Transmission electron microscopy studies of interfaces in multi-component systems

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TEM studies of interfaces in multi-component systems

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*Dark field image of the Anti-phase boundary structure in Cu$_3$Pd near an embedded MnO precipitate of the oxidized Cu$_3$Pd- 1.5 Mn at.% alloy recorded at 410 °C.*

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Chapter 1

Introduction

Metal-oxide interfaces play an important role in the field of electronic packaging, gas sensors, combustion engines, etc. The focus on the interface structure between metal and oxide interfaces is particularly relevant, because the overall properties of such materials are to a large extent determined by the very local region near these interfaces. Oxides and metals are distinctly different classes of materials, i.e. differ substantially in their material properties. Metallic bonding is characterized by the delocalization of the electrons. In contrast, most oxides, due to the high electron negativity of oxygen compared with metals, tend to have mixed ionic-covalent bonds. The performance of metal-oxide interfaces depends on the local atomic and electronic structure at the interface, which provides an answer to the type of bonding present between the different materials. The physical and chemical processes at interfaces must therefore be understood to improve the performance of technological devices relying on such interfaces. Generally speaking, the nature of adhesion between metal and oxides is still not well understood\(^1\). Some work emphasizes the importance of the electrical polarizability of the metal by the oxide (image charges induced by the oxide in the metal)\(^2\). This point of view appears to be supported by the experimental observation that so-called polar interfaces (where for instance the oxide has only oxygen ions within the terminating plane) are most stable, whereas if the metal is removed the polar oxide surfaces would have the highest surface energy. On the other hand, the direct chemical bonding of the metal atoms to the oxygen ions in the terminating oxide plane can be more important to understand the stability of this type of polar interface. Other work stresses the importance of van der Waals forces for understanding the metal-oxide adhesion\(^3\). In particular, further progress on ab-initio calculations is needed to improve our understanding of metal-oxide adhesion.

In previous work\(^4,5,6,7\) an attempt has been made to analyze misfit dislocations along metal-oxide interfaces. The basic idea was that the extent by which the misfit strain at the interface, which is in general appreciable for metal-oxide interfaces, is localized in misfit dislocations reveals the strength of bonding across the interface. Higher interaction strength is needed to generate a misfit dislocation pattern at a larger mismatch. The localization of strain at the semi-
coherent metal-oxide interfaces can be experimentally observed using High-Resolution Transmission Electron Microscopy (HRTEM). In order to translate this extent of localization into bond strength, atomistic modeling is needed. (Many-body) Interatomic potentials of metals are relatively well-known\textsuperscript{8,9}. In principle, this also holds for ionic solids, but due to the long-range of the Coulomb interactions, the calculation (Ewald summation) for deformed or defective crystals is difficult. Since oxides are in general much stiffer than metals, it is more convenient to assume the oxide being infinitely stiff avoiding the need to describe the interaction within the oxide. Finally, the interaction across the interface can be described by empirical pair potentials including many body effects. To simulate various interaction strengths across the interface this pair potential was scaled by a factor $\alpha^{10,11}$. In this way the observed localization of misfit strain at the interface can be compared with atomistic simulations for various values $\alpha$ in order to have some quantitative idea of the bond strength.

Apart from this rather unique approach to determine the bond strength at interfaces other more obvious experimental methods are for instance based on Electron Energy Loss Spectroscopy measurements with high spatial (sub-nanometer) and energy resolution\textsuperscript{12}, measurement of wetting angles\textsuperscript{13,14}, and mechanical testing where ideally the energy of debonding of the metal and oxide is measured. This last technique appears to be straightforward, but in practice is often not suitable because most of the energy for delamination, is for instance dissipated by plastic deformation in the metal and thereby obscures completely the determination of the real work of adhesion.

From a theoretical point of view ab-initio calculations, e.g. based on density functional theory, are most appropriate to investigate the nature and strength of bonding at metal oxide interfaces. Unfortunately, up to now these calculations were mostly performed on model systems, where for instance the metal-oxide interfaces were assumed to be coherent. Only recently there was a first attempt to introduce misfit dislocations at the metal oxide interface into first principles calculations\textsuperscript{15}. Based on ab-initio calculations the important interactions for more phenomenological models can be derived. Such an attempt to improve our understanding of metal-oxide bonding has also been performed recently\textsuperscript{6}. In the present thesis also considerable attention has been paid to ab-initio calculations (chapter 6).

A strong motivation for this work was that experimental HRTEM images seem to indicate that the electrical polarization of the metal by the oxide for polar interfaces was directly observable. HRTEM image simulations are based on
neutral atoms. Therefore first-principle calculations were performed to provide the input for realistic HRTEM simulations by incorporating charge redistribution, charge transfer at metal oxide interfaces (chapter 6). In chapter 3 to 5 the emphasis is more on the detailed atomic structure and the local chemistry at metal-oxide interfaces. The previous studies were focused on ‘simple’ oxides (BO or B$_x$O$_y$) in pure metals (A). In the present work (1) impurities are added to the metal A to study their possible segregation to the A-BO interfaces (chapter 3), (2) the simple metal A is replaced by a matrix that shows long range order to study the possible local effect of the interface with the oxide on the order in the metal (chapter 4) and (3) the interfaces between metal A with more complex oxides of type B$_{3-x}$C$_x$O$_4$ with various contents x are analyzed (chapter 5).

HRTEM observations are highly suitable to study the narrow region at the interface on an atomic scale. In the past, extensive investigations on metal-oxide interfaces were performed, but not correlated with elemental analysis on an atomic scale. Segregation of a third element at a metal-oxide interface may influence many important material properties. Recently appropriate techniques became sufficiently sophisticated to allow chemical analysis of hetero-interfaces near or at an atomic scale, for example (scanning) transmission electron microscopy ((S)TEM) combined with X-ray energy dispersive spectrometry (EDS) or parallel electron energy loss spectroscopy (PEELS) and High-Angle Annular Dark-Field (Z-contrast) detection. One of the difficulties is the mechanical drift of the sample and therefore misleading results may appear. In the present work a new approach is introduced that turns out to be powerful to quantify segregation (fraction of a monolayer) at heterophase interfaces (chapter 3).

Ordered alloys have been a topic of considerable interest over the last decades because of their potential use in high-temperature applications. Interfaces with these ordered alloys and oxides can provide new perspectives for better compounds with better performance. An attempt has been made to combine heating of such interfaces in-situ in the TEM with HRTEM analysis down to an atomic scale, as demonstrated in chapter 4.

Metal-oxide devices found in engineering materials are in general rather complex, consisting of several elements reacting with each other. This makes the analysis of such systems rather difficult, like segregation behavior (chapter 3) or nucleation of more complex oxides. The well-defined interfaces with pure constituents must be known prior to study further impurities or the effect of a third element on metal-oxide interfaces. The focus on an oxide with a third
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element, which is introduced into the system to study the effect on interfacial misfit and orientation relation at metal-oxide interfaces, is the subject of chapter 5.

The study of the local electron structure at the interface is necessary to understand the character of bonding. Ab-initio calculations of metal-oxide interfaces allow the calculation of this electron structure. Recently, calculations of the relaxation of the ion positions and the electron structure elucidate the interplay between bonding and geometry of interfaces. This method demands high computational efforts, but with the increasing performance of computers, it becomes a suitable method for investigating more complex systems. Ab-initio density-functional theory has become an equivalent approach to experimental electron microscopy with both high spatial (sub-nm range) and energy (sub-eV) resolutions. This allows a comparison between the theoretical calculations and the experimental observations. An optimum has to be found for the model interface (computational limits) and experimental aspects. In chapter 6 a new approach has been made presented to include the effect of charge redistribution and charge transfer at polar interfaces in HRTEM image simulations. The bonding at the interface is analyzed by comparing the ‘realistic’ interface calculations with those involving blocks of atoms with free surfaces and with those of neutral atoms.

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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 $C_s$ corrector to reach resolutions below 0.1 nm.

In this research two different transmission electron microscopes were used, a JEOL 4000 EX/II (LaB$_6$, 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 LaB$_6$. 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. LaB$_6$ 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:

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

(2.3)

where $J$ is the field-emitted current density in A/m$^2$, $E$ 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 $10^{14}$ Am$^{-2}$sr$^{-1}$ with an energy spread of 0.2 – 0.5 eV compared with $\sim 10^9$ Am$^{-2}$sr$^{-1}$ 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 ZrO$_2$ 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.
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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>Brightness (A/m²/sr)</td>
<td>(0.3-2)10⁹</td>
<td>(0.3-2)10⁹</td>
<td>10¹¹-10¹⁴</td>
<td>10¹¹-10¹⁴</td>
<td>10¹¹-10¹⁴</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>2500-3000</td>
<td>1400-2000</td>
<td>300</td>
<td>1800</td>
<td>300</td>
</tr>
<tr>
<td>Work function (eV)</td>
<td>4.6</td>
<td>2.7</td>
<td>4.6</td>
<td>2.8</td>
<td>4.6</td>
</tr>
<tr>
<td>Source size (µm)</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>Energy spread (eV)</td>
<td>3.0</td>
<td>1.5</td>
<td>0.3</td>
<td>0.8</td>
<td>0.5</td>
</tr>
</tbody>
</table>

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:

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

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:
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\[ \sigma(\vec{r}) = e^{-i\Phi(\vec{r})} \]  \hspace{1cm} (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:\5

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

\[ B(U) = E(U)e^{X(U)} \]  \hspace{1cm} (2.7)

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

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

\[ I(\vec{r}) = 1 + 2\Phi \otimes FT^{-1}[E(U)\sin(X(U))] \]  \hspace{1cm} (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 $E_\Delta$ which represent the damping by the beam convergence and the spread in defocus respectively, are described as follows:

$$E_\Delta(U) = e^{\frac{-1}{2}\pi^2 \Delta^2 U^2}$$  \hspace{1cm} (2.10)

$$E_\alpha(U) = e^{\pi^2 \alpha^2 (\Delta f + \Delta C U^2)^2 U^2}$$  \hspace{1cm} (2.11)

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 $E_\Delta$. 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: \((4/3 \cdot C_r \lambda)^{1/2}\) and the highest transferred frequency is equal to \(1.5C_r^{-1/4}\lambda^{-3/4}\).

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 microscopes⁴ |
|---------------------------------|---------------------------------|
|                                | JEOL 4000EX/II | JEOL 2010F |
| Emission                        | LaB₆ (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 and MacTempas are applied for this purpose.
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 Moodie⁹.

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 \( q(x, y) = e^{i[\sigma V(x, y) - i\mu(x, y)]} \) is calculated, where the constant \( \sigma = \frac{2\pi me\lambda}{h^2} \) 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:

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

(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.
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:

$$\Psi(\vec{r}) = \Psi_o(\vec{r}) - \frac{8\pi^2 me}{\hbar^2} \int_{\Omega_s} V(\vec{r}') \Psi(\vec{r}') G(|\vec{r} - \vec{r}'|) d\vec{r}'$$

(2.13)

with:

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

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

$$\Psi_o(\vec{r}) = e^{-2\pi i \vec{k} \cdot \vec{r}}, \quad k = \frac{1}{\lambda}$$

(2.14)

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

$$G(|\vec{r} - \vec{r}'|) = -\frac{e^{-2\pi i |\vec{r} - \vec{r}'|}}{4\pi |\vec{r} - \vec{r}'|}$$

(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: $|\vec{r} - \vec{r}'| \approx \frac{r - r'}{k}$

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 $\Psi(\vec{r}) = \Psi_o(\vec{r}) + \Psi_1(\vec{r})$. The wave-function $\Psi(\vec{r}')$ at $\vec{r}'$ is replaced by $\Psi_o(\vec{r}) = e^{-2\pi i \vec{k} \cdot \vec{r}}$ and $|\vec{r} - \vec{r}'|$ by $|\vec{r}|$. Finally, the scattered wavelet $\Psi_1(\vec{r})$ is given by:

$$\Psi_1(\vec{r}) = \frac{e^{-2\pi i \vec{k} \cdot \vec{r}}}{r} \int_{\Omega_s} V(\vec{r}') e^{-2\pi i \vec{r}' \cdot \vec{r}} d\vec{r}'$$

(2.16)

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

(2.17)

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

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

(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 \( \bar{r}_a \), 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:

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

(2.19)

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

\[ V(\bar{u}) = \int \frac{\rho(\bar{r})}{k^2} e^{2\pi i \bar{u} \cdot \bar{r}} d\bar{r} \]  

(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: 

\[ k^2 V(\bar{k}) = 4\pi \rho(\bar{k}) \]. 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
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\(^{10}\) ratio technique in the thin-film approximation:

\[
\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}
\]

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\(^{11}\). 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-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-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
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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\textsuperscript{12}. 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\textsuperscript{13}. 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 B\(_x\)O\(_y\) complex oxides to simple fcc BO type oxides (Sb in Ag/Mn\(_3\)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:

$$c_0 D_0 > c_B D_B$$  \hspace{1cm} (2.22)

Where \(c_0\) is the concentration of oxygen and \(c_B\) the concentration of B in A. \(D_0\) 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:

$$\xi = \sqrt{\frac{2c_0 D_0}{n c_B}} t,$$

(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. 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\textsubscript{2} cooling and a Gatan model 691 PIPS.

![A sketch of an ion-beam thinning device](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\textsubscript{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\textsuperscript{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.
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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\textsuperscript{26} and Kohn-Sham\textsuperscript{21} 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 $V_{\text{eff}}(\mathbf{r})$. 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\textsuperscript{21}: 

\[ 
\]
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\[
\sum_i \left[ -\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{eff}}(\vec{r}_i) \right] \Psi_i(\vec{r}_i) = \varepsilon_i \Psi_i(\vec{r}_i),
\]

with the effective potential:

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

\(V_{\text{ion}}(\vec{r})\): 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:

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

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:

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

Where \(\varepsilon_{\text{ex}}(\vec{r})\) 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, \(\varepsilon_{\text{ex}}(\vec{r})\) is split into an exchange and a correlation part:
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\[ \varepsilon_{ex}(n) = \varepsilon_x(n) + \varepsilon_c(n), \quad (2.28) \]

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:

\[ \varepsilon_x(n) = -\frac{3}{2} \left( \frac{3n}{\pi} \right)^{1/3} = -\frac{3}{2} \left( \frac{9}{4\pi^2} \right)^{1/3} \frac{1}{r_c}, \quad (2.29) \]

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 (\( \nabla n(\vec{r}) \neq 0 \)) the exchange-correlation energy functional \( E_{xc}[n] \) can be expanded as follows\textsuperscript{23}:

\[ E_{ex}[n] = \int d\vec{r} \varepsilon_{ex}(n(\vec{r}))n(\vec{r}) + \int \varepsilon_{xc}^{(2)}(n(\vec{r})) \frac{[\nabla n(\vec{r})]^2}{n^{5/3} (\vec{r})} + \ldots \quad (2.30) \]

It is obvious from (2.27) that the deviation from the LDA energy is of the order of \( \left[ \int \nabla n(\vec{r})^2 / n(\vec{r})^{5/3} \right]. \) 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:

\[ \left[ \frac{\nabla n(\vec{r})}{n^{5/3} (\vec{r})} \right]^2 \ll k_F^2 \quad (2.31) \]

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 \( (\hbar = e^2 = m = 1) \textsuperscript{32} \).
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\[ E_{XC}[n] = \int d\vec{r} n(\vec{r}) E_X(r_s(\vec{r})) F_{XC}(r_s(\vec{r}), \xi(\vec{r}), s(\vec{r})) , \]  

(2.32)

here \( E_X(r_s) = -(3/4\pi)(9\pi/4)^{1/3}/r_s \), is the exchange energy per electron in a homogeneous electron gas with the density \( n = (4\pi^3/3)^{1/3} \). The enhancement factor \( F_{XC}(r, \xi, s) \) is a function of three variables: the Seitz radius \( r_s \), the relative spin polarization \( \xi = (n_s + n_\uparrow)/n \), and the reduced density gradient \( \sqrt{n}/2kF n = (3/2\pi)^{1/3}\sqrt{\nabla n} \), where \( k_F = (3\pi^2n)^{1/3} \). 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:

\[ \Psi_{\vec{i}}(\vec{r}) = \sum_G c_{\vec{i}, \vec{k}+G} e^{i(\vec{k}+\vec{G})\cdot \vec{r}} \]  

(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):

\[ \vec{k} = x_1 \vec{b}_1 \times x_2 \vec{b}_2 \times x_3 \vec{b}_3 \]  \hspace{1cm} (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. 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 \(c_{ik,G}\) (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
Basic concepts

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.

\[ \psi(r) \text{ all electrons of } s\text{-orbitals} \]

\[ \psi_{ps} \text{ pseudo of } s\text{-orbitals} \]

**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:

$$
\vec{F}_i = \frac{\partial E_{tot}}{\partial \vec{R}_i} = \frac{\partial}{\partial \vec{R}_i} \langle \Psi | H | \Psi \rangle + \frac{\partial E_{ion}}{\partial \vec{R}_i}
$$

(2.35)

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

$$
\frac{\partial}{\partial \vec{R}_i} \langle \Psi | H | \Psi \rangle = \langle \Psi \left| \frac{\partial H}{\partial \vec{R}_i} \right| \Psi \rangle,
$$

(2.36)

and hence applying this to equation (2.35) gives:

$$
\vec{F}_i = \langle \Psi \left| \frac{\partial H}{\partial \vec{R}_i} \right| \Psi \rangle + \frac{\partial E_{ion}}{\partial \vec{R}_i}
$$

(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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Chapter 3

Competitive segregation of In and Ga at \{111\} Cu-MnO interfaces

In this chapter, a new approach is introduced to analyze Gibbsian segregation. It is applied to systems, in which abrupt and sufficiently large differences in concentration of the solvents on both sides of the interface are present. The potential of the approach is illustrated by determining the extent of segregation of In, Ga and competitive segregation behavior of Ga and In at parallel \{111\} Cu-MnO interfaces. The analytical TEM results are combined with high-resolution TEM (HRTEM) observations in order to study the behavior of gallium segregation.

3.1 Introduction

In many materials impurity or alloying elements are present that can segregate at grain boundaries or heterophase interfaces. Segregation of such elements may influence important material properties\(^1\). In contrast to homophase interfaces detailed studies of segregation at heterophase interfaces have been reported only scarcely\(^2,3\). This is due to experimental difficulties to detect small amounts of a solute material at atomic planes. Recently appropriate techniques became sufficiently sophisticated to allow chemical analysis of hetero-interfaces near or at the atomic scale\(^4,8\), for example (scanning) transmission electron microscopy ((S)TEM) combined with X-ray energy dispersive spectrometry (EDS) or parallel electron energy loss spectroscopy (PEELS) and High-Angle Annular Dark-Field (Z-contrast) detection.

Nowadays three methods are available to reveal segregation at interfaces using analytical (S)TEM at edge-on oriented interfaces in a TEM foil:
1. taking a line scan;
2. chemical mapping;
3. using a scan raster;

A drawback of line scans and maps is related to drift of the sample and/or the electron beam. Sample drift may occur due to local heating by the electron beam and cannot be eliminated completely. Both kinds of drift are harmful for a detailed analysis, because in order to detect small enrichments in just one
monolayer the steps between measurement points should be small, and the detection time per point should be made sufficiently large to record significant signals. A line scan is in general statistically inadequate to analyze strong concentration gradients at interfaces, due to the lack of a sufficient number of spots in the crucial region. In (S)TEM mode the concentrations measured are not the actual ones, but convoluted spatially with the electron probe. When the size of the fluctuations in concentration is smaller than the probe size (for instance an enrichment in only 1 monolayer with a thickness of 0.2 nm whereas the effective probe size is for instance 1 nm) the measured concentration depends sensitively on the exact position of the electron probe with respect to the concentration fluctuation. Using a line-scan or elemental mapping the position of the probe is in general not known accurately enough to obtain the actual concentrations, that is to say to perform the deconvolution. Taking a scan raster overcomes the problems of drift and inadequacy, but at the expense of a decrease in detection sensitivity due to averaging over a larger volume. Another way to circumvent this problem without losing detection sensitivity is offered by our novel approach as has been delineated in\(^9\). It should be stressed, however, that this methodology is specifically applicable to heterophase interfaces. The basic idea is that the measured solute concentration is plotted against one of the two measured solvent concentrations showing an abrupt concentration change at the interface and fitted with theoretical curves based on assumed concentration profiles that are convoluted with a (Gaussian) function mimicking the electron probe. For more details of this approach and a discussion in comparison with the other approaches reference is made to\(^9\).

### 3.2 The Model

Instead of performing a line-scan with a small electron probe across the interface, a large number of measurements are made directly on top of the edge-on interface, together with a few reference measurements on both sides of the interface. A and C are the solvents on both sides of the interface and B is the segregating solute. If the concentration A is maximum on the A-rich side and C is the minimum on the C-rich side the solute B can be related to the solvent concentration A. If there is no enrichment or depletion of the solute B at the interface, the solute concentration B plotted versus the solvent concentration A results in a straight line. When the data points in the boundary are above the straight line, the solute B segregates at the boundary. To quantify the amount of segregation at a heterophase interface \(A(B)/C(B)\), it is necessary to correlate the measured concentration to the exact position of the probe with regard to the interface. This can be realized by modeling the segregation at interfaces by
convoluting the assumed concentration profile of solute B with a Gaussian function. This Gaussian function represents the electron probe with a probe size s (see Figure 3.1). Figure 3.1 schematically depicts possible concentration profiles of solvent A and Solute B with a concentration $x$ in the bulk of the A-rich phase and a concentration $y$ of a segregant in the outermost monolayer of the A-rich phase at the interface.

![Figure 3.1](image)

**Figure 3.1** Assumed concentration profiles for the solvent A and solute B at an A(B)/C(B) heterophase interface convoluted with a Gaussian function that mimics the electron probe.

The concentration profiles seem to have one-dimensional character (Figure 3.1). The extension of the model to two dimensions, i.e. with a planar interface and rotationally symmetric Gaussian probes, yields identical results, due to the symmetric properties of the Gaussian function. Different levels of enrichment at the interface can be visualized by varying the value y. Figure 3.2 shows the calculated curves for varying solute B concentrations in the monolayer. In the model x is set to 3.1 at.% and s is 0.7 nm. It is important to notice that with the assumed concentration profiles it is possible to predict on which side at the interface segregation occurs (solid and dashed lines in Figure 3.2). The solid line holds for a concentration of 10 and 20 at.% segregant in the outermost monolayer of the metal and the dashed curves for a concentration of 10 and 20 at.% segregant in the first monolayer of the oxide side of the interface. For segregation at the oxide side of the interface, the maximum of the segregant concentration shifts to a lower metal concentration than expected for segregation at the metal side of the interface. In section 3.4 it will be demonstrated that gallium has a tendency to segregate at the oxide side of the interface, as opposed to indium that wants to segregate at the metal side of the interface. It is obvious that for various probe sizes a constant solute concentration B will be more pronounced with decreasing probe size s. This is
Competitive segregation of In and Ga at \{111\} Cu-MnO interfaces

illustrated in Figure 3.3 in which for a given enrichment the deviation from a straight line is more pronounced with decreasing probe size \(s\). The model curves are achieved with \(x = 3.1\) at.\%, \(y\) to 20 at.\% in the outermost monolayer of the metal and \(s\) varies between 0.5 and 2.1 nm.

**Figure 3.2** The concentration of solute B is plotted versus the concentration of the solvent A for B concentrations \(y\) of 10\% and 20\% in the outermost metal monolayer (solid lines) and the first monolayer of the oxide side (dashed lines) at the interface. The probe size is 0.7 nm (FWHM of the Gaussian function). The concentration \(x\) of B in the bulk solvent A was set to 3.1 at.\%.

**Figure 3.3** The solute B is plotted against the solvent A for various probe sizes \(s\). The B concentration \(y\) is set to 20 at.\% in the outermost monolayer in the A-rich phase at the interface. The solute concentration B in the bulk solvent A is set to 3.1 at.\%.
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Extracting the unknown y-value from the experimental data (where x and s are known), requires a fitting procedure of the convoluted assumed concentration profiles to the experimental data\textsuperscript{10}. This is not a straight forward procedure and is explained in the following with the definition (Figure 3.1):

\[
\Omega_A(n,x,y) = \begin{cases} 
1 - x, & 0 \leq n \leq 502 \\
1 - y, & 502 \leq n \leq 522 \\
0, & n > 0 
\end{cases} \tag{3.1}
\]

and

\[
\Omega_B(n,x,y) = \begin{cases} 
x, & 0 \leq n \leq 502 \\
y, & 502 \leq n \leq 522 \\
0, & n > 522 
\end{cases} \tag{3.2}
\]

These concentration profiles \(\Omega_A(n,x,y)\) and \(\Omega_B(n,x,y)\) are convoluted with the normalized Gauss function mimicking the electron probe:

\[
g(n,s) = Ae^{-\frac{\ln 2n^2}{(50s)^2}} \tag{3.3}
\]

The current, variable \(n\) is assigned to the position across the interface, whereas per definition \(502 \leq n \leq 522\) represent a monolayer of 0.2 nm at the interfaces (where the assumed segregation takes place) and \(s\) denotes the probe size (FWHM) of the electron beam in nm (see also \textsuperscript{9}). The convolution is\textsuperscript{10}:

\[
C_A(t,x,y) = \int_{-\infty}^{\infty} \Omega_A(n,x,y)g(n-t,s)dn
\]

\[
C_B(t,x,y) = \int_{-\infty}^{\infty} \Omega_B(n,x,y)g(n-t,s)dn
\]

The convoluted concentration profiles are shown in Figure 3.4 and 3.5. For the fitting procedure, it is not possible to use these convoluted concentration profiles directly as analytical functions (see Figure 3.2), because they are multi-valued functions. It means that there exists an ambiguous relation between the solvent/solute atomic concentrations \(y\) (at.\%) with respect to the position \(t\) at the interface. This problem can be circumvented by fitting the convoluted concentration profile \(c_A(t,x,y)\) of solvent A with a unique analytical function.

This solvent A profile can be non-ambiguously attributed to the position across the interface when fitting it with the following (Fermi-) function:
Competitive segregation of In and Ga at {111} Cu-MnO interfaces

\[ f(t, a, b, c, d) = \frac{c \cdot 100}{e^{\frac{100}{b^2} + 1}}, \]  

(3.5)

where \( a, b, c \) are the fitting parameters. The attribution of the solvent concentration \( x_A \) as measured by EDS to the position \( t \) can be done by setting \( x_A = f(t) \) and solving (3.5) to \( t_f(x_A) \):

\[ t_f(x_A, a, b, c, d) = b^d \cdot [\ln\left(\frac{c \cdot 100}{x_A}\right) - 1] + a \]  

(3.6)

Now it is possible to match the assumed convoluted profile \( C_B(t_f, x, y) \) of solute \( B \) and the EDS measured segregation \( y_B \) across the interface by calculating the minimum of the least square function:

\[ \Gamma = \left( \sum_i \left[ y_B - C_B(t_f, x, y) \right]^2 \right)^{1/2}, \]  

(3.7)

where the summation runs over all the measurement points. For segregation, the concentration \( y_B \) in the outermost monolayer of the metal at the interface depends on the convolution profile of solvent A (via \( t_f \)) and therefore influences the fitting parameters \( a, b, c \) and \( d \). The solute concentration \( x \) in solvent A and the size of the electron beam are kept constant during a fitting procedure. This drawback in the fitting procedure is not significant, because after each performed fit the obtained value \( y \) can be used as a new input variable in the assumed convoluted profile of solvent A. After 3 iterations by using \( y \) as a new input parameter the matched segregation \( y_B \) converges to a fixed value. This fitting procedure is performed analogously to quantify segregation in the first monolayer at the oxide side of the interface by redefining the rectangular functions, i.e. various assumed concentration profiles can be tested.
Figure 3.4 Convolution of $\Omega_A(n,x,y)$ with the Gaussian function $g(n,s)$. The solvent concentration is 90 at.\% in the metal side and 0 at.\% in the oxide side of the interface. A probe size of $s = 1.4$ nm was used (only the right part, $t \geq 350$, of the function used for the fitting procedure is shown).

Figure 3.5 Convolution of $\Omega_B(n,x,y)$ with the Gaussian function $g(n,s)$. The solute concentration $B$ in the metal matrix is 2.9 at.\% and 17.6 at.\% in the last monolayer at the metal side of the interface. A probe size of $s = 1.4$ nm was used (only the right part, $t \geq 350$, of the function used for the fitting procedure is shown).
3.3 Experimental Procedure

An alloy containing copper with 1 atomic percent (at. %) manganese was made in a high-frequency furnace by melting the pure constituents (99.99% by weight) in an alumina crucible under a protective atmosphere of oxygen-free argon. Ingots were homogenized (1 week at 700°C in an evacuated quartz tube) and subsequently cold-rolled from 4 mm down to 0.5 mm. The Cu-MnO interfaces were obtained by internal oxidation for 17 h at 900°C using the Rhines Pack technique\textsuperscript{11}, i.e. an envelope of copper foil was filled with the sample and Cu, CuO and Al₂O₃ powder in a volume ratio of about 1:1:1, and placed in an evacuated quartz tube. Internal oxidation of Cu 1 at.% Mn yields octahedral shaped MnO precipitates with a cube-on-cube orientation relation with the copper matrix. The MnO precipitates have a NaCl-type crystal structure and the average size of the oxide particles is 200 nm. A large mismatch of 22.9% is present at the {111} planes forming the interfaces between Cu and MnO, which leads to the formation of semi-coherent interfaces. Further details of MnO precipitates in copper matrix are extensively described in\textsuperscript{12, 13, 14}. After internal oxidation approximately 3.5 at.% gallium was placed together with the sample, without making mutual contact, inside an evacuated quartz tube for 1 week at 700°C. After 1 week nearly all gallium is dissolved more or less homogeneously in the copper matrix. Next, two different treatments were used. One consisted of introducing approximately 3.5 at.% indium in the copper matrix using the same treatment as for gallium during 1 week at 750°C. The other consisted of the same annealing treatment but without indium present.

TEM samples were prepared by grinding, dimpling and ion milling (using liquid nitrogen cooling) 3 mm disks to electron transparency. The EDS measurements were carried out using a JOEL 2010F, field emission gun TEM operating at 200 kV and equipped with an EDAX EDS spectrometer with a super ultra thin window. A double-tilt beryllium sample holder was used. The measurements were performed with an electron probe diameter characterized by an FWHM of 0.7 nm. During the EDS measurements the samples were oriented in the <110> copper matrix orientation, to ensure that the electron beam is edge-on oriented to {111}-Cu-MnO planar interfaces. The sample was always tilted towards the detector over an angle between 10 and 30°. The dead time was never larger than 40% and never smaller than 10%. This was achieved by using time constants varying between 35 and 100 μs, corresponding to an energy resolution relative to MnKα varying from 135 to 145 eV, respectively. For the quantification of the compositions the theoretical Zaluzec $k_{AB}$ factors were used\textsuperscript{15}. In the analysis of segregation we are primarily interested in the relative
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enrichment at the interface compared to the bulk and therefore the use of (in absolute sense) less accurate theoretical $k_{AB}$ factors is justified. For the determination of the composition across an interface a large number of spectra were obtained by positioning the beam for 40 s on the interface and subsequently shifting the beam (manually using the deflection coils) to other parts of the interface. These measurements were completed by a limited number of spectra from areas close to the interface on both sides of the interface. After quantification the indium and gallium concentrations were related to the copper concentration and compared with the model description as explained in section 3.2. This model description is based on assumed concentration profiles that are of simple nature, for instance the atomic fraction of gallium or indium in the copper matrix has value $x$ (then of copper has value $1-x$), in the outermost monolayer of the metal at the interface has value $y$ (then of copper has value $1-y$) and the concentrations of gallium or indium and copper are zero in the oxide. These concentration profiles are convoluted with a Gaussian function mimicking the electron probe. Note that the FWHM characterizing the probe size incorporates beam broadening. For instance the initial FWHM of the probe entering the sample surface is 1 nm and at the exit plane of TEM sample is 2 nm. Then we assume the effective probe size to be 1.4 nm (FWHM).

HRTEM images (in the JEOL 4000 EX/II) were obtained by digitizing negatives using a charge-coupled device (CCD) camera and the gray scale was adapted to achieve reasonable brightness/contrast. HRTEM images were not filtered.

3.4 Results and Discussion

3.4.1 Energy-dispersive spectrometry analyses

TEM samples with MnO precipitates in copper were analyzed after the three different segregation treatments. In the first sample only gallium was introduced (1 week 700 °C). In the second one after the gallium treatment also indium was dissolved (an additional week at 750 °C). The third one was, after the gallium treatment, subjected to the same heat treatment as for introducing indium, but without indium present. EDS results for these 3 cases for the copper matrix and the MnO precipitates are presented in Table 3.1. The errors of the measured concentrations are based on an average over five spectra (Gaussian statistics). An additional systematic error is introduced by the theoretical $k_{AB}$ factors. The measured oxygen concentration in the copper matrix
and the small amounts of copper found during the measurement in the MnO precipitates can be assigned to spurious X-rays, because all of these measurements were taken near the interfaces. From this point of view it becomes clear that no indium and gallium are dissolved in the interior of the MnO precipitates. Measurements to analyze the possible segregation of indium and gallium were repeated for three different interfaces in each sample and all three measurements showed similar segregation behavior.

Figure 3.6 shows the gallium concentration across a \{111\} Cu-MnO interface just after the introduction of gallium into the internally oxidized Cu 1 at.% Mn. There is hardly any segregation of gallium recognizable. Thus, all the measured gallium concentrations versus the copper concentration across the interface can be described with a straight line. The fitting procedure assuming an effective probe size (FWHM) of 1.4 nm already indicates a gallium concentration of 1.8 at.% per monolayer in the first two monolayers of the oxide. The reason why we assume that the gallium is in the first two monolayers of the oxide will be discussed later. Note that the gallium concentration in the copper matrix is 3.8±0.4 at.% (homogeneous).

**Table 3.1** EDS results for the copper matrix and MnO precipitates (average over 5 spectra)

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Mn</th>
<th>O</th>
<th>Ga</th>
<th>In</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper matrix</td>
<td>93.6±1.2</td>
<td>0.5±0.4</td>
<td>2.2±1</td>
<td>3.8±0.4</td>
<td>-</td>
</tr>
<tr>
<td>Cu 1at.% Mn 3.8 at.% Ga (just after introduction of Ga)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper bulk</td>
<td>91.8±1.3</td>
<td>0.4±0.2</td>
<td>2.5±1.3</td>
<td>2.0±0.3</td>
<td>3.4±0.4</td>
</tr>
<tr>
<td>MnO precipitate</td>
<td>5.7±1.2</td>
<td>51.6±7.6</td>
<td>42.2±7.1</td>
<td>0.2±0.1</td>
<td>0.2±0.2</td>
</tr>
<tr>
<td>Cu 1at.% Mn 3.8at.% Ga (after introduction of In at 750 °C for 1 week)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper matrix</td>
<td>92.4±1.7</td>
<td>0.7±0.5</td>
<td>5.1±1.7</td>
<td>1.9±0.3</td>
<td>-</td>
</tr>
<tr>
<td>Cu 1at.% Mn 3.8at.% Ga (after annealing at 750 °C for 1 week)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
After 1 week at 750 °C for the intake of indium, segregation of gallium is rather limited but already unambiguously detected. Only a small concentration of 2.5 at.% is present in the first two monolayers of the oxide side of the interface; see Figure 3.7.

**Figure 3.6** After Ga dissolution at 700 °C for 1 week into internally oxidized Cu 1 at.% Mn, about 3.8 at.% Ga is dissolved in the copper matrix. The almost straight line indicates that Ga does not significantly segregates at the interface.

After 1 week at 750 °C for the intake of indium, segregation of gallium is rather limited but already unambiguously detected. Only a small concentration of 2.5 at.% is present in the first two monolayers of the oxide side of the interface; see Figure 3.7.

**Figure 3.7** EDS results together with the model curve. The curve holds for a Ga concentration in the copper matrix of 2 at.% and a probe size of 1.4 nm. The best match of the model curve with the EDS measurement is reached with a Ga concentration of 2.5 at.% in the first two MnO monolayers at the Cu-MnO interface.
 Already at this stage the fitting procedure clearly indicates that the data are better fitted with a concentration profile that assumes the gallium to be in the first monolayer or the first two monolayers of the oxide instead of the outermost monolayer of the metal matrix. Note that now the gallium concentration in the copper matrix has dropped to 1.9±0.3 at.%. Thus, it appears that during the heat treatment and the dissolution of indium the gallium concentration at the interface obtains more or less the value that was originally present in the copper matrix. In the copper matrix itself the concentration of gallium decreases due to the segregation of gallium at grain boundaries and due to the formation of spinel-type GaₓMnᵧO₄ precipitates (see also section 3.4.2).

After the dissolution of indium, the segregation of indium occurs at the Cu/MnO interfaces as shown in Figure 3.8. The presence of indium and gallium in Cu 1 at.-% Mn results in an indium segregation of approximately 17 at.% in the terminating copper monolayer at the parallel {111} Cu/MnO interface, whereas the average indium concentration in the copper matrix was only 2.9 at.%; see Figure 3.8. Indium segregation of 17.6 at.% in the terminating monolayer is very similar to previous measurements of indium segregation of 15 at.% without the presence of gallium at the Cu-MnO interface⁹. Apparently, there is no influence of the presence of gallium on the indium segregation to {111} Cu-MnO interfaces.

![Figure 3.8](image)

**Figure 3.8** EDS results together with the model curve. The curve holds for an In concentration in the copper matrix of 3.0 at.-% and a probe size of 1.4 nm. The best match of the model curve with the EDS measurement is reached with an In concentration of 17.6 at.% in the outermost copper monolayer at the Cu-MnO interface.
In order to investigate the influence of gallium segregation without the presence of indium, heat treatment of Cu 1 at.% Mn 3.8 at.% Ga at 750 °C for 1 week in vacuo was performed. Heat treatment without the presence of indium appears to result in significantly higher gallium segregation as shown in Figure 3.9. The theoretical curve in Figure 3.9 holds for an 0.4 nm (2 monolayer) thick layer at the oxide side of the interface with a gallium concentration of 14.3 at.% per monolayer and a gallium concentration in the matrix of 2.0 at.%. From the fitted data in Figure 3.9 it becomes apparent that according to the goodness of fit the gallium segregation takes place at the oxide side of the interface and with the information obtained from HRTEM images a thickness of 2 monolayers appears to be consistent with this. The concentration of 14.3 at.% gallium may indicate that gallium and MnO are locally transformed into GaMn$_2$O$_4$. Thus, without the presence of indium, gallium segregates strongly at the oxide side of the interface and with indium present gallium only show weak signs of segregation. These results show unambiguously that indium segregation at the Cu-MnO interface seals the first monolayers at the oxide side of the boundary for the segregation of gallium.

![Figure 3.9](image)

**Figure 3.9** EDS results together with the model curve. The curve holds for a Ga concentration in the copper matrix of 2.0 at.% and a probe size of 1.4 nm. The best match of the model curve with the EDS measurement is reached with a Ga concentration of 14.3 at.% in the first two monolayers at the oxide side of the Cu-MnO interface.

Using our fitting procedure to the data Figure 3.6-3.9 showed that in the case of gallium the fitting was always better if the gallium was assumed in the first 2
monolayers of the oxide than in the outermost monolayer of the metal matrix whereas for indium clearly the opposite was indicated. All the measurements were made using an electron probe that initially has a size of 0.7 nm FWHM and after going through the sample becomes effectively about 1.4 nm. Using the smaller 0.5 nm probe size the count rate is too low when an interface close to the hole in the TEM specimen is studied and an interface in a thicker region has to be found. On the other hand the beam broadening inside the specimen has to be taken into account and varies with the thickness to the power of \(3/2\). The best interfaces are found in thin areas relatively close to the hole in the TEM foil. A compromise has to be found between a sufficient count rate and the beam broadening. For the probe size used to generate the model curves in Figure 3.6-3.9 a FWHM of 1.4 nm was estimated which includes the beam broadening in the sample. The procedure to include the beam broadening in an effective probe size is fairly accurate, although it is rather difficult to make an accurate estimate of this effective probe size. Therefore the results of our fitting procedure, for instance the 17.6 at.% indium in the outermost monolayer of the copper matrix, suggests an accuracy that is actually not present, because due to possible variations in probe sizes the relative error is probably of the order of 30%. Consequently a more realistic value for the In concentration in the outermost layer of copper is 17.6±5 at.%. Of course, there are practical solutions to know the final probe size better but at least knowledge of the drift for each data point is then necessary.

From the EDS measurements it is clear that a higher extent of segregation at heterophase interfaces results in a larger scatter among the values for the measured concentrations, especially near the maximum of the model curves. The major reason for this scatter is the drift of the sample (or electron beam) during the 40 s used to record a spectrum. The effect of drift can in principle be incorporated in the effective probe size of each individual measurement. Using the modeled curves it is assumed that the probe size is a constant for all measurement points. In practice, this will not be the case and in fact the different data points correspond to curves with different effective probe sizes (Figure 3.3). Only in the case of segregation these different effective probe sizes matter, because a straight line in the case of the absence of any segregation remains also a straight line independent of the probe size. A clear example of this is shown in Figure 3.10. It holds, because segregation of Zn at the Cu-MnO interfaces does not occur, but a small amount of Zn dissolves into the MnO. The measured Zn concentration does not show any significant scatter with respect to the straight line. All error bars in the plots of the EDS measurements Figure 3.6 - 3.10 are related to the typical errors listed in Table 3.1.
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3.4.2 HRTEM observations

Selected Area Electron Diffraction (SADP) patterns and HRTEM showed that in all samples the MnO precipitates are in minority, because about ½ to 2/3 of the precipitates have a spinel-type structure and a composition corresponding to Ga_{x}Mn_{y}O_{4} with x varying between 1 and 2 and y between 2 and 1 (as we determined using EDS) and only the rest is MnO. All results analyzed up to this stage hold for the MnO precipitates. An example of a spinel precipitate in copper is shown in the HRTEM image of Figure 3.11. A cube-on-cube orientation relation holds between the spinel and the copper and the precipitates have octahedral shapes due to the dominant {111} facets. The oxygen sublattices of the spinel and MnO are identical only the distribution of the cations over the interstitial sites in the O sublattice differs for the two phases. Analysis of the misfit between the copper and spinel indicates that the lattice constant of the spinel is 2 times 1.176 the lattice constant of Cu, i.e. using 0.3615 nm for copper this gives 0.850 nm for the spinel. This value is very close to 0.846 nm that holds for the lattice constant of the known spinel Ga_{2}MnO_{4} (JCPDS-International 1992).

Figure 3.10 EDS results of Zn concentrations across a Cu-MnO interface. It indicates clearly that Zn does not segregate to the interface. However, about 1.2 at.% Zn is dissolved in the MnO precipitate. The measurement was performed with an FWHM probe size of 0.7 nm.
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The presence of Ga$_x$Mn$_y$O$_4$ precipitates indicates that gallium has a tendency to react with the MnO to form a new phase. Therefore it is not completely surprising that gallium in MnO precipitates has a tendency to segregate to the oxide side of the interface. However, this is not a general rule, because for instance Zn has also a strong tendency to react with MnO to give spinel type Zn$_x$Mn$_y$O$_4$ precipitates, but it does not segregate at all at Cu/MnO interfaces, neither at the oxide side nor at the metal side (see for example Figure 3.10). A difference between Zn and gallium is that the former is well dissolveable in MnO as can be seen from the 1.2 at.% Zn that is already homogeneously distributed in the MnO precipitate in Figure 3.10 whereas gallium does not appear soluble in the MnO, but has to nucleate the spinel. Hence, the interface does not appear to form a barrier where enrichment occurs for Zn, whereas it does for Ga.

A HRTEM image of a Cu/MnO interface is shown in Figure 3.12 for a sample in which gallium was dissolved (1 week 700 °C) and which was annealed for an additional week in vacuo at 750 °C. The Cu-MnO interfaces are constituted by {111} planes and viewed along their common <011> direction. A thin layer, appearing less well ordered than the MnO and copper and positioned in-
between the MnO and the copper is clearly visible in Figure 3.12. The thickness of the layer is approximately 0.5 nm.

The EDS measurements revealed for this case a high gallium concentration at the oxide side of the interface. Although not clearly visible the HRTEM image indicates that the thin layer is connected more to the oxide than to the metal part. Based on mismatch it forms an intermediate between the MnO and Cu, which have a large misfit of 22.9%. The misfit of the intermediate layer is smaller with the MnO than with the Cu. Probably the phase in this intermediate layer is related to the above mentioned spinel precipitates and the spinel-type Ga$_2$MnO$_4$ (JCPDS International 1992). The lattice constant of this spinel is 0.846 nm, compared to 0.4444 nm for MnO and 0.3615 for Cu. So, the misfit at the metal/oxide interface is reduced from 22.9 % for Cu/MnO to 17.0 % for Cu/spinel, where we consider the fcc oxygen sublattice with half the lattice constant of the spinel. However, based on the chemical composition (14.3 at.% Ga) it is more likely that the layer contains GaMn$_2$O$_4$ instead of Ga$_2$MnO$_4$.

A plausible explanation for the gallium segregation at the oxide side of the Cu/MnO interface is that a thin outer Ga$_x$Mn$_y$O$_4$ layer around the MnO reduces the metal/oxide interfacial energy by reducing the mismatch energy at the
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interface. In principle one sharp Cu/MnO interface is replaced by two interfaces with a thin gradient layer in-between. From a thermodynamic point of view it is probably favorable to get rid of the spinel/MnO interface and to transform the MnO fully into Ga$_2$Mn$_2$O$_4$. However, in the system the total amount of Mn and O atoms is in principle fixed (in the evacuated quartz tube) and only gallium is supplied. Therefore the limiting factor for transformation of MnO into Ga$_2$Mn$_2$O$_4$ is the amount of oxygen. Under this limiting oxygen condition it is impossible to transform the MnO fully, but still it appears possible to form a thin layer of Ga$_2$Mn$_2$O$_4$ at the interface that apparently can reduce the interfacial energy.

The explanation for the indium segregation is straightforward. Indium atoms that segregates at the metal side of the Cu/MnO interface prefer the sites in-between the misfit dislocation cores of the network at the interface, because these sites offer more space for the relatively large indium atoms than present in the copper matrix$^9$. An explanation for the blocking effect of indium on the segregation of gallium to the oxide side of the interface is not as straightforward. There can be a kinetic reason: indium atoms are strongly fixed to the special sites at the interface that are also needed for the transport of gallium atoms from the copper matrix to the oxide precipitate or vice versa. In this way the gallium diffusion across the interface can be strongly hampered. However, there can also be a thermodynamic reason. It has to be kept in mind that annealing the Cu/MnO system in vacuo with gallium or indium vapor reduces strongly the oxygen partial pressure the system is subjected to. After internal oxidation the system had a tendency to become in equilibrium with the oxygen partial pressure corresponding to the dissociation pressure of Cu$_2$O. However, after annealing in gallium or indium vapor the oxygen partial pressure is reduced to the dissociation pressure pertaining to Ga- or In-oxide. After internal oxidation the terminating layer of MnO at the parallel {111} Cu/MnO interface will be a close packed oxygen plane, whereas after annealing in gallium or indium vapor the terminating layer of MnO will likely become a close packed Mn plane$^{17-19}$. Gallium segregation at the oxide side of the interface thus implies that the terminating close packed plane of the oxide will contain a large number of gallium atoms next to the Mn atoms. Indium segregation at the metal side of the interface thus would imply a large number of In-Ga bonds across the interface. If these bonds are not favorable, as appears the case considering the binary Ga-In phase diagram$^{21}$, then the presence of indium can destabilize the presence of gallium atoms at the oxide side of the interface. On the other hand Cu-Ga bonds across the interface can be favorable (gallium is well dissolvable in Cu, even at low temperature and can form
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several intermetallic phases with copper\textsuperscript{20}). This can explain the observed results that, without the presence of indium, gallium segregate at the oxide side of the interface and, with the presence of indium, gallium segregation is hampered.

Another even less well understood, but also intriguing observation was made with dissolution of gallium in the Cu/MnO system. Vacuum annealing MnO precipitates in pure copper exhibits the usual tendency for clustering and Ostwald ripening of the MnO precipitates in order to decrease the total amount of interfacial energy. We have already reported in previous publications that antimony is able to suppress this clustering and Ostwald ripening keeping the number and size of the MnO precipitates stable during annealing\textsuperscript{13,22}. The same holds for indium. However, with gallium the size of the MnO precipitates decreases after dissolution of gallium by a factor of 3 to 4, i.e. $200 \pm 20$ nm before, $64 \pm 17$ nm just after the introduction of gallium and $62 \pm 6$ nm after the additional week vacuum anneal.

A tentative explanation for the reduction of the precipitate size is the following. The introduction of gallium itself is not directly responsible for the shrinkage of the precipitates, because we determined that internally oxidized Cu 3 at.\% Ga forms large Ga$_2$O$_3$ precipitates with a size between 200 nm and 350 nm. The strong reduction in the oxygen partial pressure that is accompanying the gallium introduction is probably more important. After internal oxidation the precipitates are oxygen terminated\textsuperscript{16-20} and compared to the metal atoms with high affinity for oxygen (Mn in this case) excess oxygen is present. After annealing in gallium vapour the oxide precipitates become metal terminated\textsuperscript{16-19} and excess metal is present in the precipitates, i.e. the former excess oxygen can now be used for the development of additional oxide. Simultaneously gallium is introduced that wants to form Ga$_x$Mn$_y$O$_z$ precipitates (suppose with $x = 1$ and $y = 2$). Then compared to the original MnO about the double of the amount of oxygen atoms needs to be present. That amount of excess oxygen is of course not available. Still as much as possible gallium and Mn atoms wants to be oxidized, i.e. as much as possible excess metal should be present in the precipitates. The only way to increase the amount of excess metal per precipitate is to decrease the size of the precipitates by which the surface area compared to the volume of the precipitate increases. This scenario works better for relatively small precipitates (e.g. with a size of 10 nm) where the surface area to volume is already large and the change from excess oxygen to excess metal implies a significant increase of the number of metal atoms that can become connected to the oxide. It is less effective for larger precipitates, but still the gallium atoms that can leave their unfavorable position in the copper matrix
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and can be incorporated in the oxide may outweigh the increase in interfacial area and thus interfacial energy. This reduction in precipitate size is of course aided if the interfacial energy of Cu/MnO is reduced with gallium introduction as appears to be the case.

3.5 Conclusions

The present analysis shows that the earlier proposed approach for the analysis of Gibbsian segregation at hetero-interfaces applying analytical TEM to edge-on oriented interfaces is a suitable method that allows the detection of a fraction of a monolayer coverage at a heterophase interface and the determination at which side of the heterophase interface segregation occurs. Segregation of gallium and indium and their competitive behavior at parallel \{111\} Cu/MnO interfaces was analyzed using 3 different sets of samples. In the first set that was obtained after dissolving about 3.8 at.% Ga in the copper matrix (1 week at 700 °C) no significant segregation of gallium at the interfaces with the MnO precipitates was observed. In the second set produced after additionally dissolving about 3.4 at.% indium in the copper matrix (an additional week at 750 °C), weak segregation of gallium at the oxide side of the Cu-MnO interface was detected and relatively strong segregation of indium at the metal side of the interface was observed (17.6 at.% In for the terminating monolayer of the copper matrix). In the third set that was obtained after annealing of the first set in vacuo for an additional week at 750 °C (i.e. the same treatment as for introducing In), strong segregation of gallium at the oxide side of the Cu-MnO interface was observed (about 14.3 at.% per monolayer for the first two monolayers of the oxide versus 2 at.% in the copper matrix). This leads to the conclusion that indium effectively blocks gallium segregation towards the oxide side of the interface. On the other hand, the presence of gallium does not influence the segregation of indium. Explanation for the gallium segregation at the oxide side is that a thin spinel type Ga$_x$Mn$_{3-x}$O$_4$ is formed that reduces the misfit at the metal-oxide interface. Full transformation of MnO precipitates into Ga$_x$Mn$_{3-x}$O$_4$ is impossible because of the limited amount of oxygen present in the system. HRTEM images of the third set confirm that a thin outer layer (about 2 monolayers thick) of the oxide precipitates have a deviating structure with intermediate misfit between copper and MnO that may lower the interfacial energy.
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Chapter 4

Electron microscopy study of ordering in Cu$_3$Pd and at Cu$_3$Pd-MnO interfaces

High-resolution electron microscopy and dark field imaging at lower magnification have been used to analyze the state of order of Cu$_3$Pd, the structure of antiphase boundaries (APBs) and details of the long period superstructure (LPS due to APBs) in Cu$_3$Pd (L1$_2$) alloys. In-situ TEM observations of Cu$_3$Pd with an approximate concentration of 25 at. % Pd and Mn of 1.5 at. % have been carried out. Comparison between internally oxidized Cu$_3$Pd alloy and not oxidized Cu$_3$Pd alloy is performed. Finally HRTEM observations of L1$_2$ ordered Cu$_3$Pd at parallel {111} and {100} Cu$_3$Pd-MnO interfaces have been analyzed.

4.1 Introduction

Ordered alloys have been a topic of considerable interest over the last decades because of their potential use in high-temperature applications\(^1\). The transition temperature from chemical long-range order to disorder depends on elemental composition of the intermetallic compounds. In this work we will concentrate only on long-range order and not on short-range order that exists above the transition temperature. Also well-established in L1$_2$ ordered structures are so-called long period superstructures (LPS), i.e. equilibrium structures with an ordered array of parallel Anti-Phase Boundaries (APBs) with a particular periodic distance. In the binary Cu-Pd system (see Figure 4.3) L1$_0$, L1$_2$ ordering for the Cu-rich compound and one and two-dimensional LPS in this L1$_2$ have been observed\(^2\). The LPS was detected between 17 and 30 at.% Pd and was studied as a function of temperature by Broddin et. al\(^2\). A more detailed analysis of the composition range between 18 and 21 at.% Pd was carried out to study chaotic and uniform regimes in incommensurate APBs\(^3\). The transition from the L1$_2$ structure at low temperature to the LPS at higher temperatures was studied and the LPS is retained up to the order/disorder transition temperature (Guymont and Gratias)\(^4\). Near this transition temperature ($T_c$) the APBs become wetted by the disordered phase and the thickness of this wetting
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layer scales with $\log[a(T-T_c)]^{-1}$, so that only starting from about 1 K below and up to $T_c$, substantial wetting is observable.

In this chapter in-situ heating is performed, starting at 40 ºC below the order/disorder transition temperature $T_c$, to study the LPS in Cu$_3$Pd with and without the presence of MnO precipitates. Dark field imaging at lower magnification was used to study the APB structures and the L1$_2$ order in Cu$_3$Pd at parallel $\{100\}$ and $\{111\}$ Cu$_3$Pd-MnO interfaces was investigated in detail by means of High-Resolution Transmission Electron Microscopy (HRTEM).

4.2 Experimental details

A Cu$_3$Pd alloy containing 1.5 at.% Mn was prepared by melting the elements (purity 99.99 wt.%) together in an arc furnace. The ingot was homogenized (1 week 700 ºC) and subsequently cold rolled to foils of an approximate thickness of 250 µm. Internal oxidation was performed using the so-called Rhines pack technique at 900 ºC for 17 h in an evacuated quartz tube. The internally oxidized alloy was annealed at 450 ºC for 24 hrs. in vacuo and subsequently quenched in direct contact with water. Discs were punched out of the foils for TEM observations.

Thinning of the discs was performed by electro-polishing using an electrolyte containing 78 % CH$_3$OH and 22 % HNO$_3$. Voltages in the range of 15 - 20 V were applied. After electro-polishing the discs of the internally oxidized alloy were covered with a thin oxide layer (a problem that does not occur for the pure metallic Cu-Pd system). Ion milling (Gatan PIPS model 691) was used to remove these thin oxide layers and to further reduce the thickness of the oxide precipitates. The time for ion milling was kept shorter than 30 min at 2.5 kV in order to avoid as much as possible damage of the L1$_2$ ordering and disappearance of the ordered APB structures in the Cu$_3$Pd matrix. Only ion milling as a thinning method was not successful in producing suitable Cu$_3$Pd specimen. Even after long in-situ annealing in the TEM the LPS could not be retrieved. This has been also mentioned by Tichelaar et. al.

The effect of ion milling on the APB structures is illustrated in Figure 4.1 and Figure 4.2. Figure 4.1 shows a dark field image using the group spots near $\{110\}$ of oxidized Cu$_3$Pd- 1.5 at. % Mn when tilted within two-beam condition. The inset in Figure 4.2 shows the cube zone diffraction pattern of the image in which the splitting of the $\{110\}$ super-reflections with two kind of APB domains with periodicity direction $<010>$ and $<001>$ is visible. A few APBs, indicated by dark lines, are visible close to the MnO precipitate, seen in Figure 4.1. After in-situ
heat treatment at 450 °C for 30 minutes the APB structure, imaged as dark fringes, is fully recovered, see Figure 4.2.

To re-establish the order and to study the development or disappearance of ordering and LPS as a function of temperature, in-situ heating experiments in a TEM were performed. These experiments were carried out in a JEOL 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 °C. During the heating experiments the development of the L1₂ ordering in Cu₃Pd and LPS (due to the formation of ordered arrays of APBs) in a temperature range between 450 °C and 500 °C was carefully monitored.

For HRTEM a JEOL 4000 EX II, operating at 400 kV (spherical aberration coefficient: 0.97 ≤ 0.02 mm, defocus spread 7.8 ≤ 1.4 nm, beam semi-convergence angle 0.8 mrad) and Stuttgart JEOL ARM, operating at 1250 kV (spherical aberration coefficient: 2.7 mm, defocus spread 11 nm, beam semi-convergence angle 0.9 mrad) was used. The EDS measurements were carried out using the JEOL 2010F, operating at 200 kV and equipped with an EDAX X-
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ray energy-dispersive spectrometer with a super-ultra thin window. For the detection of the composition profile around an edge-on oriented parallel {111} Cu₃Pd-MnO planar interface an electron probe diameter of 0.7 nm (FWHM) was used. A detailed description of the method employed to determine the composition profile and the segregation towards heterophase interfaces can be found in chapter 3 or elsewhere⁷,⁸.

Figure 4.2 Dark-field image using {110} a super-reflection of oxidized Cu₃Pd- 1.4 at. % Mn. The micrograph was recorded after 30 minutes in-situ heating at 450 °C for the sample seen in Figure 4.1 using the same conditions. The structure of the APBs is fully established after in-situ heat treatment. The corresponding electron diffraction pattern is represented as an inset.

4.3 Results and Discussion

4.3.1 In-situ studies of LPS in oxidized and not oxidized Cu₃Pd using Dark Field Imaging

The study of the APB structures of the oxidized and not oxidized Cu₃Pd- 1.5 at. % Mn alloy was performed in-situ for different temperatures up the order/disorder transition temperature T_c.

After the internal oxidation process the presence of MnO (NaCl structure) and Mn₃O₄ (tetragonal distorted spinel, I4/amd) precipitates with a size of 100-200nm⁹ were observed. The MnO precipitates are bound by {111} planes.
Additionally the MnO precipitates have a small fraction of plate-shaped precipitates with a dominant (001) facet oriented parallel to [100] of the Cu3Pd matrix. The fraction of MnO precipitates can be increased by increasing the Mn content in the Cu3Pd matrix (before oxidation).

The measured compositions of the two systems are summarized in Table 4.1. The EDS measurement, see Table 4.1, of the oxidized Cu3Pd-1.5 at. % alloy showed that the Mn is bound to the oxide precipitates. This results in different Cu/Pd ratios between internally oxidized Cu3Pd alloy of 3.26 (Mn is bound to the MnO precipitates) and 3.00 of the not oxidized Cu3Pd alloy (see Table 4.1).

**Table 4.1 EDS measurements of the not oxidized and oxidized Cu3Pd-1.5 at.% Mn using analytical TEM (average over 10 spectra).**

<table>
<thead>
<tr>
<th></th>
<th>Cu (at. %)</th>
<th>Pd (at. %)</th>
<th>Mn (at. %)</th>
<th>Cu/Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not oxidized</td>
<td>73.68 ± 0.22</td>
<td>24.60 ± 0.22</td>
<td>1.72 ± 0.09</td>
<td>3.00</td>
</tr>
<tr>
<td>Oxidized</td>
<td>75.92 ± 0.48</td>
<td>23.30 ± 0.41</td>
<td>0.10 ± 0.09</td>
<td>3.26</td>
</tr>
</tbody>
</table>

The phase diagram of the Cu-Pd binary system, see Figure 4.3, shows in the Cu3Pd region the occurrence of one-dimensional and two-dimensional LPS. In the following the depicted dark field images were recorded after 1 hr. at each temperature to reach mechanical stability for recording of the dark field images.

The spots near the [110] super reflections of the <001> zone axis diffraction pattern, seen inside the white circle, were taken to visualize the APB structures. This is illustrated in Figure 4.4. The periodicity of the APBs according to the splitting of the {100} and {010} satellites around the {110} super reflection at 480 °C is M = 8 ±1 for both the oxidized Cu3Pd-1.5 at. % Mn alloy and for the not oxidized alloy.

Figure 4.5 shows APB structures at 480 and 485 °C for the oxidized Cu3Pd-1.5 at. % Mn (left side) and the not oxidized Cu3Pd-1.5 at. % Mn (right side). At 480 °C, the oxidized system reveals that the sharp APBs are confined to cube planes with small domains of about 50 nm. In contrast, the not oxidized Cu3Pd-1.5 at. % Mn at 480 °C shows both diffuse APBs in thicker region of the TEM foil and sharp APBs close to the edge of the foil. In the following all the dark field images (Figure 4.5 - 4.7) recorded using a {110} super-reflection near the <001> viewing direction tilted to two-beam condition. In all dark field images (Figure 4.5 and 4.6) an overlap of the (100) and the (010) domains can exist due to the finite thickness of the foil. This is indicated, e.g. in Figure 4.5 top right dark field image, by a white circle. At the bottom of Figure 4.5 the dark field images recorded at 485 °C are shown. For the oxidized Cu3Pd-1.5 at.% Mn alloy the APBs grow mainly along (100) at the expense of the (010) domains, whereas for
the not oxidized system no significant changes of the APB structures at 480 °C can be recognized (see Figure 4.5 bottom right). At the temperature of 490 °C the oxidized Cu₃Pd- 1.5 at. % Mn the L1₂ starts to disorder. The dark field image of Figure 4.6 left for the oxidized system illustrates the beginning of the disordering where the APBs persisting up to the order/disorder temperature.

In contrast, the not oxidized system shows at 490 °C (see Figure 4.6 right) a slight tendency to change from diffuse APBs to sharp APBs, which are oriented mainly along the (100) direction. The not oxidized Cu₃Pd- 1.5 at. % Mn alloy shows 5-10 °C below the order disorder transition temperature a further growth of the APBs along the (100) direction at the expense of the (010) direction. The dark field images at 495 and 500 °C, shown in Figure 4.7, reveals that at the temperature at 595 °C the (010) APB domains completely disappear. This can be seen in the diffraction pattern in Figure 4.7 on the left hand side, indicated by the diffraction spots in the white circle. The (100) APBs domains merge together 5 °C below the order disorder transition temperature. Just before reaching the transition temperature of 505 °C the LPS can be still observed. In the present case, at a temperature of 40 °C below the order/disorder temperature T_c, the one-dimensional LPS with a periodicity of M = 8 ± 1 and Pd concentration of 23-25 at. % seems the stable configuration.
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Figure 4.4 Electron diffraction pattern recorded at 480 °C for viewing along the <001> direction. A {110} super spot is taken to visualize the APB structure. The white circle indicates the size and position of the objective aperture used to obtain the dark field images shown in Figure 4.5-4.7. 
$2\Delta = 1/\text{Ma}$, $a$: lattice constant and $M$: spacing of the APBs.

Figure 4.5 Dark field images show the APB structure at 480 and 485°C (for recording condition see the inset in the top left image, Figure 4.4 and main text). The oxidized and not oxidized Cu$_3$Pd–1.5 Mn at. % alloy are seen on the left hand side and right hand side, respectively.
The mixed composition along the columns can be a result of local disorder or of APB meandering (ledges). In this case APBs can be considered as a smooth profile modulation. A slight but systematic decrease in $M$ with increasing temperature has been observed by Kubo and Adachi. Therefore the number of diffused planes (responsible for the diffused APBs) strongly depends on the value of $M$, which itself varies significantly with Cu/Pd ratio. However, the
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periodicity $M$ between 450 and 480 °C determined from the diffraction pattern and HRTEM observations is $M = 8 \pm 1$. This nearly constant value of the APB spacing $M$ suggests that the observed temperature range is too small to change $M$ significantly. The observation of diffuse APBs (see Figure 4.8) at 450 °C indicates that the thermal equilibrium is not reached after 1 hr in the thicker region of the TEM samples. In Figure 4.8, the diffuseness extends over several atomic planes and this is similar to what is observed by Broddin et al. Normally at temperature $> 440$ °C the two-dimensional LPS can be observed for Pd concentration of 245 at.% in Cu$_3$Pd alloys. To observe two-dimensional LPS in the present Cu$_3$Pd- 1.5 at. % Mn alloys the samples may have to be annealed for a longer time.

In the oxidized Cu$_3$Pd- 1.5 at. % Mn alloy, with an oxygen content according to EDS spectra of $4 \pm 2$ at.% O, the modulation period $M^{13}$ in the metal matrix is not significantly changed. However, the presence of oxygen in Cu$_3$Pd is responsible for the less diffuse character of the APBs. This less diffuse character of APBs can be observed in higher order satellites detected in SAD pattern$^{13}$. The observed modulation profiles $M$ from meandered APBs in the not oxidized Cu$_3$Pd- 1.5 at. % Mn alloy to the sharp APBs in the oxidized Cu$_3$Pd- 1.5 at. % Mn alloy, seen in Figure 4.5 and 4.6 can be explained from the characteristics of the electronic structure$^{14}$:

Figure 4.8 HRTEM images during in-situ heating at 450 °C viewed along the <001> direction. For both images, the oxidized (left side) and the not oxidized (right side) Cu$_3$Pd- 1.5 at. % Mn alloy the one-dimensional LPS showing APBs with diffuse character with a substantial width.
Flat sheets of a well defined Fermi surface produce a deep minimum in $V(k)$ at $2k_f$ ($k_f$ is the Fermi wave vector perpendicular to the flat sheets). Oxygen may have a strong influence on the Fermi surface. Oxygen atoms tend to be strong electron scatterers in the Cu$_3$Pd alloy. This enhanced scattering due to the presence of oxygen in Cu$_3$Pd will reduce the lifetime of the electronic states. This leads to a blurring of the Fermi surface. It is this blurred Fermi surface that broadens the minimum in $V(k)$ in Cu-Pd-O alloys, which accounts for the squaring (means sharpening of the APBs) of the modulation function. The modulation period $M$ of the one-dimensional LPS remains relatively constant with different amount of oxygen in the Cu$_3$Pd matrix it implies that the position of the Fermi surface remains unaltered with oxygen addition.

The increase in the order/disorder temperature with 15 °C in the not oxidized Cu$_3$Pd- 1.5 at. % Mn alloy is caused by the presence of Mn in the Cu$_3$Pd matrix. The difference in the Cu/Pd ratio cannot be responsible for the difference in $T_c$, because according to the phase diagram (Figure 4.3) it would have opposite effect than observed. Sato and Toth$^{15}$ investigated the effect of additional elements on the LPS structure and order/disorder transition temperature $T_c$. They revealed that the increase of the Pd content in the CuAu II matrix increases the transition temperature (from ordered to disordered state)$^{15}$. Similarly, it is likely that the presence of O and/or Mn in the Cu$_3$Pd matrix may increase the order/disorder transition temperature, rather than the oxygen present in the Cu$_3$Pd matrix after oxidation.

### 4.3.2 L1$_2$ ordering at {100} and {111} Cu$_3$Pd-MnO interfaces

All HRTEM observations were carried out after the sample was heated in-situ at 480 °C for 1 h and subsequently cooled down by switching of the heating device. Although the sample is in vacuo the cooling in the thin areas of interest for TEM occurs very fast due to the very limited specimen thickness (order of 20 nm). The used temperature of 480 °C, according to the temperature control of the heating device, is 10 °C below the order disorder transition temperature $T_c$ of 490 °C. The HRTEM micrograph, seen in Figure 4.9, shows a Cu$_3$Pd-MnO interface in the <100> viewing direction. Using this projection the {001} APBs are separated by $M = 8 \pm 1$ planes and strike the projected parallel {111} Cu$_3$Pd-MnO interface under an angle of 45° (see Figure 4.9). However, in this projection the Cu$_3$Pd-MnO interface is inclined, preventing an accurate structure determination close to the interface.
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However, for the Mn$_3$O$_4$ plate-shaped precipitates it is possible to observe an edge-on interface in the <100> projection. This is illustrated in Figure 4.10 and 4.11. It is clearly visible that the L1$_2$ ordering in Cu$_3$Pd exists up to the {001} Cu$_3$Pd-Mn$_3$O$_4$ interface (Figure 4.10 and 4.11). Figure 4.10 shows at the recording temperature of 480 °C that the APBs oriented perpendicular the Cu$_3$Pd-MnO interface is not changing its behavior when approaching the interface. Apparently, this parallel {001} type of interface between Cu$_3$Pd and Mn$_3$O$_4$ does not change the structure of the APBs (e. g. deflection or wetting of the APBs) and does not influence the L1$_2$ ordering in the Cu$_3$Pd matrix, as seen in Figure 4.10 and 4.11.

In contrast, the polar {111} Cu$_3$Pd-MnO edge-on interface, as can be seen in Figure 4.12 reveals a different degree of the L1$_2$ ordering at the interface. In order to determine the degree of L1$_2$ order in Cu$_3$Pd as a function of distance to the parallel {111} Cu$_3$Pd-MnO interface, line-scans parallel to the interface with a width of 3 pixel (perpendicular to the interface) were taken directly on top of the atomic columns. The 8 bit gray scale values of the line profiles from the HRTEM micrographs along <112> parallel to the projected interface of Cu$_3$Pd using Fast Fourier Transformation (FFT) to extract the regular {200} spacing and the {100} spacing caused by the L1$_2$ ordering of Cu$_3$Pd alloys.
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Figure 4.10 HRTEM image in the <100> projection of Cu$_3$Pd-Mn$_3$O$_4$ interface recorded in situ at 480 °C in the Stuttgart JEOL ARM 1250. The L1$_2$ ordering and the APBs (perpendicular to the interface) persist up to the interface. Due to the heating at 480 °C in the TEM the Mn$_3$O$_4$ precipitates start to reduce to MnO.

Figure 4.11 HRTEM image in the <100> projection of Cu$_3$Pd-Mn$_3$O$_4$ interface recorded at RT. The L1$_2$ ordering occurs up to the interface (APBs are parallel to the interface). Specimen was in bulk state annealed at 480 °C for 24 and subsequently quenched in water after which the TEM sample was prepared.
This procedure is illustrated in Figure 4.12 and 4.14. In Figure 4.14, the Fast Fourier Transform on a line-scan close to the Cu₃Pd-MnO interface and a line-scan in the Cu₃Pd matrix (illustrated in Figure 4.12, because highlighted by the white lines) shows clearly the disappearance of the {100} super reflections close to the interface. Finally, the ratio of the amplitude of the {100} and {200} peaks were taken to determine the degree of ordering as a function of distance in the metal to the Cu₃Pd-MnO interface. The degree of ordering is seen in Figure 4.13. This plot shows that the ordering gradually disappears when approaching the {111} Cu₃Pd-MnO interfaces within a length scale of about 10 monolayers for different defoci. Different defoci used for recording the HRTEM images resulted in different {100}/[200] intensity ratios in the Cu₃Pd matrix, i.e. at relative large distance to the interface (see Figure 4.13). HRTEM image simulations (MacTempas¹⁶) for perfectly ordered Cu₃Pd show that the {100}/[200] ratio depends sensitively on the TEM specimen thickness and on the defocus used. Despite this strong sensitivity and the large variation that can occur for the {100}/[200] ratios it can be concluded that the experimentally obtained ratios are in agreement with the simulated ones (see Table 4.2).

Table 4.2 {100}/[200] ratio in the Cu₃Pd matrix of experimental HRTEM images (see Figure 4.14) and simulated images of ordered Cu₃Pd for different defoci. The values listed under simulation correspond to a thickness of 10 nm/12 nm.

<table>
<thead>
<tr>
<th>Defocus</th>
<th>Experiment</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/-1.2 nm</td>
<td>2.91</td>
<td>4.27/3.21</td>
</tr>
<tr>
<td>-12 nm</td>
<td>2.30</td>
<td>2.63/1.26</td>
</tr>
<tr>
<td>-24 nm</td>
<td>0.97</td>
<td>4.81/0.58</td>
</tr>
</tbody>
</table>

The TEM samples are in-situ heated at 480 °C and this leads to thicker areas under investigation. In order to reduce its relative surface area the specimen retracts the thinnest parts and the wedge shaped specimen becomes more blunt. On the other hand, if HRTEM images of Cu₃Pd-MnO interfaces with a reasonable atomic resolution are recorded the specimen cannot be too thick (e.g. < 20 nm). Therefore an intermediate thickness of 10 to 12 nm used in the simulations gives a proper match to the experimental thickness of the HRTEM micrographs. A problem can be that a thickness gradient along the interface occurs, due to the wedge shape of the TEM specimen. We have tried to minimize this effect by using for the analysis shown in Figure 4.12 - 4.13 interfaces that ran parallel to the edge with the hole in the TEM specimen.
Electron microscopy study of ordering in Cu$_3$Pd and at Cu$_3$Pd-MnO interfaces

Figure 4.12 HRTEM image of a \{111\} Cu$_3$Pd-MnO interface in the <110> viewing direction. The first and the tenth line profile, highlighted by white solid lines along the interface, are Fourier transformed and the result of this procedure is depicted in Figure 4.14.

Figure 4.13 \{100\}/\{200\} ratio at 480 °C to visualize degree of L1$_2$ ordering in Cu$_3$Pd at \{111\} Cu$_3$Pd-MnO interfaces for different defoci.
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Yet, since the measured ratio is strongly dependent on thickness, it may cause deviations between the experimentally obtained and simulated \{100\}/\{200\} ratios. The same of course does not apply only to the ratios measured for bulk Cu$_3$Pd, but for the whole profile as a function of distance to the interface. Particularly, at an interface between dissimilar materials like MnO and Cu$_3$Pd the presence of thickness variation perpendicular to the interface can hardly be avoided. This may also be the reason why not all the shapes of the profiles for the different defoci are identical. The gradually disappearance of the L1$_2$ ordering in the <110> projection at polar \{111\} Cu$_3$Pd-MnO interfaces can be confirmed also in the <112> projection, as illustrated in Figures 4.15. and 4.16. Also in the <112> projection the gradually disappearance of the L1$_2$ ordering is demonstrated by now performing a line-scan perpendicular to the interface in Figure 4.15 (width of 400 pixel) across the \{111\} Cu$_3$Pd-MnO interface. This result is depicted in Figure 4.16. The comparison of the \{100\}/\{200\} ratios seen in Figure 4.13 for the <110> projection at the line profile across the polar \{111\} Cu$_3$Pd-MnO interface shown in Figure 4.16 reveal that the intermediate region from order to disorder at the interface appears over about 10 monolayers. Thus the present results clearly indicate that at parallel \{001\} Cu$_3$Pd-MnO interfaces disordering does not occur (as observed both at high temperature and after cooling to RT), whereas at parallel \{111\} Cu$_3$Pd-MnO interfaces disordering does occur as observed using both <110> and <112> projections.

**Figure 4.14** Fast Fourier Transform of line-scans taken for planes line 1 and 10, seen in Figure 4.12. The \{100\} peak of the super spots caused by the ordering of Cu$_3$Pd can be hardly seen in line 1, whereas in line 10 the \{100\} peak is clearly visible.
Electron microscopy study of ordering in Cu₃Pd and at Cu₃Pd-MnO interfaces

Figure 4.15 HRTEM image of a (111) Cu₃Pd-MnO interface in the <112> viewing direction. The degree of L1₂ ordering gradually disappears when approaching the (111) Cu₃Pd-MnO interface.

Figure 4.16 Lineprofile with a width of 400 pixel across the Cu₃Pd-MnO interface in the <112> projection shows clearly the disappearance of the L1₂ ordering when approaching the interface of about 10 monolayers by counting the peaks in the gradually disordered region.
An important question is if the interface gives rise to local composition variations in the Cu₃Pd that may explain the presence of disorder. In Chapter 3 we presented a new approach to measure and quantify segregation at heterophase interfaces that has advantages compared to line scans, chemical maps or the use of scan raster⁷,⁸. We now applied this approach to the Cu₃Pd-MnO interface and the result is shown in Figure 4.17. It shows the measured Pd concentration as a function of the measured Cu concentration (i.e. across the interface) together with the fitted segregation curve. A linear relation between the Pd and Cu concentrations would indicate that segregation does not occur. The result of the fitting shows a weak Pd segregation at the interface with 26.6 at.% Pd in the metal monolayer (ML) most near the interface compared to a measured Pd concentration of 21.5 at.% (the oxygen content of approx. 2.2 at. % was considered in this quantification) in the Cu₃Pd matrix. This means Pd enrichment in a single ML is about 20%. Comparing these concentrations with the Cu-Pd phase diagram and knowing that for the matrix concentration in-situ annealing was performed 10 °C below Tₐ, the higher Pd concentration at the interface then would be above Tₐ. So it is very well possible that during annealing the monolayer most near to the interface tends to be disordered. Fast cooling of the TEM specimen does not allow the order to (re-) develop. However, the conclusion is that the very local enrichment in one ML cannot be responsible for the gradually disappearing of the L1₂ ordering over a longer range of about 10 MLs.

An important characteristic of the {111} facet of the MnO is that it gives rise to a polar interface, because after internal oxidation the outer atomic layer of the MnO is occupied by negative oxygen ions only¹⁷,¹⁸. Perpendicular to the interface a repeat unit with alternating positive Mn and negative O ions occurs, i.e. establishing an electrical dipolar field. For a free surface (oxide-vacuum interface) such a dipolar field would cause a diverging surface energy and thus would never correspond to a stable surface. The free surface will reconstruct in order to arrive at a finite surface energy. Ab-initio calculations on polar {0001}-surfaces of ZnO demonstrated that the electronic structure in ZnO is disturbed by the polar free surface of about 16 atomic layers into the bulk¹⁹. For polar oxide-metal interfaces, the situation is in essence different compared with non polar interfaces: (i) a larger work of adhesion and charge transfer (e.g. 0.08e for (100) and 0.18e for (111) Cu over O interface²⁰), (ii) larger shifts in the layer potentials relative to the bulk and (iii) small amplitude electron density oscillation extending at least 5 Å²⁰ away from the interface into the metal. The metal is very effective in screening the electrical charges in the outer monolayer.
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of the oxide, but the metal induced gap states (MIGS) in the oxide are supplied by the charges of the bulk metal, rather than the interface layer alone²¹, ²².

![Figure 4.17](image)

**Figure 4.17** EDS results together with the model curve. The best match of the model curve with the EDS measurement is reached with a Pd concentration of 26.6 at.% in the outermost Cu₃Pd monolayer at the {111} Cu₃Pd-MnO interface compared with the measured Pd concentration in the Cu₃Pd matrix of 21.9 at.%. A probe size of 1.4 nm was assumed for the fitting procedure between model curve and EDS data.

Fluctuating charge density develops along the interface following the alternating positively and negatively charged layers of the oxide, but with strong damping of these oscillations in electron density in the metal. Ab-initio calculations for the polar parallel {111} Cu/MgO interface confirmed the presence of these charge oscillations in the metal²⁰, but due to the limited size of the computational cell it was not possible to be conclusive on the range of this interaction. However, it is not impossible that it extends over about 10 MLs.

A principal point is that small changes in the interatomic potentials may have a large effect on \( T_c \), because, only considering pairwise interactions, \( T_c \) is more or less a linear function of \( w_{ij} = v_{ij} - \frac{v_{ij} + v_{ji}}{2} \) with \( v_{ij} \) the nearest neighbor bond energy between atoms i and j. So, small changes in \( v_{\text{Cu-Pd}} \), \( v_{\text{Cu-Cu}} \) or \( v_{\text{Pd-Pd}} \) may result in a substantial change of \( w_{\text{Cu-Pd}} \) that in return clearly changes \( T_c \). Another reason could be the interface separation (bond length) in polar and non-polar interfaces. In section 6.2.2 the calculated separation of the Ag-O bond for the polar Ag-MgO interface is 1.55 Å which is much smaller than the interplanar
distance of 2.2 Å in the Ag bulk. In contrast, Benedek et al. calculated that the Cu-O bond length of 2 Å for a non-polar interface is slightly bigger than the d-spacing in the Cu bulk. This difference in interface separation between non-polar and polar interfaces can change the interatomic potentials at the interface. If the polar interface affects the interatomic potentials in the metal over a relative large range (10 MLs) it can affect the order in this range and can be the cause for the observed disordering profile.

Further support for the long-range effect of heterophase interfaces on the order (also for temperatures clearly below $T_c$ and in particular for the parallel {111} interface in contrast to the (100) and (110) interfaces), comes from thermodynamic calculations presented in. The interface between Al$_3$Li and Al is considered in most detail for a parallel (100) configuration, but also for the parallel (110) and (111) ones. The calculations are based on first principles to arrive at the interatomic potentials (up to second nearest neighbors) that are used as input in the Cluster Variation Method to obtain the composition profiles (including the degree of short and long-range order) perpendicular to the interface. It is shown that the obtained width of the interface boundary is a linear function of $T$ without indication that it diverges when approaching $T_c$. This is in clear contrast to the wetting of APBs where the width of the disordered wetting layer is proportional to $\log[a(T-T_c)]^{-1}$. It should be noted that in this latter case the definition of the width is unambiguous whereas in the former case it has a much more arbitrary basis. Nevertheless, in the sense of the width of the disorder layer we observe in Figure 4.12 and 4.15 the width of the diffuse region from order to complete disorder for the (100) Al$_3$Li-Al interface at 400 K (280 K below $T_c$) is already 12 (100) planes or 2.4 nm. In the light of these results it is not surprising that for the presently considered (more extreme) polar interface, cooled down after annealing 10 K below $T_c$, a region of 10-15 MLs is found where the order vanishes when approaching the interface.

4.4 Conclusions

This chapter shows, using HRTEM images recorded for the <110> and <112> projection that the L1$_2$ ordering at polar {111} Cu$_3$Pd-MnO interfaces gradually disappears. On the other hand the non-polar {001} Cu$_3$Pd-Mn$_3$O$_4$ interfaces has no influence of the L1$_2$ order even close to the interface and near to $T_c$. Dark field imaging at lower magnification showed that oxygen dissolution in the copper matrix after internal oxidation had a sharpening effect on the APB structure and keeps the nearly constant value of the APB spacing M of 8 ±1
Electron microscopy study of ordering in Cu₃Pd and at Cu₃Pd-MnO interfaces compared with the not oxidized samples. The presence of Mn and/or the absence of O in the copper matrix of the not oxidized sample probably increased the order-disorder transition temperature.

References

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Chapter 5

Misfit along interfaces between $\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$ and Ag

In this chapter, we investigate how the tetragonality of $\text{AB}_2\text{O}_4$ spinel structures embedded in a cubic matrix depends on the chemical composition. Zinc manganites $\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$ are interesting candidates, because Zn is located on the tetrahedral side (A site), whereas the Mn$^{3+}$ prefers the octahedral site (B site) of the spinel phase$^1$. Mn$^{3+}$ is responsible for the tetragonal distortion of $\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$. We focus on a wide range of $\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$ precipitates in a Ag matrix with $x$ varying between 0 and 1.5. This variation of $x$ could be obtained by internal oxidation of Ag-2at.% Mn-4at.%Zn in air and annealing in vacuo at different temperatures. It has been demonstrated that the Zn concentration in $\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$ has a major influence on the interfacial misfit and orientation relation between Ag/$\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$.

5.1 Introduction

Aminoff$^2$ measured with X-ray powder diffraction the tetragonal distortion of $\text{Mn}_3\text{O}_4$. The lattice constants are $a = 5.75 \, \text{Å}$ and $c = 9.42 \, \text{Å}$ (SG: I4/amd). Compared to the (cubic) spinel $\text{AB}_2\text{O}_4$ it is more convenient to consider $\text{Mn}_3\text{O}_4$ with $a = 8.14 \, \text{Å}$ (i.e. $\sqrt{2}$ times 5.75 Å) and $c = 9.42 \, \text{Å}$ (SG: Fd3m), i.e. [100] and [010] in spinel correspond to [110] and [011] for I4/amd$^3$. The distortion of the crystalline lattice ($c/a > 1$) arises from the presence of the Mn$^{3+}$ on the octahedral sites of the spinel lattice$^4$. An analysis of the electronic configuration of the 3$d$ transition series shows (e.g. for Mn$^{3+}$, Cu$^{2+}$) that the doublet states cannot be degenerated in the crystal field and therefore in the case of orbital degeneracy the octahedron is deformed ($c/a > 1$). On the other hand, for the tetrahedron the deformation leads to $c/a < 1$. These deformations caused by the cooperative Jahn-Teller (JT) distortion takes the dynamic JT effect at higher temperatures into account by including anisotropic (nonlinear) JT couplings. A calculation of the tetragonal distortion in spinels was performed$^4$, where the molecular field treatment was applied for relative high temperatures ($T \geq 100 \, \text{K}$). The decrease of the Mn$^{3+}$ concentration on the octahedral sites or the increase of the temperature is generally known to result in the order-disorder transition. The phase diagram ZnO/Mn$_3$O$_4$ shows that the tetragonal phase is stable up to
1100 ºC in air. Above this temperature a reversible tetragonal to cubic transition occurs. This anneals the cooperative JT distortion and the cubic structure is observed.

For zinc manganites Zn$_x$Mn$_{3-x}$O$_4$ the Zn$^{2+}$ ions have a preference to be present on the tetrahedral sites of the spinel lattice. From $x = 0$ up to $x = 1.5$ the tetragonal distortion decreases gradually from $c/a = 1.16$ to $c/a = 1$ at room temperature. It was shown that the transition temperature from tetragonal to cubic decreases with the increase of the zinc content. For zinc concentrations $x \geq 1$ the Zn$^{2+}$ cations start to exchange with the Mn$^{3+}$ cations. This reduces the Mn$^{3+}$ concentration on the octahedral sites of the spinel structure according to the structural formula:

$$Zn^{2+} (Zn^{2+}_x Mn^{4+}_x Mn^{3+}_{2-2x})O_4$$ (5.1)

Equation (5.1) indicates that the concentration of the JT ion Mn$^{3+}$ on the octahedral sites decreases whereas the Mn$^{4+}$ concentration increases, thereby reducing the tetragonality.

Internal oxidation of Ag-3 at.% Mn resulted in octahedral shaped Mn$_3$O$_4$ precipitates due to the {111} facets inside the silver matrix. The orientation relation between Ag and Mn$_3$O$_4$ and the dislocation structure at these metal-oxide interfaces was investigated in detail by HRTEM and atomistic calculations. The tetragonal distortion leads to a configuration where only a few planes and directions of Ag and Mn$_3$O$_4$ can be parallel simultaneously whereas other planes show mutual tilting (up to 7.6º) or both tilting and twisting.

The present work focuses on Zn$_x$Mn$_{3-x}$O$_4$ precipitates in a silver matrix with a wide variation of the zinc concentration. The misfit and orientation relation as a function of the zinc content $x$ between Ag and Zn$_x$Mn$_{3-x}$O$_4$ by means of HRTEM have been scrutinized.

### 5.2 Experimental details

A silver alloy containing 2 atomic percent (at.%) Mn was made in a high-frequency furnace by melting the pure components (Purity 99.99% by weight) in one aluminum crucible under argon protective oxygen free atmosphere. The silver alloy was cold rolled down to 100 µm and homogenized in an evacuated quartz tube for one week at 700 ºC. During the homogenization process a piece corresponding to 4 at.% Zn was positioned separately in the evacuated quartz tube and dissolved into the silver alloy. Oxide precipitates in the silver matrix were obtained by oxidation of the alloy in air. Five different sample systems
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with different oxidations and annealing steps of Ag - 2at.%Mn - 4at.%Zn were fabricated, as follows:
1. Internal oxidation in air at 900 °C for ½ h.
2. Internal oxidation in air at 800 °C for 5h.
3. Internal oxidation in air at 900 °C for ½ h and annealing in vacuum at 900 °C for 5h
4. Internal oxidation in air at 800 °C for 5 h and annealing in vacuum at 800 °C for 24h
5. Internal oxidation in air at 800 °C for 5 h, annealing in vacuum at 800 °C for 24h and re-internal oxidation in air at 900 °C for ½ h.

TEM samples were prepared by grinding, dimpling and ion milling 3 mm discs to electron transparency. HRTEM imaging was performed with a JEOL 4000 EX/II, operating at 400 kV (spherical aberration coefficient: 0.97 ± 0.02, spread of defocus: 7.8 ± 1.4 nm, beam semi convergence angle: 0.8 mrad). The HRTEM micrographs were obtained from digitized negatives. EDX measurements were carried out using a JEOL 2010 F operating at 200 kV with a probe-size of about 1 nm (FWHM). Each measured composition of precipitates was determined by averaging over about 15 EDX measurements.

5.3 Results

5.3.1 Precipitate formations

Table 5.1 gives an overview over the different measured compositions after oxidizing in air and annealing in vacuo of Ag-2at%Mn-4at%Zn. Internal oxidation at 900°C and 800°C (½ h and 5 h, respectively) results according to the EDX measurements and HRTEM images in octahedral shaped ZnMnO precipitates (cubic spinel Fd3m). A HRTEM image of a ZnMnO precipitate with a size of approximately 5 nm is shown in Figure 5.1. After internal oxidation in air at 900 °C and 800 °C the samples were annealed at the same temperature in vacuo for 5 h and 24 h, respectively. The cubic spinel phase ZnMnO decomposes into two different types of oxide precipitates. The treatment at 900 °C results in small elongated octahedral shaped ZnO precipitates (tetragonally distorted spinel) precipitates (Figure 5.3) and approximately 2-10 times longer plate-shaped precipitates of ZnO (Figure 5.2). Basically, the plate precipitates have a hexagonal wurtzite structure, but in many cases HRTEM images show that strong stacking disorder of the basal planes is present locally leading to the fcc based sphalerite stacking (Figure 5.4).
Misfit along interfaces between ZnₙMn₃₋ₙO₄ and Ag

Annealing at 800 °C in vacuo also leads to plate-like ZnₙMn₁₋ₙO, but with a lower Zn concentration of $x = 0.88$. On the other hand, the spinel phase of ZnₙMn₃₋ₙO₄ is not present. In contrast, after this annealing at 800 °C and 900 °C small inclusions with a maximum size of 5 nm are present in the silver matrix, as seen in Figure 5.2. Analytical TEM reveals that these inclusions are fcc phase Mn₀.₈₆Zn₀.₁₄O (i.e. have the rocksalt structure).

After re-internal oxidation, the inclusions transfer back to octahedral shaped Zn₁₀₄Mn₁₉₆O₄ with a size of 5-10 nm. In the plate-like precipitates the Zn concentration increases from $x = 0.88$ to $x = 0.96$. So, compared to the first internal oxidation treatment with only Zn₁₅Mn₁₅O₄ precipitates, after re-oxidation a kind of phase separation into ZnMn₂O₄ and ZnO has occurred. Coupled to this picture, some plate-like precipitates are visible that split into two phases: cubic spinel phase Zn₁₄₇Mn₁₅₃O₄ directly connected to the ZnO-based wurtzite/sphalerite structure (Figure 5.4). Besides these plate-like precipitates also wurtzite and sphalerite ZnₙMn₁₋ₙO forms into truncated trigonal shaped precipitates as could be observed in some cases after annealing at 900 °C and 800 °C. Detailed observation of ZnO precipitates with wurtzite and sphalerite structure in Ag and Pd have been published earlier⁹,¹⁰. In the following, only the spinel phased precipitates will be considered.
Table 5.1: Characterization in concentration x, shape, size and crystallographic structure of the formed ZnxMn3-xO4 precipitates for different oxidation and annealing steps of Ag -2at.% Mn -4at.%Zn.

<table>
<thead>
<tr>
<th>Ag -2at.% Mn-4at.% Zn</th>
<th>Phase of the precipitates</th>
<th>Zn concentration</th>
<th>Shape of the precipitates</th>
<th>Dimension of the precipitates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation at 900 °C for ½ h in air</td>
<td>ZnxMn3-xO4 (SG: Fd3m)</td>
<td>x = 1.5 ± 0.1</td>
<td>Octahedrally shaped precipitates bounded by [111] planes in Ag</td>
<td>5 – 15 nm</td>
</tr>
<tr>
<td>Oxidation at 800 °C for 5 h in air</td>
<td>ZnxMn3-xO4 (SG: Fd3m)</td>
<td>x = 1.5 ± 0.1</td>
<td>Octahedrally shaped precipitates</td>
<td>5 – 15 nm</td>
</tr>
<tr>
<td>Oxidation at 900 °C for ½ h in air + annealing in vacuo at 900 °C for 5 h</td>
<td>ZnxMn3-xO4 (SG: I4/amd) wurtzite/sphalerite ZnxMn1-xO (SG: P63mc/ F43m)</td>
<td>x = 0.56 ± 0.1 x = 0.93 ± 0.03</td>
<td>Elongated - and octahedrally shaped ZnxMn3-xO4 Plate like/truncated trigonal shaped ZnxMn1-xO</td>
<td>length: 10 – 25 nm, width: 5 – 10 nm, length: 50 – 120 nm, width: 8 – 25 nm</td>
</tr>
<tr>
<td>Oxidation at 800 °C for 5 h in air + annealing in vacuo at 800 °C for 24 h</td>
<td>ZnxMn1-xO f.c.c. (SG: Fm3m) wurtzite/sphalerite ZnxMn1-xO (SG: P63mc/ F43m)</td>
<td>x = 0.15 ± 0.04 x = 0.88 ± 0.05</td>
<td>Octahedrally shaped Mn2Zn1-xO Plate like/truncated trigonal shaped ZnxMn1-xO</td>
<td>5 - 10 nm, length: 50 –100 nm, width: 10 –15 nm</td>
</tr>
<tr>
<td>Oxidation at 800 °C for 5 h in air + annealing in vacuo at 800 °C for 24 h + oxidation in air at 900 °C for ½ h</td>
<td>ZnxMn3-xO4 (SG: I4/amd) wurtzite/sphalerite ZnxMn1-xO (SG: P63mc/ F43m) and ZnxMn3-xO4/ Zn(Mn)O</td>
<td>x = 1.03 ± 0.14 x = 0.96 ± 0.02 x = 1.47 ± 0.02</td>
<td>Octahedrally shaped ZnxMn3-xO4 Plate like/truncated trigonal shaped ZnxMn1-xO, ZnxMn3-xO4/ Zn(Mn)O</td>
<td>5 – 10 nm, length: 50 –100 nm, width: 10 –15 nm</td>
</tr>
</tbody>
</table>

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**Figure 5.2** Plate-shaped precipitate of Zn$_{0.98}$Mn$_{0.02}$O after internal oxidation at 900 °C for $\frac{1}{2}$ and annealing in vacuo at 900 °C for 5 h.

**Figure 5.3** HRTEM image showing an elongated octahedral Zn$_{0.54}$Mn$_{2.46}$O$_4$ in the $<110>$ viewing direction of an internal oxidized Ag- 2at%Mn- 4at%Zn (900 °C for $\frac{1}{2}$ h) annealed at 900 °C for 5 h in vacuo.
5.3.2 Mismatch and orientation relation (OR) between Zn$_{x}$Mn$_{3-x}$O$_{4}$ and Ag

The mismatch between Zn$_{x}$Mn$_{3-x}$O$_{4}$ and Ag changes by varying the concentration $x$. The lattice parameter and degree of tetragonal distortion for different Zn concentrations of Zn$_{x}$Mn$_{3-x}$O$_{4}$ was given in 5. The OR between the octahedral shaped Zn$_{x}$Mn$_{3-x}$O$_{4}$ and the Ag matrix (Figure 5.1) can be regarded as parallel topotaxy (cube-on-cube) where the interfaces are formed by the parallel $\{111\}$ of metal and oxide. In contrast, due to the tetragonality of Zn$_{x}$Mn$_{3-x}$O$_{4}$, as shown in Figure 5.3, with a-axis of 0.808 nm and c-axis of 0.920 nm only one or two direction and planes can be simultaneously parallel.

For viewing the interface between the Zn$_{x}$Mn$_{3-x}$O$_{4}$ and the Ag matrix, the Ag crystal is tilted into the $<110>$ zone axis. The tetragonality of Zn$_{x}$Mn$_{3-x}$O$_{4}$ can easily be observed in HRTEM images (using the Ag crystal as reference), because of the difference between the c-and a-axis. The tetragonality can be detected by measuring the blunt angle between $\{111\}$ planes of the precipitate: $\{111\}$ planes of a cubic crystal such as Ag make a blunt angle of 109.5$^\circ$ in all possible $<110>$ projections. For tetragonal distorted spinel, however, in the $[110]$ viewing direction an angle larger than 109.5$^\circ$ is observed (with $1/3$ probability) and in the $[101]$ and $[011]$ directions less than 109.5$^\circ$ is observed (with $2/3$ probability). Figure 5.5 depicts the blunt angle between $\{111\}$ planes of

![HRTEM image showing a precipitate where cubic spinel Zn$_{1.47}$Mn$_{1.53}$O$_{4}$ is connected to wurtzite/sphalerite Zn$_{0.96}$Mn$_{0.04}$O. These precipitates grow after internal oxidation at 900 ºC for ½ h of a sample that was previously annealed in vacuo, see Table 5.1.](image)

Figure 5.4

[85]
Misfit along interfaces between $\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$ and Ag when viewed along [110] or [101]/[011] for different Zn concentrations $x$ based on the lattice constants given in $^5$.

The calculated misfit between $\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$ and Ag at parallel $\{111\}$ interfaces along [112] varies from 10.3% ($x = 0$) to 2.4% ($x = 1.5$) based on the $a$ and $c$ lattice constants, as seen in Figure 5.6. Note that the mismatch in the perpendicular $[\bar{1}10]$ direction varies from -0.4% ($x = 0$) to +2.4% ($x = 1.5$).

Using HRTEM images of $\{111\}$ heterophase interfaces the misfit between metal and oxide can be directly observed with Bragg filtering of $\{111\}$ planes. This is demonstrated in Figure 5.7 and 5.8. The modulation of the line profiles in Figure 5.7 and 5.8 corresponds to the mismatch of 10.4% and 2.4% (approx. 11 periods in the metal vs. 10 periods in the oxide and 42 periods in the metal vs. 41 in the oxide, respectively) in the $\{111\}$ lattice fringes at Ag-$\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$ with $x = 0$ and $x = 1.47$, respectively (Figure 5.7 and 5.8). The line profile of the Ag-$\text{Mn}_3\text{O}_4$ interface (Figure 5.7) shows that the magnitude of the intensity modulation reveals the possibility to distinguish between the Burgers vectors of type $1/3\ <112>$ and $1/6\ <112>$ that were observed and calculated to be present along the Ag-$\text{Mn}_3\text{O}_4$ interface$^7$. This different degree of modulation results from the undulation of the outmost Ag monolayer at the interface$^7$. The $1/3\ <112>$ Burgers vector corresponds to a stronger lattice distortion than the $1/6\ <112>$. However, for the line profile seen in Figure 5.8 bottom panel of the $\{111\}$ Ag-$\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$ interface the modulation intensity cannot be unambiguously interpreted, because of the two-dimensional network of misfit dislocations.

Figure 5.5 Angle between $\{111\}$ planes of octahedral $\text{Zn}_x\text{Mn}_3\text{O}_4$ by variation of zinc concentration $x$. See angles in Figure 5.2 and 5.4.

<table>
<thead>
<tr>
<th>Angle (°)</th>
<th>$x$ in $\text{Zn}<em>x\text{Mn}</em>{3-x}\text{O}_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td>115</td>
<td>-</td>
</tr>
<tr>
<td>110</td>
<td>-</td>
</tr>
<tr>
<td>105</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>-</td>
</tr>
</tbody>
</table>

86
present at the interface. I.e. the mismatch of 2.4% is present along all directions whereas at the Ag-Mn$_3$O$_4$ interface a more or less one-dimensional mismatch occurs, where the misfit dislocations can be observed end-on.

![Figure 5.6](image)

**Figure 5.6** Misfit at {111} Ag-Zn$_x$Mn$_{3-x}$O$_4$ interfaces along <112> decrease by increasing the amount of x in Zn$_x$Mn$_{3-x}$O$_4$ because the c/a ratio decreases.

The degree of modulation can be directly confirmed with simulated HRTEM images of relaxed {111} Ag-Mn$_3$O$_4$ interfaces, as seen in Figure 5.9. The calculation of the relaxed atomic configuration of the Ag atoms at the {111} Ag-Mn$_3$O$_4$ interface was obtained by the program described in$^8$ and is fully discussed in$^7$. Inverse FFT on Bragg filtered {111} spots make it possible to distinguish between the Burgers vectors of type 1/3 <112> and 1/6 <112> (Figure 5.9 bottom panel), however for the disregistry where the misfit dislocation at Ag-Mn$_3$O$_4$ interfaces is exactly located, additional determination of the position of the Ag atoms and the position of the oxygen atoms along the interface must be performed in real space, as described in$^7$

In contrast, inverse FFT on Bragg filtered {111} spots on unrelaxed {111} HRTEM simulated Ag-Mn$_3$O$_4$ interfaces show constant degree of modulation in the line profiles, as see in Figure 5.10. Thus, comparing Figure 5.7, 5.9 and 5.10 clearly indicates that {111} Ag-Mn$_3$O$_4$ is a semi-coherent and not an incoherent interface.
Misfit along interfaces between $\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$ and Ag

Figure 5.7 Visualization of the mismatch between Ag and $\text{Mn}_3\text{O}_4$. Top panel shows the HRTEM image of an (111) Ag-$\text{Mn}_3\text{O}_4$ interface. The middle panel shows the inverse FFT of the Bragg filtered (111) spots of the HRTEM image. The white line along the Ag-$\text{Mn}_3\text{O}_4$ interface (middle panel) indicates the line profile of the (111) Ag-$\text{Mn}_3\text{O}_4$ interface, as seen in the bottom panel. The minima in the line profile correspond directly to the misfit between Ag and $\text{Mn}_3\text{O}_4$. 
Figure 5.8 Visualization of the mismatch between Ag and Zn$_{1.5}$Mn$_{1.5}$O$_4$. Top panel shows the HRTEM image of an (111) Ag-Zn$_{1.5}$Mn$_{1.5}$O$_4$ interface. The middle panel shows the inverse FFT of the Bragg filtered (111) spots of the HRTEM image. The white line along the Ag-Zn$_{1.5}$Mn$_{1.5}$O$_4$ interface (middle panel) indicates the line profile of the (111) Ag-Zn$_{1.5}$Mn$_{1.5}$O$_4$ interface, as seen in the bottom panel. The minima in the line profile correspond directly to the misfit between Ag and Zn$_{1.5}$Mn$_{1.5}$O$_4$. 
Misfit along interfaces between $\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$ and Ag

**Figure 5.9** Visualization of the mismatch between Ag and $\text{Mn}_3\text{O}_4$. Top panel shows the HRTEM image simulation of an relaxed{111} Ag-$\text{Mn}_3\text{O}_4$ interface (defocus -6nm, thickness 4 nm, beam tilt of 1.3 mrad$^\circ$). The middle panel shows the inverse FFT of the Bragg filtered {111} spots of the simulated HRTEM image. The white line along the Ag-$\text{Mn}_3\text{O}_4$ interface (middle panel) indicates the line profile of the {111} Ag-$\text{Mn}_3\text{O}_4$ interface, as seen in the bottom panel. The variations of the intensity modulation in the line profile correspond directly to the misfit dislocation between Ag and $\text{Mn}_3\text{O}_4$. 

![HRTEM image simulation](image.png)
5.4 Discussion

The direct nucleation of Mn$\textsubscript{3}$O$_4$ in Ag compared with the presence of MnO precipitates in Cu is probably caused by the different partial pressure of oxygen during oxidation of Ag and Cu. Ag is oxidized in air, whereas Cu is oxidized as the partial pressure pertaining to the equilibrium between Cu/Cu$\textsubscript{2}$O (powder). Another possible explanation is the difference of the oxygen permeability through Ag and Cu. At 900 °C $c_0D_0$, with $c_0$ the oxygen solubility and $D_0$ the diffusion coefficient of oxygen within the matrix, is about two orders of magnitude larger in Ag than in Cu\textsuperscript{12}. The presence of Zn and Mn in the silver matrix results after internal oxidation at 900 °C and 800 °C in cubic Zn$_{1.5}$Mn$_{1.5}$O$_4$ octahedrally shaped precipitates. The main reason for this cubic spinel is likely to be the similar diffusion constants of Mn and Zn ($D_{\text{Mn}} = 7.92 \cdot 10^{-9}$ cm$^2$/s (at 900 °C)$^{13}$ and $D_{\text{Zn}} = 8 \cdot 10^{-9}$ cm$^2$/s (at 900 °C)$^{14}$) and after the oxidation front during the oxidation process the same amount of Zn and Mn are present when the precipitates grow. After annealing in vacuo the Zn$_{1.5}$Mn$_{1.5}$O$_4$ octahedrally shaped precipitates decompose to MnO and ZnO precipitates. From thermodynamic point of view the change of the Gibbs-free energy for the bulk oxidation of Mn into several oxide phases is different if the Mn concentration is limited or the O concentration is limited. In the first case the calculation based

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**Figure 5.10** Visualization of the mismatch between Ag and Mn$\textsubscript{3}$O$_4$. The line profile shows the HRTEM image simulation of an unrelaxed[111] Ag-Mn$\textsubscript{3}$O$_4$ interface (defocus -6nm, thickness 4 nm, beam tilt of 1.3 mrad$^1$). The mismatch of 10.0 % between Ag and Mn$\textsubscript{3}$O$_4$ is visible, but without any misfit dislocation, as seen in Figure 5.9.
on the Gibbs-free energy per Mn (atom or mole)\(^{15}\) shows that Mn\(_3\)O\(_4\) precipitates are thermodynamically preferred, whereas in the second case the calculation of the Gibbs-free energy per O (atom or mole) reveals that MnO precipitates are favored\(^{15}\). The same applies here. After internal oxidation, where sufficient oxygen is available and the amount of Mn and Zn is limited Zn\(_{1.5}\)Mn\(_{1.5}\)O\(_4\) is favored. On the other hand, during annealing in vacuo the amount of oxygen is limited and decomposition in the more stable MnO and ZnO phases occurs. At 900 °C decomposition can occur much faster than at 800 °C. This is probably the reason that the Mn concentration found within the ZnO precipitates is still higher at 800 °C than at 900 °C. However, at 900 °C also a small amount (about 2%) of elongated octahedral shaped Zn\(_{0.56}\)Mn\(_{2.44}\)O\(_4\) (tetragonally distorted) precipitates is present. The partial oxygen pressure can be high enough after internal oxidation at 900 °C. Figure 5.11 depicts the dissolution of oxygen in Ag at P\(_{O_2}\) = 1 atm as a function of temperature. The oxygen dissolution in Ag at 900 °C is almost two orders of magnitude higher than at 800 °C\(^{17}\), as can be seen in Figure 5.11. This higher oxygen content after a heat treatment at 900 °C can be the reason that after annealing in vacuo the spinel phase develops, because of the sufficient amount of oxygen present in the Ag matrix. After re-internal oxidation the MnO inclusion transfer to Zn\(_{1.03}\)Mn\(_{1.97}\)O\(_4\) octahedrally shaped precipitates. Usually the well-defined compound ZnMn\(_2\)O\(_4\) is obtained at 900 °C after long annealing time\(^{16}\). In thermal equilibrium (\(T = 900 °C\)) Zn\(_x\)Mn\(_{3-x}\)O\(_4\) has a low zinc content of x < 1.08\(^{16}\). For a higher zinc content (\(x > 1.08\)) the cubic phase ZnMnO\(_3\) is observed\(^{16}\), in addition to the spinel phase, in agreement with our observations.

![Figure 5.11 Dissolution of oxygen in Ag at P\(_{O_2}\) = 1 atm as a function of temperature. The data are taken from literature\(^{17}\).](image)
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5.5 Conclusions

The main result shown is that it is possible to vary the Zn content $x$ in ZnxMn$_{3-x}$O$_4$ precipitates in Ag matrix by applying several oxidation and annealing steps. The transformation from tetragonally distorted to cubic ZnxMn$_{3-x}$O$_4$ (from $x = 0$ to $x = 1.5$) formed inside the silver matrix was studied. Atomic scale studies of the mismatch and misorientation of {111} Ag-Zn$_x$Mn$_{3-x}$O$_4$ interfaces reveal clearly the decreasing misfit between Ag and Zn$_x$Mn$_{3-x}$O$_4$ with increasing amount of zinc in the spinel phase. Bragg filtering is a simple method to visualize the misfit and misfit dislocations at {111} Ag-Zn$_x$Mn$_{3-x}$O$_4$ interfaces and therefore to get qualitative information about the bond strength present along the metal-oxide interface.

References

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Chapter 6

Ab-initio HRTEM simulations of \{111\} Ag-MgO interfaces

In this chapter, first principle calculations are incorporated in HRTEM simulations by converting the electron charge density into electron scattering factors. The objective is to examine the influence of charge transfer, charge redistribution and ionicity on the dynamical electron scattering and on HRTEM images. The corrected HRTEM image simulation of the contrast differs from simulated images where neutral atoms are considered. This will be exemplified on \{111\} MgO and \{111\} Ag-MgO interfaces.

6.1 Introduction

Metal ceramic interfaces play an important role in the performance of many advanced materials\(^1\). Examination of the atomistic structure with HRTEM microscopy may lead to insight of the adhesion and the nature of bonding between dissimilar materials\(^1\). To resolve the atomistic structure of interfaces it is essential that experimental HRTEM micrographs are compared with image simulations. Quantitative structure retrieval from HRTEM micrographs has demonstrated the need of incorporating atomic bonding, i.e. a more accurate description of the electron scattering in thin crystals\(^3\). HRTEM image simulations rely on scattering factors of neutral atoms. The standard calculation of dynamic electron diffraction starts with a superposition of the scattering potential of the atoms (atomic form factors) at the position of the atoms. These factors for all elements (neutral and a few types of ions) are presented in literature\(^5\), but only at specific sampling points. To interpolate the atomic form factors for any spatial frequency the data are fitted as a sum of Gaussian functions as introduced by Doyle & Turner\(^5\). The difference between neutral and ionic scattering was pointed out to be significant\(^6\). On the other hand detailed investigations on structure factors obtained experimentally by CBED\(^7\) revealed that the effect of ionicity is rather small. Reliable results including ionicity in TEM simulations by means of first principles calculations was carried
Ab-initio HRTEM simulation of {111} Ag-MgO interfaces

out on sapphire by Gemming et. al. A ‘realistic’ simulation of sapphire showed that there is no significant difference with respect to simulated images of neutral atoms. On the other hand Fresnel-like features are expected to be present at places where the mean inner potential changes rapidly\textsuperscript{9,10}. This could be relevant for metal-oxide interfaces.

In this chapter an attempt will be made to include the effect of charge redistribution and charge transfer at polar Ag-MgO interfaces. The bonding at the interface is analyzed by comparing the ‘realistic’ interface calculations with those involving atomic blocks with free surfaces and with those of neutral atoms. This study addresses the question if the ‘realistic’ image simulations of HRTEM images lead to deviations from the simulation involving neutral atoms. Furthermore, the effect of bonding between individual atoms will be incorporated in HRTEM image simulations. Finally, the HRTEM simulations will be compared qualitatively with experimental HRTEM micrographs of polar \{111\} Ag-MnO and Ag-Mn\textsubscript{3}O\textsubscript{4} interfaces.

### 6.1.1 Experimental background

Ag-MnO interfaces were obtained by internal oxidation of Ag-3 at.% Mn at 900 °C for 1 hr, which results in Mn\textsubscript{3}O\textsubscript{4} (tetragonal distorted spinel, I\textsubscript{4}/amd) precipitates bound by {111} planes with sizes of 5-20 nm\textsuperscript{11}. Figure 6.1 shows an example of a HRTEM image of in the \langle110\rangle viewing direction of a polar \{111\} Ag-Mn\textsubscript{3}O\textsubscript{4} interface. After the introduction of Zn into the Ag matrix the Mn\textsubscript{3}O\textsubscript{4} precipitates transform to MnO precipitates with {111} facets, because of the oxygen affinity of Zn\textsuperscript{12}. However, during annealing in zinc vapor the oxygen partial pressure is reduced to the dissociation pressure pertaining to zinc oxide. After internal oxidation the terminating layer of Mn\textsubscript{3}O\textsubscript{4} at a \{111\} oriented Ag-Mn\textsubscript{3}O\textsubscript{4} interface will be a closed packed oxygen plane, whereas after annealing in zinc vapor the terminating layer of Mn\textsubscript{3}O\textsubscript{4} may becomes a close packed Mn plane\textsuperscript{13,14}. In contrast, MgO precipitates in Ag after internal oxidation showed no clear facets and were nearly spherical with a size of 5 nm\textsuperscript{15} and are therefore not suitable for the present comparison with Ab-initio HRTEM simulations.

The drawback of studying \{111\} Cu-MgO interfaces is the large mismatch between MgO and Cu of 16.6 % compared with the misfit in \{111\} Ag-MnO (8.6 %) and \{111\} Ag-Mn\textsubscript{3}O\textsubscript{4} (10.4 %). Along interfaces with a large mismatch periodic strain fields can be observed in experimental HRTEM micrographs and TEM image simulations of \{111\} Cu-MgO interfaces\textsuperscript{16}. An advantage of the parallel \{111\} Ag-Mn\textsubscript{3}O\textsubscript{4} interface is the one-dimensional misfit along the interface due to the tetragonality of Mn\textsubscript{3}O\textsubscript{4}. This gives an array of misfit
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dislocations, which can be observed in end-on HRTEM images. Usually a two-dimensional network of misfit dislocations is present at semi-coherent metal-oxide interfaces, which leads to a mismatch along various viewing directions on the interface plane. A two-dimensional network projected onto a one-dimensional misfit makes a reliable interpretation rather difficult. Therefore, the {111} Cu-MgO and {111} Cu-MnO interfaces with large misfits of 16.6 % and 22.9 %, respectively are not suitable for comparison with HRTEM image simulations of coherent Ag-MgO interfaces. Polarization of the Ag layer at oxide interfaces, which was observed for adhesion of Ag to the spinel substrate might be responsible for the Fresnel-like feature observed at Ag oxide interfaces.

Calculations for MnO performed with the local density approximation (LDA) with a plane wave basis set is not able to provide the correct electronic structure due to the strongly correlated nature of interactions in this oxide. Because of the rather localized character of the 3d electrons the plane wave method is not well applicable as a basis set, even when the pseudo-potential approach is applied. A more appropriate method is to perform calculations using a linear combination of atomic orbitals (LCAO) with Gaussian basis functions. Therefore electronic structure calculations on Ag-MgO were performed to circumvent this problem. Electron charge transfer and charge redistribution of Ag-MgO and Ag-MnO should produce similar results.

Figure 6.1 Experimental HRTEM micrograph of an {111} Ag-Mn3O4 interface in the <110> viewing direction. The bright line at the outermost monolayer at the metal side of the interface is indicated by a white arrow.
Ab-initio HRTEM simulation of \{111\} Ag-MgO interfaces

6.1.2 HRTEM simulations with screened ionic scattering factors

Incorporation of ionicity in the HRTEM image simulation at metal-oxide interfaces can be performed by replacing the neutral atom scattering factors by the 'free-ion' scattering factors. Using X-ray scattering factors based on relativistic Dirac-Fock calculations\(^{18}\) it is possible to convert the X-ray scattering factors to electron scattering factors using the well-known Mott formula:

\[
\begin{equation}
2
f_{\text{el}} = \frac{m e^2}{8 \pi \hbar^2 \varepsilon_0} \cdot \frac{Z - f_X(s)}{s^2},
\end{equation}
\]

where \(Z\) is the atomic number, \(s (= \sin \Theta / \lambda)\) represents the normalized scattering angle in \(\text{nm}^{-1}\), \(m\) represents the mass of the electrons, \(e\) is the electron charge, \(\hbar\) is Planck’s constant and \(\varepsilon_0\) is the dielectric constant of vacuum. The factor \(1/s^2\) results in singularities when \(s\) approaches to zero (the relation \(f_{\text{el}}(0) = Z\) holds for neutral atoms). These difficulties are due to the Coulomb field associated with the excess charge of an isolated free ion. The Coulomb field is proportional to \(1/r\) and therefore does not decrease fast enough with increasing distance from the ion to achieve convergence for most lattice sums. A solution can be found by adding singularities of opposite sign\(^5\). In practice, this summation leads to numerical errors and the sum does not converge. Because the charge of the neighboring ions leads to an effective shielding of the long range Coulomb potential, a shielding factor of the charge of the nucleus can be introduced:

\[
\Phi = \frac{\Delta Z e}{4 \pi \varepsilon_0} \frac{1}{r} e^{-r/r_0}\]

with a shielding radius \(r_0\). Figure 6.2 shows the ionic scattering factors of \(\text{Ag}^{2+}\) and \(\text{O}^{2-}\) with shielding radii \(r_0 \to 0\) \(\text{nm}\). The shielding radius \(r_0 \to 0\) \(\text{nm}\) corresponds exactly to the separation of the Coulomb charge proposed by Doyle and Turner\(^5\). However, Gemming et al.\(^8\) demonstrated that the ionic scattering factors are sensitive with respect to the choice of the shielding radius. A reasonable choice for the shielding radius \(r_0\) is the nearest neighbor distance. In our case the Ag-Mn\(_2\)O\(_4\) interface has a complicated coordination of atoms at the interface. In the present approach the \(\text{Ag}^{2+}\) and \(\text{O}^{2-}\) ions are assumed to behave as objects that scatter electrons like neutral atoms by calculating the ionic scattering factors with shielding radii approaching 0, as seen in Figure 6.2. A more realistic approach would be to chose the ionicity of \(\text{Ag}^{+}\) and \(\text{O}^-\), but these scattering factors are not available in literature, e.g. Rez et. al\(^{18}\).
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The ionic scattering factors of Ag$^{2+}$ and O$^{2-}$ are fitted with the parameterized function introduced by Doyle and Turner:

$$f_{el}(s) = \sum_{i=1}^{3} a_i \exp(-b_i s^2) + c$$  \hspace{1cm} (6.3)

The parameterized scattering factors of Ag$^{2+}$ and O$^{2-}$ are applied at the \{111\} Ag-Mn$_3$O$_4$ interface by replacing the neutral with ionic scattering factors at the terminating monolayer of oxygen and silver. This can be realized by replacing the $a_i$ and $b_i$ parameters of the neutral atoms by the ionic ones in the image simulation package EMS$^{19}$. The HRTEM image simulation including ionic scattering factors in the terminating Ag and O monolayer is shown in Figure 6.3 with a defocus of -650 Å and thickness of 60 Å. The ionization of oxygen to O$^{2-}$ (Figure 6.3 image c) shows no difference of the contrast compared with simulation with only neutral atoms (Figure 6.3, image a). In contrast, the ionization of the outermost Ag monolayer clearly shows (Figure 6.3, image b and d) an increase of the brightness compared with neutral Ag atoms in the bulk. In fact, the same behavior occurs in experimental HRTEM images of \{111\} Ag-Mn$_3$O$_4$ interfaces, as seen in Figure 6.1. However, the sensitivity of the simulated pattern for changes of the shielding radius makes it hardly possible to attain unambiguity when incorporating ionization in HRTEM image simulation. An ab-initio calculation of the electronic structure might contribute.
Ab-initio HRTEM simulation of {111} Ag-MgO interfaces to a higher reliability of HRTEM simulations. This will be the subject in the following sections.

6.2 Electron charge density calculations

First principles calculations were performed to calculate the charge distribution $\rho(\mathbf{r})$ of {111} Ag-MgO interfaces. This method is based on solving the Schrödinger equation iteratively by constructing the potentials and wave-functions self-consistently. This was carried out using the software packages CASTEP$^{20}$, included as a module in the CERIUS2 (Accelrys) package and DACAPO (developed at CAMP, Lyngby, Denmark$^{21}$). CASTEP and DACAPO allows us to find the total energy, electron charge density and electronic structure of a system consisting of electrons and nuclei within the plane wave Density Functional Theory (DFT), using so-called ultrasoft pseudopotentials$^{22}$. In all our calculations, a cut-off energy of the plane-wave basis set of 340 eV was taken, which suffices to stabilize MgO in the ground state-structure. The local density-approximation (LDA) with exchange-correlation functional ‘PZ’$^{23}$ was applied in CASTEP and the general gradient approximation (GGA) within ‘PW91’$^{24}$ as exchange-correlation functional was applied for calculations in DACAPO. This is in accordance with the generated Vanderbilt ultra-soft pseudo-potentials in both DFT codes. Otherwise, GGA calculations using pseudo-potentials derived within LDA may differ significantly from the

![Figure 6.3 HRTEM simulation of ionized rows of terminating O and Ag layer at the {111} Ag-Mn$_3$O$_4$ interface: (a) only neutral scattering factors (b) Ag$^{2+}$ scattering factors implemented in the outermost Ag monolayer, (c) O$^2$ scattering factors used in the first O monolayer and (d) a combination of b and c. For the simulations a defocus of -650 Å and thickness of 60 Å are used.](image)
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pseudo-potentials generated in GGA mode\textsuperscript{25}. Therefore, the exchange-correlation interaction between valence and core electrons was performed at the same theoretical level.

6.2.1 Bulk MgO and sapphire

The charge density difference $\Delta \rho(\vec{r})$ was calculated by subtracting an atom model using the superposition of the neutral atoms from the relaxed ionic crystal environment obtained by DFT calculations. With CASTEP a full self-consistent calculation in the $\langle 110 \rangle$ projection of MgO was performed to get the relaxed ‘ionic’ charge density. The corresponding neutral atom model was obtained by using only a single atom placed in the center of the supercell. This procedure requires for each different kind of atom (e.g. Ag, Mg, O) an additional CASTEP run. After the calculation is finished for each atomic species neutrality of the crystal is obtained by superposition of the charge density of the neutral single atoms on all their positions in the real crystal. Subsequently the charge density difference was obtained by subtracting the charge from the ‘ionic’ atom charge density map. For comparison, a second procedure was applied using DACAPO. A full self-consistent calculation of $\langle 110 \rangle$ MgO was performed to get the ‘ionic’ charge density map in DACAPO. The calculation was repeated, but was stopped after the first loop to obtain the ‘initial’ charge density of the individual atoms. For this case the pseudo-potentials of the neutral individual atoms, the electronic configuration must be generated in the ground state. Finally, the charge density difference map in DACAPO is the difference between the full self-consistent calculation and initial charge density map. For MgO in the $\langle 110 \rangle$ projection the cell dimensions are $a = 5.94$ Å, $b = 4.2$ Å and $c = 5.94$ Å and a k-point mesh of $4 \times 6 \times 4$ was performed in the calculations (spacing $0.04209 \times 0.03968 \times 0.04209$ 1/Å) for sufficient sampling. The Brillouin zone of sapphire in the $[1120]$ projection ($a = 12.991$ Å, $b = 4.121$, Å, $c = 4.759$ Å) was sampled by $1 \times 3 \times 2$ (spacing $0.07698 \times 0.08089 \times 0.10508$ 1/Å).

6.2.2 Polar $\{111\}$ Ag-MgO interface

The $\{111\}$ Ag-MgO interface is known to be semi-coherent with a mismatch of 3.07 %. The ratio of the MgO and Ag lattice constants is approximately 34/33 and the smallest possible periodic structure with the smallest interface unit cell would contain at least 999 Mg or O atoms and 1156 Ag atoms which is far too many for first principles calculations. But this small mismatch implies that a
Ab-initio HRTEM simulation of \{111\} Ag-MgO interfaces

substantial fraction of regions at the interface is coherent (and that only locally the mismatch is accounted for by misfit dislocations). Therefore, calculations for the \{111\} coherent Ag-MgO interface provide realistic information about the coherent patches of the real interface. The small mismatch of the Ag-MgO interface was compensated by adapting the lattice parameters of both Ag and MgO to 4.20 Å to get the fully coherent interface. The relaxation of the Ag atoms with respect to the MgO was carried out by applying an evacuated region at both sides of the interface. The Brillouin zone of the Ag-MgO was sampled sufficiently by $1 \times 4 \times 8$ (spacing of $0.04059 \times 0.04860 \times 0.04209$ Å$^{-1}$). The model of the polar Ag-MgO interface is depicted in Figure 6.4. At both sides of the interface an evacuated layer of 5.42 Å was applied to minimize the interaction of the faces of adjacent crystals slabs across the evacuated region. The periodic slab geometry of ($4 \mid 3,2$) (Ag$\mid$O,Mg) layers for the oxygen terminated interface and ($4 \mid 2,3$) (Ag$\mid$O,Mg) for the magnesium terminated interface in the ABCABcabc stacking sequence was applied to keep the computational effort manageable. Due to the vacuum the Ag atoms are free to relax perpendicular to the interface (parallel to the interface periodic boundary conditions holds) with a convergence criteria of 0.02 eV/Å using BFGS algorithm (Broyden-Fletcher-Goldfarb-Shanno$^{26-29}$ procedure) for the ionic minimization.

The interface separation of the Ag-O bond after the relaxation of the Ag block across the \{111\} Ag-MgO interface was 1.55 Å for the oxygen terminated interface and 2.20 Å for the magnesium-terminated interface (interface separation). The interplanar spacing between Ag layers in the bulk was about 2.19 Å. The free surface of the MgO side of the interface has an O and Mg

\textbf{Figure 6.4} Schematic illustration of the \{111\} Ag-MgO model with vacuum on both sides of the interface. This model is used to obtain the relaxed Ag coordinates for a model without the presence of a vacuum see Figure 6.5.
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alternating layer (Figure 6.4) to keep MgO stoichiometric. Calculations of the same model, but using a reconstructed surface by tapering the MgO side (for more details see\textsuperscript{30}) yield the same results for the relaxed coordinates of the Ag atoms. Due to the polarity of MgO with a dipole perpendicular to the interface, tapering might affect the results and therefore has to be checked. During the calculation the dimension of the supercell \((23.55 \text{ Å} \times 5.144 \text{ Å} \times 2.97 \text{ Å})\) and \((24.97 \text{ Å} \times 5.144 \text{ Å} \times 2.97 \text{ Å})\) for the oxygen and Mg terminated interface was fixed. A comparison of calculated polar \{222\} MgO-Cu interfaces with slab geometry \((3,3|3)\) (MgO|Cu) layers in the ABCabc stacking sequence and \((5,5|5)\) (MgO|Cu) yielded similar results\textsuperscript{31}. Subsequently, the relaxed Ag coordinates with respect to MgO were used as an input for a new polar Ag-MgO model where the coordinates of Mg and O are unchanged, see Figure 6.5. Figure 6.5 shows an periodic slab geometry of \((7|4,3)\) (Ag|O,Mg) layers in the CABCABCabcabca stacking sequence without the presence of a vacuum.

\[
\begin{align*}
\text{Figure 6.5} & \quad \text{Schematic depiction of the \{111\} Ag-MgO model interface.}
\end{align*}
\]

On the charge redistribution and charge transfer during electronic calculation of the Ag-MgO interface (Figure 6.5). In principle, the calculation holds for a multilayer. To extract the charge transfer across the interface and the electron redistribution due to metal-oxide bonding the charge density difference must be calculated. This was performed with CASTEP in the following way: First, the charge density of the Ag-MgO interface is calculated. Afterwards the calculations for the individual slabs of MgO and Ag are carried out by just removing for each case the block of Ag atoms or the one with the Mg and O atoms in the supercell, respectively. In all calculations, the number of k-points and cutoff energy were kept constant. The calculated charge density of the Ag-MgO interface was subtracted from the charge density of the Ag and MgO slab to obtain the charge density difference \(\Delta \rho(\vec{r})\), which represents the charge redistribution due to the bonding across the Ag-MgO interface. The charge density \(\Delta \rho(\vec{r})\) including the bonding environment in the bulk was calculated using DACAPO by subtracting the fully self-consistent calculation from the
density given from the initial charge of the individual atoms in the ground state. This \( \Delta \rho(\vec{r}) \) includes beside the electron charge transfer and electron redistribution at the interface also the ionicity and bonding in the bulk at both sides of the interface. This procedure is of course not rigorously correct, but is the best approximation that we can use, in particular, when comparing HRTEM image simulations, where the errors due to the approximation are likely to be unimportant.

### 6.3 Ab-initio HRTEM image simulation

The charge density calculated with the method described in the previous section gives only relative values with an unknown offset due to the use of pseudo-potentials. Application of the electron charge density difference as a correction term in TEM simulations circumvents this problem. The calculation of the projected potential used for multislice HRTEM image simulations is connected with the charge density via the two-fold integration of Poisson’s equation in reciprocal space. The implementation of the charge-density difference \( \Delta \rho(\vec{r}) \) is carried out by introducing a correction term for the projected potential. This relation is described in the following equation:

\[
V(\vec{k}) = \frac{2me}{4\pi^2 \varepsilon_0 \hbar^2} \left\{ \sum_{n,j} \left[ \frac{\rho_{n,j} e^{2\pi ik \cdot \vec{r}}}{k^2} d\vec{r} \right] - \sum_{nx,ny,nz} \left[ \frac{\Delta \rho(nx,ny,nz)e^{2\pi ik \cdot \vec{r}}}{k^2} d\vec{r} \right] \right\}, \tag{6.4}
\]

which demonstrates the splitting of the charge density into two parts for the calculation of the projected potential \( V(\vec{k}) \). The charge density \( \rho_{n,j} \) denotes the charge of nucleus \( j \) including the electron shell for the neutral atom at position \( n \) represented by the electron scattering factors as described by Doyle and Turner\(^5\) and the second term represents the correction term \( \Delta \rho(\vec{r}) \). The charge density difference \( \Delta \rho(\vec{r}) \) is integrated over the CASTEP or DACAPO grid \( nx, ny, nz \) of the supercell, see equation (6.4). The charge density difference \( \Delta \rho(\vec{r}) \) was implemented as a correction term in the source code of the EMS software package within the program sc4\(^19\). Note that in all HRTEM image simulations the Debye-Waller factor and absorption coefficient were set equal to zero.

The use of the reciprocal grid renders the representation of the data independently of the sampling density, because the Fourier transformations automatically adapt the CASTEP or DACAPO grid to the EMS grid. This method avoids the need of interpolation of the charge density on the EMS grid\(^8\).
but the accuracy is limited by the spatial frequency up to which the charge density calculations were carried out. Nevertheless, the current approach accounts for non-spherical components and charge redistribution of the charge density. Atomic form factors, which represent rotational symmetry of the charge density of atoms are thus not applied in the present approach.

6.4 Comparison between ab-initio and standard HRTEM simulations

With charge density difference calculations, it is possible to check the image contrast provided by a standard TEM simulation program, e.g. EMS with Doyle & Turner neutral electron scattering factors, with the more precise calculation of the electron scattering including the correction term based on ab-initio calculations, as explained in section 6.2 and 6.3. In all cases, the EMS program sc4 was used to simulate the HRTEM images. The input parameters for the simulated images correspond to the ones of JEOL 4000EX/II in Groningen, operating at 400 kV with an information limit of 1.4 Å (spherical aberration coefficient, 0.97 ± 0.02 mm; defocus spread, 7.8 ±1.4 nm; beam semi convergence angle, 0.8 mrad).

6.4.1 Bulk MgO and sapphire

Figure 6.6 shows a HRTEM image simulation of MgO in the <110> viewing direction (thickness 71 Å, defocus -750 Å). Image (a) in Figure 6.6 shows a conventional image simulation of MgO, image (b) shows the corresponding simulation corrected with a charge density map obtained from CASTEP and the image (c) is corrected with the charge density map performed with DACAPO. In both corrected HRTEM images (CASTEP and DACAPO correction term) the ionic environment of MgO is incorporated in the projected potentials. In Figure 6.6 it is clearly visible that the contrast has the tendency to invert the brightness contrast at a defocus value of -750 Å. The inversion of the contrast between conventional image simulation and image simulation corrected with charge density maps can be clearly seen in the line profiles, as shown in Figure 6.7 of the simulated HRTEM images of Figure 6.6. The convergent beam electron diffraction technique (CBED) and DFT calculations revealed that the charge density could be described as a superposition of spherical Mg\textsuperscript{2+} and O\textsuperscript{2-} ions\textsuperscript{32}. This high degree of ionicity might be responsible for the shift in contrast including the ionicity in HRTEM image simulation (see Figure 6.6). The ab-initio charge density maps for sapphire do not differ significantly from simulated images of neutral atoms\textsuperscript{8}. This is confirmed by the present work, as
Ab-initio HRTEM simulation of {111} Ag-MgO interfaces

shown in Figure 6.8 in the same sequence as Figure 6.6. Apparently, for MgO the effect of the environment is important, whereas it is not so for sapphire.

**Figure 6.6** HRTEM image simulation of MgO in the <110> viewing direction for the imaging parameters of a JEOL 4000 EX/II. (a) conventional simulation, (b) corrected with charge density difference map using CASTEP and (c) corrected with charge density difference map calculated with DACAPO. For all simulations a thickness of 71 Å and a defocus value of -750 Å were used.

**Figure 6.7** Line profiles of simulated images corresponding to Figure 6.6. A white frame shows over which area the line profile is taken (integration width 30 pixel). The profile reveals the inversion of the contrast between conventional image simulation (EMS) and corrected simulations (CASTEP and DACAPO).
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6.4.2 {111} Ag-MgO interface (O-terminated)

In the following, three different cases for the correction term of {111} Ag-MgO interfaces will be evaluated with HRTEM simulations:

1. Standard TEM simulation using Doyle & Turner scattering factor
2. Standard simulation + correction term including the charge transfer and charge redistribution only at the interface (CASTEP).
3. Standard simulation + correction term including case (b) and all the individual atomic bonding, e.g. the ionicity in MgO (DACAPO).

Figure 6.8 HRTEM image simulation of sapphire in the [20] viewing direction for the imaging parameters of a JEOL 1250 ARM (1250 kV). (a) conventional simulation, (b) corrected with charge density difference calculated with CASTEP and (c) corrected with charge density difference map calculated with DACAPO. For all simulations a thickness of 76 Å and a defocus value of -500 Å were used. See also under 8 for further details.

Figure 6.9 Charge density difference 
\[ \Delta \rho(\vec{r}) = \rho_{\text{Ag-MgO}}(\vec{r}) - [\rho_{\text{Ag slab}}(\vec{r}) + \rho_{\text{MgO slab}}(\vec{r})] \] of Ag-MgO interface (CASTEP). The cross section of the contour plot goes through [0.5,0,0] to get a cross section of a Ag-O bond at the interface. The range ± 0.1 e/Å³ is chosen for a better visualization. The actual \( \Delta \rho \) values range from -1.026 to 0.453 e/Å³.
Ab-initio HRTEM simulation of \{111\} Ag-MgO interfaces

Both contour plots of the charge density difference (through [0,5,0,0] to get a cross section of a Ag-O bond of case b and c as seen in Figure 6.9 and Figure 6.10, respectively) reveal similar behavior of the charge redistribution at the interface, but as expected not for the bulk phases.

From the contour plots it is hardly possible to conclude the character of bonding, e.g. if net charge transfer occurs. Calculation of the layer-projected densities of states was performed with DACAPO to obtain the interface electronic spectra of the \{111\} Ag-MgO interface. For the layer projected DOS an ionic radius of 1 Å was chosen. Figure 6.11 shows the density of states of the first and second MgO layer adjacent to the interface and terminating Ag layer at the interface. Note that one MgO layer contains one oxygen monolayer and the adjacent Mg monolayer. The first MgO layer shows a peak just below the Fermi level, within the bulk MgO band gap (MgO band gap gray region, see Figure 6.11). It seems that the Ag-O bond is a hybrid between the occupied Ag 4d and O 2p states\(^{17}\) and a shift of the O 2s band to a slightly higher energy at the interface (compare 1. MgO layer with the 2. MgO layer) is observed, which represents an electrostatic potential shift of roughly 0.3 eV. This is much smaller than the MgO band gap of 7.8 eV\(^{33}\). This occurrence of states in the band gap whose intensity decays exponentially with increasing distance from the interface\(^{33}\) is known as metal induced gap states (MIGS). Metal-induced gap states (MIGS) at the MgO side of the interface reduce the electron charge redistribution and charge transfer, due to the less ionic character of the interface. An additional effect of the MIGS is the reduction of the electrostatic

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.10.png}
\caption{Charge density difference $\Delta \rho(\vec{r}) = \rho_{\text{Ag-MgO}}(\vec{r}) - [\rho_{\text{Agneutral}}(\vec{r}) + \rho_{\text{MgOneutral}}(\vec{r})]$ of Ag-MgO interface (DACAPO). The cross section of the contour plot goes through [0.5,0,0] to get a cross section of a Ag-O bond at the interface. The range ± 0.1 e/Å\(^3\) is chosen for a better visualization. The actual $\Delta \rho$ values range from -0.243 to 0.393 e/Å\(^3\).}
\end{figure}
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potential shift as well. In contrast, considerable electro negativity would indicate an ionic type of interface, but a calculated layer-by-layer charge transfer determined with Mulliken charge population analysis does not exceed 0.18 e/atom, which is in agreement for polar Cu-MgO interface. The metal induced band gap states at the oxide side should be a general feature of any metal-oxide interfaces, as mentioned by Finnis.

A set of TEM simulated images of \{111\} Ag-MgO interface is seen in Figure 6.12 and Figure 6.13. The arrows in Figure 6.12 and Figure 6.13 indicate the interface between terminating oxide and silver layer. Figure 6.12 shows TEM simulations for three different defocus values of -480, -600 and -720 Å for cases (a), (b) and (c) with a constant thickness of 74 Å. The terminating oxide monolayer changes the contrast between the three different cases; especially a difference exists between the contrast of the standard TEM simulation (case a) and the corrected TEM simulation (see case c) for a given defocus value. Including the bonding of individual atoms in the correction term (case c) the brightness is slightly increased at the terminating oxide monolayer compared with the brightness of

Figure 6.11 Calculated layer-projected density of states for oxygen terminated \{111\} Ag-MgO interface. The zero of energy indicates the Fermi level. The projected DOS of the terminating oxygen layer exhibit states in the MgO band gap close to the Fermi level (metal induced gap states MIGS) whose intensity decays exponentially with increasing distance from the interface. The shift of the 2s band to a slightly higher energy at the interface reflects the electrostatic potential shift of roughly 0.3 eV. This will be expected for an interface dipole.
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the oxygen layer in the bulk observed for different thickness values, see Figure 6.13 right column. For all defocus-thickness variations a contrast change in the corrected TEM simulations in the outmost Ag layer at the Ag-MgO interface can be hardly detected. The electrons on the metal side at the interface are delocalized and may prevent a local contrast change at the metal side of the interface.

![Figure 6.12 HRTEM image simulation of Ag-MgO in the <110> viewing direction using defocus values -480, -600 and -720 Å and a thickness of 74 Å.](image)

![Figure 6.13 HRTEM image simulation of Ag-MgO in the <110> viewing direction using defocus value of -750 Å and a thickness of 45, 59, 74 and 84 Å.](image)

Line profiles of simulated images across {111} Ag-MgO interface (O terminated) using defocus value of -750 Å and a thickness of 74 Å are shown in Fig.6.14. These line profiles correspond to the simulated images in the third row of Figure 6.13. The line profile of the corrected image simulation of case c shows that the contrast minima and maxima are inverted compared with simulation of neutral MgO (case a and b), whereas in the bulk of Ag similar contrast behavior is observed in all cases (see Figure 6.14).
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6.4.3 {111} Ag-MgO interface (Mg-terminated)

The same procedure as performed on the oxide terminated {111} Ag-MgO interface (section 6.2.2 and 6.4.2) is applied to the Mg terminated {111} Ag-MgO interface. A contour plot of the charge density difference through [0.5,0,0] to get a cross section of an Ag-Mg bond of case b (including only the charge redistribution at the interface) is displayed in Figure 6.15. Figure 6.15 indicates that the charge redistribution in the terminated Ag layer is less pronounced by the Mg-terminated layer than in the case of an oxygen-terminated interface (Figure 6.9). A set of TEM simulated images is shown in Figure 6.16 of an Mg terminated {111} Ag-MgO interface. The arrows in Figure 6.16 indicate the interface between terminating magnesium and silver layer.

Figure 6.14 Line profiles of simulated images across {111} Ag-MgO interface (O terminated) using defocus value of -750 Å and a thickness of 74 Å. These line profiles correspond to the simulated images in the third through four of Figure 6.13.
Ab-initio HRTEM simulation of {111} Ag-MgO interfaces

The line profile of the corrected image simulation of case c shows that the contrast minima and maxima are inverted compared with simulation excluding the bonding environment of the bulk MgO (case a and b), whereas in the bulk of Ag similar contrast behavior is observed in all cases, as seen in Figure 6.17. At the terminating Ag and Mg layers, the contrast does not change significantly (compare Figure 6.16 and 6.17). This is in agreement with the small charge redistribution present at the Ag-terminated {111} Ag-MgO interface compared with the corresponding O-terminated interface (compare Figure 6.9 versus 6.15).

Figure 6.15 Charge density difference
\[ \Delta \rho(\vec{r}) = \rho_{\text{Ag-MgO}}(\vec{r}) - [\rho_{\text{Ag slab}}(\vec{r}) + \rho_{\text{MgO slab}}(\vec{r})] \] of Ag-MgO interface. The cross section of the contour plot goes through [0.5,0,0] to get a cross section of an Ag-Mg bond at the interface. The range ± 0.1 e/Å³ is chosen for a better visualization. The actual \( \Delta \rho \) values range from -0.1473 to 0.0425 e/Å³.

Figure 6.16 HRTEM image simulation of a Mg terminated Ag-MgO interface in the <110> viewing direction using defocus values -120 Å and -750 Å with a thickness of 74 Å. The panels (a), (b) and (c) correspond to the defined correction terms, as described in 6.4.2.

The line profile of the corrected image simulation of case c shows that the contrast minima and maxima are inverted compared with simulation excluding the bonding environment of the bulk MgO (case a and b), whereas in the bulk of Ag similar contrast behavior is observed in all cases, as seen in Figure 6.17. At the terminating Ag and Mg layers, the contrast does not change significantly (compare Figure 6.16 and 6.17). This is in agreement with the small charge redistribution present at the Ag-terminated {111} Ag-MgO interface compared with the corresponding O-terminated interface (compare Figure 6.9 versus 6.15).
6.5 Comparison with experiment

An experimental HRTEM image of a \{111\} Ag-MnO interface recorded with a JEOL 4000EX/II is depicted in Figure 6.18. In Figure 6.18 a bright line is present at the outermost Ag layer at \{111\} Ag-MnO interface. The interface between Ag and MnO is indicated by a white line. The same occurs, but less pronounced on the oxide side at the interface. The brightness is slightly higher compared with the brightness in the bulk (see Figure 6.18). For a better visualization of the contrast across the \{111\} Ag-MnO interface a line-profile of the HRTEM image (Figure 6.19) was performed, as seen in Figure 6.19. Figure 6.18 and Figure 6.19 show clearly the higher brightness at the terminating monolayers compared with the brightness in the bulk of Ag and MnO.
The comparison between the experimental micrograph (Figure 6.18) with the HRTEM image simulation for case a and c (Figure 6.13) and the corresponding line profiles of Figure 6.14 third through four panels, as seen in Figure 6.13 show a tendency of increasing the brightness in the termination oxygen layer compared with the brightness in the bulk for high defocus values. This seems also to be the case in experimental HRTEM observations of the {111} Ag-MnO interface, seen in Figure 6.1. The outermost Ag layer at {111} Ag-MnO interface (Figure 6.1) is indicated by a white arrow. The study of corrected HRTEM simulated images indicates that the bright line observed in the experimental HRTEM micrographs might belong to the oxide side of the interface, as seen in Figure 6.1. This would clearly provide experimental evidence that the bright line present on the terminating oxygen layer in HRTEM images is reproduced by the ab-initio calculations and it directly reveals the presence of bonding at the interface. On the other hand the bright line observed at {111} Ag-MnO interfaces (Figure 6.18) on the outermost Ag monolayer can be related to a Mn-terminated interface. This is the case after annealing of Ag-MnO interfaces in vacuo. In contrast, the higher brightness in the terminating Ag monolayer (see Figure 6.16 at defocus –120 Å) at Mg-terminated interfaces mainly originates from the position of the Ag ions at MgO, and is not a full evidence of bonding across the interface.
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From an analysis of interfacial films performed with Fresnel-fringe technique\textsuperscript{9,10} artifacts due to potential wells and surface grooving at interfaces can be estimated. In particular TEM sample preparation can damage the interfaces and would give rise to surface grooves. Usually thicker specimens will reduce the effect of surface grooves, but for HRTEM image observations of edge-on heterophase interfaces the foil thickness is limited (max 15 nm). For such a thickness, a surface groove can significantly change the projected potential at the interface. On the other hand, these artifacts due to surface groove at interfaces would extend over several monolayers. In contrast, the present case (Figure 6.18 and Figure 6.1) the observed bright line at the polar Ag-MnO and Ag-Mn\textsubscript{3}O\textsubscript{4} interfaces is confined to just one monolayer.

6.6 Discussion

The metal induced gap states (MIGS) diminish the ionic character of metal oxide bonding, associated with less charge transfer and electrostatic potential shift at the interface. Therefore, the observed change in contrast between conventional and ab-initio HRTEM image simulations concludes that not only the ionicity in oxides is important to consider. Also the directional components of the bonding environment alters the contrast (means anisotropic scattering

![Figure 6.19 Line profile of the experimental HRTEM micrograph of an [111] Ag-MnO interface in the <110> viewing direction from Figure 6.18. The increase of the brightness in the terminating monolayers of Ag and MnO at the interface is clearly visible.](image)
Ab-initio HRTEM simulation of {111} Ag-MgO interfaces

around atomic sites) in HRTEM image simulations. At the present state substantial effort is necessary to calculate ab-initio charge density difference maps, but this method can help to increase the reliability in quantitative image matching. In particular, the difference of the pattern between conventional and ab-initio HRTEM image simulations of oxides can lead to a misinterpretation of the experimental image. For instance, the estimated thickness obtained with image matching of the experimental image revealed that the calculated image is thinner using screened potentials (incorporating the ionicity in HRTEM image simulations) than using the neutral potential\textsuperscript{34}. The initial start of any HRTEM image simulation is the determination of atomic scattering factors to calculate the projected potential. It should be pointed out that the scattering factors from Doyle and Turner\textsuperscript{5}, parameterized as the sum of four Gaussians, are only valid up to 2.0 nm\textsuperscript{-1}. This lead to an underestimate of the scattering greater than 2.0 nm\textsuperscript{-1}, but for a 400kV high-resolution microscope with a resolution of 0.16 nm resolves scattering angles to about 10 mrad (2.0 nm\textsuperscript{-1} is equivalent with 33 mrad at 400 kV). On the other hand the calculated atomic scattering factors from Rez et al.\textsuperscript{18} are quite similar to those of Doyle and Turner\textsuperscript{5}. Thus, the atomic scattering factors are not the source of error.

6.7 Conclusions

The ionicity of oxides and the charge redistribution at interfaces play a significant role when incorporated in HRTEM image simulations. Ab-initio calculations were used as a correction term to take the ionic character of bulk MgO into account. It has been shown that for a defocus of -750 Å a reversal of the contrast of bulk MgO in the <110> projection occurs. On the other hand, it seems that the ionicity is not important for sapphire in HRTEM image simulations\textsuperscript{8}. This was verified in the present work. This is directly opposed to the findings of Stobbs and Stobbs\textsuperscript{6} where the ionicity in sapphire seems to be important for HRTEM image simulations. The chosen high defocus value of -750 Å in most of the HRTEM image simulations (Figure 6.6, 6.13 and 6.16) reflect the maximum difference between the conventional HRTEM image simulation (Doyle and Turner scattering factors\textsuperscript{5}) and corrected HRTEM image simulation using ab-initio calculations. Performing ab-initio HRTEM image simulations on polar {111} Ag-MgO interfaces reveal differences in contrast compared with conventional image simulations:
• Both ab-initio charge density difference maps calculated with CASTEP or DACAPO for oxygen-terminated \{111\} Ag-MgO show a slightly brighter row of atoms in the outermost Ag layer at the interface, but this effect is weak, as seen in Figure 6.13 and 6.14.

• In contrast to the metal side of the interface (O-terminated Ag-MgO), including the ionicity of MgO and charge redistribution (DACAPO) at the interface shows that the first oxygen layer at the interface is much brighter than for the neutral atoms. This is also slightly the case when the ionicity or bonding environment of the bulk is not included, i.e. when only the charge transfer and redistribution at the interface (e.g. using CASTEP) is taken into account in the HRTEM simulation, as shown in Figure 6.13 and 6.14.

• The Mg-terminated \{111\} Ag-MgO interface shows hardly any differences between conventional and corrected HRTEM image simulations at the interface, as seen in Figure 6.16. At a defocus value of -120 Å bright dots are present on the Ag atoms in the outermost layer at the interface and at a defocus value of -750 Å the bright dots are present in the terminating Mg layer of the oxide for all three cases (Figure 6.16 and 6.17). The contrast reversal in the MgO at a defocus value of -750 Å remains when the ionicity of the oxide is included in the correction term as demonstrated for bulk MgO and the O-terminated interface (Figure 6.7 and 6.14).

• At oxygen-terminated \{111\} Ag-MgO the bonding between metal and oxide (interface separation 1.5 Å) is responsible for the difference in contrast at the interface between conventional and ab-initio HRTEM image simulations. In contrast, the magnesium-terminated \{111\} Ag-MgO interface (interface separation 2.2 Å) shows no contrast change between conventional and ab-initio HRTEM image simulations. Therefore, the enhanced contrast compared with the contrast in the bulk structure at the interface likely originates from the position of the Ag atoms at the interface.
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Chapter 7

Summary and Outlook

This chapter presents a summary and an outlook of future research on metal-oxide interfaces. Chemical analysis in sub-nm range is necessary to interpret HRTEM observations and metal-oxide bonding. With in-situ heating experiments, it is possible to understand the behavior at metal-oxide interfaces at elevated temperatures. Sub-nm spatial and high-energy resolution PEELS (parallel electron energy loss spectrometry) measurements will provide more experimental information on the electronic structure of metal-oxide interfaces. Combining these PEELS measurements and quantitative HRTEM combined with first-principles DFT calculations still offer room for improvements attaining more insights into bonding between metals and oxides.

7.1 Summary

In order to understand the bonding between metals and oxides, interfaces were studied with high-resolution transmission electron microscopy, analytical TEM, in-situ experiments down to an atomic scale and first-principles Density Functional Theory (DFT) calculations. It was possible to combine HRTEM observations with the analysis of the chemical composition within one monolayer at the metal-oxide interfaces. With in-situ experiments, a detailed visualization of order-disorder transitions on an atomic scale at metal-oxide interfaces could be realized. A computer code was developed to relate HRTEM observations to charge transfer (ionicity) and charge redistribution along metal oxide interfaces. The interfaces of interest were fabricated by internal oxidation to obtain many small oxide precipitates inside a metal matrix. This method produces many clean interfaces for investigations in each sample and such internally oxidized samples are easy to prepare for transmission electron microscopy.

In chapter 3 the extent of segregation of In, Ga and competitive segregation behavior of Ga and In at parallel \{111\} Cu-MnO interfaces were determined using 3 different sets of samples. The analytical TEM results were combined with high-resolution TEM (HRTEM) observations to study the behavior of gallium segregation. The new approach allowed us measuring enrichments of a fraction of monolayer coverage at a heterophase interface and to determine at
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which side of the heterophase interface segregation occurs. The new approach is based on assumed concentration profiles convoluted with a Gaussian function that mimics the electron probe. Then, the segregating solute is plotted as a function of one of the solvents on one side of the interface. The experimental data were collected from many EDS measurements with a nano probe on an edge-on {111} Cu-MnO interface with a few reference measurements on both sides of the interface. These experimental data were fitted with an assumed convoluted concentration profiles to determine the segregation at interfaces. Our approach leads to the conclusion that indium effectively blocks gallium segregation towards the oxide side of the interface. On the other hand, the presence of gallium does not influence the segregation of indium to the metal side of the interface. The analytical TEM observation of the gallium segregation at the oxide side of the interface was confirmed with HRTEM observations.

In chapter 4, the combination of in-situ heating experiments with HRTEM studies on Cu3Pd-MnO interfaces was performed to reveal the state of order of Cu3Pd, the structure of anti-phase boundaries (APBs) and details of the long period superstructure (LPS due to ordering of APBs) in Cu3Pd and at Cu3Pd-MnO interfaces. It turned out that the method of TEM sample preparation plays an important role to visualize the APBs and the L12 ordered structure. The use of ion milling for sample preparation destroyed the APB structure and damaged the L12 ordering. The solution was to perform electrochemical polishing prior to the final thinning process of the specimen. A thin oxide layer of the internally oxidized sample remained after electrochemical polishing and had to be removed with ion milling within the shortest time lapse possible so as to prevent the damage of the APB structure and the ordering. Nevertheless, in-situ heating was needed to restore the order. Dark field imaging at lower magnification showed that oxygen dissolution in the Cu3Pd matrix after internal oxidation had a sharpening effect on the APB structure and the presence of Mn and/or O in the Cu3Pd matrix of the not oxidized sample probably increased the order-disorder transition temperature. The analysis of HRTEM images of Cu3Pd-MnO interfaces in the <110> and <112> projection showed that the L12 ordering at polar {111} Cu3Pd-MnO interfaces gradually disappeared when approaching the interface. In contrast, for the non-polar {002} Cu3Pd-MnO viewed along <100> no influence on the L12 order and the APB structure, even close to the interface, could be detected.

In chapter 5, the zinc concentration was altered within Ag-Zn3Mn3-xO4 over a wide range of x and interfaces between these oxide precipitates and Ag were
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studied. With the increase of the zinc content $x$ in Zn$_{x}$Mn$_{3-x}$O$_{4}$, the oxide transformed from tetragonally distorted to cubic spinel. This variation of $x$ could be obtained by internal oxidation of Ag-2at.% Mn-4at.% Zn in air and annealing \textit{in vacuo} at different temperatures. HRTEM was performed to study the misfit and misorientation between Ag and Zn$_{x}$Mn$_{3-x}$O$_{4}$. The different degree of misfit from 10.4% at Ag-Mn$_{3}$O$_{4}$ to 2.4% at Ag-Zn$_{1.5}$Mn$_{1.5}$O$_{4}$ could be clearly visualized using Bragg filtering. The latter is a simple method to visualize the misfit and misfit dislocations at \{111\} Ag-Zn$_{x}$Mn$_{3-x}$O$_{4}$ interfaces and therefore to determine qualitatively the adhesive interaction strength present across the metal-oxide interface. The line profile obtained for the Ag-Mn$_{3}$O$_{4}$ interface showed that the magnitude of the intensity modulation reveals the possibility to distinguish between the Burgers vectors of type $1/3$ $<$112$>$ and $1/6$ $<$112$>$ present at the interface.

The objective of chapter 6 was a combination of ab-initio DFT calculations with HRTEM image simulation to examine the influence of charge transfer, charge redistribution and ionicity on the dynamical electron scattering and on HRTEM images. The charge density calculations were incorporated in HRTEM image simulation software. The idea was to transfer the calculated charge density maps into the difference atom-projected potentials and to use them as a correction term for the neutral atom-projected potentials. This correction term for the contrast differed from simulated images where only neutral atoms (conventional HRTEM image simulation) were considered. This was demonstrated on bulk MgO and Ag-MgO in the $<$110$>$ projection. The Mg-terminated {111} Ag-MgO interface showed hardly any differences between conventional and corrected HRTEM image simulations at the interface. In contrast, the O-terminated Ag-MgO interface showed that the bonding between Ag and MgO was responsible for the difference in contrast at the interface between conventional and ab-initio HRTEM image simulations. The incorporation of the ionicity in MgO showed a contrast reversal between corrected ab-initio and conventional (neutral atom model) HRTEM image simulation for relative high defocus values. The present work shows for the first time the importance of combining DFT calculations directly with HRTEM image simulations.
Summary and Outlook

7.2 Outlook

A phenomenological explanation was found why the In segregation occurs at the outermost monolayer on the metal side of \{111\} Cu-MnO\(^1\). The relaxation of an atomistic model of the oxygen-terminated \{111\} Cu-MnO interface (the Cu atoms are free to move, the oxide is assumed to be rigid) is performed with interatomic potentials\(^2,3\). This simulation indicates that a trigonal network of misfit dislocations with line direction \(<110>\) and Burgers vector \(1/6 <112>\) is present\(^4\). In general, there are two types of triangle. In one type the layers are correctly fcc stacked, whereas for the other a stacking fault exists at the interface. The In atoms have a larger atomic radius (167 pm) than Cu atoms (128 pm) and thus the In atoms tend to move to areas where they have more space compared with the space in the Cu matrix. This is fulfilled at the center of the triangles at the Cu-MnO interface where the Cu atoms are stretched to match the planes of the MnO compared with the planes in the bulk. The more phenomenological description of In segregation at Cu-MnO can be verified with ab-initio DFT calculations or semi-empirical calculations\(^6\) on (in)coherent Cu-MnO interfaces to calculate the segregation energy. Wang at. al\(^5\) calculated the Influence of C on adhesion of the coherent Al\(_2\)O\(_3\)-Al interface and it was found that the presence of C at the interface increases the work of separation by a factor of 3 compared with corresponding clean interface. This calculation can also be performed on Cu-MnO interfaces incorporating the misfit and to determine the adhesion with the presence of In at the interface. In general, it would be possible to distinguish between the segregation energy of the correctly fcc stacked triangles and the triangles with stacking faults. Progress on calculations on semi-coherent interfaces\(^6\) and adhesion on the surface with defects\(^7\) combined with the improvements of computer codes can realize this calculation on segregation at heterophase interfaces in more realistic manner. The phenomenon of segregation at heterophase interface could be used to make interfaces more coherent at originally incoherent interfaces.

The disappearance of the L1\(_2\) ordering close to polar \{111\} Cu\(_3\)Pd-MnO interfaces probably comes from the change of the interatomic potentials of the Cu-Pd bond at the polar Cu\(_3\)Pd-MnO interface. This may have a large effect on the order disorder transition temperature \(T_c\). Thus, the disordered region at the interface reaches the order disorder transition temperature, whereas the whole system is below \(T_c\). Therefore, small changes in the effective interatomic potentials \(v_{ij}\) \((i=\text{Cu}, j=\text{Pd})\) of Cu-Pd, Cu-Cu or Pd-Pd may result in a substantial change of the \(w_{ij}=v_{ij}(v_{ii}+v_{jj})/2\) that in return directly changes \(T_c\). The precise relation between electron redistribution and charge transfer at polar metal-
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oxide interfaces and the interatomic potentials must be examined in more detail and the possible inaccuracy of DFT calculations must be carefully considered. The sensitivity of the change of interatomic potentials on the order disorder transition temperature in Cu3Pd at the Cu3Pd-MnO interface must be quantified to draw stronger conclusions.

The evaluation of polar {111} Zn$_x$Mn$_{3-x}$O$_4$-Ag interfaces in chapter 5 was performed more qualitatively, because it was not possible to solve the right crystallography in Zn$_x$Mn$_{3-x}$O$_4$. The idea was to perform iterative forward calculations, meaning iterative matching of various model images with the experimental Zn$_x$Mn$_{3-x}$O$_4$-Ag interface in the <110> projection. A quantitative HRTEM evaluation of the Zn$_x$Mn$_{3-x}$O$_4$-Ag interface in the <110> projection was not reproducible with this method. For experimental HRTEM observations of the spinel phase, the symmetry is lowered compared with calculations of HRTEM images. One of the reasons can be the kinematically forbidden {002} reflections in the <110> projection that have an influence on the formation of the experimental HRTEM image. This should be checked with the examination of the influence of charge transfer and redistribution on dynamically forbidden reflections forming in Zn$_x$Mn$_{3-x}$O$_4$.

Another important point is the sample preparation of spinel oxides for TEM. In general, ion milling (chapter 2) as a TEM sample preparation technique is performed. The ion milling can be aggressive in such a way that the stoichiometry in the spinel oxide is changed. For instance, the crystallographic phase of MgAl$_2$O$_4$ where Fd$ar{3}$m regarded as the accepted space group according to literature$^{10}$ is energetically close to the non-centrosymmetrical space group F43m$^{11}$. The deviation from the conventionally accepted centrosymmetrical structure arises from oxygen displacements. This presumption can be proved by DFT calculations of the total energy between stoichiometric spinel oxides and the presence of impurities and lattice vacancies for the space group Fd$ar{3}$m and F43m. The appreciation of the lowering of the symmetry of experimental HRTEM images compared with HRTEM image simulation is of importance in order to perform quantitative HRTEM on {111} Zn$_x$Mn$_{3-x}$O$_4$-Ag interfaces.

Another difficulty is the observed bright line at the Mn$_3$O$_4$-Ag interface in the <110> projection (see section 6.1.1) for quantitative analysis. A straightforward method is the quantitative measurement of the mean inner potential at heterophase interfaces by electron holography$^{12}$. This result can be used as an input for HRTEM image simulation to reproduce behaviors at metal-oxide interfaces (e.g. reproduce the observed bright line at Zn$_x$Mn$_{3-x}$O$_4$-Ag interfaces).
Summary and Outlook

In general, the combination of quantitative HRTEM, high spatial and energy resolution PEELS, high spatial resolution electron holography and (ab-initio) first principles calculations is very powerful to improve our detailed understanding of interface behaviors at atomic scale. In-situ deformation experiments like deformations or indentations provide a possibility to reveal the mechanical stability of metal-oxide interfaces. The effect between covalent (carbides) and less ionic (nitrides) type of precipitates with the metal matrix can be an interesting subject for the future.

References

Samenvatting

Grensvlakken tussen een metaal en een oxide spelen een belangrijke rol in het vakgebied van de materiaalkunde. Elektronische componenten (IC of chips), gassensoren, verbrandingsmotoren zijn eclatante voorbeelden daarvan. Een cruciaal aspect van de hechting tussen metalen en oxiden wordt evenwel slecht begrepen. Dit proefschrift concentreert zich op het ontrafelen van de atomaire structuur langs metaal/oxide grensvlakken gedaan met als doel een beter inzicht te krijgen in de eigenschappen.

Metaal/oxide grensvlakken werden onderzocht met hoge resolutie transmissie elektronen microscope (HR TEM), analytische TEM, in situ experimenten tot op atomaire schaal en ab-initio berekeningen op basis van de zogenaamde Density Functional theorie. HRTEM opnamen werden gecombineerd met analyses van de chemische samenstelling binnen één monolaag aan metaal/oxide grensvlakken. Met behulp van in situ experimenten kon een gedetailleerd beeld van orde-wanorde overgangen op een atomaire schaal aan metaal/oxide grensvlakken worden verkregen. Een computerprogramma is ontwikkeld voor het relateren van HRTEM opnamen aan ladingsoverdracht (ioniciteit) en ladingsverdeling langs metaaloxide grensvlakken. De grensvlakken zijn gemaakt met interne oxidatie waarbij kleine oxide precipitataten in de metallische matrix werden gefabriceerd. Deze methode levert schone grensvlakken op en maakt transmissie elektronen microscopisch onderzoek goed uitvoerbaar.

In hoofdstuk 3 is de mate van segregatie van In en Ga en de competitie van segregatie tussen In en Ga aan parallelle {111} Cu-MnO grensvlakken aangetoond door gebruik te maken van drie verschillende typen preparaten. De analytische TEM resultaten zijn gecombineerd met HRTEM opnamen om het gedrag van de Ga segregatie te onderzoeken. Met deze nieuwe meetprocedure bleek het mogelijk om de verrijkingen van een fractie van een monolaag aan hetero-fase grensvlakken te bepalen en te onderzoeken aan welke kant van het grensvlak de segregatie optreedt. Deze nieuwe procedure is gebaseerd op
Samenvatting

veronderstelde concentratieprofielen die geconvolueerd worden met een Gaussische functie die de elektronenbundel representeert. Daarna wordt de segregerende solute uitgezet tegen één van de solvents die in overmaat aan één kant van het grensvlak aanwezig is. De experimentele data werden verkregen door EDS metingen uit te voeren met een bundel van de afmeting van een nanometer op een rechtopstaand grensvlak met enkele referentiemetingen aan beide zijden van het grensvlak. De voorgestelde procedure leidt tot de conclusie dat indium de segregatie van gallium naar de oxide-kant van het grensvlak effectief blokkeert. Aan de andere kant heeft de aanwezigheid van gallium geen invloed op de segregatie van indium aan de metaalkant van het grensvlak. De waarnemingen met analytische TEM bleken werden bevestigd met HRTEM opnamen.

In hoofdstuk 4 zijn in situ verhittingsexperimenten gecombineerd met HRTEM studies aan Cu₃Pd-MnO grensvlakken om de mate van orde in Cu₃Pd te bepalen, d.w.z. de stuktuur van antifase grenzen (APBs) en details van de lang-periode superstructuur in Cu₃Pd en aan Cu₃Pd-MnO grensvlakken. De methode voor het maken van TEM preparaten bleek een belangrijke rol te spelen bij het observeren en analyseren van APBs en de L₁₂ geordende structuur. De techniek van ionenfrezen voor het maken van preparaten vernietigde de APB structuur en beschadigde de L₁₂ ordening. De oplossing was het uitvoeren van elektrochemisch polijsten voor het uiteindelijk dunner maken van het preparaat. Een dunne oxidelaag bleef echter achter op het intern geoxideerde materiaal en moest verwijderd worden door middel van zo kort mogelijke ionenfrezen om zo min mogelijk schade aan APB structuur en de ordening aan te brengen. Desalniettemin was in situ verhitting nodig om de schade te herstellen. Donker-veld opnamen bij lage vergroting toonde aan dat de opgeloste zuurstof in de Cu₃Pd matrix na interne oxidatie een aanscherpend effect heeft op de APB structuur en dat Mn in de matrix van het niet-geoxideerde materiaal waarschijnlijk de temperatuur van de orde-wanorde overgang verhoogt. De analyse van HRTEM opnamen van Cu₃Pd-MnO grensvlakken in de <110> en <112> projectie toonde aan dat de L₁₂ ordening bij polaire {111} Cu₃Pd-MnO grensvlakken geleidelijk verdwijnt bij nadering van het grensvlak. Daarentegen bleek het non-polaire {002} Cu₃Pd-MnO grensvlak geen invloed op de L₁₂ ordening en de APB structuur, zelfs dicht bij het grensvlak, te hebben.

Hoofdstuk 5 rapporteert over experimenten waarin het zinkgehalte in Ag-ZnₓMn₃₋ₓO₄ gevarieerd wordt en over de grensvlakken tussen deze oxide precipitaten en Ag. Met de toename van het zinkgehalte in ZnₓMn₃₋ₓO₄
transformeert het oxide van vervormd tetragonaal naar kubisch spinel. Deze variatie als functie van x kon verkregen worden door interne oxidatie van Ag-2at.%Mn-4at.%Zn in lucht en het gloeien in vacuüm bij verschillende temperaturen. HRTEM is gebruikt voor het bestuderen van de mispassing en misoriëntatie tussen Ag en Zn\textsubscript{x}Mn\textsubscript{3-x}O\textsubscript{4}. De verschillende mate van mispassing van 10.4% bij Ag-Mn\textsubscript{3}O\textsubscript{4} tot 2.4% bij Ag-Zn\textsubscript{1.5}Mn\textsubscript{1.5}O\textsubscript{4} kon gevisualiseerd worden door gebruik te maken van een zogenaamd Bragg filter. Dit filter levert een simpele methode om mispassing en misfitdislocaties bij \{111\} Ag-Zn\textsubscript{x}Mn\textsubscript{3-x}O\textsubscript{4} af te beelden en daarbij dus kwalitatief de interactiesterkte te onderzoeken die aanwezig is over het grensvlak. Het lijnprofiel van het Ag-Mn\textsubscript{3}O\textsubscript{4} grensvlak toonde aan dat de grootte van de intensiteitsmodulaties het mogelijk maakt om een onderscheid te maken tussen de Burgers vectoren van het type 1/3<112> en 1/6<112> die aanwezig zijn aan het grensvlak.

Hoofdstuk 6 beschrijft een combinatie van ab-initio berekeningen op basis van de zogenaamde ‘Density Functional Theory’ (DFT) en HRTEM beeldsimulaties om de invloed van ladingsoverdracht, ladingsverplaatsing en ioniciteit op de dynamische elektronen diffractie en HRTEM beelden te onderzoeken. De ladingdichtheid berekeningen zijn geïncorporeerd in een computercode voor HRTEM beeldsimulaties. Het idee was om de berekende ladingdichtheid maps om te zetten in geprojecteerde potentialen per atoom die het verschil met neutrale atomen representeren en die vervolgens te gebruiken als correctieterm voor de neutrale atoom geprojecteerde potentialen die standaard in HRTEM beeldsimulaties aanwezig zijn. Deze procedure is toegepast op MgO en Ag-MgO in de <110> projectie. Het Mg getemineerde \{111\} Ag-MgO grensvlak toonde geen noemenswaardig verschil tussen de standaard en de gecorrigeerde HRTEM beeldsimulaties voor het grensvlak. Het O getemineerde \{111\} Ag-MgO grensvlak daarentegen toonde aan dat de binding tussen Ag en MgO verantwoordelijk is voor het verschil in contrast aan het grensvlak tussen de standaard en de ab-initio HRTEM beeldsimulaties. Het incorporeren van de ioniciteit van MgO toonde een contrastomkering tussen de gecorrigeerde ab-initio en de conventionele (neutraal atoommodel) HRTEM beeldsimulaties voor relatief grote defocuswaarden. Het huidige werk toont voor het eerst aan dat DFT berekeningen gekoppeld kunnen worden aan HRTEM beeldsimulaties om de structuur en eigenschappen van metaal-oxide grensvlakken te kunnen onderzoeken.
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[Signature]