Content

Electron Microscopy I
Dagmar Gerthsen

1. From light microscopy to electron microscopy
2. Practical aspects of transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM)
   2.1 The transmission electron microscope
   2.2 Sample preparation
   2.3 Beam damage
3. Electron diffraction in solids: kinematical diffraction theory
   3.1 Interaction of electrons with single atoms
4. Conventional TEM (and STEM) imaging of objects from solid state physics and materials science
5. Dynamical electron diffraction
6. Imaging of the crystalline lattice by high-resolution transmission electron microscopy (HRTEM)
7. Scanning transmission electron microscopy (STEM)
8. Electron holography
9. Transmission electron microscopy with phase plates
2.1 The transmission electron microscope

Sufficient sample, lens-current and electron-beam stability by extreme requirements regarding laboratory conditions

- Temperature variations < ± 0.5 degrees/hour
- Electromagnetic stray field variation < ± 30 nT
- Small mechanical floor vibration amplitudes (1.1 m thick concrete foundation in CFN building)

Pairs of “coils” in condensers, objective, diffraction lens and projection lenses for beam tilt and beam shift

Sets of apertures with different diameter in the condenser lens system and diffraction pattern and intermediate image plane (not all shown in scheme)
2.1 The transmission electron microscope

TEM imaging and diffraction mode

Change between imaging and diffraction mode by change of focal length of the intermediate lens

Control of the imaging mode by the diameter of the objective aperture in the back focal plane of the objective lens

Selection of a sample region for diffraction analysis by the diameter and position of the selected area aperture in the 1\textsuperscript{st} intermediate image

SAED: selected area electron diffraction

Figure 9.12. The two basic operations of the TEM imaging system involve (A) projecting the diffraction pattern on the viewing screen and (B) projecting the image onto the screen. In each case the intermediate lens selects either the back focal plane or the image plane of the objective lens as its object.

2.1 The transmission electron microscope

Condensor: adjustment of beam intensity, convergence und coherence of the electron wave

Scanning transmission electron microscopy (STEM)

Role of the C2 aperture diameter

D.B. Williams, C.B. Carter, Transmission Electron Microscopy, Fig.9.1 – 9.3

Several fixed settings for C1 („spot size“), focusing of C2 focus und control of C2 aperture diameter by operator
2.1 The transmission electron microscope

Scanning transmission electron microscopy (STEM) in a transmission electron microscope: principle of image formation

Focused electron beam

Scan coils

Beam scans sample area

Detector

Display screen, digital image

Synchronization

Magnification = \( \frac{L}{l} \)

\( l \): size of scanned area

\( L \): size of display screen

Measurement of local transmitted electron charge at \((x,y)\) by STEM detector determines brightness of pixel at the equivalent position on the display screen \((x',y')\)

No lenses for image formation necessary!

Adapted from Williams, Carter, Transmission Electron Microscopy, Abb. 9.17
2.1 The transmission electron microscope

STEM

Generation of an electron beam with small diameter (electron „probe“)

- Beam diameter depends on aberrations of the lowermost focusing lens and convergence angle $\alpha_0$ and can be varied between several nm and $\sim 0.05$ nm (in microscopes with a probe corrector) depending on the desired resolution and imaging mode.
- The beam convergence angle is determined by the $C_2$ aperture diameter.
- A diffraction pattern is formed in the back focal plane of the objective lens.
- No imaging lenses necessary for image formation!
- The imaging lens system images the diffraction pattern on the detector plane and allows variations of the magnification of the diffraction pattern (different camera lengths).
2.1 The transmission electron microscope

Effect of beam convergence angle on the diameter of Bragg reflections in diffraction patterns

The diameter of Bragg reflections in diffraction patterns increases with beam convergence angle.

Parallel beam → spot-like Bragg reflections
Convergent beam → Bragg disks → convergent beam electron diffraction (CBED)
2.1 The transmission electron microscope

**STEM detectors**
- For electrons scattered in different angular ranges
- Scattering angle range can be also modified by camera length of imaging lens system

![Diagram of electron scattering angles]

**BF:** bright-field detector for unscattered electrons or electrons scattered in small angles
**ADF:** annular dark-field detector for electron scattered in larger angles
**HAADF:** high-angle annular dark-field detector for electrons scattered in large angles
2.1 The transmission electron microscope

Alignment of transmission electron microscope: What is important?
2.1 The transmission electron microscope

- **Analytical double-tilt holder** for solid-state samples
- specimen diameter 3 mm

Special specimen holders:
- Cooling, heating, specimen holders with electrical leads
- "environmental cells“ for experiments under elevated gas pressures or in fluids
- Sample holders for deformation testing

Fotos: L. Dieterle (LEM)

Reservoir for liquid nitrogen for cooling holder
2.2 Sample preparation

TEM sample preparation
Goals:
• Electron-transparent sample with maximum thickness of a few 10 nm for high-resolution TEM and up to maximal ~ 1 μm for conventional TEM
• Dependence of maximum specimen thickness on atomic number/density of sample material, electron energy and desired resolution
• Preparation artifacts must be avoided

• Cutting a thin slice from bulk material and drilling a disk with 3 mm diameter
• Grinding the disk to a thickness of about 200 μm thickness

Light microscopy image of TEM specimen
2.2 Sample preparation

TEM sample preparation

Dimple grinding to a thickness of only a few \( \mu \text{m} \) in the center of the disk

E. Hornbogen, B. Skrotzki, Werkstoffmikroskopie, Fig.2.1

Sputtering with \( \text{Ar}^+ \)-ions until a hole in the center of the sample appears
\( \text{Ar}^+ \)-ion energies between few keV and few 100 eV under a shallow incidence angle between 3 and 20 degrees
Parameters need to be optimized for each sample material

E. Hornbogen, B. Skrotzki, Werkstoffmikroskopie, Fig.2.10
2.2 Sample preparation

Preparation of cross-section samples: side view of thin-film systems

Further preparation techniques:
• electrochemical / chemical etching (metals, semiconductors)
• Ultramicrotomy with diamond knife („Soft Matter“: polymers, samples from life sciences → ultrathin sections with minimum thicknesses of 50 nm
• ...

all other preparation steps like in standard procedure
2.2 Sample preparation

TEM sample preparation with a focused-ion-beam (FIB) system

Milling of a thin lamella from a bulk sample with a beam of focused Ga\(^{+}\)-ions (1 - 30 keV ion energy)

- Preparation from bulk material at precisely defined location
- Implantation of Ga in the sample and knock-on damage by high-energy Ga\(^{+}\)-ions possible

More details of FIB and scanning electron microscopy in EMII lecture course
2.3 Beam damage in the electron microscope

„Direct“ radiation damage
• atom displacement („knock-on“) damage
• electron excitation damage / radiolysis

Atom-displacement damage

- Formation of vacancies and interstitials, if binding energy of atom < transferred energy during collision
- Formation of extended defects (stacking faults, cavities) if high vacancy and interstitial concentrations are present
  
  Limitation of illumination / observation time, reduction of electron energy

e.g. for
Si $E_0 > 145$ keV
Al $E_0 > 170$ keV
2.3 Beam damage in the electron microscope

Knock-on damage

Grain boundary in Si imaged at 300 keV

Electron-beam induced rod-to-tube transformation


FIG. 1. Z-contrast images and derived structures of the $\Sigma = 25 \{710\} \{001\}$ symmetric tilt boundary at two stages of exposure to electron irradiation: (a) a nearly unaffected core with all columns visible but those shaded showing reduced intensity; (b) a partially affected core with several columns appearing darker.

R. Popescu (LEM)
Radiolysis in electrical insulators

- Structural rearrangement of atoms by excitation of their electrons in higher-energy bound states or conduction band states
- Reduction of radiolysis by sample cooling in a liquid-nitrogen cooled sample holder and/or increase of electron energy
- Radiolysis in electrically conducting samples insignificant
- Frequent damage mechanism in ionic crystal, (electrically insulating) oxide ceramics, life science samples and polymers
2.3 Beam damage in the electron microscope

„Indirect“ radiation damage
• Contamination
• Electron-beam-induced sample heating

Contamination

Polymerization of hydrocarbon molecules $C_nH_m$ from
• Remnant gas atmosphere (pump oils, grease from rubber sealings)
• contamination from sample preparation on the sample surface by the electron beam illumination

Precautions:
• work under clean conditions (gloves)
• final sample cleaning in Ar/O-plasma
• best possible vacuum by, e.g., cold trap at liquid-nitrogen temperature (condensation of $C_nH_m$ molecules on cold trap)
• liquid-nitrogen cooled sample holder (reduction of surface diffusion)

L. Reimer, Transmission Electron Microscopy, Fig. 10.10
2.3 Beam damage in the electron microscope

Electron-beam-induced sample heating

- Few experimental data available
- Heat conductivity of sample and thermal coupling to sample holder decisive
- Melting of nanoparticles and small precipitates observed *without intentional sample heating* (extreme examples)
- Calculation: dissipated heat by the electron beam = power transferred by heat conduction

Table 10.3. Rise of specimen temperature $\Delta T$ in the centre of a circular diaphragm ($R = 50 \, \mu m$) covered with a supporting film and irradiated with 100 keV electrons

<table>
<thead>
<tr>
<th>Substance</th>
<th>Uniform illumination  $R = 50 , \mu m$, $j = 10^{-2} , A , cm^{-2}$</th>
<th>Small-area illumination  $r_0 = 0.5 , \mu m$, $j = 1 , A , cm^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formvar</td>
<td>62 °C</td>
<td>6 °C</td>
</tr>
<tr>
<td>Glass (SiO)</td>
<td>27 °C</td>
<td>2.5 °C</td>
</tr>
<tr>
<td>Metal (Cu)</td>
<td>0.3 °C</td>
<td>0.03 °C</td>
</tr>
</tbody>
</table>

L. Reimer. Transmission Electron Microscopy, Fig. 10.2 und Table 10.3
3. Electron diffraction in solids: kinematical diffraction theory

Contrast in TEM due to interaction between electrons and sample

Interpretation of contrast on the basis of a detailed understanding of the interaction between electrons and solid

Interaction between electrons and single atoms

Interaction with a crystalline solid

Kinematical diffraction theory (single electron scattering)

Dynamical diffraction theory (multiple electron scattering)

Chapter 5

General validity of kinematical diffraction theory for electrons, X-rays and neutrons
### 3.1 Interaction of electrons with single atoms

**Elastic and inelastic scattering processes**

*Elastic scattering:*
Momentum and energy conservation

*Inelastic scattering:*
Generation of excited states or ionization of target atom
In a solid: excitation of phonons, plasmons, ...

Elastic collision of an electron with a single atom with transferred energy $E'$:
“Billiard“ physics without detailed knowledge of interaction type

\[
E' = \frac{2E(E + 2E_R)}{Mc^2} \sin^2 \theta / 2 = \frac{E(E + 1.02)}{496A} \sin^2 \theta / 2
\]

- $E$: kinetic energy of the incident electron (in units of MeV)
- $E_R$: electron rest energy 0.511 MeV
- $M$: atom mass of target atom in $A \, m_p$ ($m_p$: atomic mass unit)
- $c$: speed of light
- $\theta$: scattering angle
3.1 Interaction of electrons with single atoms

Elastic scattering

Energy transfer to the atom = energy loss of the electron

<table>
<thead>
<tr>
<th>θ</th>
<th>E = 100 keV</th>
<th></th>
<th>E = 1 MeV</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C (A = 12)</td>
<td>Cu (A = 63.5)</td>
<td>Au (A = 197)</td>
<td>C</td>
<td>Cu</td>
</tr>
<tr>
<td>0.5°</td>
<td>0.5 meV</td>
<td>0.1 meV</td>
<td>0.03 meV</td>
<td>9 meV</td>
<td>1.7 meV</td>
</tr>
<tr>
<td>10°</td>
<td>0.15 eV</td>
<td>29 meV</td>
<td>9 meV</td>
<td>2.7 eV</td>
<td>0.5 eV</td>
</tr>
<tr>
<td>90°</td>
<td>10 eV</td>
<td>1.9 eV</td>
<td>0.6 eV</td>
<td>179 eV</td>
<td>34 eV</td>
</tr>
<tr>
<td>180°</td>
<td>20 eV</td>
<td>3.8 eV</td>
<td>1.2 eV</td>
<td>359 eV</td>
<td>68 eV</td>
</tr>
</tbody>
</table>

For small scattering angles θ in TEM holds in a good approximation: energy and wavelength unchanged for elastic scattering!

Knock on damage for \( E > 100 \text{ keV} \) for elastic scattering into large scattering angles (rare!) and typical binding energies of atoms in a solid between 5 and 30 eV
3.1 Interaction of electrons with single atoms

Description of elastic electron scattering: Particle description

Classical description by Rutherford (1911): Coulomb interaction between atom nucleus with charge $+Ze$ and electron without consideration of screening electron cloud

$\theta$: scattering angle
$d\Omega$: solid angle
$Z$: atomic number of the atom

Differential scattering cross-section: $\frac{d\sigma(\theta)}{d\Omega}$

Probability for scattering process with scattering angle $\theta$
3.1 Interaction of electrons with single atoms

Rutherford differential scattering cross-section (non relativistic)

\[ \frac{d\sigma(\theta)}{d\Omega} = \frac{e^4 Z^2}{4(4\pi\varepsilon_0)^2 m^2 \nu^2 \sin^4 \frac{\theta}{2}} \]

\( Z \): atomic number of target atom  
\( \nu \): electron velocity  
\( m \): electron mass  
\( e \): elementary charge

Differential scattering cross-section diverges for \( \theta \rightarrow 0 \)

Solution of the problem by taking into account the screening electron cloud by quantum mechanical calculation: Solution of the stationary Schrödinger equation  
\[ \text{screened differential Rutherford scattering cross-section} \] (Electron microscopy II)

In addition consideration of spin-orbit coupling for small distances between the electron and atom nucleus:  
\[ \text{differential Mott scattering cross-sections} \]
3.1 Interaction of electrons with single atoms

Description of elastic scattering: Wave description (stationary)

Incident plane electron wave

$$\psi = \psi_0 \exp(2\pi i k \vec{r})$$

$\vec{r}$: position

$k$ : wave vector of electron wave

Scattering at point charge $\rightarrow$ spherical wave

$$\psi_s = \psi_0 f(\theta) \frac{\exp(2\pi i k r)}{r}$$

$f(\theta)$: atomic form factor gives angle dependence of amplitude of the scattered wave

Resulting wave

$$\psi = \psi_0 \left( \exp(2\pi i k \vec{r}) + i f(\theta) \frac{\exp(2\pi i k r)}{r} \right)$$
3.1 Interaction of electrons with single atoms

Origin of $f(\theta)$: Electron scattering electron at an atom with charge density $\rho(\vec{r}_i)$

\[
\rho(\vec{r}) = \rho_i + \rho_s = \rho_i + \frac{2\pi m e}{\hbar^2} \int_{\text{Atom}} V(\vec{r}_i) \frac{\exp(2\pi i k |\vec{r} - \vec{r}_i|)}{|\vec{r} - \vec{r}_i|} \psi(\vec{r}_i) d^3 \vec{r}_i
\]

- Incident (plane) wave
- Total wave function at $\vec{r}_i$
- Green's function

Integral Schrödinger equation (Green's function formulation)

\[
-\frac{\hbar^2}{8\pi^2 m} \Delta \psi - eV(r)\psi = E\psi
\]
3.1 Interaction of electrons with single atoms

1. Born approximation

\[ eV(\vec{r}_i) \ll E_0 \quad \text{Intensity of incident wave not substantially weakened:} \quad \psi(\vec{r}_i) = \psi_i \quad |\psi_s| \ll |\psi_i| \]

\(|\vec{r}| \) and \(|\vec{r} - \vec{r}_i| \gg |\vec{r}_i| \)

\[ \psi_s = \frac{\exp(2\pi i k \vec{r}) 2\pi me}{r \hbar^2} \int V(\vec{r}_i) \exp\left(2\pi i (\vec{k} - \vec{k}') \vec{r}_i\right) d^3\vec{r}_i \]

Atom

with

\[ \vec{k} - \vec{k}' = \vec{g} \]

- scattered wave proportional to the Fourier transform of the potential
- atomic form factors depend on charge distribution within the atom
3.1 Interaction of electrons with single atoms

Atomic form factor takes into account screening by the electron cloud, relativistic effects (using 1. Born approximation)

\[ f(\theta) = \frac{2\pi m e^2}{\varepsilon_0 h^2} \left( \frac{\lambda}{\sin \left( \frac{\theta}{2} \right)} \right)^2 [Z - f_x(\theta)] \]

Mott-Bethe equation

\( m \): electron mass  
\( \varepsilon_0 \): vacuum permittivity  
\( Z \): atomic number of target atom  
\( \lambda \): electron wave length  
\( f_x \): scattering amplitude for X-rays (well known) – describes screening by electron cloud

Calculated atomic form factors for electron scattering at single atoms e.g. by Doyle und Turner, Acta Cryst. A24, 390 (1968)

- description of atoms in ionic und covalent crystals not optimal (error some %)  
- charge density distribution of atoms in crystal must be well known for accurate computation of \( f(\theta) \)