Part 4

High-Resolution Transmission Electron Microscopy
Significance

- high-resolution transmission electron microscopy (HRTEM):
  - resolve object details smaller than 1nm (10\(^{-9}\) m)

- image the \textit{interior} of the specimen
  - compare, e. g., scanning tunneling microscopy: atomic resolution, however only at the surface

- local
  - compare, e. g., X-ray diffraction: averaging, “statistical” information

- direct imaging
  - HRTEM images can be »intuitively« interpretable (however, severe restrictions apply – see below)

- direct imaging of atom arrangements (in projection)
  - crystals (and quasi-crystals)
  - in particular: structural defects
    - interfaces (grain boundaries, interphase interfaces)
    - stacking faults, anti-phase boundaries, inversion domain boundaries, …
    - crystals dislocations, disclinations, misfit dislocations, …
  - however: projection
    \(\Rightarrow\) \textit{no} (individual) point defects
    \(\Rightarrow\) defects need to be parallel to the viewing direction
• techniques
  – HRTEM (high-resolution transmission electron microscopy)
    • since 1980ies
    • »steady« improvement of conventional TEM
    • widespread application
    • focus of interest in this course
  – holography
    • high-resolution electron holography is relatively new
    • record amplitude and phase (not just intensity) of the electron wave in the image plane
  – HAADF (high-angle angular dark-field) imaging (“z-contrast”)
    • new method
    • scanning transmission electron microscopy
    • requires annular (HAADF) detector

HRTEM versus CTEM (conventional TEM)

• contrast formation in CTEM
  – sometimes absorption contrast, mostly *diffraction* contrast:
    • crystallites (grains) of different structure (different phases) or orientation
    • distortions induced by particles, dislocations, …
    • variation of the scattering amplitude by stacking faults, grain boundaries, …

• CTEM bright-field imaging
- CTEM dark-field imaging
• example: Co precipitates in CuCo

– bright-field image

– distortion field introduced by the particles (plane bending) changes diffraction conditions in the matrix ⇒»coffee bean« contrast

• principle of CTEM:

– different specimen regions generate Bragg reflections of different intensity

– contrast: either Bragg reflections or transmitted beam do not contribute to the image

⇒ consequence: interatomic spacings cannot be resolved
Abbe Theory of Resolution

• ideal object (↔ crystal): lattice with period $d$

• coherent illumination: plane waves, wavelength $\lambda$

\[
\text{Sin} \left[ \varphi_z \right] = \frac{z \cdot \lambda}{d}
\]

• diffraction:
  – path difference between waves emitted from neighboring slits must equal an integer number of wavelengths, $z \cdot \lambda$
  – diffracted beams make angles $\varphi_z$, with the plane of the lattice, and

• Abbe: only the diffracted beams carry information about the spacing $d$
  $\Rightarrow$ to image the lattice, the optical system must at least include one diffracted beam ($z = 1$)
⇒ generalization:
to resolve an object under coherent illumination, the image formation must include at least the first diffraction maximum of the object

⇒ the aperture semi-angle $\alpha$ introduces a limit for the spatial resolution:

$$\Rightarrow \sin[\varphi_1] = \frac{\lambda}{d} < \sin[\alpha]$$

⇒ resolution limit $\delta$:
smallest distance $d$ that can be resolved

$$\sin[\varphi_1] = \sin[\alpha] \Rightarrow \delta = \frac{\lambda}{\sin[\alpha]}$$

⇒ resolving interatomic distances requires larger aperture than CTEM imaging and interference of (at least two) different Bragg reflections
⇒ transition from CTEM to HRTEM:

- instrumental pre-requisites for interference images
  - illumination with a high degree of coherence (small source, small spread of the wavelength)
  - mechanics and electronics sufficiently stable
  - electron lenses with small aberrations (spherical and chromatic aberration, astigmatism)

- remove objective aperture

- ultra-thin specimen to avoid absorption and inelastic electron scattering (destroys coherence)

- orient the specimen to generate suitable Bragg reflections

- “ideal” HRTEM imaging (neglecting lens aberrations)

⇒ high resolution, but no contrast!
Phase Contrast

- consider *thin* specimen, plane electron wave $\psi_0$, no absorption
  
  $\Rightarrow$ specimen just introduces *small, locally varying* phase shift
  (refractive index $\leftrightarrow$ electrostatic potential)

- express exit wave $\psi_e(x)$ as sum of incident wave $\psi_0$ and scattered wave $\psi_s(x)$

\[
\psi_e(x) = \psi_0 + \psi_s(x)
\]
• phase of \( \psi_s[x] \) is shifted by \(-90^\circ\) versus \( \psi_0 \):

\[
\psi_e[x] = \psi_0 - i \psi_s[x]
\]

\( \Rightarrow \) intensity:

\[
|\psi_i[x]|^2 = |\psi_e[x]|^2 \approx |\psi_0[x]|^2
\]

\( \Rightarrow \) no contrast!

• must convert locally different phase shifts to locally different intensities (contrast \( \Leftrightarrow \) intensity variation)

\( \Rightarrow \) if the optics introduces an additional phase shift of the scattered wave by \(-90^\circ\),

\[
|\psi_i[x]|^2 = |\psi_0[x] - \psi_s[x]|^2 < |\psi_0[x]|^2
\]

• problems:
  
  – \(-90^\circ\) phase shift cannot be realized in an ideal manner
  
  – for TEM there exists no “\(\lambda/4\) plate” as for light-optical microscopy
  
  – in HRTEM, the required phase shift is introduced by
    
    • the spherical aberration of the objective lens
    
    • defocusing of the objective lens
  
  – the image, which is obtained by interference of coherent electron waves, often has a complex relationship with \( \psi_e \), the electron wave function at the exit surface of the specimen

• consequence:

  Correct interpretation of HRTEM images requires a *quantitative* understanding of image formation.
• example: $\text{Al/MgAl}_2\text{O}_4$ interface
  
  – HRTEM in $<110>$ projection
  
  – microscope: JEM-ARM 1250 (Stuttgart)

• where are which atoms?!
  
  – Al, Mg, O atom columns: “white” or “black”? 
  
  – relative visibility of the ions in the spinel?
Electron Optics

- HRTEM:
  - interference → wave properties
  - “wave model” of electron mandatory
- exact treatment of electron interference: quantum mechanics
- however: simpler wave optics also yields correct results – apart from image rotation and adjustments of the wave length $\lambda$

Properties of Fast Electrons

Physical Constants

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>rest mass</td>
<td>$m_0 = 9,1091 \cdot 10^{-31}$ kg</td>
</tr>
<tr>
<td>charge</td>
<td>$Q = -e = -1,602 \cdot 10^{-19}$ C</td>
</tr>
<tr>
<td>kinetic energy</td>
<td>$E = e , U$</td>
</tr>
<tr>
<td></td>
<td>$1$ eV $= 1,602 \cdot 10^{-19}$ Nm</td>
</tr>
<tr>
<td>velocity of light</td>
<td>$c = 2,9979 \cdot 10^8$ m s$^{-1}$</td>
</tr>
<tr>
<td>energy at rest</td>
<td>$E_0 = m_0 , c^2 = 511$ keV $= 0,511$ MeV</td>
</tr>
<tr>
<td>Planck constant</td>
<td>$h = 6,6256 \cdot 10^{-34}$ N m s</td>
</tr>
</tbody>
</table>
Electrons in Motion

<table>
<thead>
<tr>
<th>property</th>
<th>non-relativistic</th>
<th>relativistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newton’s law</td>
<td>$F = \frac{d}{dt} p = m_0 \frac{d}{dt} v$</td>
<td>$F = \frac{d}{dt} p = \frac{d}{dt} (m v)$</td>
</tr>
<tr>
<td>mass</td>
<td>$m = m_0$</td>
<td>$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$</td>
</tr>
<tr>
<td>energy</td>
<td>$E = eU = \frac{1}{2} m v^2$</td>
<td>$m c^2 = E_0 + E = m_0 c^2 + eU$</td>
</tr>
<tr>
<td>velocity</td>
<td>$v = \sqrt{\frac{2e}{m_0}}$</td>
<td>$v = c \sqrt{1 - \frac{1}{\left(1 + \frac{E}{E_0}\right)^2}}$</td>
</tr>
<tr>
<td>momentum</td>
<td>$p = m_0 v = \sqrt{2m_0 E}$</td>
<td>$p = m v = \frac{1}{c} \sqrt{2 E E_0 + E^2}$</td>
</tr>
<tr>
<td>de Broglie wavelength</td>
<td>$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_0 E}}$</td>
<td>$\lambda = \frac{hc}{\sqrt{2 E E_0 + E^2}}$</td>
</tr>
</tbody>
</table>

- de Broglie wavelength as a function of the accelerating voltage:
• velocity as a function of the accelerating voltage:

\[ \frac{v}{c} \]

\[ [kV] \]

• kinetic and potential energy of the electrons on their way through the microscope

specimen:
- electrostatic potential varies ⇒ diffraction
- free surfaces → average positive
- “inner potential” \( U_i \), attractive for electrons
- acceleration, increase of the average velocity
- wave length \( \lambda \) becomes smaller
Fraunhofer Diffraction

- Fresnel diffraction $\rightarrow$ Fraunhofer diffraction:
  - plane incident wave, diffraction pattern at “infinite” distance
  - alternatively: diffraction pattern at back-focal plane of a lens

\[ \frac{1}{f} = \frac{1}{b} + \frac{1}{g} \]

- wave at the exit surface of the specimen: $\psi_e$

- focal plane: rays that leave the specimen under the same diffraction angle $\theta$ intersect in the same point of the focal plane

- note:
  - path difference between neighboring rays
→ phase shift, to be taken into account when calculating the amplitude in the back focal plane

- path difference for scattering of a plane incident wave at two scattering centers $P$ and $Q$:

- ray through $P$ has longer path than ray through $Q$

- path difference:

$$\Delta s_g = u_0 \cdot \Delta r - u \cdot \Delta r = -\lambda (k - k_0) \cdot \Delta r = -\lambda q \cdot \Delta r$$

$u_0, u$: unit vectors; $q$: scattering vector.

⇔ phase $\varphi_P$ of the ray through $P$ lags behind compared to phase $\varphi_Q$ of the beam through $Q$

- phase difference:

$$\Delta \varphi_g = \varphi_P - \varphi_Q = -\frac{2\pi}{\lambda} \Delta s_g = 2\pi q \cdot \Delta r$$
• ray path for HRTEM (see above):
  – for a given diffraction angle \( \theta \) consider phase difference \( \varphi_g \) between ray through \( \mathbf{r} \) and ray through origin of the object plane (\( \mathbf{r} = 0 \)):
    \[
    \Delta \mathbf{r} = \mathbf{r} = (x, y, 0)
    \]
    \[
    \Delta \varphi_g = \varphi_g[\mathbf{r}] := \varphi[\mathbf{r}] - \varphi[0]
    \]
    \( \varphi[0] \): focal-plane phase of the ray emitted at \( \mathbf{r} = 0 \) with angle \( \theta \), \( \varphi[\mathbf{r}] \): focal-plane phase of the ray emitted at \( \mathbf{r} \) with angle \( \theta \).
  – TEM: small wavelength, small diffraction angles
    \( \Rightarrow \) \( \mathbf{q} \) is approximately \textit{parallel} to the focal plane
    \[
    \mathbf{q} = |\mathbf{k} - \mathbf{k}_0| = 2k \sin \left[ \frac{\theta}{2} \right] \approx \frac{\theta}{\lambda}
    \]
• in the focal plane all rays with the same scattering vector \( \mathbf{q} \) intersect in a point, which is displaced from the origin in the direction of \( \mathbf{q} \)
• distance of the intersection point from the focus (origin of focal plane):
    \[
    f\theta = f\mathbf{n} \mathbf{q}
    \]
    \( \Rightarrow \) use \( \mathbf{q} \) as coordinate vector in the focal plane
    (a vector of length \( ||\mathbf{r}|| \) in the focal plane corresponds to \( \mathbf{q} = ||\mathbf{r}||/f\lambda \))
    \[
    \psi_f[\mathbf{q}] = \int_{S_e} \psi_e[\mathbf{r}] \text{Exp}[i\varphi_g[\mathbf{r}]] d\mathbf{S}
    \]
    \[
    = \int_{S_e} \psi_e[\mathbf{r}] \text{Exp}[2\pi i \mathbf{q} \cdot \mathbf{r}] d^2\mathbf{r}
    \]
    \( S_e \): object plane.
“weighed sum”

- plane waves with the same scattering vector $q$ (and the same wave vector $k$) but different phases $2\pi i q \cdot r$
- contribution of each wave is proportional to the amplitude of the wave function at the exit surface of the specimen

→ Fourier transformation!

The wave function $\psi_f$ in the (back-) focal plane corresponds to the Fourier transform of the object wave function $\psi_e$ (at the exit surface of the specimen):

$$\psi_f = \mathcal{F}[\psi_e]$$

- however: this is strictly correct only for a perfect, ideal lens

- *real* lenses: see below …

- wave function in the image plane:
  - consider point $r = (x, y)$ of the object
  → conjugate point in the image plane (image):

$$r' = -Mr$$

$M$: magnification.

- this implies:

$$\psi_i[r] = \psi_e \left[ -\frac{1}{M} r \right]$$

- amplitude $\psi_i[r']$ at point $r'$ in the image:

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- since the image of an area is $M^2$ larger than the area itself, the image intensity must decrease as $M^2$

$\Rightarrow$ amplitude decreases as $M^{-1}$

- sum over contributions from all points of the focal plane, taking into account the respective phases

- phase difference of neighboring rays that intersect at image point $r'$:

  - consider ray intersecting with the focal plane at $f \lambda q$ away from the focus ($q = 0$):

    \[
    \begin{align*}
    s_g &= f \cdot q \cdot \theta' = f \cdot q \cdot \frac{r}{f} = \lambda qr \\
    s_g &= \lambda qr = -s_g
    \end{align*}
    \]

- path difference to the ray through the focus:
⇒ the phase shift introduced between the focal plane and the image plane exactly compensates the phase shift introduced between the object plane and the focal plane:

\[ \varphi_g' = -\frac{2\pi}{\lambda} \Delta \mathcal{S}_g = -2\pi q \cdot r \]

*(ideal lens: different rays emerging from the same point of the object arrive at the image point without relative phase shifts)*

⇒ amplitude at \( r' \) in the image plane:

\[ \psi_i[r'] = \frac{1}{M} \int_{\mathcal{S}_f} \psi_f[q] \exp[-2\pi i q \cdot r'] d^2q \]

\[ = \frac{1}{M} \int_{\mathcal{S}_f} \psi_f[q] \exp[-2\pi i q \cdot \left( -\frac{r'}{M} \right)] d^2q \]

\( \mathcal{S}_f \): focal plane.

• often one neglects the magnification and the inversion of the image, and expresses the image with respect to the coordinate system of the object (let \( M = 1, r' = r \)):

\[ \psi_i[r] = \int_{\mathcal{S}_f} \psi_f[q] \exp[-2\pi i q \cdot r] d^2q \]

⇒ inverse Fourier transformation!

The wave function \( \psi_i \) in image plane corresponds to the inverse Fourier transform of the wave function \( \psi_f \):

\[ \psi_i = \mathcal{F}^{-1}[\psi_f] \]

⇒ result for the complete imaging process *(ideal lens, \( M = 1, r' = r \)):
The wave function $\psi_i$ in the image plane corresponds to the inverse Fourier transform of the Fourier transform of the object wave function $\psi_e$:

$$\psi_i = \mathcal{F}^{-1}[\mathcal{F}[\psi_e]]$$

- **ideal** lens, $M = 1$, $r' = r$: perfect restoration of the object wave function in the image

- **“real”** imaging:
  - finite aperture $\rightarrow$ truncates the Fourier spectrum in the focal plane
  - lens aberrations introduce *additional* phase shifts
    $\rightarrow$ the objective lens shifts the phases of the plane waves of which $\psi_e$ is composed in a complex way versus each other
    $\Rightarrow$ $\psi_i$ does not exactly correspond to $\psi_e$
  - limited coherence
    $\rightarrow$ attenuation of the interference, diffuse background
  $\Rightarrow$ interpretation of “real” images requires in-depth understanding of Fourier transformation
Fourier Transformation

**General Properties**

- definition of the Fourier transform
  \[
  F[f(x)] = \mathcal{F}[f]:= \int_{-\infty}^{\infty} f(r) \exp[2\pi i xu] \, dx
  \]

- inverse Fourier transform:
  \[
  F^{-1}[\mathcal{F}[f]] = f(x):= \int_{-\infty}^{\infty} \mathcal{F}[f] \exp[-2\pi i xu] \, du
  \]

- extension to \(n\) dimensions:
  \[
  F[f(x)] = \mathcal{F}[f]:= \int_{\mathbb{R}^n} f(x) \exp[2\pi i xu] \, d^n x
  \]
  \[
  F^{-1}[\mathcal{F}[f]] = f(x):= \int_{\mathbb{R}^n} \mathcal{F}[f] \exp[-2\pi i xu] \, d^n u
  \]

- convention
  - factor \(2\pi\) in the exponent
  - sometimes neglected (in quantum mechanics, for example), but this requires to multiply
    - either \(F[]\) or \(F^{-1}[]\) by factor \((2\pi)^{-1}\), or
    - each, \(F[]\) and \(F^{-1}[]\), by \((2\pi)^{-1/2}\)
• properties of the Fourier transform

<table>
<thead>
<tr>
<th>real space</th>
<th>Fourier space</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f[x] )</td>
<td>( F[u] )</td>
</tr>
<tr>
<td>( af[x] + bg[x] )</td>
<td>( af[u] + bg[u] )</td>
</tr>
<tr>
<td>( f^*[x] )</td>
<td>( F^*[-u] )</td>
</tr>
<tr>
<td>( f[x - a] )</td>
<td>( F[u] \exp[2\pi au] )</td>
</tr>
<tr>
<td>( f[ax] )</td>
<td>( \frac{1}{a} F\left[\frac{u}{a}\right] )</td>
</tr>
<tr>
<td>( \frac{d}{dx} f[x] )</td>
<td>( (-2\pi u) F[u] )</td>
</tr>
<tr>
<td>( \frac{d^n}{dx^n} f[x] )</td>
<td>( (-2\pi u)^n F[u] )</td>
</tr>
<tr>
<td>( \exp[-2\pi ax] )</td>
<td>( \delta[u - a] )</td>
</tr>
<tr>
<td>( \delta[x - a] )</td>
<td>( \exp[2\pi au] )</td>
</tr>
<tr>
<td>( f[x] \cdot g[x] )</td>
<td>( \int_{-\infty}^{\infty} F[u'] \cdot G[u - u'] , du' \equiv (F \ast G)[u] )</td>
</tr>
<tr>
<td>( \int_{-\infty}^{\infty} f[x'] \cdot g[x - x'] , dx' \equiv (f \ast g)[x] )</td>
<td>( F[u] \cdot G[u] )</td>
</tr>
</tbody>
</table>
Delta Function

- definition of the delta “function”
  (actually a “distribution,” since it is not defined for every argument)

\[
\delta[x - a] := \begin{cases} 
0 & x \neq a \\
\infty & x = a 
\end{cases}
\]

\[
\int_{-\infty}^{\infty} \delta[x - a] = 1
\]

- visualization:

- delta function correspond to a normal distribution in the limit of vanishing standard deviation:
\[ \delta[x] = \lim_{\sigma \to 0} \left( \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{x}{\sigma} \right)^2 \right] \right) \]

- under an integral the delta function “selects” a value of the integrand function:
\[ \int_{-\infty}^{\infty} \delta[x - a] \cdot g[x] \, dx = g[a] \]

- concerning Fourier transforms, the following relation is particularly important:
\[ \int_{-\infty}^{\infty} \exp[2\pi i ux] \, dx = \delta[u] \]

**Convolution**

- definition of the convolution integral of two functions \( f[x] \) and \( g[x] \):
\[ (f * g)[x] := \int_{-\infty}^{\infty} f[x'] \cdot g[x - x'] \, dx' \]

- substitution \( y' = x - x' \), \( dx' = -dy \) reveals that the convolution is symmetric with respect to exchanging the argument functions:
\[ (f * g)[x] = -\int_{-\infty}^{\infty} f[x - y] \cdot g[y] \, dy = \int_{-\infty}^{\infty} g[y] \cdot f[x - y] \, dy = (g * f)[x] \]

- interpretation:
  spread function \( f \) with the function obtained by inverting function \( g \)
Example of a Convolution

\[ (f * g)[x] = \int_{-\infty}^{\infty} f[x'] \cdot g[x - x'] \, dx' \]

\[ \downarrow \]

\[ g[x_1 - x'] \]

\[ g[x_2 - x'] \]

\[ \int_{-\infty}^{\infty} f[x'] \cdot g[x_1 - x'] \, dx' \]

\[ \int_{-\infty}^{\infty} f[x'] \cdot g[x_2 - x'] \, dx' \]

\[ (f * g)[x] \]