Chapter 2
Basic Concepts

This chapter presents an outline of the basic tools used in this research. In particular an overview of basic concepts of transmission electron microscopy and the theory of image formation is given. At the end of this chapter a brief introduction to the density functional theory (DFT) is presented. Experimental HRTEM imaging, DFT calculations and HRTEM image simulations are performed to retrieve information from metal oxide interfaces.

2.1 Transmission Electron Microscopy

The wave-like characteristics of electrons were first postulated in 1925 by Louis de Broglie, with a wavelength far less than visible light. In 1926 H. Busch revealed that an electromagnetic field might act as a focusing lens on electrons. The first electron microscope was constructed in 1932 by Ernst Ruska. For his research, he was awarded in 1986 the Nobel price together with Binnig and Rohrer who invented the scanning tunneling microscope. The Electron microscope opened new horizons to visualize materials structures far below the resolution reached in light microscopy. The most attractive point is that the wavelength of electrons are much smaller than atoms and it is at least theoretically possible to see details well below the atomic level. However, currently it is impossible to build transmission electron microscopes with a resolution limited by the electron wavelength, mainly because of imperfections of the magnetic lenses (see section 2.1.2). In the middle of the 70's the last century commercial TEMs became available that were capable of resolving individual columns of atoms in crystalline materials. High voltage electron microscopes, i.e. with accelerating voltages between 1 MV and 3 MV have the advantage of shorter wavelength of the electrons, but also radiation damage increases. After that period HRTEMs operating with intermediate voltages between 200 kV – 400 kV were designed offering very high resolution close to that achieved previously at 1MV. More recently, developments were seen to reconstruct the exit wave (from a defocus series) and to improve the directly interpretable resolution to the information limit. New developments for
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increasing the resolution in high resolution electron microscopy is the use of a monochromator and an Cs corrector to reach resolutions below 0.1 nm. In this research two different transmission electron microscopes were used, a JEOL 4000 EX/II (LaB₆, 400 kV) for atomic structure observations and a JEOL 2010F (FEG, 200kV) for EDS analysis and in-situ heating experiments. Williams and Carter have written an excellent introductory textbook in the field of modern electron microscopy. For a theoretical textbook of TEM reference is made to.

2.1.1 Illumination System

Electrons are generated in an electron gun, accelerated towards the anode and focused at the specimen with condenser lenses. High resolution TEM requires planar coherent electron waves, since high-resolution micrographs are formed by phase contrast, see more details in the next section 2.1.2. For elemental analysis, it is also important to have the possibility to focus the electron beam within a diameter (FWHM) of the order of 1 nm to determine chemical compositions in the nanometer range. Several demands must be fulfilled: high brightness, small source size and little energy spread of the electrons. The brightness of the beam is an important parameter and is defined as follows:

\[
B = \frac{I}{A\Omega}
\]  

i.e. the brightness value \( B \) is related to the electron current \( I \) emitted from the area \( A \) (which also determines the spatial coherency) into the spatial angle \( \Omega \). The conventional way to generate electrons is thermionic emission. A tip is heated so that the energy of the electrons can exceed the energy of the so-called work function and leave the tip. This can only be realized with materials with high melting temperature (such as tungsten) or with low work function like LaB₆. The saturated current density of the thermionic emitted electrons is described by the Richardson-Dushman's law that includes the work function \( \Phi \) of the tip material and the temperature \( T \):

\[
J = CT^2 e^{\frac{-\Phi}{kT}}
\]

with the current density \( J \) at the tip and \( C \) the so-called Richardson-Dushman's constant depending on the material used for the tip. LaB₆ tips are commonly used (instead of tungsten filaments), because of the lower operating temperature that reduces the energy spread of the emitted electrons and increases the brightness.
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An alternative method to generate electrons from a source is to apply high electric fields at a small tip. At the tip (with radii typically 10-50 nanometer) fields in the order of $10^7 - 10^8$ V/cm are created enabling electrons to tunnel through the potential barrier. For electric fields $E > 10^7$ V/cm the electron current density $J$ can be described according the modified Fowler-Nordheim relation:

$$J = \frac{1.54 \times 10^{-6}}{\Phi t^2(y)} E^2 e^{-6.8 \times 10^{-7} v(y) \Phi^{1/2}},$$  \hspace{1cm} (2.3)

where $J$ is the field-emitted current density in A/m², $E$ is the applied electric field at the tip, and $\Phi$ is the work function in eV. The functions $v$ and $t$ of the variable $y = 3.79 \times 10^4 E^{1/2}/\phi$ depend weakly on the applied electric field and have been tabulated in literature. The advantage of this cold field emission guns (cold FEG) is the small size of emitting area in the order of nanometers with a brightness that is three orders of magnitude higher than for thermionic sources. In the FEG-TEM it is therefore possible to focus the beam to a very small probe for chemical analysis at a sub-nanometer range and produce a beam with high spatial coherence over a large area of the specimen. The small (virtual) source size reaches values for the brightness in the order of $B = 10^{11}$ to $10^{14}$ Am²sr⁻¹ with an energy spread of 0.2 – 0.5 eV compared with $\sim 10^9$ Am²sr⁻¹ and an energy spread of 0.8 – 1 eV for thermionic emission. However, FEG sources need UHV to keep the surface of the emitter clean and high demands on the stability of the high voltage power supply. Further drawbacks are the need for extra magnetic shielding around the emitter and the limited lifetime of FEGs.

A moderate heating of the FEG can circumvent some disadvantages associated with cold FEG emitters. For thermal assisted FEGs the work function is often reduced by coating the tip with ZrO₂ which keeps the emission stable (Schottky emitter). This increases the energy spread of the emitted electrons by about a factor of 2 and some reduction of the temporal coherency compared with cold FEGs. The Schottky emitter is widely used in commercial FEG-TEMs, because of the stability, lifetime and high intensity. Table 2.1 gives an overview of the technical data of the different electron sources.
After the (plane) electron wave strikes the specimen a part of the electrons experience a phase shift. This phase shift is caused by (inelastic) elastic scattering of the electrons within the specimen and results in the exit wave when the electron front leaves the specimen. Responsible for the image formation is the elastically scattered electrons, the inelastically scattered electrons appear as diffuse background in TEM micrographs. The essential part of image formation in TEM is the transformation of the phase shift stored in the exit wave into amplitude modulation, and therefore into visible contrast. With the assumption that the specimen is a pure phase object the phase shift can be described with the object function:

\[ \lambda = h \left[ 2m_0eE_0 \left( 1 + \frac{eE_0}{2m_0c^2} \right) \right]^{-1/2} \]  

(2.4)

Transmission electron microscopes operate generally between 80 kV and 1300 kV meaning that the velocity of the electron includes relativistic effects. This must be taken into account applying the De Broglie relationship to calculate the wavelength:

For 400 kV electrons this results in a wavelength of \( \lambda = 1.64 \) pm which is much smaller than the information limit of any high-resolution microscope. The point resolution of 0.1-0.2 nm of high-resolution microscopes is limited by the spherical aberration coefficient \( C_s \) of their objective lenses and not by the wavelength.

### 2.1.2 Image formation

After the (plane) electron wave strikes the specimen a part of the electrons experience a phase shift. This phase shift is caused by (inelastic) elastic scattering of the electrons within the specimen and results in the exit wave when the electron front leaves the specimen. Responsible for the image formation is the elastically scattered electrons, the inelastically scattered electrons appear as diffuse background in TEM micrographs. The essential part of image formation in TEM is the transformation of the phase shift stored in the exit wave into amplitude modulation, and therefore into visible contrast. With the assumption that the specimen is a pure phase object the phase shift can be described with the object function:

**Table 2.1 Technical data of different electron sources**

<table>
<thead>
<tr>
<th></th>
<th>Tungsten</th>
<th>LaB₆</th>
<th>Cold FEG</th>
<th>Schottky</th>
<th>Heated FEG</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Brightness</strong></td>
<td>(0.3-2) (10^9)</td>
<td>(0.3-2) (10^9)</td>
<td>(10^{11-10^{14}})</td>
<td>(10^{11-10^{14}})</td>
<td>(10^{11-10^{14}})</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>2500-3000</td>
<td>1400-2000</td>
<td>300</td>
<td>1800</td>
<td>300</td>
</tr>
<tr>
<td><strong>Work function</strong></td>
<td>4.6</td>
<td>2.7</td>
<td>4.6</td>
<td>2.8</td>
<td>4.6</td>
</tr>
<tr>
<td><strong>Source size</strong></td>
<td>20-50</td>
<td>10-20</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td><strong>Energy spread</strong></td>
<td>3.0</td>
<td>1.5</td>
<td>0.3</td>
<td>0.8</td>
<td>0.5</td>
</tr>
</tbody>
</table>
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\[ \sigma(\vec{r}) = e^{-i\Phi(\vec{r})} \]  (2.5)

For sufficiently thin objects the phase can be considered as weak \( \Phi(\vec{r}) \ll 1 \) and \( \sigma(\vec{r}) \) can be approximated to first order: \( \sigma(\vec{r}) = 1 - i\Phi(\vec{r}) \)

A possibility to visualize the phase contrast in TEM was introduced by Scherzer. Perfect lenses show no amplitude modulation, but imaging introduces an extra phase shift between the central beam and the beam further away from the optical axis of the objective lens (deviation from the ideal Gaussian wave front). Deviations from the ideal Gaussian wave front in lenses is known as spherical aberration. For particular frequencies the phase contrast of the exit wave will be nearly optimally transferred into amplitude contrast. Therefore the observed contrast in TEM micrographs are mainly controlled by the extra phase shift of the spherical aberration and the defocus. The influence of the extra phase shift on the image contrast can be taken into account by multiplying the wavefunction at the back focal plane with the function describing the extra phase shift as a function of the distance from the optical axis. The lenses can be conceived cylindrical symmetric, and will be represented as a function of the distance of the reciprocal lattice point to the optical axis \( U = (u^2 + v^2)^{1/2} \), where \( u \) and \( v \) are the angular variables in reciprocal space. The extra phase factor \( X(U) \) describes in two terms the spherical aberration and defocus:

\[ X(U) = -\pi\lambda\Delta f U^2 + \frac{1}{2}\pi C_s \lambda^3 U^4 \]  (2.6)

with \( \Delta f \) the defocus value and \( C_s \) the spherical aberration coefficient. The function that multiplies the exit wave is the so-called transfer function \( B(U) \):

\[ B(U) = E(U) e^{X(U)} \]  (2.7)

For the final image wave after the objective lens, assuming a weak phase object:

\[ b(\vec{r}) = FT^{-1}[FT(\sigma(\vec{r})) \otimes B(U)] = \sigma_{\text{object}} \otimes B(\vec{r}), \]  (2.8)

where \( FT \) and \( FT^{-1} \) are symbols to represent the Fourier transform and inverse Fourier transform, respectively. After the multiplication of equation (2.8) with its complex conjugate and neglecting the terms of second order and higher the image formation results in:

\[ I(\vec{r}) = 1 + 2\Phi \otimes FT^{-1}[E(U)\sin(X(U))] \]  (2.9)
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Under ideal imaging conditions the wave aberration must be \( \pi/2 \) or \( \sin(X(U)) = 1 \) for all spatial frequencies \( U \). Therefore \( \sin(X(U)) \) is called the contrast transfer function (CTF). The CTF converts the phase information from the specimen into intensity information by the phase shift introduced by the objective lens and thus defines the weight with which each elastically scattered beam is transferred into the image intensity spectrum. Further, even thin HRTEM samples are too thick to be considered as a pure phase object because also the amplitude of the object wave will change (inelastic scattering).

The interpretation of the contrast in TEM micrographs in terms of atomic structure is therefore not straightforward and needs evaluation with HRTEM simulations to extract the atomic positions. Further difficulties arise from the combination of the energy spread of the electrons, fluctuations of the lens current, mechanical vibration of the specimen and usage of a partly converged beam. These factors cause a loss of spatial and temporal beam coherence. Such effects result in a smearing of the image, and deteriorate the ultimate resolution, since for high frequencies, the CTF function is damped and approaches zero.

The damping envelopes \( E_\alpha \) and \( E_\Lambda \) which represent the damping by the beam convergence and the spread in defocus respectively, are described as follows:

\[
E_{\Lambda}(U) = e^{-\frac{1}{2}x^2\Delta^2 U^4}
\]

\[
E_{\alpha}(U) = e^{\pi^2\alpha^2(\Delta f + \Delta c U^2)^2 U^2},
\]

where \( \Delta \) is the half-width of a Gaussian spread of focus and \( \alpha \) is the semi-angle of the convergence cone at the specimen surface. The resulting contrast transfer function (CTF) for the JEOL 4000 EX/II and the JEOL 2010F are plotted in Figure 2.1 with the damping envelopes \( E_\alpha \) and \( E_\Lambda \). From the plot of the contrast transfer function it is not clear how the resolution in HRTEMs is defined. There are several resolutions possible as stated by O’Keefe:

1. Fringe or lattice resolution. This is related to the highest spatial resolution present in the image. The sign of \( \sin(X(U)) \) is not known and the structure is not related to the image. Maybe in thicker crystals second-order or non-linear interference can occur. This resolution is limited by the beam convergence and the spread of defocus.

2. Information limit. This resolution is similar to the lattice resolution and is related to the highest spatial frequency transferred linearly into the intensity spectrum. A definition used is that the information limit is defined as the frequency where the overall value of the damping envelopes corresponds to \( e^{-2} \) (e.g. the damping is 5% of the CTF intensity).
3. Point resolution. This is the definition of the first zero point in the contrast transfer function, right hand side of the Scherzer band. For higher spatial frequencies, the image contrast and thus the structure cannot be unambiguously interpreted. The optimal transmitted phase contrast is defined as a Scherzer defocus: $(4 / 3 \cdot C_{\mu} \lambda)^{1/2}$ and the highest transferred frequency is equal to $1.5 C_{\mu}^{-1/4} \lambda^{-3/4}$.

In Figure 2.1 the CTF's of the JEOL 4000EX and JEOL 2010F at optimum defocus are plotted with the damping envelopes. The corresponding electrical-optical properties are listed in Table 2.2. For the two microscopes with a different illumination system, it is clearly visible that with the JEOL 2010F a rapid oscillation of the CTF occurs. These oscillations arise because the spatial coherence is higher for the 2010 F (spread of defocus and in particular beam convergence is smaller) than for the 4000 EX/II. Correspondingly, the information limit of the JEOL 2010F is better than of the 4000EX/II. For the JEOL 2010F the information limit is a factor 2 higher compared with the point resolution. For microscopes with higher operating voltages (e.g. 1250 kV), a FEG will not significantly increase the information limit, because the higher the voltage the larger the energy spread of the electrons and the damping envelope is limited by the spread of defocus, instead of beam convergence.

| Table 2.2 Technical data of the used microscopes$^4$ |
|---------------------------------|-----------------|
|                                 | JEOL 4000EX/II | JEOL 2010F      |
| Emission                        | LaB$_6$ (filament) | FEG (Schottky emitter) |
| Operating voltage (kV)          | 400             | 200              |
| Spherical aberration coefficient (mm) | 0.97          | 1.0              |
| Spread of defocus (nm)          | 7.8             | 4.0              |
| Beam convergence angle (mrad)   | 0.8             | 0.1              |
| Information limit (nm)          | 0.14            | 0.11             |
| Point resolution (nm)           | 0.165           | 0.23             |
| Optimum defocus (nm)            | 47              | 58               |
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For lower (≤ 200 kV) voltage TEMs the situation is clearly more favorable and a FEG thus significantly improves the information limit. For the interpretation of HRTEM micrographs it is essential to align the sample carefully along a zone axis. This can be achieved in diffraction mode with the help of Kikuchi pattern and/or even distribution of the spot intensities. Kikuchi bands arise from the inelastically scattered electrons and are more pronounced in thicker regions of the specimen. The misalignment of the zone axis of a crystal is in this way reduced to a fraction of a mrad. To correct for beam tilt is not a straightforward task, because of the misalignments in the imaging system after the objective lens. For a good correction of beam tilt a coma-free alignment is necessary. This can be obtained by wobbling the beam tilt in x-directions symmetrically around a central value until the power spectra of imaged amorphous areas are identical for positive and negative tilt around the central value. Then the procedure has to be repeated for the y-direction. This procedure can only be performed accurately with computer controlled microscopes equipped with a CCD camera and is not used in the current work. A compromise is to use the voltage center alignment which results in some residual beam tilt of the order of 1-2 mrad. The two-fold astigmatism can be easily corrected by the objective stigmator, because of its distortion and blurring effect on the image (of an amorphous edge). All these parameters together with the thickness and defocus value must be carefully considered. Without using image simulation software it is hardly possible to interpret HRTEM images and take possible slightly misaligned image parameters into account. Therefore, TEM image simulation packages as EMS or JEMS\textsuperscript{7} and MacTempas\textsuperscript{8} are applied for this purpose.
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Figure 2.1 Contrast transfer functions and damping envelopes of the JEOL 4000 EX/II (top) and JEOL 2010F (bottom) at optimum defocus of 47 and 58 nm, respectively. The highly coherent electron source used in the 2010F, a FEG, is apparent from the many oscillations in the CTF of the 2010F.
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2.1.3 Interaction with matter

Elastically scattered electrons generate the basis of the image formation in HRTEM and are the predominant fraction of the transmitted electrons for small sample thickness (< 15 nm). In contrast, the thicker the sample the more electrons become inelastically scattered and this must be prevented as much as possible, because they contribute mostly to the background intensity of the image. Therefore, the thinner the specimen (≤ 2 nm) the better the quality of the HRTEM images. The inelastic scattered electrons can be removed by inserting an energy filter in the microscope between specimen and recording device. In the following section on image formation, only the elastic scattered electrons are considered.

2.1.3.1 Multislice Method

To retrieve structural information it is necessary to calculate the trajectory of the electron wave through the crystal. In the kinematical approximation, the multiple scattering of the electrons is neglected and results in a (non-diffracted) central beam that always keeps its initial intensity. This approximation already fails for thin crystals (order of nm) and even for (heavy) single atoms. Multiple scattering of the electrons in the specimen occurs and can be properly described with dynamical diffraction theory. This accounts for all the scattered beams and their mutual exchange of the intensity during the multiple scattering process in the specimen. A full dynamical calculation would exceed the available computer power. Using the fact that back-scattering of the high energetic electrons can be considered to be negligibly small in thin crystals, electrons are assumed to scatter only in a forward direction with small diffraction angles. With this approximation the crystal can be divided in sub-slices with a thickness Δz perpendicular to the incident beam. In-between the slices the wave front propagates as shown in Figure 2.2. This kind of approach was proposed by Cowley and Moodie\(^9\).

The principle of multislice simulations:

1. Construct a structure model of the atoms, which corresponds to the spatial distribution of the electrostatic potential (Coulomb fields of atoms)
2. The electrostatic potential \(V(x, y)\) with in-plane coordinates \(x, y\) of the sliced crystal or supercell is projected for each subslice of the included atoms onto its exit surface. This projection can be performed, because of the assumed small diffraction angles of the electrons and the small thickness of the slice.
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\[ V(x, y) = \int V(x, y, z)dz \] is the two-dimensional projection of the potential (see further section 2.1.3.2).

3. On the basis of \( V(x, y) \) the phase grating \( q(x, y) = e^{-i[\sigma V(x, y) - \mu(x, y)]} \) is calculated, where the constant \( \sigma = 2\pi m e \lambda / h^2 \) defines the interaction strength of the electrons with the matter and \( \mu(x, y) \) is the local absorption (inelastic scattering effects).

4. Calculate the propagation of the exit wave \( \Psi_{n+1} \). This can be described by convoluting \( q(x, y) \) with the Fresnel propagator: \( p(x, y) = e^{-i\pi(x^2 + y^2) / \lambda \delta} \).

The multislice method is based on Huygens' principle. The real-space exit wave function after the \( n \)th slice \( \Psi_n(x, y) \) is:

\[
\Psi_n(x, y) = [\Psi_{n-1}(x, y) \otimes p_{n-1}(x, y)] \cdot q_n(x, y), \tag{2.12}
\]

where the object is replaced by an infinite number of point sources emitting spherical wavelets (see Figure 2.2 indicated by the small arrows). This approach results in efficient computation, because the convolution can be replaced by a multiplication of Fourier Transformations. The quality of the simulation increases with decreasing slice thickness and increasing number of beams (Bragg reflections) included in the calculation.

**Figure 2.2** Multislice method as sequence of transformation and propagation.

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2.1.3.2  **Formalism of the projected potentials**

There exists a direct equivalence between the multislice method and the solution of the time independent Schrödinger equation, which is commonly applied in scattering theory. For the exit wave function the scattering integral has the following solution:

$$\Psi(\bar{r}) = \Psi_0(\bar{r}) - \frac{8\pi^2 me}{\hbar^2} \int_{\Omega_s} V(\bar{r}') \Psi(\bar{r}') G(|\bar{r} - \bar{r}'|) d\bar{r}'$$  \hspace{1cm} (2.13)

with:

- $G(\bar{r})$ : Green operator
- $\Omega_s$ : the scattering volume

In vacuo, the incident electron wavefront is described as a plane wave with vector $\bar{k}$:

$$\Psi_0(\bar{r}) = e^{-2\pi ikr}, \quad k = |\bar{k}| = \frac{1}{\lambda}$$  \hspace{1cm} (2.14)

$\lambda$ is the wavelength of the electrons. The Green operator $G(|\bar{r} - \bar{r}'|)$ is given by:

$$G(|\bar{r} - \bar{r}'|) = -\frac{e^{-2\pi i|r-r'|}}{4\pi|r-r'|}$$  \hspace{1cm} (2.15)

The formalism can be simplified to that of Rayleigh-Sommerfeld formulation, since the point of observation is at a distance much larger than the size of the scattering center: $|\bar{r} - \bar{r}'| \approx r - \frac{r - r'}{k}$

A further (first order) assumption is that the amplitude of the secondary spherical wavelet is much weaker than the amplitude of the transmitted wave. This is equal to the first Born approximation with $\Psi(\bar{r}) = \Psi_0(\bar{r}) + \Psi_1(\bar{r})$. The wave-function $\Psi(\bar{r}')$ at $\bar{r}'$ is replaced by $\Psi_0(\bar{r}) = e^{-2\pi ikr}$ and $|\bar{r} - \bar{r}'|$ by $|\bar{r}|$. Finally, the scattered wavelet $\Psi_1(\bar{r})$ is given by:

$$\Psi_1(\bar{r}) = \frac{e^{-2\pi ikr}}{r} \left[ \int_{\Omega_s} V(\bar{r}') e^{-2\pi i\bar{k} \bar{r}'} d\bar{r}' \right]$$  \hspace{1cm} (2.16)

The essential part is the correct calculation of the crystal potentials $V(\bar{r}')$ and they are related to the electron scattering factors $f_{\alpha}(\bar{u})$ of individual atoms by:
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\[ f_{cl}(\vec{u}) = \int_{\Omega} V(\vec{r}) e^{2\pi i \vec{u} \cdot \vec{r}} d\vec{r} \]  \hspace{1cm} (2.17)

The Fourier coefficients of the crystal potential \( V(\vec{u}) \) are calculated with:

\[ V(\vec{u}) = \sum_{\Omega_c} f_{cl}(\vec{u}) \text{Occ}(\vec{r}_a) e^{-B_a |\vec{r} - \vec{r}_a|^2} e^{2\pi i \vec{u} \cdot \vec{r}} \]  \hspace{1cm} (2.18)

- \( B_a \): the Debye-Waller factor that takes the thermal vibration into account (typically 0.005 nm\(^2\)),
- \( \text{Occ} \): the occupancy of the atoms in the crystal of side \( \vec{r}_a \), and
- \( \Omega_c \): the cell volume.

In the multislice method the crystal potential is projected onto a sub-slice \( \Delta z \).

Finally the projected potential \( V_p(x,y) \) is described as follows:

\[ V_p(x,y) = c \int_0^1 V(x,y,z) dz = \sum_{n=1}^N V_{n,p}(x,y) \]  \hspace{1cm} (2.19)

Instead of using electron scattering factors \( f_{cl}(\vec{u}) \) it is more straightforward to calculate the projected potential directly from the charge density of the structure model:

\[ V(\vec{u}) = \int \frac{\rho(\vec{r})}{k^2} e^{2\pi i \vec{u} \cdot \vec{r}} d\vec{r} \]  \hspace{1cm} (2.20)

The projected potential and the electron density in the solid is related to the two-fold integration of the Poisson's equation in reciprocal space:

\[ k^2V(\vec{k}) = 4\pi \rho(\vec{k}) \].

This direct implementation of charge density calculation as a correction term in HRTEM image simulation is treated in more detail in chapter 6, where the charge density is obtained from ab-initio calculations.

### 2.2 Quantitative X-Ray Microanalysis

Quantitative X-ray microanalysis was performed using a JEOL 2010F analytical transmission electron microscope. Additionally to the operation in the TEM-mode (parallel incidence of the electron beam) there exists also the possibility to operate in X-ray energy-dispersive spectrometry (EDS) and nano-beam-diffraction (NBD) mode. In the NBD-mode the convergences angle \( \alpha \) of the beam incidence is smaller, whereas in the EDS-mode these angles are larger. In the latter case, the diameter of the electron probe can be reduced to
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approximately 0.5 nm (FWHM) and thus enables very localized chemical analysis. The NBD-mode will be not considered in the present work. In the following a brief introduction and operation of EDS microanalysis in the analytical TEM will be given.

In EDS the inelastic scattered electrons are essential. In general, the highly accelerated primary electrons are able to remove one of the tightly bound inner-shell electrons of the atoms in the irradiated sample. This “hole” in the inner-shell will be filled by an electron from one of the outer-shells of the atom to lower the energy state of the configuration. After recombination each element emits its specific characteristic X-rays or an Auger electron. The electron of the incident beam also interacts with the Coulomb field of the nuclei. These Coulomb interactions of the electrons with the nuclei lower their velocity and produce a continuum of Bremsstrahlung in the spectrum. The results is that the characteristic X-rays of a detected element in the specimen appear as Gaussian shaped peaks on top of the background of Bremsstrahlung. This background of the EDS spectrum must be taken into account in quantitative analysis. The interface between microscope and EDS detector is schematically depicted in Figure 2.3.

![Figure 2.3 Schematically set-up of the EDS detector mounted in the transmission electron microscopy.](image)

A Si(Li)-detector is mounted between the objective pole pieces with a ultra-thin window in front of it. This has the advantage that X-rays from light elements down to boron can be detected. The EDS unit in an analytical TEM has three main parts: the Si(Li)-detector, the processing electronics and the multi-channel analyzer (MCA) display. After the X-rays penetrate the Si(Li)-detector a charge
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pulse proportional to the X-ray energy will be generated that is converted into a voltage. This signal is subsequently amplified through the field-effect transistor. Finally, a digitized signal is stored as a function of energy in the MCA. After manual subtraction of the background from the X-ray dispersive spectra the quantification of the concentration $C_i$ $(i = A,B)$ of elements $A$ and $B$ can be related to the intensities $I_i$ in the X-ray spectrum by using the Cliff-Lorimer\textsuperscript{10} ratio technique in the thin-film approximation:

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}$$

(2.21)

For the quantification, the Cliff-Lorimer factor $k_{AB}$ is not a unique factor and can only be compared under identical conditions (same: accelerating voltage, detector configuration, peak-integration, background-subtraction routine). The $k_{AB}$ factor can be user-defined or theoretical $k_{AB}$ values are stored in the library of the quantification software package\textsuperscript{11}. With modern quantification software, it is possible nowadays to obtain an almost fully automated quantification of X-ray spectra using the MCA system. The intensities $I_A$ and $I_B$ are measured, their background is subtracted and they are integrated. For the quantification the K$_\alpha$-lines are most suitable, since the L- or M-lines are more difficult due to the overlapping lines in each family. However, highly energetic K$_\alpha$-lines (for energies > 20 keV non-linear effects in the Si(Li)-detector) should be excluded for quantification in heavy elements and L- or M-lines must be taken into account instead. The possible overlapping peaks in X-ray spectra must be carefully analyzed. Poor counting statistics, because of the thin foil can be a further source of error in particular for detection of low concentrations. A longer acquisition time increases the count rates (better statistics), but this may have the drawback of higher contamination and sample drift during the recording of the spectra. Sample drift is extremely disadvantageous in experiments where spatial resolution is essential, like segregation studies at grain boundaries or interfaces (chapter 4).

The correction procedure in bulk microanalysis is often performed with the ZAF correction; $Z$ for the atomic number, $A$ for absorption of X-rays and $F$ for fluorescence of X-rays within the specimen. For thin electron-transparent specimen the correction procedure can be simplified, because the A- and F factors are very small and only generally the Z-correction is necessary.

All acquisitions of the present work were performed using a double-tilt beryllium specimen holder. The beryllium holder prevents generation of detectable X-rays from parts of the specimen holder. A cold finger near the
specimen (cooled with liquid nitrogen) reduces hydrocarbon contamination at the surface of the specimen.

2.3 In-situ heating

Many phenomena occur at elevated temperatures and they are of fundamental interest. The use of specimen heating during TEM observation allows the possibility to study direct phase transformations, such as nucleation and growth, dissolution processes, etc. In the present work heating of Cu3Pd alloys have been carried out in a JOEL 2010F equipped with a Gatan double tilt specimen heating holder, model 652. The temperature of the heating element is controlled with an accuracy of ± 1 ºC and the specimen can be heated to 900 ºC. The furnace of the heating holder is constructed of tantalum, because of its high temperature stability and resistance to solid state welding to most technical materials including silicon. Tantalum anti-welding rings between the specimen and the furnace prevents any damage of the furnace if welding of the specimen does occur.

2.4 Creation of oxide interfaces

To study fundamental aspects of metal-oxide bonding it is necessary to study well-defined model systems. There are several methods to create these interfaces. One approach is to use Molecular Beam Epitaxy (MBE) to produce high quality structures with monolayer control. An advantage of this technique is that metal can be deposited on an oxide substrate in several chosen orientations. The difficulty is the preparation of suitable TEM samples of these grown layers. For interface studies a cross-section must be prepared thin enough for HRTEM observations. This can be troublesome for brittle oxide layers. A second method to produce metal-oxide interfaces is the use of solid state bonding as proposed by Burger, Mader and Rühle. In this case the metal and oxide are carefully oriented and heated in vacuum. In this way, it is possible to choose an orientation for both materials, but the interface reconstructs sometimes to a lower energy configuration. To some extent this method has the same difficulties as the MBE method in sample preparation, but the metal block gives a better strength to the configuration as a whole. It should be realized that observations of a single interface does not always provide enough statistical information. Another disadvantage is that it is difficult to create really clean interfaces, e.g. without impurities.
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For the present study internal oxidation is performed to obtain a large number of oxide precipitates inside a metal matrix. The advantages here are:

1. The large number of clean straight oxide interfaces with negligible impurity segregation because of the large total interface area to volume ratio\(^{14}\)
2. Possibility to obtain reliable statistics
3. The easy way of HRTEM samples preparation.

Further annealing of the internally oxidized sample in \textit{vacuo} at different temperatures might change the phase of the oxide precipitates (see e.g. chapter 5) or the introduction of a third element into the metal matrix reduces \(\text{B}_2\text{O}_y\) complex oxides to simple fcc BO type oxides (Sb in \(\text{Ag/Mn}_3\text{O}_4\))\(^{14}\). The reverse process is the internal reduction, where a metal oxide inside another oxide is reduced in the presence of reducing gas flow. This is demonstrated for Cu inclusions inside MgO by Backhaus-Recoult et. al\(^{15}\) by heating MgO-CuO in a CO/CO\(_2\) gas flow. The orientation and shape of the oxide precipitates are controlled by the mismatch between metal and oxide and interfacial energies for different planes (Wulff construction). The 3D shape of the precipitates can be deduced from the cross sectioned 2D image, as described by Hooke\(^{16}\).

2.4.1 Internal oxidation

Internal oxidation of metals is quite extensively studied\(^{4,17}\), because of the precipitation hardening to impede the glide of dislocation in metals. Meijering\(^{18}\) has written an elaborate review of internal oxidation. A few conditions must be fulfilled for internal oxidation:
Binary alloys containing a majority metal A and a minority metal B is subjected to an oxidizing atmosphere. The metal B will oxidize if the oxygen affinity is higher compared with metal A and the oxygen pressure is high enough to oxidize B and not A. In addition, the following relation is of importance:

\[
 c_0 D_O > c_B D_B \tag{2.22}
\]

Where \(c_0\) is the concentration of oxygen and \(c_B\) the concentration of B in A. \(D_O\) and \(D_B\) are the corresponding diffusion constants of oxygen and B in A. The internal oxidation process can be simplified with a few approximations\(^{18}\):

- \(D_B\) can be neglected, so that the internal oxidation takes place inside the metal.
- The reaction takes place at a sharp boundary
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- The oxygen solubility is small
- The oxygen concentration at the surface is equal to the solubility $c_0$.

If these approximations can be applied, the depth of the oxidation front is described by:

$$\xi = \frac{2c_0 D_0}{nc_B} t,$$  \hspace{1cm} (2.23)

with half the valence of $B$ is called $n$ (the formed oxide of $BO_n$). This equation is fulfilled if the concentration $B$ is not too large. The growth of the precipitates takes place just after the oxidation front has passed by dissociation and diffusion of the just oxidized atoms. A theoretical analysis of the interplay between metallic and oxide phases during the oxidation process is given by Wagner\textsuperscript{19}. In many cases, the oxidation is fast along grain boundaries, which results in preferential oxidation at the grain boundaries. The growth of the precipitates is controlled by diffusion of the oxidized B atoms toward the oxide agglomerates (difference between $D_0$ and $D_B$). For diffusion, probably dissociation of the B-oxide has to take place, which is easier if the difference in oxygen affinity between A and B is smaller. A small difference of the oxygen affinity between A and B will result in large precipitates. A higher processing temperature results also in an increase of the size of the precipitates.

2.5 Sample preparation for TEM

After internal oxidation of the metal alloy the material has to be thinned for the observation in the TEM. A mechanical punch of the thin sheet of the metal alloy is performed to get 3 mm round disks with an approximate thickness of 100 µm. The 3 mm discs are dimpled to a final thickness of around 20 µm in the center of the specimen. With an argon ion beam the remaining material in the center of the specimen is milled away until a hole appears. The area close to the hole should reach electron transparency of a few nanometers. Another method can be applied for thinning specimen using electrochemical polishing. Both sample preparation technique were performed in the present work and will be briefly explained.

2.5.1 Ion milling

An argon ion bombardment on the thin TEM specimen is performed to sputter material from the film until it is thin enough to be studied in the TEM. The main variables, which control the ion milling process are the angle of incidence on the
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sample and the accelerating voltage of the ion beam. A typically accelerating voltage of 2.5 – 6 kV is used. An ion milling device is schematically shown in Figure 2.4. An angle of incidence of $\leq 6^\circ$ is used to prevent compositional thinning. The ion milling equipment used here is a Gatan model 690 dual ion mill with possible liquid N$_2$ cooling and a Gatan model 691 PIPS.

![Figure 2.4](image)

**Figure 2.4** A sketch of an ion-beam thinning device: Argon gas bleeds into an ionization chamber where a potential up to 6 kV creates a Ar ion beam applied to a rotating specimen. The whole device is under vacuum (10$^{-5}$ -10$^{-6}$ bar) and the specimen may be cooled down with liquid N$_2$.

### 2.5.2 Electrochemical polishing

Electrochemical polishing can be applied only on electrically conducting materials such as metal-based alloys. With this method, a sample can be prepared within a couple of minutes. Electrochemical polishing was performed using a TENUPOL III device, as shown in Figure 2.5. A pump and nozzle system sprays electrolyte by two jets on both sides of the specimen. An appropriate voltage is applied in order to get a current due to the anodic dissolution of the specimen to create a polished surface rather than etching or pitting. The correct process temperature, the electrolyte solution chemistry, applied voltage, polishing current are given for various metals in tables$^{20}$, but nevertheless this method is a “black art” with trial and error to achieve proper thin TEM samples.

For creation of metal oxide interfaces, the ion milling rate of the ion beam must be approximately the same for both the oxide and metal. If this would not be the case oxide particles will either stick out of the surface creating shadowing
Basic concepts

effects or become too thin and drop out of the metal matrix. This problem exists with electrochemical polishing, because the polishing rates are generally different for oxides and metals. Only if this difference is not too large or the oxide precipitates are small electrochemical polishing of internally oxidized samples can be applied followed by a short ion-milling step. This method can be useful to reduce irradiation damage of the ion beam significantly. This will be illustrated in chapter 4.

![Figure 2.5 schematic set-up of the TENUPOL III polishing device. The positively charge specimen is held in a Teflon holder between two jets. A control unit (not shown here) monitors the polishing.](image)

2.6 First Principles Density Functional Theory (DFT)

The aim of this section is to give a brief review of first principles density functional theory (DFT) calculations in solids. The usefulness of the quantum total-energy technique to calculate the total energy of a system of electrons and nuclei will be pointed out. DFT calculations are capable to predict the configuration of the system (aggregates of atoms) with the lowest total energy. For instance to determine the equilibrium lattice constant of a single crystal. In chapter 6 DFT calculations are performed on \{111\} Ag-MgO interfaces and corresponding bulk materials to extract the electronic distribution and therefore the nature of the bonding within such systems.
2.6.1 Approximation in DFT calculations

DFT calculations predict the electronic of solids and geometric structure at interfaces and minimize the total energy with respect to the electronic and nuclear coordinates. Using the fact that the mass of the nuclei is much larger than the mass of electrons, the coordinates of the nuclei are assumed to be frozen, in contrast with the instantaneous response of the electrons. This assumption, leading to the splitting of the electron and nuclear coordinates in many body theories, is known as the Born-Oppenheimer approximation. The many body problem of electrons in a solid is still not solvable for even simple systems (for a typical solid with \( \sim 10^{23} \) degrees of freedom) to minimize the energy of the electron configuration. Electronic many particle problems can be only solved for rather small systems, like atoms, molecules and clusters. Further simplification must be introduced to describe the electron-electron interaction performed with density functional theory and the electron-ion interaction is approximated with the pseudo-potential theory. The density functional theory was first proposed by Hohenberg-Kohn and Kohn-Sham to allow an iterative minimization technique to relax the electronic coordinates and find unambiguously the true ground state densities of a system. The minimum value of the total energy is equivalent to a set of self-consistent one-electron equations. Due to the Pauli exclusion principle for electrons (fermions) the wave functions of a many-electron system must be anti-symmetric. From the Pauli principle a spatial separation of electrons arises with parallel spin and therefore lowers the Coulomb energy of the electronic system. This lowering of the Coulomb energy due to the antisymmetry of the wave-function is called the exchange energy. The incorporation of the exchange energy in the total energy calculation is known as the Hartree-Fock approximation. Hartree-Fock calculations in general overestimate the total energy, because the Coulomb energy of electrons with opposite spins can be further reduced at the cost of higher kinetic energies. The difference between the true many body Hamiltonian and the Hartree-Fock Hamiltonian is called the correlation energy. The difficulty is to determine the exchange correlation energy of the electrons. Kohn and Sham showed that the ground state of the electronic system can be described by single electron equations instead of applying the many body Hamiltonian. The electron-electron and ion-electron interaction are integrated in an effective potential \( V_{\text{eff}}(\vec{r}) \). It is essential to find a set of wave functions \( \Psi_i \) that minimize the Kohn-Sham energy \( \varepsilon_i \) and to solve the Kohn-Sham (single particle) Hamiltonian in a consistent manner:
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\[
\sum_i \left[ \frac{-\hbar^2}{2m} \nabla_i^2 + V_{\text{eff}}(\vec{r}) \right] \Psi_i(\vec{r}) = \varepsilon_i \Psi_i(\vec{r}) ,
\]  
(2.24)

with the effective potential:

\[
\Psi_{\text{eff}}(\vec{r}) = V_{\text{ion}}(\vec{r}) + V_{H}(\vec{r}) + V_{\text{ex}}(\vec{r}) ,
\]  
(2.25)

\( V_{\text{ion}}(\vec{r}) \): The static total electron-ion potential

\( V_{H}(\vec{r}) \): The Hartree-Fock potential of the electrons given by

\[
V_{H}(\vec{r}) = e^2 \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r'
\]

\( V_{\text{ex}}(\vec{r}) \): The exchange-correlation potential given by the functional derivative:

\[
V_{\text{ex}}(\vec{r}) = \frac{\delta E_{\text{ex}}[n(\vec{r})]}{\delta n(\vec{r})}
\]

The electron density is written as a sum over single-particle wave functions:

\[
n(\vec{r}) = \sum_i |\Psi_i(\vec{r})|^2
\]  
(2.26)

It must be mentioned that the Kohn-Sham Hamiltonian is exact, but the exchange-correlation function is not known. Therefore a successful approximation of exchange-correlation potential must be developed.

In the local density approximation (LDA) the exchange-correlation energy functional (in general inhomogeneous) of the interacting electron system is approximated as follows:

\[
E_{\text{ex}}[n(\vec{r})] = \int E_{\text{ex}}(\vec{r}) n(\vec{r}) d^3r ,
\]  
(2.27)

Where \( E_{\text{ex}}(\vec{r}) \) is the exchange-correlation energy per electron of a homogeneous electron gas with the corresponding local density \( n(\vec{r}) \) of an inhomogeneous electron system. This approximation is only rigorous for a homogeneous electron gas, but it should still be a sufficient approximation if the density varies slowly as a function of position. There exist several parameterizations to find a link between exchange-correlation energy of high-density electrons, intermediate and low-density electron gases. For the parameterization, \( E_{\text{ex}}(\vec{r}) \) is split into an exchange and a correlation part:
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$$\varepsilon_{\text{ex}}(n) = \varepsilon_x(n) + \varepsilon_c(n),$$  \hspace{1cm} (2.28)

in which the exchange part is equivalent to the Hartree-Fock term related to the homogeneous electron gas. The HF term can be analytically expressed (e.g. “Solid State Physics”, N. W. Ashcroft, N. D. Mermin\textsuperscript{22}) with the result:

$$\varepsilon_x(n) = -\frac{3}{2} \left( \frac{3n}{\pi} \right)^{1/3} = -\frac{3}{2} \left( \frac{9}{4\pi^2} \right)^{1/3} \frac{1}{r},$$  \hspace{1cm} (2.29)

with the parameter \( r_c = (3/4\pi n)^{1/3} \), which is the average distance of the electrons in a homogeneous electron gas. Unfortunately, the correlation energy cannot be described exactly. A common form of \( \varepsilon_c(n) \) is parameterized by Perdew and Zunger\textsuperscript{23} from the Monte Carlo simulations of a homogeneous electron gas by Ceperley and Adler\textsuperscript{24}.

However, in the HF approximation there is still no correlation between electrons with different spins, which would be present because of their Coulomb repulsion. This repulsion creates a correlation hole around each electron, which further reduces the energy. In many materials and atoms the density of “spin-up” and “spin-down” electrons is not equal. This will be not explained further and reference is made to\textsuperscript{25}.

The LDA approximation is exact for a homogeneous electron gas, for which the gradient of the electron density is zero. For the non-homogeneous electron gas \( (\tilde{\nabla} n(\vec{r}) \neq 0) \) the exchange-correlation energy functional \( E_{xc}[n] \) can be expanded as follows\textsuperscript{23}:

$$E_{\text{ex}}[n] = \int d\vec{r} \varepsilon_{\text{ex}}(n(\vec{r})) n(\vec{r}) + \int \varepsilon_{xc}^{(2)}(n(\vec{r})) \frac{[\tilde{\nabla} n(\vec{r})]^2}{n^{5/3}(\vec{r})} + \ldots$$  \hspace{1cm} (2.30)

It is obvious from (2.27) that the deviation from the LDA energy is of the order of \( [\tilde{\nabla} n(\vec{r})]^2 / n^{5/3}(\vec{r}) \). The Fermi momentum \( k_F \), apart from prefactors is equal to \( n^{1/3} \), the condition for the validity of the LDA can be given as:

$$\left[ \frac{[\tilde{\nabla} n(\vec{r})]}{n^{5/3}(\vec{r})} \right]^2 \ll k_F^2$$  \hspace{1cm} (2.31)

In general, the gradient term in (2.31) provides an accurate correction to LDA for slowly varying densities, but the quality of the results decrease for realistic electronic densities. However, the calculations are improved by the generalized gradient approximation (GGA), e.g by Perdew et al\textsuperscript{31} of the form \( (\hbar = e^2 = m = 1) \).
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\[
E_{\text{XC}}[n] = \int d\tilde{r} n(\tilde{r}) \varepsilon_X(r_s(\tilde{r})) \sum_{s} F_{\text{XC}}(r_s(\tilde{r}), \xi(\tilde{r}), s(\tilde{r})),
\]

(2.32)

here \( \varepsilon_X(r_s) = -(3/4\pi)(9\pi/4)^{1/3}/r_s \), is the exchange energy per electron in a homogeneous electron gas with the density \( n = (4\pi r_s^3 / 3)^{-1} \). The enhancement factor \( F_{\text{XC}}(r, \xi, s) \) is a function of three variables: the Seitz radius \( r_s \), the relative spin polarization \( \xi = (n_\uparrow + n_\downarrow)/n \), and the reduced density gradient \( \nabla n / 2k_F n = (3/2\pi)^{1/3} \left| \nabla r_s \right| \), where \( k_F = (3\pi^2 n)^{1/3} \). This factor defines the form and the level of the approximation for the exchange-correlation energy and can be more accurate than the LDA calculations. Bulk structural properties are often not improved within the GGA. GGA calculations often overestimate the lattice parameters, whereas LDA has a tendency for overbindings. A closer agreement performing GGA calculations is reported for alkali metals, 3d metals and some 4d metals\(^{31,34} \). For metal-oxide interfaces the interface spacing increases by about 0.08 Å performing GGA calculation on \{111\} Cu-MgO interfaces\(^{33} \) compared with LDA. At this moment there exists no clear universal rules which XC functional, either of LDA or GGA should be applied. The use of LDA or GGA calculations still lead to different conflicting results in the literature. More experience with GGA calculations needs to be built up, in order to possibly solve the inconsistencies.

### 2.6.2 Periodic Supercells

For the present studies (chapter 6) the DFT calculations are performed using ultra-soft pseudopotentials\(^{27} \) and a plane wave basis set\(^{28} \).

The valence electrons in a crystal move in a static potential of the nuclei of atoms or ions. The Schrödinger equation can be solved applying the Bloch theorem to the electron wave functions. Several conditions must be fulfilled: The system must be infinitely and periodic in all 3 dimensions and the electrons in the solid experience from electrostatic potentials (ions) as a small perturbation (quasi free electron model). Thus each electron in the system can be written as a sum of plane waves:

\[
\Psi_i(\tilde{r}) = \sum_{G} \tilde{c}_{i,\tilde{k}+G} e^{i(\tilde{k}+\tilde{G})\tilde{r}}
\]

(2.33)

An infinitely extended system is described by the first Brillouin zone in the reciprocal space. The calculation of each k-point \((k \in \mathbb{R}) \) inside the Brillouin zone, which contributes to the electron potential in the crystal would result in an infinite calculation. However, adjacent k-points result in almost identical values. This means, that the calculation of finite numbers of k-points can be
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performed by summing values for an integrand (e.g. the charge density) at a finite number of points in the Brillouin zone, called the k-point mesh. The coordinates of the k-points are given as vectors spanning a small polyhedron of the same shape as the Brillouin zone (Monkhorst and Pack):\

\[
\vec{k} = x_1 \vec{b}_1 \times x_2 \vec{b}_2 \times x_3 \vec{b}_3
\]  

(2.34)

The positive, integer values \(x_i\) specify how many tiles spread along the \(\vec{b}_i\) over the whole Brillouin zone by translations of the tile. The k-point pattern of a smaller Brillouin zone, which corresponds to a larger unit cell in real space may be unfolded in the Brillouin zone of the system. For this case the pattern consists an only of single point at the center of the tile. An appropriate choice of the k-point mesh must be found to obtain a balance between accuracy and an efficient calculation. Increasing the number of k-points does not lead to a monotonous behavior of the total energy. Therefore, several convergence tests of systems under investigation with different k-point meshes must be performed\(^{30}\). In general, for metallic systems the k-point mesh should be denser, due to the complexity of the Fermi surface in metals (e.g. necked form close to the edge of the Brillouin zone). In contrast, the energy states of electrons in insulators will be represented as a (nearly) Fermi sphere and thus only a few k-points are needed to calculate the total energy of non-metallic systems.

A plane wave basis for the representation of electrons in a solid is very poorly suited for the tightly bound core electrons, which would require a very large set of plane waves to describe the rapid fluctuations of the electron density in the core region. Such large plane wave basis set would increase the computation time to perform an all-electron calculation. The physical properties of solids depend mostly on the valence electrons rather than on the core electrons. A solution to this problem is the introduction of potential approximations by removing the core electrons and by replacing them with a weaker pseudopotential that acts on a set of pseudo wave functions rather than the true valence wave functions.

The coefficients in \(c_{i,k,G}\) (2.34) are typically more important for plane waves with small kinetic energy than those with higher kinetic energy. Thus the plane wave basis set can be truncated to include only electrons with a kinetic energy below a certain cut-off energy. An all electron wave function with a corresponding pseudo wave function is illustrated in Figure 2.6. The valence wave function oscillates rapidly in the region occupied by the core electrons due to strong interaction with the ionic potential. Important for the pseudo wave function is that the orthogonality with the core wave function must be
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maintained (due to the exclusion principle). Outside a defined core radius $r_c$ the pseudopotential and the full potential must be identical. This softening (smoothening in the core region) of the potentials using pseudopotentials reduces the number of plane waves and therefore the computational efforts are reduced dramatically, too. Norm-conserved pseudopotentials are conserved at the core region. This does not hold for ultrasoft pseudopotentials, but these potentials are much softer compared to norm-conserved pseudopotentials. Therefore, the ultrasoft pseudopotentials are used in the present work (chapter 6), because they are more suitable to first-row and transition metal systems. For example, the first row elements have a rapid change of the electron density (the nucleus is not screened well by the core electrons) and thus need a high energy cutoff of the plane-wave basis set to represent these rapid changes of the electron density. Ultrasoft pseudopotentials are much softer and this reduces the cutoff energy by about a factor 2 compared with norm-conserved pseudopotentials.

The application of the plane wave basis set for a system that contains a defect is not possible. In both systems, an infinite number of plane waves would be necessary and this is independent of the cut-off energy chosen for the basis set. Because of translational invariance a system with a single defect becomes a system with an array of defects (periodic boundary condition). Therefore it is essential that the defect in neighboring cells, e.g. an interface, are independent of each other. This can be achieved by increasing the cell size until the calculated total energy has converged and the defects do not interact anymore.

![Figure 2.6](image.png)

*Figure 2.6 Schematic depiction of all-electron wave function (solid line) and pseudo wave function (dotted line).*
2.6.3 Relaxation of the atomic coordinates

In section 6.2.2, the Ag atoms are free to relax perpendicular to the interface until the forces acting on the atoms approach zero.

The force acting on ion i is given by:

\[ \vec{F}_i = \frac{\partial E_{\text{tot}}}{\partial \vec{R}_i} \]

\[ = \frac{\partial}{\partial \vec{R}_i} \langle \Psi | H | \Psi \rangle + \frac{\partial E_{\text{ion}}}{\partial \vec{R}_i} \] (2.35)

where \( E_{\text{ion}} \) is the energy of interaction between the ions. The Hellmann-Feynman theorem states that if \( \psi \) is an eigenstate of \( H \), then:

\[ \frac{\partial}{\partial \vec{R}_i} \langle \Psi | H | \Psi \rangle = \left\langle \Psi \frac{\partial H}{\partial \vec{R}_i} | \Psi \right\rangle, \] (2.36)

and hence applying this to equation (2.35) gives:

\[ \vec{F}_i = \left\langle \Psi \frac{\partial H}{\partial \vec{R}_i} | \Psi \right\rangle + \frac{\partial E_{\text{ion}}}{\partial \vec{R}_i}, \] (2.37)

when the electron coordinates have relaxed to a minimum of the total energy, the forces (better DFT forces) acting on the ions are efficiently calculated.

References

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