM.

- Lenses in an TEM/STEM utilize either or combinations of magnetic and electrostatic fields to direct the beams as desired.
Electrons with particles and wavelike properties.

\[ p = h \kappa = h \left( \frac{1}{\lambda} \right) \]
\[ \lambda = \frac{h}{p} = \frac{h}{mv} = \frac{h}{\sqrt{2mE}} \]

\( h \): Planck’s constant, \( m \): electron mass, \( v \): electron velocity
Electrons are treated as wave-like, rather than particle-like. Because the wavelength of high-energy electrons is a few thousandths of a nanometer,
http://www.seallabs.com/how-sem-works.html

**FIG. 2.16** Schematic drawing of a transmission electron microscope.
- a: not diffracted.
- Diffracted e’s enter the objected lens at a slightly different angles, converge to form at b.
- Simultaneous reflections from a number of planes
  => Diffraction pattern (I₁)
- These rays pass through b will form an image of the specimen at I₂, superimposed over that from the direct beam.

**FIG. 2.17** Images can be formed in the transmission electron microscope corresponding to the direct beam or to a diffracted beam. (Images from more than one diffracted beam are also possible.)
TEM Diffraction and Image Modes

Figure 2.12 - The two basic operations of the TEM imaging system involve (A) projecting the diffraction pattern on the viewing screen and (B) pro-

Adjust which to focus
Selected area diffraction (SAD)

- Selected area diffraction (SAD) is referred to as "selected" because the user can easily choose from which part of the specimen to obtain the diffraction pattern.

- Located below the sample holder on the TEM column is a selected area aperture. This is a thin strip of metal that will block the beam. It contains several different sized holes, and can be moved by the user.
An aperture diaphragm at $I_1$ to allow the corresponding beams to pass through.

**Fig. 2.18** The use of a diaphragm to select the desired image

- An aperture diaphragm at $I_1$ to allow the corresponding beams to pass through.
Thicker regions of the sample, or regions with a higher atomic number will appear dark, whilst regions with no sample in the beam path will appear bright. (compare with p. 70).

**TEM:**
The STEM was invented in the 1930s along with TEM and offers imaging modes and enhanced microanalysis capabilities not available with a TEM.
Advantages of STEM over TEM

1. Bright field imaging in STEM: by using a large detector and angle of travel, a STEM can be used to image much thicker samples than a TEM is capable of imaging.

2. High-angle annular dark-field imaging (HAADF)
3. As in the SEM, secondary or backscattered electrons can be used for imaging in STEM; but higher signal levels and better spatial resolution are available by detecting transmitted electrons.

⇒ comparatively high accelerating voltage is used.

Figure 22.13. Schematic of the HAADF detector set-up for Z-contrast imaging in a STEM. The conventional ADF and BF detectors are also shown along with the range of electron scattering angles gathered by each detector.
For DF imaging, the annular detector (HAADF) collects more electrons than a diaphragm, and less noisy.

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**FIG. 2.19** This stereographic projection of a cubic crystal shows the principle planes whose zone axis is [100].

*Zone axis*
In a real space

\[ d_{011} = \frac{d_{100}}{\sqrt{2}} = 0.0707 \text{ nm} \]

\[ d_{100} = 0.1 \text{ nm} \]

\( \sqrt{2} d_{100} \)

**FIG. 2.10** Simple cubic lattice. Relative inter-planar spacing for \{100\} and \{110\} planes. Note the unit cell of this lattice is a cube with atoms at its eight corners.
• Reciprocal space \((1/d) = 2\sin\theta/n\lambda\): a powerful tool for understanding diffraction pattern.

• The symmetry present in direct space appears in reciprocal space.

\[ \mathbf{k} - \mathbf{k}_0 = \mathbf{g}_{hkl} \]
\[ |\mathbf{g}_{hkl}| = 1/d_{hkl} = l_{hkl} \]

**FIG. 2.20** The diffraction pattern corresponding to a beam directed along [100] in a cubic crystal

\[ |\mathbf{a}_{011}| = \sqrt{2} \]
(001) standard stereographic projection

BCC crystals

x: Forbidden reflections
Selection rules
Ewald Sphere Construction by Paul Peter Ewald, a German physicist and crystallographer.

- $1/d = 2\sin\theta/\lambda$
- $0 \leq \sin\theta \leq 1$
- $\Rightarrow 0 \leq (1/d = 2\sin\theta/\lambda) \leq 2/\lambda$

$k_0$: incident beam

$k$: diffracted beam

$g$: reciprocal lattice vector
• Any reciprocal lattice vector $g_{hkl}$, drawn from the origin to the reciprocal lattice point (hkl), will be normal to the reflecting planes that have the Miller indices (hkl) in direct space.
Electron diffraction vs X-ray diffraction

1. Both, ED and XRD, are caused by constructive interference of scattered waves, and the same fundamental laws (e.g., Bragg law, extinction rules) can be applied for the interpretation of the resulting diffraction patterns.

ED shows some unique characteristics:
4. This has the advantage that the diffracted electron beams have a high intensity and exposure times are in the order of a few seconds. ED patterns can directly be observed on the viewing screen of the electron microscope. Thus, orienting a crystal along a direction can be easily achieved by tilting while observing changes of the ED pattern simultaneously.

http://www.microscopy.ethz.ch/ED-XRD.htm
• Typically, in X-ray diffraction only one reciprocal lattice point is on the surface of the Ewald sphere at one time.

• Electron diffraction can obtain several planes in a zone at the same time is due to:

1. $\lambda$ of the incident electron beam
   \[ \lambda \downarrow \Rightarrow (2/\lambda) \uparrow \]  
   Bigger Ewald Sphere

2. The effect of the specimen shape
• The key point is that when the sphere cuts through the reciprocal lattice point, the Bragg condition is satisfied.
Figure 17.2. The relrod at $g_{hk\ell}$ when the beam is $\Delta\theta$ away from the exact Bragg condition. The Ewald sphere intercepts the relrod at a negative value of $s$ which defines the vector $k = g + s$. The intensity of the diffracted beam as a function of where the Ewald sphere cuts the relrod is shown on the right of the diagram. In this case the intensity has fallen almost to zero.
Figure 17.3. (A) For a thin specimen, every point is replaced by a red rod. (B) The Ewald sphere cutting the rods in (A) when the crystal is tilted slightly off the 001 axis. (C) The effect of the tilt in (B) on the DP. Notice that all of the spots in the DP are displaced relative to their positions on the square grid (the projection of the spots at zero tilt), but that the magnitude of the displacement varies depending on the sign and size of $s$. Of course, spots on the Ewald sphere must still be the “correct” distance from 000.
2.11 Scanning Electron Microscope (SEM)

- SEM greatly extends the usefulness of the optical microscope: higher magnifications and greater depth
- No tedious specimen preparation procedures needed
- Normally 1,500 to 50,000X
The detector is biased at +200 V, to draw e⁻'s.
2.12 Topographic Contrast

- Topographic contrast:
  Contrast origin: surface inclination of the surface relative to detector.

![Diagram showing topographic contrast](image)

**FIG. 2.24** An illustration of how the scanning electron microscope can reveal surface relief when used with a secondary electron detector.
**FIG. 2.25** An SEM micrograph of a fractured Cu–4.9 at. % Sn specimen. Note the large depth of field exhibited in the picture, which shows that the specimen failed by both transgranular (across the grains or crystals) and intergranular (along the grain boundaries) fracture.
2.12 Topographic Contrast

- Backscattered electrons may also be used as a source of the signal.

**Fig. 2.26** Backscattered electrons are also able to reveal surface relief.
In (B)

- Phase A: lower Z, darkest
- Phase B: gray
- Phase C: white

**FIG. 2.27** A comparison of images from the same area of a specimen surface, obtained with (A) secondary electrons and (B) backscattered electrons.
2.13 The Picture Element (Pixel) Size

- Picture element size (PES): the area of the raster surface that supplies information to a single spot on the CRT screen

  \[ \text{PES} = \text{the actual pixel size of the CRT/magnification} \]

- e.g.: 1000 steps along a 10 cm line => 100\(\mu\text{m/step} \]

  \[ \Rightarrow \text{PES}=100\mu\text{m/M} \]

For fixed beam size of 12.5 nm; equivalent M for PES is 8000X (100×1000/12.5)
2.14 SEM Depth of Focus

- One of the great advantages of SEM images is the unusually great depth of focus they exhibit.
2.14 SEM Depth of Focus

- The e\textsuperscript{-} beam has a very small angle of divergence.
• There is a region below and above the plane of optimum focus: the beam size is smaller than PES => sharp focus.
⇒ Beyond that region: the beam size is larger than PES => blurry

• D: The depth of focus (field)

\[
\frac{\text{PES}}{2} = \frac{D}{2} \times \alpha \Rightarrow
\]
2.10 Electron Spectrum:

- 45° incident beam & a detector normal to the surface
- $E_0$: incident electron energy (low)
- I: Peak closed to $E_0$; heavier mass (atomic number ↑) specimen => peak sharper, close to $E_0$.
- II: inelastic processes: energy loss
- III: secondary electrons: peak at ~ 3-5 eV
• When a sample is bombarded with electrons, the strongest region (III) of the electron energy spectrum is due to secondary electrons.
• Secondary electrons are produced when an incident electron excites an electron in the sample and loses some of its energy in the process.

http://www4.nau.edu/microanalysis/microprobe/Interact-SE.html
• Their energies are a function of $E_0$ and the surface work function, $E_w$, which defines the amount of energy needed to remove electrons from the surface of a material.

http://www4.nau.edu/microanalysis/microprobe/Interact-SE.html
2.15 Microanalysis of Specimens

- The scanning electron microscope can be easily converted into an instrument capable of chemically microanalyzing specimens.

1. Electron probe x-ray microanalysis
2. Auger electron spectroscopy

1. Electron probe x-ray microanalysis
- Using the characteristic peaks of the x-ray spectrum resulting from the bombardment of the specimen by the beam electrons.
- The $\lambda$ and strength yield valuable info about the chemical composition of the specimen.
2.17 The Characteristic X-Rays

- Characteristic X-ray originates from electron transfer between different energy levels.

**Diagram Description**

**Figure 2.31** Illustration of how \( K_\alpha \) radiation and Auger electrons are formed. (A) The ejection of an electron from the \( K \) shell is the first step. (B) If an atom from the \( L \) shell falls into the hole in the \( K \) shell, it is possible for a \( K_\alpha \) photon to be released. (C) Alternatively, the drop of an \( L \) shell electron into the \( K \) shell hole may result in the ejection of an Auger electron from the \( L \) shell.
• X-Ray spectrum varies with the incident e- s energy.

**FIG. 2.30** The effect of the accelerating potential, applied to the electrons in the electron beam, on the X-ray spectrum of a molybdenum specimen.  
(A) When the electrons are accelerated by a potential of 20,000 volts, only a continuous X-ray spectrum is obtained.  
(B) When the potential is raised to 25,000 volts, two small characteristic peaks are superimposed upon the continuous spectrum.  
(C) Further increasing the potential applied to the electrons to 35,000 volts greatly increases the magnitudes of the characteristic lines.
• Molybdenum (Mo): Kα₁ actually consists of two lines: Kα₁ and Kα₂, slightly different λ.

• Kα₁: L3 to K, Kα₂: L2 to K
- Diameter of e⁻ beam: 10 nm
- The area of the specimen surface where x-ray emitted: 1 μm
- The depth below the surface: 1 μm
- Spatial resolution: 1 μm
- Detection limit: 100 ppm

Low x-ray yield for light elements
2.18 Auger Electron Spectroscopy (AES):

- Ejection of a second outer shell electron
- Auger e⁻s: dominates for an atomic number < 15

**Characteristic x-ray**

**Inner shell**

**Fig. 2.31** Illustration of how $K_\alpha$ radiation and Auger electrons are formed. (A) The ejection of an electron from the $K$ shell is the first step. (B) If an atom from the $L$ shell falls into the hole in the $K$ shell, it is possible for a $K_\alpha$ photon to be released. (C) Alternatively, the drop of an $L$ shell electron into the $K$ shell hole may result in the ejection of an Auger electron from the $L$ shell.
- Three $e^-$s reaction: KLL
- No Auger analysis for H, He

**FIG. 2.32** Auger electron spectra of silver with an incident beam energy of 1 keV. Derivative and integral spectra are compared (After N. C. MacDonald)

Auger signal superimposed on a strong background due to back-scattered $e^-$s.
Elastically scattered electrons (no energy loss)

Background:
back-scattered & secondary electron

Energy loss due to electronic and plasma excitations

Energy (eV); log scale

Intensity (a.u.)