Bonding along metal-oxide interfaces
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In this chapter, the results of calculations on different Cu/MgO-interfaces are presented. Calculations have been performed on the Cu(100)/MgO(100)-interface and the Cu(111)/MgO(111)-interface. The latter system has an oxide terminated interface plane. The chapter is organized as follows: after a short introduction an explanation will be presented how the parameters of the parameterized potentials are determined (§3.2). In the two subsequent sections the results for the different orientations of the interface are presented. The results of these calculations will be compared to values published in literature (§3.5) and in §3.6 conclusions are drawn.

3.1 Introduction

To understand the nature of metal-oxide bonding it is advisable to study first the structure of simple metal-oxide interfaces. Calculations have been performed on interfaces between copper and magnesium oxide for two different orientations. These calculations are performed as a first check to see if our model is able to describe correctly the interactions across the interface. To this end, the results are compared with results derived both from experimental observations and from quantum mechanical calculations.

The atomic structure of the interface can be revealed with the help of high-resolution electron microscopy and cross-checked with a predicted atomic structure from lattice statics calculations. In order to image metal-oxide interfaces in a HRTEM and derive the atomic structure the interface must be
observed edge-on to view the atomic structure un-obscured by moiré effects. Another necessity is the need to view the metal structure along a low-index zone axis to resolve separate atomic columns. In that way, small deviations in

Fig. 3-1: HRTEM image of an edge-on Cu/MgO {111} interface viewed along ⟨110⟩ in a Jeol 4000EX/II (Groningen) near optimum defocus (~48 nm). Black dots in Cu correspond to positions of atomic columns.¹

Fig. 3-2: HRTEM image of an edge-on Cu/MgO {111} interface viewed along ⟨112⟩ in the Stuttgart Jeol ARM 1250. Defocus is about ~55 nm and atomic columns of Cu correspond to black dots.¹
the atomic structure can be observed and measured. With nowadays instruments it is in general quite impossible to resolve the oxide structure atomically (i.e. both cations and anions), even along a low index zone.

The interfaces have to be straight and without steps along the beam direction to be able, to interpret the structure as formed by the interactions across the interface and not by a projection of steps at the interface. HRTEM images of edge-on observed Cu/MgO interfaces pertaining to parallel topotaxy of metal and oxide with \{111\} parallel to the interface are shown in Figs 3-1 and 3-2 for viewing along \langle 110 \rangle 1 and \langle 112 \rangle 2.

In several studies the interfacial atomic configuration and interfacial energies of metal-oxide interfaces were determined using ab-initio calculations as shown by Benedek3, Schoenberger et al.4 and Smith et al.5 or by using models based on charge interactions6,7,8. However, in these calculations only coherent interfaces (e.g. by straining the metal to match the oxide) were considered. At present, lattice statics calculations appear more suited for determination of the relaxed atomic structure of semi-coherent interfaces. The description of the inter-atomic interaction across the metal-oxide interface is however a problem, since it is poorly understood. A first important point is the range of interaction, i.e. is it short or long range? Based on the image-charge scheme, long-range Coulomb and dipole-moment interactions are involved.

### 3.2 Determination of the interaction parameters

Quantum mechanical calculations are performed on simplified model descriptions of this particular interface. In fact, this model system is quite small containing only a limited number of atoms. Information is extracted from the results of these calculations to be able to fit the parameters of the potentials that are used to give a simplified description of the interactions between the atoms.

Three different interactions can be characterized:

Interactions between two atoms, which are both located in the metal; these are the interactions between two copper atoms.

Interactions across the interface; these are interactions between a copper atom in the metal and an oxide or magnesium ion in the ceramic.
Interactions between two ions; these are the interactions that occur within the ceramic.

The latter interactions are neglected because magnesium oxide is much stiffer than copper and consequently most of the atomic relaxations will take place in the copper.

First, the determination of the parameters for the interactions between copper atoms is presented, followed by the results of the parameters for the interactions across the interface.

3.2.1 Parameters of the copper interactions

Quantum mechanical calculations are performed on different computational cells with copper atoms in the face centered cubic structure; the results are used for the fitting procedure of the parameterized potentials. A different value for the lattice parameter has been used for each quantum mechanical calculation. The energies obtained are used to fit the values of the parameters.

Additional quantum mechanical calculations have been performed, where the copper atoms are positioned in a slab of three atoms thick, with vacuum on both sites. The same geometry is used for the determination of the parameters of the interactions across the interface. However, in these calculations there is also a slab with oxide and magnesium ions present in the computational cell. Because the atoms are not longer in symmetric positions, they will experience forces. These forces as well as the calculated energies are used in the fitting procedure of the parameters.

Subsequently, with the parameters thus obtained the forces and energies for the structures are calculated and the relative deviation is calculated with respect to the results of the quantum mechanical calculations. The averages of the deviations are calculated for the forces as well as for the energies. The combination of the average deviations is then used to determine the optimum values of the parameters. This is done by minimizing the average deviations.

The set of parameters that give the best agreement between the results of the quantum mechanical calculations and the values calculated with the parameterized potentials is used in further calculations (i.e. for the fitting of the
parameters of the interactions across the interface and for the structure relaxations). The average deviation in the energy for this particular set is equal to 3.8% and the average relative deviation in the forces is 1.8%.

With this set of parameters, further calculations have been performed on bulk copper in order to determine material constants, and for a detailed comparison with experimental observations, reported in literature.

**Table 3-1: Material constants of copper calculated with the fitted parameters.**

<table>
<thead>
<tr>
<th></th>
<th>Calculated (GPa)</th>
<th>Experimental (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{11}</td>
<td>169.8</td>
<td>169; 168.4 and 176.9^{10}</td>
</tr>
<tr>
<td>C_{12}</td>
<td>130.4</td>
<td>122; 121.4 and 132.8^{10}</td>
</tr>
<tr>
<td>C_{44}</td>
<td>66.3</td>
<td>75; 75.4 and 73.7^{10}</td>
</tr>
<tr>
<td>Bulk constant</td>
<td>143.6</td>
<td>138', 140^{11}</td>
</tr>
</tbody>
</table>

From the values of the elastic constants, also the Poisson’s ratio was determined, it was found to be equal to 0.33. The value of the Poisson’s ratio reported in literature^{11} is 0.34.

With the determined parameters, further calculations have been performed to find the lattice parameter with the lowest energy. The lattice parameter that was found in these calculations was equal to 3.600Å compared to 3.615Å as reported in literature^{11}.

With the lattice, for which the energy has its minimal value, the cohesive energy is calculated and it is found to be equal to 3.71 eV. In the literature, an experimental value of 3.49 eV is reported^{12}. In addition, the cohesive energy for a cluster of copper atoms is given, which is reported to be 2.33 eV.
3.2.2 Parameters of the interactions across the interface

After the values of the parameters describing the interactions between the copper atoms, have been determined it is possible to find values of the parameters for the interactions across the interface.

These parameters are determined with the help of quantum mechanical calculations using a simplified model of the Cu/MgO-interface. The computational cell in that case consists of: three copper atoms, three magnesium ions and three oxide-ions. For the different quantum mechanical calculations, the distance between the copper block and the magnesium oxide block is varied. In order to keep the size of the computational cell constant for all the calculations, the choice is made that a part of the computational cell is vacuum. Therefore, only one interface is present in the computational cell, for which the distance is varied, and on the other side is vacuum, which should be wide enough so that the interactions across the vacuum can be neglected.

Fig. 3-3 displays one computational cell for the quantum mechanical calculations. At the right hand side of the block with three layers of magnesium and oxide ions can be seen, next to it is the block with three layers of copper atoms. At the left hand side is the first layer, with magnesium and oxide ions, of the next computational cell; this is the same layer as the last layer on the right. Some of the atoms are shared between multiple computational cells, therefore it seems that there are more than nine atoms in each computational cell.

From the quantum mechanical calculations, the energies and the forces on the

![Fig. 3-3: One of the computational cells used for the quantum mechanical calculations on the Cu/MgO-interface.](image-url)
copper atoms are extracted, so that they can be used to describe the parameters of the interactions across the interface. These energies and forces are also calculated with the parameterized potentials and from these values the average relative deviation is calculated for the energies and the forces. These two values are minimized to find the optimal values of the parameters.

After optimization, the average relative error in the calculated energies was 1.6% and the average relative error in the forces was equal to 3.8%.

3.3 Structure relaxations of the Cu(100)/MgO(100)-interface

The Cu(100)/MgO(100)-interface is the one for which a calculation of the structure relaxation has been carried out. In this system, both end-planes of copper and magnesium oxide terminate with a cubic structure. In the terminating end-plane of the magnesium oxide layer both magnesium as well as oxide ions are present. The different ions are on sub-lattices that are shifted with respect to each other.

The experimental lattice parameter of magnesium oxide is equal to 4.2112Å, and the lattice parameter of copper is 3.6149Å. The intention is to perform structure relaxation for a computational cell in which both the magnesium oxide and the copper are not strained already prior to the relaxations. To achieve this the number of unit cells of both materials in one computational cell describing the interfacial structure, i.e. in the two directions parallel to the interface, should be taken in such a way that the two materials almost perfectly match each other. On the other hand, the number of atoms in the computational cell determines how long it will take to perform the calculations; therefore, it is desired to have the smallest number of atoms in the computational cell as possible.

The above mentioned constraints are best met by choosing six unit cells of magnesium oxide and seven unit cells of copper, in both directions parallel to the interface. In this case, the computational cell is 25.2672Å if the lattice parameter of the magnesium oxide is used and 25.3043Å in the case of the lattice parameter of copper. This small mismatch is corrected by scaling the distances in the copper such that the two lengths match. This is done by reducing the lattice parameter by 0.15%.
The first layers from the interface, for both the magnesium oxide and the copper, are shown in Fig. 3-4. In this figure the copper atoms are depicted as large white circles. The ions in the magnesium oxide layer are shown as small circles, where the oxide ions are white and the magnesium ions are black. In this figure, also the edges of the computational cell are shown. These are indicated by the square shown in the figure.

Structure relaxations have been carried out using the resulting computational cell. The relaxations result in a displacement of the copper atoms in the layers close to the interface. The displacements can be divided into two directions: the direction parallel and perpendicular to the interface. The displacements in both directions are visualized in Fig. 3-5 this is done for the copper atoms in the first layer from the interface. The small white circles indicate the oxide ions and the small black ones are the magnesium ions, like in Fig. 3-4. In Fig. 3-5 the copper atoms are displayed in different gray scales, the brightness is an indication of the distance of the atom away from the terminating layer of the magnesium.

**Fig. 3-4**: First layers from the interface. Large white circles are Cu-atoms, small white are $O^{2-}$-ions and small black are Mg$^{2+}$-ions. The box lines give the border of the computational cell.
oxide; the black colored atoms are located closest to the interface at a distance of 2.2Å and the white atoms the farthest at a distance of 2.7Å. The original in-plane positions of the copper atoms are also indicated by the dashed circles.

When only concentrating on the height of the copper atoms, it can be seen that the atoms, which are located directly opposite to an oxide ion, are the closest to the terminating layer of the magnesium oxide. The atoms, which are situated the farthest from the interface, are the copper atoms, which are facing a magnesium ion.

From the in-planar displacements, it can be seen that, in the area where the copper atoms almost follow the oxide ions, the atoms are farther apart from each other in order to get a better match between the periodicity in the magnesium oxide and the periodicity in the copper. This stretching of the
copper is compensated in the areas where the copper atoms are opposite to magnesium ions.

From the data acquired in the simulations, it is possible to calculate the components of the strain tensor associated with the first metal layer from the interface. The components of the strain are calculated with respect to the positions of the copper atoms in bulk material. The component of the strain along the [100] direction is visualized in Fig. 3-6 and it is calculated by dividing the change in displacement along the [100]-direction by the distance along the [100]-direction, this is done for combinations of three neighboring atoms.

In Fig. 3-6, the atoms are not drawn, but the edges of the computational cell are shown at the same place as in Fig. 3-4 and Fig. 3-5. Therefore, the area where the strain has its highest values, indicated by the dark color, is where the copper atoms are located in the positions where they face the oxide ions. In this area the distance between the atoms along the [100]-direction is about 7% larger than in bulk copper. This is about half of the strain that is needed to match the periodicity of the magnesium oxide, which would result in about 15% strain. The brighter areas in Fig. 3-6 indicate the places where the copper atoms and the magnesium ions are facing each other.

The strain in the other in-plane direction is quite similar, only rotated over 90°. The component of the strain along the [100]-direction does not change much when moving along the [010]-direction, or vice versa. The deviations are in the order of 1%.
When performing further analyses it is found that the interface separation, i.e. the average distance between the first copper layer and the first magnesium oxide layer, is equal to 2.43Å, with an error of 0.15Å. The average length of the bonds between the copper atoms, in the first layer, and the ions, in the first magnesium oxide layer, is found to be equal to 2.56Å, with an error of 0.20Å.

In our model, the ions in the ceramic are not relaxed. This results in a situation where the internal interactions are the same with and without a metal crystal next to the ceramic. Therefore, the work of adhesion that is calculated is the result of energy change of the interactions within the metal and the interactions across the interface. The work of adhesion that is calculated for this interface is 868 mJ/m².

3.3.1 Effects of charge variations in the MgO

The description of the interface that has been used so far is for a perfect interface between copper and magnesium oxide: it is atomically flat over infinite distances and no impurities are present in either one of the dissimilar materials. In reality, both requirements are not met and therefore it would be interesting to see what the effects of these conditions are on the work of adhesion and the structural relaxations. However, the description of an infinitely large interface finds its origin in the methodology we applied to calculate the interacting forces and therefore its effects cannot be examined while maintaining the idea of a repeat unit cell. Nevertheless, the effects of point defects can be investigated. Here it should be kept in mind that due to the use of computational cells a high concentration of impurities can be present at the interface.

The correct modeling of the interface with impurities requires a physical description of the interactions between the impurity atoms and the other atoms and ions. The impurity atoms will in general primarily interact with the copper atoms and the ions in the magnesium oxide. There will be almost no interactions among the impurity atoms because of the larger distances between these impurity atoms due to the low concentration. To fit the interactions correctly the interactions in the computational cell for the quantum mechanical calculations should be comparable to the ones during the structure relaxations,
this would mean large computational cells and therefore long computation times.

To be able to calculate the effect of impurities to some extent, calculations have been performed in which the effect of charge variations in the magnesium oxide are studied. This is done by putting an additional charge on one of the oxide ions in the terminating magnesium oxide layer. This charge can be either positive or negative. In order to keep charge neutrality an opposite charge is distributed over the remaining ions. A second method is applied by putting a charge on one of the oxide ions and the opposite charge on one of the magnesium ions, both of them are in the terminating layer, again the charge can be positive and negative. In all the cases, the absolute value of the charge change on the oxide ion is equal to 0.1e (=1.6 $10^{-20}$ C).

In Fig. 3-7 the charge differences in the first copper layer are visualized, the charge differences are caused by a more negatively charged oxide ion, located almost in the center of the computational cell, and a more positively charged magnesium ion, which is located in the lower left corner of the computational cell. The mentioned oxide and magnesium ion are indicated in Fig. 3-7 with a

![Fig. 3-7: Charge differences in first copper layer, due to a more negative charge on one of the $O^-$ ions in the center and a more positive charge on the $Mg^{2+}$ ion in the lower left corner.](image)

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small – respectively a small +, on the place where the ion is positioned.

The changes in the calculated charges of the copper atoms are quite localized, i.e. only the atoms located directly opposite to ions of which the charges are changed experience a significant change in the potential, causing a significant change in the calculated charge. The influence of the charge variations is also quite localized along the direction perpendicular to the interface, i.e. the changes on the atoms in the second copper layer are already quite small in comparison to the changes in charge on the copper atoms that are directly facing the ions, where the charge has been altered.

For the other variations of the investigated charges, the results are quite similar regarding the effect on the copper atoms. For all the calculations the changes in the charge affect primarily the atoms directly opposite to the ions on which the charge is varied. In Table 3-2 the results for four different systems are presented. Here, the relative change in the work of adhesion, the minimum and maximum changes of the charges and the minimum and maximum changes in height are given. A positive value of the change in height means that the atom moved closer to the terminating layer of the magnesium oxide.

<table>
<thead>
<tr>
<th>Charge variation</th>
<th>$\Delta W_{\text{adh}}$ (%)</th>
<th>$\Delta \text{charge}$ (e)</th>
<th>$\Delta \text{height}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O^2-$</td>
<td>-0.25</td>
<td>-0.020</td>
<td>0.002</td>
</tr>
<tr>
<td>$-0.1e$</td>
<td>0.54</td>
<td>0.001</td>
<td>0.022</td>
</tr>
<tr>
<td>$+0.1e$</td>
<td>-0.48</td>
<td>-0.021</td>
<td>0.012</td>
</tr>
<tr>
<td>$-0.1e$</td>
<td>+0.1e</td>
<td>0.77</td>
<td>-0.013</td>
</tr>
<tr>
<td>$+0.1e$</td>
<td>+0.1e</td>
<td>0.77</td>
<td>-0.013</td>
</tr>
</tbody>
</table>

An increase of the absolute charge of the oxide ion results in an increase of the bonding across the interface and a decrease of the distance between the terminating copper layer and the terminating magnesium oxide layer. A decrease of the absolute charge results in the opposite, i.e. a decrease of the bonding and a larger distance between the two terminating layers. When also the charge of the magnesium ion is altered, this effect becomes stronger. The work of adhesion increases or decreases significantly, but the effect on the distance between the two materials is of minor importance.
In these calculations, the changes of the charges on the oxide and magnesium ions are rather small. The absolute value of the charge variations is only 0.1e, whereas in reality impurities are more likely to have charge differences, which are ten times larger. Of course, this lower value of the charge differences would result in an underestimate of the change of work of adhesion but the general trend will be similar. Another effect that may produce an overestimate of the effect on the work of adhesion is still the rather high concentration of impurity ions. Due to the periodicity that is necessary for the calculations, still one or two ions of the 72 ions in the terminating magnesium oxide layer have an altered charge. Normally the concentration of impurities is much lower than this.

Due to the limitations of the model and the non-linear response, it is hard to extrapolate the results to more realistic situations, but it seems likely that effects of localized charges in the magnesium oxide on the work of adhesion are rather indirect. A large difference in localized charges due to impurities along the interface can be compensated by a depletion or an enhanced concentration of vacancies, which affects the work of adhesion. Probably other effects, like the difference in size of the impurity atoms, will have also an effect on the work of adhesion and the structure of the atoms near the interface.

3.4 Structure relaxations of the Cu(111)/MgO(111)-interface

The second Cu/MgO-interface for which calculations of the structure relaxation have been carried out is the Cu(111)/MgO(111)-interface. For this system, both the copper and the magnesium oxide have a six-fold rotational symmetry, which are revealed in the 111-layers. The magnesium oxide layer is terminated either by a layer consisting of only magnesium ions or oxide ions. The calculations of the relaxations have been carried out on a Cu(111)/MgO(111)-interface, where the magnesium oxide is terminated by an oxide layer. This is done so because according to reported quantum mechanical calculations this termination is energetically more favorable than terminating with magnesium. Further, from the calculations on Cu(100)/MgO(100) it was also found that the bonding between copper and oxide is stronger than the bonding between copper and magnesium.

Because the structure of both copper and magnesium oxide are quite similar, and because the same crystallographic orientations of the terminating layers are
considered, it is possible to use the same number of unit cells in both directions, parallel to the interface, as was used for the Cu(100)/MgO(100)-interface. Therefore, again, 6 unit cells of magnesium oxide and 7 unit cells of copper are used.

Because the atoms in the terminating layers are placed in a hexagonal structure, it is necessary to use two different orientations parallel to the interface to define the computational cell. Along one axis the [11-2]-direction is used for both materials. For both materials, the interatomic distance along this direction is equal to $\sqrt{6}/2 \cdot a_0$, where $a_0$ is the lattice parameter of the unit cell. Using the above-mentioned 6 to 7 ratio, this should give computational cells for magnesium oxide and copper of comparable sizes. For magnesium oxide this gives a computational cell with one side of $6\sqrt{6}/2 \cdot 4.2112 = 30.95\text{Å}$, and for the same side for copper this gives $7\sqrt{6}/2 \cdot 3.6149 = 30.99\text{Å}$. Therefore, compressing the copper in this direction by 0.15% gives a perfect match between the two systems.

The direction in the (111)-plane and perpendicular to the [11-2]-direction is the [1-10]-direction. In this direction, the distance between two atoms is equal to $\sqrt{2} \cdot a_0$. Thus for magnesium oxide it results in a side of $6\sqrt{2} \cdot 4.2112 = 35.73\text{Å}$, and for copper the side has a length of $7\sqrt{2} \cdot 3.6149 = 35.79\text{Å}$. So also, in this direction the distances between the copper atoms need to be compressed by 0.15%.

For the calculations of the structure relaxations a square, in the plane of the interface, computational cell is used. It should be noted that one computational cell contains four repeat unit cells, each of which having the same size and atomic structure. The method used to calculate the interactions of the charges and dipole-moments is restricted to computational cells of which the sides are perpendicular to each other; this is a consequence of the use of the expansions in the Fast Multipole Method. Therefore, the repeat unit cell cannot be used in these calculations and a more complex computational cell is required.

In Fig. 3-8 the computational cell that is used to calculate the structure relaxations of the Cu(111)/MgO (111)-interface is shown. The viewing direction is perpendicular to the interface. In the figure, the atoms in the first layer of the copper are shown. These atoms are indicated with the larger circles. In addition, the ions in the first two layers of magnesium oxide are shown. The ions in the first magnesium oxide layer are indicated by the smaller white circles. These circles all represent oxide ions, whereas the ions in the second layer are
displayed by small black circles. The second layer consists fully of magnesium ions. The edges of the computational cell are represented by the large rectangle. The edges of one of the repeat unit cells have been indicated in the center of the computational cell.

In Fig. 3-9 the atoms in the first copper layer and the ions in the first two magnesium oxide layers are depicted. This time the structure relaxation is visualized. The positions of the atoms in the two directions parallel to the interface are quite easily recognized, but the visualization of the coordinates perpendicular to the interface is more difficult. In order to visualize the distance from the interface, the atoms are depicted with a gray scale. Each gray scale indicates a certain height, ranging from $-1.1\text{Å}$, indicated by the black color, to
The copper atoms to the right of the repeat unit cell are colored black or almost black. This means that these atoms are located closest to the terminating magnesium oxide layer. These atoms are located in the hollow sites of both the first and second magnesium oxide layer from the interface. The atoms that are located also in the hollow sites of the first layer but directly opposite to the ions in the second layer, are a bit farther away from the terminating magnesium oxide layer. These are the atoms at the left side of the repeat unit cell. The copper atoms that are farthest away from the magnesium oxide layers are the

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**Fig. 3-9:** Top view of the Cu/MgO-interface, the structure of the atoms in the first Cu layer is shown after relaxation, the height of the atoms is visualized with gray level.
ones located directly opposite to the oxide ions. These are the bright colored atoms on the corners of the repeat unit cell.

After a close examination, it is possible to see the displacements of the copper atoms in the terminating layer parallel to the interface. These displacements can be visualized by using the components of the strains along the different directions. The strains are calculated with respect to the atomic configuration in bulk copper.

To calculate the strain first the displacements of all the atoms with respect to the atomic configuration in bulk copper are calculated. The displacements are calculated for both directions parallel to the interface, that is the [1-10]- and the [11-2]-direction. Then, with the help of three neighboring atoms, which is the minimum required, the change of the displacements is calculated as a function of the atomic positions in the plane of the interface. The strains are then calculated by dividing the change in displacement by the change in the coordinate. Both the change in displacement and the change in the coordinate can be either along the [1-10]- or the [11-2]-direction. Therefore, four possible strains are calculated: one along the [1-10]-direction, one along the [11-2]-direction and two for the remaining possible combinations of the two directions. The first two refer to uni-axial tensile and compressive strains of the material. The latter represent the shear strain components of the material and they should be equal to each other, therefore the average of the two values is reported.

In Fig. 3-10 the strains calculated by dividing the change of displacements, along the [11-2]-direction, by the change of coordinates, also along the [11-2]-direction, are visualized. It can be seen that the strain reaches values of around 0.16, this means that the distance between the copper atoms is increased by 16%, which results in a distance between the copper atoms equal to the distance between the oxide ions. Thus, the copper atoms, in the first layer from the interface, in the center right and the center left region of the repeat unit cell follow locally the periodicity of the oxide ions in the terminating magnesium oxide layer. The atoms in the center right part of the repeat unit cell have a slightly better match with the oxide ions than the atoms in the center left part. The atoms in the center right part of the repeat unit cell are atoms that are located in the hollow sites of the oxide ions in the first layer, as well as in the hollow sites of the magnesium ions in the second layer. In addition, the atoms
in the center left part are located in the hollow sites of the oxide ions. They are placed directly opposite to the magnesium ions.

The stretching of the material in some of the areas requires corrections in other parts of the repeat unit cell. The corrections are found prominently at the corners of the repeat unit cell and on the shorter axis. The corners of the repeat unit cell are in areas where the copper atoms are located directly opposite to the oxide ions. The short axis (of the repeat unit cell along the [1-10]-direction) is the area where a transition takes place from the hollow positions of the magnesium ions to the positions directly opposite to these ions.

**Fig. 3-10:** Strains in the terminating copper layer, this is the change of the displacement along the [11-2]-direction divided by the displacement along the [11-2]-direction.
In Fig. 3-11, the strains, calculated by taking the change in displacements and in coordinates both along the [1-10]-direction, are visualized. In this direction the distances between the atoms in the center right part of the repeat unit cell along the [1-10] -direction are also increased by about 16% in order to match the distances between the oxide ions in the adjacent layer.

Again, the stretching of the material is compensated on the corners of the repeat unit cell, by compressing the material in those places along the [1-10]-direction. A substantial difference with the previously described strain field is that the stretching in the center left part of the repeat unit cell is quite limited in this case, whereas previously a value of almost 0.16 was found. Another significant difference is the behavior of the atoms along the short axis of the repeat unit

Fig. 3-11: Strains in the terminating copper layer, this is the change of the displacement along the [1-10]-direction divided by the displacement along the [1-10]-direction.
cell. The distances between these atoms along the [11-2]-direction are compressed by almost 16%, while along the [1-10]-direction the distances between the atoms are increased by almost 16%. The atoms along the short axis of the repeat unit cell form a boundary between the atoms that are located in the hollow positions of the first two magnesium oxide layers and the atoms that are located in the hollow site of the first layer and the atop position of the second magnesium oxide layer. This transition requires a translation of the atoms in one of those areas and it results in a compression of the atoms on the short axis along the [11-2]-direction. Along the short axis is a row of oxide ions and a row of copper atoms. These rows are located directly on top of each other. The most favorable place for the copper atoms in this row is the positions precisely between two oxide ions. It produces a strong driving force to the copper atoms to follow the periodicity of the oxide ions along the [1-10]-direction.

The strains calculated by dividing the change in displacements along the [1-10]-direction by the change of coordinates along the [11-2]-directions and vice versa, should be equal to each other. Probably due to the limited number of sampling points some small differences arise between the calculated values of these strains, the average of the two calculated values are presented in Fig. 3-12.

It can be seen that these strains are limited to the edges of the repeat unit cell. Again, these are the boundaries between the two areas for the orientations of the copper atoms with respect to the second layer of the magnesium oxide, just like the boundary along the short axis of the repeat unit cell. The transition across the short axis results in a translation perpendicular to the axis of the copper atoms on one site of the boundary. In this case, this is also what happens, but because the boundaries don’t fall along the [1-10]- or the [11-2]-direction a shear strain is formed at these boundaries.

From the strain components, it can be concluded that copper has the best bonding to magnesium oxide at places where the copper atoms are located in both the hollow sites of the first as well as the hollow sites of the second magnesium oxide layer. In these areas the distance between the atoms is increased, such that the periodicity of the copper matches the periodicity of the magnesium oxide. In places where the copper atoms are in the hollow sites of the first layer and in the atop position of the second layer the distances between the atoms are also increased, but to a less extent. Stretching of the copper in these areas is compensated by compression on the boundaries between the
areas. The compression is most prominent in areas where the copper atoms are located directly opposite to the oxide ions in the terminating layer.

The average distance between the atoms in the first copper layer to the first magnesium oxide layer is 1.47Å, with a spread of 0.22Å. This spread in the distance is a result of the height distribution within the first copper layer. The bond length between an atom in the first copper layer with an ion in the first magnesium oxide layer is on average 2.04Å, with a spread of 0.04Å.

The work of adhesion calculated for the relaxed interface is 5.25 J/m².

Fig. 3-12: Strains in the terminating copper layer, this is the change of the displacement along the [11-2]-direction divided by the displacement along the [1-10]-direction.
3.5 Comparison with the literature

In literature\textsuperscript{13} it is reported that for MgO precipitates grown by internal oxidation in a Cu matrix, primarily Cu(111)/MgO(111)-interfaces are observed, suggesting that these interfaces have a higher work of adhesion than the Cu(100)/MgO(100)-interface. The octahedrally shaped MgO precipitates, with [111] facets, are terminated\textsuperscript{14,15,16,17,18} with a layer containing only oxide ions. The termination with oxide ions instead with magnesium ions is supported by the results of quantum mechanical calculations on coherent interfaces\textsuperscript{19}. The preference of a (111) termination over a (100) termination is confirmed by the presented results, as can be seen from the large difference of the work of adhesion for two different orientations.

In the model that has been used it is assumed that the interfaces are chemically and structurally sharp, so no chemical contamination in the interface region or structural changes. For the Cu(111)/MgO(111)-interface this is confirmed by experiments both chemically\textsuperscript{18,20} and structurally\textsuperscript{21,22}.

Calculations have been reported for a single copper atom in the vicinity of a MgO(001)-surface\textsuperscript{23} and for a layer of copper on magnesium oxide. The results of the calculations, with respect to the interface separation and the work of adhesion, are presented in Table 3-3.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Configuration</th>
<th>Interface separation (Å)</th>
<th>Work of adhesion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benedek et al.\textsuperscript{13}</td>
<td>Over O</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Over Mg</td>
<td>2.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Li et al.\textsuperscript{21}</td>
<td>Over O</td>
<td>1.9</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Over Mg</td>
<td>2.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Hollow</td>
<td>1.9</td>
<td>1.0</td>
</tr>
</tbody>
</table>

From the reported values it can be seen that the atop oxide configuration is the most favourable one. This supports the conclusion drawn from the calculations that the oxide-ions are more attractive for the copper atoms than the magnesium ions, with the hollow positions having an energy between these two extremes. The calculated average distance from the first magnesium oxide
layer to the first copper layer is equal to 2.4Å. This value is between the literature values for the atop oxide and atop magnesium configuration. In addition, the value for the work of adhesion (868 mJ/m$^2$) is in agreement with the reported values of the copper block, and it is slightly less than the reported value of one copper atom atop of a magnesium ion.

Assuming that the average distance from the interface is the average of the distance of the atoms atop of an oxide ion and the atoms atop of a magnesium ion, we can calculate from the reported quantum mechanical calculations (see Table 3-3) an average distance to be of 2.3Å or 2.2Å. The average of the calculated work of adhesion is 1080 mJ/m$^2$ or 1700 mJ/m$^2$, where the first value is supposed to be more accurate because of the copper that is used instead of the single copper that is used for the second value. It can be concluded that both the average interface distance and the work of adhesion indicate in this case a slight underestimation of the strength of the bonding across the interface.

### Table 3-4: Reported values for the Cu(111)/MgO(111)-interface.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Cu/MgO-ratio, Configuration</th>
<th>Interface separation (Å)</th>
<th>Bond lengths (Å)</th>
<th>Work of adhesion (eV/interaction O-ion)</th>
<th>Work of adhesion (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benedek et al.</td>
<td>1/1, hollow, Mg-terminated</td>
<td>2.1</td>
<td>2.7</td>
<td>1.7</td>
<td>3500</td>
</tr>
<tr>
<td></td>
<td>1/1, hollow, O-terminated</td>
<td>1.3</td>
<td>2.1</td>
<td>2.9</td>
<td>6100</td>
</tr>
<tr>
<td>Benedek et al.</td>
<td>1/1, atop O</td>
<td>1.8</td>
<td>1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/1, hollow</td>
<td>1.3</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5/4</td>
<td>1.6</td>
<td>1.9, 2.1, 2.3 (*)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benedek et al.</td>
<td>7/6</td>
<td>1.6</td>
<td>1.9(**)</td>
<td>3.6</td>
<td>7500</td>
</tr>
</tbody>
</table>

*: The reported values are for atoms in different positions. These are respectively: the atop of an oxide position, the hollow position of both the first (oxide) as well as the second (magnesium) plane and the position that is the hollow position of the oxide and the atop position of the magnesium.

**: For atoms in the atop of the oxide ion position.

Different quantum mechanical calculations have been reported for the Cu(111)/MgO(111)-interface, due to the lattice mismatch, and the resulting large computational cells. The first calculations were performed on interfaces where the lattice parameters of the two materials were the same$^{13,19}$. In one of
these papers, results are reported of calculations on an interface with 5x5 Cu layer unit cells opposite to 4x4 MgO layer unit cells. With the advances of computer technology it became possible to perform first principle calculations\textsuperscript{3} on the Cu(111)/MgO(111)-interface system, with the lattice misfit included.

These calculations are performed on thin slabs so that the total number of atoms in one computational cell is 399. Results from all these calculations are presented in Table 3-4. The calculated values are given for the interface separation, the bond lengths and the work of adhesion.

From the calculations in \textsuperscript{3} it has been concluded that the largest displacements occur in the copper layer, with some displacements in the first ceramic layer and almost no displacements in the ceramic layers further away from the interface. Thereby justifying that only the atoms in the metal are displaced in our model, and that the ions in the ceramic are at fixed positions.

For both the interface with the 5/4 Cu/MgO-ratio as well for the interface with the 7/6 Cu/MgO-ratio the average interface separation is reported to be equal to 1.6Å. This is slightly more than the 1.5Å that is found in the calculation that is performed with the present model. This difference also comes back in the bond lengths across the interface; in the quantum mechanical calculations the bond lengths are found to be 2.1Å on average and in our calculations we find an average bond length of 2.0Å.

The work of adhesion reported for the quantum mechanical calculations on the interface with the 7/6 Cu/MgO-ratio is larger than the work of adhesion found in our calculations, 7500 and 5250 mJ/m\textsuperscript{2}, respectively. However, it should be noted that in one of the reports it is stated that the hollow position above the terminating oxide ions is energetically the most favorable one. This would mean that the reported value of 6100 mJ/m\textsuperscript{2} is the maximum value for the work of adhesion and for other positions smaller values are expected.

When comparing the values reported in literature to those found in our calculations it can be seen that we find a slightly shorter distance between the copper and the magnesium oxide indicating a slightly stronger bonding, but when looking at the work of adhesion our values seem to indicate a slightly weaker bonding.
3.6 Conclusions

From our calculations we find that the (111) termination, of both the copper and the magnesium oxide is preferred with respect to the (100) termination. This is in accordance with experimental observations. When comparing the results with quantum mechanical calculations it can be seen that our model performs well, despite the generalizations and approximation that are made.

3.7 References

11. www.webelements.com