In this chapter, the results of calculations on Pd/Mn$_3$O$_4$-interfaces are presented. Experimental observations with high-resolution transmission electron microscopy on these precipitates are used for the particular orientation relationships in this system. From the calculated interface energies of the different orientation relations conclusions are drawn with respect to the size of the terminating facets of manganese oxide precipitates in a palladium matrix. The results are compared with the results for Ag/Mn$_3$O$_4$.

5.1 Introduction

The equilibrium shape of small inclusions, specified by the orientation relation (OR) together with interface orientations (IOs), is determined by both interfacial energy and strain energy. In the absence of strain, a construction analogous to Wulff\textsuperscript{1}, based on a polar plot of interface energy as a function of interface normal, provides uniquely the equilibrium shape of the precipitate\textsuperscript{2}. Depending on the magnitude of the strain, the elastic energy may become appreciable and results in deviations of the equilibrium shape associated with the Wulff construction. In certain systems, strain can be the dominant factor controlling the shape. Such systems can be found in the class of coherent metallic inclusions in a metal matrix in the presence of anisotropic strains. Then, the equilibrium shape can be predicted by approaches based on minimization of elastic-strain energy\textsuperscript{3,4,5,6,7,8}. Closely related approximations, although based on geometrical arguments, involve the search for invariant planes\textsuperscript{9,10} or invariant lines. Most of
the work on oxide precipitates in a metal matrix was conducted on NaCl-type oxides (e.g. MgO, MnO, NiO, CdO) in an fcc metal matrix\textsuperscript{11,12}, see also Chapter 3. For studying the relative importance of the misfit on the shape of oxide precipitates, these systems are not particularly interesting because an isotropic mismatch between precipitate and matrix is present. As a consequence Mn\textsubscript{3}O\textsubscript{4} becomes interesting, because it is related to the NaCl-type oxides in the sense that the fcc O sub-lattice is tetragonally distorted with a c/a ratio of 1.157. Therefore, apart from the expected strong anisotropy in interfacial-binding energy, also, a strong anisotropy in the misfit is added for the system of Mn\textsubscript{3}O\textsubscript{4} precipitates in an fcc-metal matrix and hence the competition between these two factors can be studied.

In particular, transmission electron microscopy\textsuperscript{13,14} revealed Mn\textsubscript{3}O\textsubscript{4} precipitates with two types of dominant shapes in Pd-3at.\%Mn that was internally oxidized in air at 1000 °C. Other phases of manganese-oxide were not observed. One type is octahedrally shaped and bounded by \{111\} planes of Mn\textsubscript{3}O\textsubscript{4}. This system will be compared with Ag/Mn\textsubscript{3}O\textsubscript{4} in section 5.5. Interestingly, the octahedrons show a relatively larger truncation by (002) in Pd than in Ag. In addition, a second type of precipitate shape, comprising about 1/3 of all the precipitates in Pd, was not observed in Ag. It corresponds to a plate-like structure, showing an orientation relation where the tetragonal axes of Mn\textsubscript{3}O\textsubscript{4} are parallel to the cube axes of Pd, with as habit plane normal the c-axis of Mn\textsubscript{3}O\textsubscript{4}. HRTEM observations revealed the presence of a square misfit dislocation network with line direction \textless 110\textgreater{} and Burgers vector $\frac{1}{2}<110>$ at these interfaces with (002)Mn\textsubscript{3}O\textsubscript{4}//{200}Pd, see Fig. 1-1, Chapter 1. A summary of the TEM findings is as follows:

Fig. 5-1 shows a bright-field TEM image of a Mn\textsubscript{3}O\textsubscript{4} precipitate in Pd as viewed along their common \textless 110\textgreater{} direction together with the corresponding SAED (selected area electron diffraction) pattern. The Mn\textsubscript{3}O\textsubscript{4} precipitate is bounded by two pairs of edge-on observed \{111\} and one pair of edge-on observed (002). The Mn\textsubscript{3}O\textsubscript{4} has its long c-axis in the plane of projection. The SAED pattern shows that the \{111\} of Mn\textsubscript{3}O\textsubscript{4} are aligned parallel to the \{111\} of Pd for only one pair of facets. For the other pair of \{111\} facets a tilt of 7.6 ° around the \textless 110\textgreater{} viewing direction is present in-between the \{111\} of Pd and Mn\textsubscript{3}O\textsubscript{4}. In-between the (002) of Mn\textsubscript{3}O\textsubscript{4} and Pd a tilt of 3.8 ° occurs.
Fig. 5-1: Bright-field TEM image and corresponding Selected-Area Electron Diffraction pattern of a (002) truncated octahedrally shaped Mn$_3$O$_4$ precipitate in Pd as viewed along their common <110> axis (note that this is the only common direction for Mn$_3$O$_4$ and Pd$^{13,14}$. For one pair of facets the (111) of Mn$_3$O$_4$ and Pd are aligned parallel and then for the other pair of facets their (111) planes show a mutual tilt of 7.6° (where the tilt axis is parallel to the <110> viewing direction).
Fig. 5-2: HRTEM images of the edge-on observed \{111\} interfaces of the Mn$_3$O$_4$ precipitate in Pd as shown in Fig. 5-1.$^{13,14}$ In (a) the tilt of 7.6° between the \{111\} of Mn$_3$O$_4$ and Pd is clearly illustrated; the tilt is relieved by ledges in the Pd with height $\frac{1}{4}<112>$ and direction $<110>$ (i.e. parallel to the $<110>$ viewing direction). In (b) the interface with parallel \{111\} of Mn$_3$O$_4$ and Pd is shown.
Fig. 5-2a and 5-2b show HRTEM images of parts of the 7.6° tilted and parallel {111} Mn₃O₄/Pd interfaces, respectively. At the tilted interface (Fig. 5-2a) ledges in the Pd with direction <110> (viewing direction) and height 1/4<112> (perpendicular to the interface plane and the viewing direction) can be observed with a mutual distance of 7 to 8 Pd {111} planes making a large angle with the interface.

Due to the tetragonality of Mn₃O₄, parallelism of the principal axes implies that the eight {111} facets of Mn₃O₄ cannot all be parallel to the {111} planes of Pd; the normal of the {111} planes in Mn₃O₄ make an angle of 58.6° with the [001] axis, whereas for a cubic structure this angle is 54.7°. Along the ⟨110⟩ Pd zone axis the precipitate is projected as a lozenge with two identical sharp and two identical blunt angles. The situation is shown schematically in Fig. 5-3. This blunt corner corresponds to an angle of 117.1° in the case of ⟨110⟩ Mn₃O₄ and 105.8° in the case of ⟨101⟩ Mn₃O₄, whereas the corresponding angle between {111} planes in a cubic system is equal to 109.5°. The tilt between the eight {111} facets of Mn₃O₄ and the {111} planes of Pd in the case of parallelism of principal axis is 3.83° (with [110] or [1 1 0] as the tilt axis). For a tilt with this magnitude ledges (in the metal) with [110] or [1 0 1] direction along all faces of the octahedron can be expected (see Fig. 5-3). For the 3.83° tilt ledges on, for example, the ⟨1 1 1⟩ face with direction [110] and height 1/4⟨1 1 2⟩ can be expected each 14 1/4⟨1 1 2⟩ (i.e. each 14 ⟨1 1 1⟩ planes) and the corresponding projection to be expected for viewing along the [110] projection is shown schematically in Fig. 5-3.

Parallelism of the principal axes of Mn₃O₄ and the cube axes of Pd implying a tilt of 3.8° between all four pairs of {111} observed for Mn₃O₄ in Pd, but much less frequently than the orientation shown above where the Mn₃O₄ is rotated around a <110> (perpendicular to the c-axis) to bring {111} of Mn₃O₄ and Pd parallel for one pair of facets. All these observations for Mn₃O₄ octahedrons in Pd are exactly similar to the observations for Mn₃O₄ octahedrons in Ag. However, two important differences occur: (i) the Mn₃O₄ are about a factor 10 larger in Pd than in Ag and (ii) the (002) truncation of the octahedrons is substantial in Pd (see Fig. 5-1) and not in Ag. In fact, truncation in Ag only becomes present after annealing in vacuo. The larger size of Mn₃O₄ precipitates in Pd compared to Ag is caused by the much lower oxygen permeability (cₒDₒ) with cₒ the solubility and Dₒ the diffusion coefficient of oxygen in the metal matrix) in Pd than in Ag. Oxygen permeates through Pd much slower so that the Mn has more time to develop to larger oxide precipitates. Generally, a
smaller difference in oxygen affinity between metallic element to be oxidized and the metal of the matrix is responsible for larger precipitates, but this argument does not hold for the present difference in sizes of the Mn$_3$O$_4$ precipitates in Pd and Ag.

Besides the octahedron-shaped precipitates, which comprise about 2/3 of all the precipitates, plate-like shaped precipitates were also observed, comprising the rest of the precipitates. The mismatch between inter-planar distances in Mn$_3$O$_4$ and in Pd is relatively large. The a-axes of Mn$_3$O$_4$ is 4.6% longer than twice the lattice constant of Pd and the c-axis is 21.1% longer than twice the lattice constant of Pd. Comparing the fct (face centered tetragonal) O sub-lattice of Mn$_3$O$_4$ and the fcc (face centered cubic) Pd lattice this factor 2 drops. The c-axis of Mn$_3$O$_4$ makes the largest mismatch with the corresponding directions in Pd and from a point of view of minimizing strain/mismatch on interfaces, it is clear that the Mn$_3$O$_4$ facet with its normal along the c-axis is preferred. Possibly this explains the occurrence of the plate-shaped precipitates with a habit plane normal the Mn$_3$O$_4$ c-axis.

The general conclusions of the TEM analysis are:

- The anisotropy in the interface energy for oxide precipitates in a metal matrix is substantial due to the ionic nature of the oxide, giving well defined shapes associated with the Wulff construction.
- The influence of the misfit energy on the precipitate shape as bounded by semi-coherent interfaces is important only if sufficient anisotropy in mismatch is present and if the matrix is sufficiently stiff.

- The stronger coupling strength due to electronic binding effects across the interface in Pd compared to Ag is responsible for the formation of the dislocation network structures for larger misfits.

For the orientation relationships and for the structure relaxations the unit cell of Mn$_3$O$_4$ is described by a tetragonally distorted spinel crystal structure, with the a-axes of 0.814 nm and the c-axes of 0.942 nm. The atomic structure is displayed in Fig. 5-4 from different viewing directions. In fact, the crystal structure is I4/amd with the a-axes $\frac{1}{2}\sqrt{2}$ times 0.814 nm and the c-axis 0.942 nm where the a-axes of tetragonal spinel and I4/amd are related by a rotation of 45° around the c-axis. However, to allow a close comparison between the fct O sub-lattice of Mn$_3$O$_4$ and the fcc lattice of Pd here the larger tetragonally distorted spinel unit-cell will be used as the crystallographic basis for Mn$_3$O$_4$.

To compare the results of our model with these observations, calculations have been performed on all the interfaces with the abovementioned orientation relations; thus two (002) interfaces, one parallel and one with an angle of 3.8°, and three (111) interfaces, one parallel, one with an angle of 3.8° and one with an angle of 7.6°.

5.2 Determination of the interaction parameters

Before the structure relaxations can be performed, it is necessary to determine the values of the parameters of the potentials that describe the interactions between the different atoms.

First, the interactions between the palladium atoms are determined. This is done using first principle calculations, which are performed on a computational cell of palladium with different lattice parameters. In addition, some computational cells are used in which the atomic structures are distorted. In particular, this is done to enhance the accuracy of the forces, which are calculated with the parameterized potentials. With the calculated energies and forces on the atoms, the parameters are determined.
With the values of the parameters that are found, some material constants are calculated. The calculated values are presented in Table 5-1 together with reported values taken from literature.

**Table 5-1: Material constants calculated for Pd with the parameters and reported in literature.**

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Reported</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Tight Binding$^{16}$</td>
</tr>
<tr>
<td>$a$(Å)</td>
<td>3.93</td>
<td>3.85</td>
</tr>
<tr>
<td>$C_{11}$(GPa)</td>
<td>200</td>
<td>233</td>
</tr>
<tr>
<td>$C_{12}$(GPa)</td>
<td>143</td>
<td>163</td>
</tr>
<tr>
<td>$C_{44}$(GPa)</td>
<td>81</td>
<td>63</td>
</tr>
<tr>
<td>Bulk elastic constant(GPa)</td>
<td>162</td>
<td>212</td>
</tr>
</tbody>
</table>

It can be seen that the values of the lattice parameter and the bulk constant have deviations with experimental data and these deviations are comparable to the errors found in the tight binding and the first principle calculations. For the bulk elastic constant the error is even smaller than the error found with both
tight binding and other first principle calculations. The error in $C_{44}$ is comparable to the error found in the tight binding approach but much larger then the deviation found in other first principle calculations. The deviations in the values of $C_{11}$ and $C_{12}$ are larger than those found with tight binding and other first principle calculations.

The Poisson’s ratio is calculated from the material constants and is found to be 0.32, whereas in literature a value of 0.39 is reported. The cohesive energy is calculated 3.705 eV.

For the determination of the parameters of the interactions across the interface, first principle calculations are performed using simplified models for the interface system. From the results of these first principle calculations, the energies and the forces on the atoms are used to determine the values of the parameters.

The parameters are determined by calculating the relative average error in the energies and in the forces and then minimizing these values. After optimizing the values of the parameters, the error in the energies is 6.8% and the error in the forces is 10%.

5.3 Structure relaxations

In the following section the structure relaxations for the interfaces with the different orientation relationships will be presented.

$Pd/Mn_3O_4 (002)$-interface

The interface used for the structure relaxations of the Pd/Mn$_3$O$_4$-interface is formed by the joining of two free surfaces, i.e. one of palladium and one of manganese oxide. The periodicities of both palladium and manganese oxide are given by the lattice parameters along the [100]-direction, divided by the square root of 2. The lattice parameters for palladium and manganese oxide are 3.8907Å and 8.14Å, respectively. A computational cell is created with sides of 5.75Å, in the two directions parallel to the interface, [110] and [1-10]. This requires straining of palladium of 4.4%. 

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Calculations of the structure relaxations are performed with the constructed computational cell. Fig. 5-5 shows the side view of the computational cell shown after the structure relaxations. The computational cell is viewed along the [1-10]-direction of both the palladium and the manganese oxide unit cells. On both sides, the borders of the computational cell are indicated by thin vertical lines. The top part of the pictures depicts the part of the manganese oxide that is closest to the interface, with the oxide ions indicated by the small circles. The manganese ions are shown as plusses and crosses. Ions with a charge of 2+ are crosses and plusses indicate ions with a charge of 3+. The layers in which there are both oxide and manganese ions, contain only manganese ions with a charge of 3+, and the ions in the layers with only manganese ions are all charged 2+.

It can be seen that the largest part of the structure relaxations takes place in the first layer of the palladium. In Fig. 5-6 a top view (along the [002]-direction) is given of the first layers from the interface. This is done to study the relaxations of the atoms in the first palladium layer in more detail. In Fig. 5-6 the ions in the first manganese oxide are shown. These are oxide ions and manganese ions with a charge of 3+. The oxide ions are indicated with the small circles and the Mn$^{3+}$-ions are indicated with plusses. In addition, the second manganese oxide layer is shown. This is a layer with only manganese ions with a charge of 2+

![Diagram](image.png)

**Fig. 5-5:** The relaxed Pd/Mn$_2$O$_4$(002)-interface, viewed along the [1-10]-direction. In the bottom are the Pd atoms and in the top are the O$^{2-}$, Mn$^{2+}$ and Mn$^{3+}$ ions.
These ions are indicated with the crosses. The atoms in the first layer of palladium are indicated by the large circles. For these atoms, also the height is shown in the figure. The atoms that are closest to the interface are colored black; these atoms are 1.5Å below the first layer of manganese and oxide ions. The bright atoms are the ones farthest from the terminating manganese oxide layer, which is 1.9Å.

The atoms that are closest to the interface are the atoms that are located at positions with no Mn$^{3+}$-ions in the vicinity. This can be seen from Fig. 5-6, where the palladium atoms are farther away from the interface (colored white) when they are near manganese ions with a charge of 3+ (the plusses). This indicates that the oxide ions have a stronger attractive interaction with the palladium atoms, while the manganese ions have a stronger repulsive interaction. In addition, the manganese ions in the second layer from the interface have a repulsive interaction with the palladium atoms. This can be seen from the lighter gray level of the palladium atoms directly opposite to a manganese ion in the second layer (the crosses).

The work of adhesion calculated for this interface is 2250 mJ/m$^2$. The surface energy of only the palladium surface is calculated, it is found to be 1250 mJ/m$^2$. This value will be used for the calculation of the sizes of the different facets in §5.4.
Pd/Mn$_3$O$_4$ (002)-interface with 3.8° rotation

The second (002)-terminated interface has a rotation of 3.8° around the [1-10]-direction. The palladium has a periodicity of two layers along the [002]-direction. This means that the size of the computational cell needs to be chosen in such a way that over the length of one computational cell the palladium needs to have a multiple of two steps. One step is a height difference of half the lattice parameter of palladium. Therefore per computational cell a height difference of one lattice parameter is required, or a multiple. With a rotation of 3.8°, this results in a length along the [110]-direction of 57.5Å. This is ten times the size of the computational cell, which was used for the calculations without a rotation.

To keep the shape of the computational cell like a square, the size of the computational cell along the [1-10]-direction is also multiplied by a factor ten. This way the computational cell is a square shaped along the direction parallel to the interface.

In Fig. 5-7 the Pd/Mn$_3$O$_4$ (002)-interface is shown along the [1-10]-viewing direction. It can be seen that the major part of the relaxations takes place in the first two palladium layers from the interface. Before the structure relaxations the terminating palladium layer contained two steps, but after the structure relaxations these steps are not clearly visible anymore. It can be seen that the

![Diagram of Pd/Mn$_3$O$_4$ (002)-interface with 3.8° rotation](image)

**Fig. 5-7:** Side view of the first layers from the interface, for the Pd/Mn$_3$O$_4$(002)-interface with a rotation of 3.8° around the [1-10]-direction, viewed along the [1-10]-direction.
first layers from the interface are parallel to the interface due to the relaxations, while the deeper lying palladium layers still show the angle of 3.8° with the interface.

In Fig. 5-8 the relaxed structure depicted again, but now along the [002]-viewing direction. For the palladium atoms the distance to the terminating manganese oxide layer is indicated by the gray level. The atoms that are closest to the interface are colored black; they are 1.3Å from the first ceramic layer, while the atoms at a distance of 3.1Å are colored white.

In general, the atoms seem to be following a structured pattern, with some localized displacements. The largest displacements can be observed at positions where the steps are used to be located. In addition, along the [1-10]-direction some distortions can be observed.

The work of adhesion that is calculated for the Pd/Mn₃O₄(002)-interface is 1650 mJ/m². In addition, the surface energy of the palladium is 1100 mJ/m².

Fig. 5-8: Top view of the first layers from the interface, for the Pd/Mn₃O₄(002)-interface with a rotation of 3.8° around the [1-10]-direction, viewed along the [002]-direction.
For the Pd/Mn$_3$O$_4$(111)-interface a larger computational cell is needed than for the Pd/Mn$_3$O$_4$(002)-interface. This is because of the different lattice parameters of the two materials. To construct the unit cell for the Pd/Mn$_3$O$_4$(111)-interface the two materials need to be matched along the [1-10] and the [11-2]-directions.

For palladium, the periodicity along the [1-10]-direction is 2.75Å, and for the Mn$_3$O$_4$ it is 5.76Å. With these values it is possible to take 19 periodicities of Pd and 9 periodicities of Mn$_3$O$_4$. The total length for palladium and manganese oxide is then 52.27Å and 51.80Å, respectively. By compressing the Pd lattice by 0.91% it is possible to match the two materials to each other. This is done for the computational cell used in the structure relaxations calculations.

The periodicities along the [11-2]-direction of palladium and manganese oxide are 4.77Å and 11.04Å, respectively. By taking seven periodicities of the palladium a total length of 33.36Å is found. By taking three periodicities almost the same value is found for the manganese oxide; three periodicities results in 33.12Å. Thus by compressing palladium by 0.72% it can also be matched to manganese oxide along the [11-2]-direction.

Fig. 5-9: The relaxed Pd/Mn$_3$O$_4$(111)-interface, viewed along the [1-10]-direction, the Pd atoms are in the bottom part and the oxide and manganese ions are in the top part.
The computational cell formed in this way is used to perform structure relaxation calculations. In Fig. 5-9 the relaxed structure is shown along the [1-10]-viewing direction. It can be seen that the position of the palladium atoms are almost unchanged; only the atoms in the top layers show small displacements along the direction perpendicular to the interface. In Fig. 5-10, a top view is given for the layers closest to the interface. This figure can be used to investigate the displacements along the directions parallel to the interface.

For the calculations of the structure relaxations of the Pd/Mn₃O₄(111)-interface we are dealing with a first layer in manganese oxide consisting of only oxide ions; the second layer contains only manganese ions with charge 3+, again followed by a layer of only oxide ions. The next three layers contain only manganese ions, where the outer two layers contain manganese ions with charge 2+ and the center layer consists of manganese ions with charge 3+. In Fig. 5-10, only the ions of the first two layers of manganese oxide are shown along with the atoms of the first layer of the palladium. The oxide ions are indicated by small circles, the manganese ions are indicated by plusses and the palladium atoms by the large circles. The height of the palladium atoms is indicated by the gray level of the large circles; the atoms closest to the terminating manganese oxide are black and they are located at 2.2Å from the first layer. The atoms that are the farthest away from the terminating layer are white and are found at a distance of 2.4Å.

Fig. 5-10: The relaxed Pd/Mn₃O₄(111)-interface, viewed from the top. The terminating layer of the Mn₃O₄ consists of only oxide ions (o), followed by a layer with only Mn³⁺-ions (+).
It can be seen that all the displacements in the first layer of palladium are quite small; the maximum height difference is 0.2Å, while the maximum height difference for the Pd/Mn₃O₄(002)-interface is 0.4Å (see §5.3.1). In addition, the displacements in the plane parallel to the interface are quite small. In fact they are hardly noticeable and this is quite different from the relaxations near the Al/Al₂O₃-interface, see Chapter 4.

The work of adhesion that is found for this interface is 200 mJ/m². The surface energy that is calculated for the palladium is 1050 mJ/m².

\textit{Pd/Mn₃O₄ (111)-interface with 3.8° rotation}

The next orientation relationship under investigation is the Pd/Mn₃O₄(111)-interface, where the palladium is rotated around the [1-10]-direction. The rotation is over an angle of 3.8°.

The rotation does not affect the relation between the manganese oxide and the palladium along the [1-10]-direction, thus in this direction the same periodicity is chosen as for the Pd/Mn₃O₄(111)-interface without the rotation of the palladium.

The (111)-terminated palladium surface has a stacking order with three different layers: …ABCABC…. To get a periodic computational cell after the rotation it is important that the newly formed layers contain only one of the three possible layers: A, B or C. The minimum size of the computational cell allowing this to happen is the one where an A layer coincides with the next A layer. The height difference between two A layers of palladium is 6.74Å. Using an angle of about 3.8°, this results in a length of the computational cell of almost 100Å. In §5.3.3, it was noted that manganese oxide has a periodicity of 11.04Å along the [11-2]-direction. Thus for each computational cell in the structure relaxation we should take nine manganese oxide unit cells.

The results of the structure relaxation for this orientation relationship are depicted in Fig. 5-11. In this figure the interface is shown from the side along the [1-10]-direction. In the top part of the figure, the ions in manganese oxide can be seen; the palladium atoms are in the bottom part.

Initially the rotation results in steps at the interface, i.e. on the side of the palladium, similar to the steps that can be seen at the bottom of the picture. These steps show a tendency to collapse, resulting in a smoother terminating
layer at the interface. For the steps to occur, it is necessary that some of the atomic columns be displaced with respect to each other. This has been indicated at the right hand side of the picture by the horizontal lines. It can be seen that the lines at the right are located half way between the lines on the left.

In Fig. 5-12 the top view of the interface is given viewed along the [111] direction. Again, only the first two layers of manganese oxide are shown; this is the terminating layer with only oxide ions and the layer with only Mn$^{3+}$-ions. Both the displacements along the direction perpendicular to the interface and parallel to the interface are shown for the atoms in the terminating palladium layer. The height of these atoms is indicated by the gray level, black indicating a height difference between the atom and the terminating manganese oxide layer of 1.8Å, and white indicating a difference in height of 2.7Å.

The height differences due to the steps can be clearly seen. Also, some minor height differences can be recognized; these minor height differences are caused by the location of the palladium atoms with respect to the ions in the terminating manganese oxide layer. Further, it can be noted that the relaxations parallel to the interface are relatively small.

The depth of the collapses of the steps cannot be determined from Fig. 5-11. This is due to the limited number of palladium planes. From the structure relaxations a depth is found of approximately 24Å.
The work of adhesion calculated for the Pd/Mn$_3$O$_4$-interface with this orientation relationship is 400 mJ/m$^2$. For palladium, a surface energy is calculated of 1800 mJ/m$^2$.

**Pd/Mn$_3$O$_4$ (111)-interface with 7.6° rotation**

For the interface between palladium and manganese oxide, where both materials are terminated by (111)-surfaces and where the palladium lattice is rotated by 7.6° around the [1-10]-direction, a computational cell is used with the same size in the case of a rotation of 3.8°. Because the rotation angle is twice as large, the computational cell becomes half the size or the steps should occur twice as often. A reduction of the size of the computational cell by a factor 2 would result in 4.5 unit cells along the [11-2]-direction. Because this is not an option, the number of steps per computational cell is doubled, i.e. from three to six. This can also be seen in Fig. 5-13, where the computational cell for the
structure relaxations are shown; the viewing direction is along the [1-10]-
direction. Fig. 5-13 shows the atomic configuration after the structure 
relaxation. It can be seen that only three of the six steps have collapsed during 
the relaxation.

This can also be deduced from Fig. 5-14; here the interface is shown along the 
[111]-viewing direction. The first two layers of the manganese oxide lattice are 
shown, i.e. the oxide ions in the terminating layer are shown as small white 
circles, and the manganese ions in the second layer from the interface are 
shown as small black circles. The large white circles are palladium atoms that 
are at a distance of 3.8Å from the terminating layer of the manganese oxide; the 
large black circles are palladium atoms at 1.8Å from the interface. Interstitial 
distances are indicated by different gray levels; the gray level is linearly 
dependent on the distance of the atom from the interface.

The three steps that have failed to collapse during the structure relaxations can 
be recognized clearly. Due to the large spread in distances from the interface, no 
local variations can be distinguished, because they are too small compared with 
the variations perpendicular to the interface. The displacements in the plane 
parallel to the interface are so small that they can hardly be seen in Fig. 5-14.

In addition, for the Pd/Mn₃O₄(111)-interface with a 7.6° rotation, the depth of 
the steps is analyzed. One would expect that the depth of the collapses would 
be halved upon placing twice as many steps in one computational cell. 
However, the same depth is found for the system with the rotation of 3.8° and 
the one with a rotation of 7.6°, if only the collapsed steps are taken into account.

Fig. 5-13: side view of the Pd/Mn₃O₄(111)-interface with 7.6° rotation around the [1-10]-
direction.
For the rotation of 7.6° a depth is found of 23Å, whereas for a rotation of 3.8° the depth is 24Å, which is not a significant difference.

The reason why almost the same depths are found may be due to the collapse of only three out of the six steps that are initially present in the computational cell for the structure relaxation for the Pd/Mn$_3$O$_4$(111)-interface with a rotation of 7.6°.
The work of adhesion that is found from the structure relaxation calculations for this interface is equal to 200 mJ/m$^2$. The surface energy of the palladium is 1300 mJ/m$^2$.

### 5.4 Sizes of the facets of the precipitates

In §5.1 it is mentioned that the observed manganese oxide precipitates in a palladium matrix have two possible forms: one possible shape is a truncated octahedron; the other one is a plate-like precipitate. In fact, the latter shape is an extreme case of the former, i.e. the truncation is much larger.

The shape of the precipitates is determined by the energies associated with the different interface orientation relationships that occur. To investigate further the shape of the precipitates, we write the energy of a precipitate as a function of the sizes of the facets and the interface energy for each facet.

In Fig. 5-15 a schematic picture is given of a truncated octahedron, of which only the top- and bottom corner are truncated. All sides of the perfectly shaped

![Figure 5-15: Model for a truncated octahedral shaped precipitate, terminated by (111) and (002) interfaces.](image)

...
octahedron have a length \( l \). The small pyramids that have been removed from the top and the bottom of the octahedron have sides with length \( f \cdot l \).

The volume of a pyramid with sides of length \( x \) is given by the following equation:

\[
V_{\text{pyr}} = \frac{1}{6} \sqrt{2} \cdot x^3
\]

The total volume of the truncated octahedron is equal to the volume of two pyramids with sides \( l \) minus two pyramids with sides \( f \cdot l \), this can be written as:

\[
V_{\text{trun.oct.}} = \frac{1}{3} \sqrt{2} \cdot f^3 \left( 1 - f^3 \right)
\]

In the determination of the optimal value of \( f \) as function of the interface energies of the two interface orientations, it is necessary to keep the total volume of the truncated octahedron constant. Thus increasing the value of \( f \), this will also result in a larger value of \( l \).

The energy of the precipitate is the sum of the surface of each facet times the interface energy of that particular facet. Therefore it is necessary to know the total surface of the (111)- and (002)-facets. The surface of a triangle with three equal sides with length \( x \), is given by:

\[
A_{\text{triangle}} = \frac{1}{4} \sqrt{3} x^2
\]

Using Eq. (5.3) the total surface of all the (111) facets can be determined; the result is given by:

\[
A_{(111)} = 2 \sqrt{3} l^2 \left( 1 - f^2 \right)
\]

The total of the (002)-facets is twice the surface of a square with sides with a length \( f \cdot l \).

\[
A_{(002)} = 2 f^2 l^2
\]

With these equations, it is possible to write the total energy of the precipitate. To keep the equation simple, it is presented as a function of the interface energies \((\gamma_{002} \text{ and } \gamma_{111})\), the length of the sides of the perfect octahedron \( l \) and the part of the octahedron that has been removed \( f \).
It is important to keep in mind that the value of $l$ depends on the value of $f$, assuming that the volume of the truncated octahedron is constant.

The shape of the truncated octahedron is determined by the value of $f$ that leads to a minimum total energy of the precipitate. The optimal value of $f$ depends on the interface energies of the different facets. The surface energies of a palladium and a manganese oxide surface are required to calculate the interface energy from the work of adhesion. Both the work of adhesion and the surface energy of palladium are calculated and reported in the previous sections. It is not possible to calculate the surface energy of manganese oxide with the model that is used to perform the calculations of the structure relaxations. Therefore, an estimate of the surface energy is used of $2500 \text{ mJ/m}^2$. This estimate is based on values reported for $\text{Al}_2\text{O}_3$-surfaces where the surface energy ranges from $1590^{21}$ to $2590^{22} \text{ mJ/m}^2$.

In table 5-2 an overview is given of the calculated values of the work of adhesion and the surface energy of palladium for the different interface orientations. In addition, the interface energies, based on the assumption that the surface energy of all the manganese oxide surfaces is $2500 \text{ mJ/m}^2$, are given.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Rotation</th>
<th>$W_{\text{adh}}$ (mJ/m$^2$)</th>
<th>$\sigma_{\text{Pd}}$ (mJ/m$^2$)</th>
<th>$\gamma$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>002</td>
<td>0.0°</td>
<td>2250</td>
<td>1250</td>
<td>1500</td>
</tr>
<tr>
<td>002</td>
<td>3.8°</td>
<td>1650</td>
<td>1100</td>
<td>1950</td>
</tr>
<tr>
<td>111</td>
<td>0.0°</td>
<td>200</td>
<td>1100</td>
<td>3350</td>
</tr>
<tr>
<td>111</td>
<td>3.8°</td>
<td>400</td>
<td>1800</td>
<td>3900</td>
</tr>
<tr>
<td>111</td>
<td>7.6°</td>
<td>200</td>
<td>1300</td>
<td>3600</td>
</tr>
</tbody>
</table>

It is interesting to see what the optimum shape of the precipitate is in accordance with the calculated values of the interface energies obtained with the calculations of the structure relaxations. Two precipitates will be considered:
- precipitates where the (002)-interfaces have not rotated and the (111)-interfaces possess a rotation of 3.8°.

- precipitates where the (002)-interfaces have a rotation of 3.8° and half of the (111)-interfaces have not rotated and the other half has rotated over 7.6°. For the latter precipitate the average value of the interface energies that are found for the two (111)-interfaces is used for the interface energy of the (111)-interfaces.

**Table 5-3: Optimum value of f, and the energy of a precipitate (V=1Å³).**

<table>
<thead>
<tr>
<th>Rotation of (002)-interface</th>
<th>( \gamma_{002} ) (mJ/m²)</th>
<th>( \gamma_{111} ) (mJ/m²)</th>
<th>Optimal value f</th>
<th>Energy precipitate (V=1Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0°</td>
<td>1500</td>
<td>3900</td>
<td>0.78</td>
<td>1.12 eV</td>
</tr>
<tr>
<td>3.8°</td>
<td>1950</td>
<td>3500</td>
<td>0.68</td>
<td>1.10 eV</td>
</tr>
</tbody>
</table>

Two conclusions can be drawn from Table 5-3:

The energy of the precipitate is lower if the (002)-interface has been rotated over 3.8° around the [1-10]-direction. This is in agreement with experimental observations (described in §5.1), this can be concluded from the fact that two third of the observed precipitates have this rotation, leading to the conclusion that this configuration is energetically favorable.

The precipitates, without a rotated (002)-interface, have a larger value for the optimum value of \( f \) than those with a rotation. A larger value of \( f \) means that the octahedron is more truncated, thus their shape becomes more plate-like. This has also been observed experimentally.

The optimum value of \( f \) determined from experimental observations and from the calculations shows some deviations, both for the truncated octahedron as well as for the plate-like precipitates. The shapes found in the experimental observations are more extreme than those found from the calculations of the structure relaxations. The experimentally observed truncated octahedron is less truncated than the one from the calculations; experimentally a value of \( f \) of around 0.4 is found.
5.5 Comparison with Ag/Mn$_3$O$_4$

The mismatch between Mn$_3$O$_4$ and Ag is anisotropic; the $a$ axis of the tetragonal spinel is almost exactly twice the lattice constant of Ag (-0.4 % mismatch) and the $c$-axis is 15.3 % longer than twice the lattice constant of Ag. Based on the mismatch, i.e. strain energy, the expected shape of the precipitate is a plate with (001) as dominant facet. However, in electron microscopy observations, this shape is not observed; it is an octahedron with {111} facets. Apparently, the interfacial energy between Ag and Mn$_3$O$_4$ dominates over the strain energy. The decrease in interfacial energy by changing the (001) facet into {111} facets outweighs the increase in strain energy. The difference in interfacial energy between the [001] and the {111} can be readily understood since at the {111} interface the terminating layer of the precipitate is most likely a close-packed oxide layer, while at the [001] interface the less-densely and less-regularly packed terminating layer consists for example of both oxide and manganese ions in a ratio of 2:1. A summary of the electron microscopy observations is given below:

With reference to the introductory section 5.1. and Fig. 5-3, the tilt between the 8 {111} facets of Mn$_3$O$_4$ and the {111} planes of Ag in case of parallelism of principal axes is 3.83° (with [110] or [1 $\overline{1}$0] as the tilt axis). For a tilt with this magnitude, ledges (in the metal) with [110] or [1 $\overline{1}$0] direction along all faces of the octahedron can be expected. For the 3.83° tilt ledges on the (1 $\overline{1}$1) face with direction [110] and height 1/4[1 $\overline{1}$2] can be expected each 14 1/4[1 $\overline{1}$2] (i.e. for each 14 ( $\overline{1}$11) planes) and the corresponding projection to be expected for viewing along the [110] direction is shown schematically in Fig. 5-3a. The HRTEM image shown in Fig. 5-16 for viewing in [110] direction corresponds well with the expected situation. The two {111} planes in the projection make an angle at the blunt corner which is clearly larger for Mn$_3$O$_4$ than for Ag (117.1° versus 109.5°) and the misalignment and hence "ledges" occur at each of the 2 {111} facets pairs in the projection. The distance between the "ledges" along the interface as can be observed in Fig. 5-16 is 14 and twice 11 1/4<112>, the last being near to, but somewhat smaller than the expected distance of 14 1/4<112>. A smaller distance between the ledges is expected if the height of the ledges is less than a full 1/4<112> step. This is often the case. Local plane bending in Ag however may reduce the tilt of 3.83° and thus an increase of the distance between ledges is expected.
Nevertheless, the situation that misalignment and ledges are present on all eight \{111\} facets as shown in Fig. 5-16\textsuperscript{24} is not so frequently encountered. Actually, HRTEM show that most octahedrons tend to be tilted approximately $3.8^\circ$ (with [110] or [1\textoverline{1}0] as the tilt axis) with respect to the matrix to bring \{111\} faces in Ag and Mn$_3$O$_4$ parallel for a pair of facets. Then, at another pair of facets the \{111\} planes of oxide and metal become less aligned. The theoretically expected projection for this situation, for viewing along the [110] direction and with the rotation axis parallel to the viewing direction, is shown schematically in Fig. 5-3b. The experimental HRTEM image corresponding to this situation is shown in Fig. 5-17\textsuperscript{24}. In this case the [110] of Mn$_3$O$_4$ is still parallel to the [110] of Ag, whereas in all other cases the <101> of Mn$_3$O$_4$ are not parallel to the corresponding directions of Ag. It can be clearly seen in the projection of Fig. 5-17 that one pair of facets corresponds to parallel \{111\} planes and the other pair of facets corresponds to tilted \{111\} planes showing several ledges. Theoretically a tilt of $7.67^\circ$ is expected for the nonparallel \{111\} interface. Then, on for example the (1\textoverline{1}1) face ledges with direction [110] and height $1/4[1\textoverline{1}2]$ can be

![HRTEM image of a Mn$_3$O$_4$ precipitate in Ag as seen when viewed along the common <110> of Mn$_3$O$_4$ and Ag showing a nearly equal tilt of 3.8° on all interfaces, which is relieved by ledges in the Ag along the <110> with height 1/4[1\textoverline{1}2].](image)

**Fig. 5-16:** HRTEM image of a Mn$_3$O$_4$ precipitate in Ag as seen when viewed along the common <110> of Mn$_3$O$_4$ and Ag showing a nearly equal tilt of 3.8° on all interfaces, which is relieved by ledges in the Ag along the <110> with height 1/4[1\textoverline{1}2].
expected theoretically each 6.67 1/4[112] (i.e. for each 6.67 (111) planes; cf. Fig. 5-3b). In the experimental image the separation between the three ledges observed on each of the two facets is 7±1 1/4<112>, which agrees well with the expected distance.

An analysis of the "rotation" of Mn$_3$O$_4$ with respect to the Ag crystal for a large number of precipitates indicates that the rotation is not discretely 0° or ±3.83° but exhibits a continuous distribution. Probably, not the exact parallelism of {111} planes in oxide and metal determines directly the rotation, but the degree of parallelism necessary to result in a pair of facets without ledges and this is also possible when small deviations from ±3.83° occur. This leads to the conclusion that a tendency exists to align {111} planes nearly parallel in oxide and metal for one pair of facets in such a way that no ledges have to be present on this pair of facets.

Now we return to the computational part. Before calculations of the structure relaxations can be performed, it is necessary to determine the interaction

![Diagram](image-url)

**Fig. 5-17:** HTEM image of a Mn$_3$O$_4$ precipitate in Ag as seen when viewed along the common <110> of Mn$_3$O$_4$ and Ag showing a parallel and a 7.6° tilted pair of interfaces; the tilted interfaces exhibit ledges in Ag along the <110> with height 1/4<112>.
parameters that give the mathematical description of the interactions between the different elements in the vicinity of the interface. The parameters that describe the interactions between the atoms in bulk silver can be determined from calculations for computational cells containing only a couple of atoms. For the interactions between silver atoms, several first principle calculations have been performed on somewhat deformed unit cells of silver. Part of the deformations was the straining or compressing of the unit cell in all the three principle directions, but also some deformations were created by displacing one or more atoms in the unit cell. The latter calculations were mainly used to be able to get a better fit of the forces by including the forces, which resulted from the deformation of the unit cell, into the parameter fitting procedure.

With the set of parameters, various calculations are performed to determine material constants. A summary is listed in table 5-4.

| Table 5-4: material constants for Ag calculated with the fitted parameters and reported in literature. |
|--------------------------------------------------|-----------------------------|-----------------------------|-----------------------------|
|                                                   | Calculated                  | Reported                    | Experimental²⁷               |
|                                                   | a(Å)                        | Lattice Mechanical Model²⁵   | Lattice Mechanical Model²⁶   |                             |
|                                                   | 4.17                        | 88.2                        | 107.6                       | 4.0853²⁸                   |
|                                                   | C₁₁(GPa)                    | 124                         | 107.6                       | 131.5                      |
|                                                   | C₁₂(GPa)                    | 94                          | 52.8                        | 57.3                       |
|                                                   | C₁₆(GPa)                    | 44                          | 47.5                        | 51.1                       |
|                                                   | Bulk constant(GPa)          | 104                         | 71.0                        | 108.7, 100²⁸               |

The calculated values, except the value of C₁₂, are in reasonable agreement with experimentally observations. With additional first principle calculations the parameters, that give the mathematical description of the possible interactions across the interface, are evaluated. Next, using the parameterized formulation energies and forces are calculated at different interface separations, and compared with the predictions from first principle calculations. The first principle calculation is used as a reference point because it gives the most accurate description. The deviations that are found for the calculated energies
seems to be quite good with a relative error of 3.3%, but the relative error for the calculated forces can be quite high, i.e. up to 43%.

*Ag/Mn₃O₄ (002)-interface*

For the (002)-interface the periodicity of the silver and the manganese oxide in both the [100]- and the [010]-direction are important. These periodicities determine the size of the computational cell in the two directions parallel to the interface. For silver the periodicity in both the [100]- and the [010]-direction is 4.085 Å, and for manganese oxide the periodicity is 8.14 Å in both directions. A computational cell can be constructed by matching two unit cells of silver to one unit cell of manganese oxide, in both directions. The construction of such a computational cell requires the compression of the silver by a fraction of one percent.

It is possible to construct a smaller computational cell by matching the periodicities along the [110]- and the [1-10]-directions of both materials; these periodicities are smaller by a factor of the square root of two. This results in a computational cell that is half the size of the computational cell that is constructed from the [100]- and [010]-directions. An additional advantage is that the constructed computational cell can be easily used for the calculations.

![Fig. 5-18: Top view of the first layers from the interface, for the Ag/Mn₃O₄ (002)-interface, viewed along the [002]-direction.](image)
where the silver is rotated over 3.8° around the [110]-direction.

In Fig. 5-18 a top view is shown of the resulting atomic structure near the interface. The atoms located the closest to the interface are colored black; these silver atoms are at a distance of 2.0Å from the first ceramic layer. The white colored atoms are the atoms in the first metallic layer that the farthest from the first ceramic layer, these are located 3.5Å from the first ceramic layer.

It can be seen that the atoms located directly opposite to a manganese ion with a charge of 3+, are the atoms that are located the closest to the terminating ceramic layer. From this it can be concluded that the dominating part of the attractive interaction between the metal and the ceramic comes from the interaction between the silver atoms and these manganese ions.

There is no attraction between the silver atoms and the oxide ions; this is in contrast to what was seen for the calculations on the Pd/MnO$_4$-interfaces in the section. For this interface a work of adhesion is calculated of 1.5 J/m$^2$, and the surface energy of the silver is calculated as being 0.7 J/m$^2$.

**Ag/Mn$_3$O$_4$ (002)-interface with rotation**

In this calculation the silver block is rotated 3.8° around the [1-10]-direction. To maintain the periodicity along the directions parallel to the interface, the size of the computational cell needs to be increased. This should be done such that the periodicity of the computational cell is maintained at the borders, despite the rotated layers in silver. This means that the height difference of one layer due to the rotation, over one computational cell, needs to be equal to the height difference between two similar layers.

The height difference between two similar layers is equal to the lattice parameter of silver, which is 4.0857Å. It is easily found that a computational cell with a side of 11 times the periodicity of manganese oxide along the [110]-direction results in an angle of 3.7°. The size of the computational cell along the [110]-direction is thus 63.3Å. Along the [1-10]-direction the periodicity stays the same as for the interface where the silver and the manganese oxide layers are parallel to each other; this means that the size of the computational cell along the [1-10]-direction should be a multiple of 5.8Å. To keep the lengths of the two sides about the same size, the sides along the [1-10]-direction have a length of 28.8Å.
Like in the structural relaxations for the Ag/Mn$_3$O$_4$ (002)-interface, it is found that the silver atoms are attracted toward the manganese ions in the first ceramic layer while they are repelled by the oxide ions in the same layer. The attraction of the silver atoms toward the manganese ions is not strong enough to cause a structural change in the metal. This structural change would cause the silver to deform such that one or more layers directly adjacent to the manganese oxide become parallel to the layers in the ceramic, and therefore would leave no large spaces between the metal and the ceramic. For the relaxed interface the work of adhesion is calculated to be 1.2 J/m$^2$ and a surface energy for silver is 0.7 J/m$^2$.

*Ag/Mn$_3$O$_4$ (111)-interface*

For the (111)-interface the size of the computational cell is determined by the periodicity of both silver and manganese oxide along the [1-10]-direction and the [11-2]-direction. One period of manganese oxide, along the [1-10]-direction, is almost equal to two periods of silver, in the same direction; the difference between the two materials in this direction is less than 1%. The difficulty for this interface is matching the periodicities along the [11-2]-directions.

The period of the silver along the [11-2]-direction is 5.0Å, while the period of manganese oxide in this direction equal is to 11.0Å. Combining these two values gives a computational cell with a side of 55.2Å. To achieve this the silver periodicity is repeated eleven times and the periodicity of the manganese oxide is repeated five times. To keep about the same lengths for the two sides of the computational cell, 5 periods along the [1-10]-direction are used, resulting in a side of 28.8Å.

The interface distance found here is about 5Å, which is about the maximum range of the short-range potentials. It seems that the metal and ceramic repel each other as a result of the short-range potentials, but the attractive nature of the charge and dipole interactions seems to prevent that the two materials separate. In addition, the value of the work of adhesion indicates that the bonding between the two materials is extremely weak. The surface energy of the silver is calculated to be 0.65 J/m$^2$. 
CHAPTER 5

Ag/Mn₃O₄ (111)-interface with rotations

For the calculations on this interface the part with the silver atoms is rotated 3.8° round the [1-10]-direction. The rotation does not affect the periodicity along the [1-10]-direction; therefore, the same length is used as for the calculations on the (111)-interface where the planes in the silver and the manganese oxide are parallel. The size of the computational cell along the [11-2]-direction has to be chosen in such a way that the rotated silver layers continue across the borders. The periodicity of the silver along the direction perpendicular to the interface is 7.1Å. Thus a rotation of 3.8° has to result in a height difference of 7.1Å, this results in a side of 110.4Å. Like for the (111)-interface without a rotation, also for this interface a large interface separation is found and a slightly negative work of adhesion (-0.15 J/m²). For the surface energy of the silver a value is calculated of 0.70 J/m², whereas for Ag/Mn₃O₄ (111)-interface with 7.6° rotation the work of adhesion increases, but still near zero. In the latter case 0.75 J/m² is found for the surface energy for the silver.

Because of the work of adhesion of the (111)-interfaces is almost absent, the calculated truncation for the precipitates is much too high; in experiments rarely any truncation is observed for this system. If these values for the work of adhesion would have been more positive, then the interface energies for these interfaces would have been lower and (111)-interfaces would have form a larger portion of the terminating interfaces of the precipitate. Actually, if the interface energies of the (111)-interfaces were of the order of 1250 mJ/m² no truncation of the precipitates would have occurred.

Possible reasons for the unexpected values for the interface energies are:

- The chosen mathematical form of the potentials is not capable of capturing all the necessary information needed to calculate the relaxations correctly.

- The set of first principle calculations used in the fitting procedure has been too limited.

- Despite the efforts to prevent it, the fitting procedure of the parameters found a local minimum, instead of the absolute minimum.
5.6 Conclusion

The deviations that have been found between the experimental observations and the calculated optimal structure can be explained by some of the limitations in the model. Probably the main limitation is the fact that the ions in manganese oxide are assumed to be on fixed positions, and that they are unable to relax.

Despite the simplicity of the model to perform structural relaxations on the different interfaces of Pd/Mn$_3$O$_4$, we have been able to find strong resemblance between the optimum shape of a manganese oxide precipitate in a palladium matrix found in experimental observations and the optimum shape determined from the results of the structure relaxations. The calculations on the Ag/Mn$_3$O$_4$ system show that despite the success for Pd/Mn$_3$O$_4$, there is no guarantee that structural relaxations on a similar interface system can be predicted equally well.

5.7 References

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