Spin-dependent transport across anti-phase boundaries in magnetite films

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5.1 Introduction

Epitaxial Fe$_3$O$_4$ ultra-thin films have physical properties that differ significantly from those of the bulk. They exhibit magneto-resistance [27, 29, 104], larger electrical resistivity [25, 26] and the magnetisation does not saturate in high fields [23]. These properties are a consequence of the high density of anti-phase boundaries (APBs) present in epitaxially grown thin films. The shift vector at the boundary can be: $1/4[110], 1/4[1\bar{1}0], 1/2[100], 1/4[101], 1/4[10\bar{1}], 1/4[011]$ and $1/4[01\bar{1}]$, where the first three are referred to as in-plane shifts (i.e. plane of the film) and the last four as out-of-plane shifts. At the APBs a strong anti-ferromagnetic coupling can be present [23, 24], which influences the magnetic, conducting and magneto-resistance properties of the epitaxial films. It is therefore important to have knowledge about the APB character, the relationship between the shift and the boundary plane, and the way it influences the magnetic coupling across the APB.

In the previous chapter we have shown that the anti-phase boundaries that occur in epitaxial Fe$_3$O$_4$ films are not static, but are able to migrate via a thermally activated diffusional process. The domain size in the Fe$_3$O$_4$ films is greatly dependent on the film thickness, growth temperature, post-annealing time and oxygen flux [111]. The domain size increases with film thickness and with increasing growth or annealing temperature.

In this chapter we present a study of the distribution of the APB shift vectors in Fe$_3$O$_4$ films, the directionality of the APBs, and the relation-
ship between the APB shift vector and the average boundary plane. The consequences for the magnetic exchange coupling across the APB will also be discussed. We will show that when the exchange interactions on both the octahedral and tetrahedral sites are taken into account, a net anti-ferromagnetic coupling is not always present across the APBs.

5.2 Experimental

The Fe$_3$O$_4$ films were grown using molecular beam epitaxy (MBE) in an ultra-high vacuum system with a background pressure of $10^{-10}$ mbar. Standard samples were grown using an iron flux of 1.2 Å/min, an oxygen pressure of $10^{-6}$ mbar and a growth temperature of 250 °C. Using these conditions, films of 6, 12, 25 and 50 nm thickness have been grown. To determine the structural quality and purity, the films were analysed in-situ using RHEED, LEED and XPS. The thickness of the films was determined both during growth from the oscillation period of the RHEED specular spot intensity and after growth using X-Ray reflectivity. The iron flux was measured using a quartz crystal balance. Oxygen was admitted via a gas delivery system that consists of a small buffer volume. The O$_2$-gas is let into the buffer volume via a leak valve. The buffer pressure is measured with a baratron. The stoichiometry of the films was determined using Mössbauer spectroscopy. All films were highly stoichiometric, the deviation from stoichiometry, as expressed by writing the composition as Fe$_{3-\delta}$O$_4$, was as low as $\delta < 0.008$. The APB morphology was studied by transmission electron microscopy (TEM). Specimens were prepared by dissolving the MgO substrate and floating the Fe$_3$O$_4$ films off in a 4 wt.% ammonium sulphate solution at 70°C. The Fe$_3$O$_4$ films were picked up on a copper grid and analysed in a JEOL 2000FX transmission electron microscope operating at 200 keV.

5.3 Results

5.3.1 APB morphology

The APB morphologies of four Fe$_3$O$_4$ films of different thickness from 6 to 50 nm are shown in Fig. 5.1. The figure shows an increase in domain size with increasing thickness. The increase in domain size can also clearly be seen in post annealed samples as shown in Fig. 5.2 for a 12 nm thick film post annealed at 300°C for 2 and 4 hours. Figures 5.1 and 5.2 show four changes with increasing thickness and annealing time: i) an increase in domain size, ii) a decrease in curvature, iii) an increase in directionality, and iv) a decrease in the number of boundary intersections and boundaries per intersection. The latter
Figure 5.1: TEM dark field images of (a) 6 nm, (b) 12 nm (c) 25 nm and (d) 50 nm thick Fe₃O₄ films on cleaved MgO grown at 250 °C. Images were taken near the [001] direction using the 220 type reflection.

three are less obvious in the thicker films (> 25 nm) because of the larger projected width of the APBs.

The above trends in the APB morphologies were also observed with increasing growth temperature and annealing temperature [111]. The increase in domain size and the decrease in the number of boundary junctions is a consequence of the APBs annealing out of the films with time at temperature during growth and similarly with annealing time. Note that in these ultra-thin films stacking-fault-like fringes in APBs are absent because the thickness is significantly less than an extinction distance of Fe₃O₄ (213 nm for the 220-reflection).

In the remainder of this section, we will first present results of the directionality of the APBs as a function of film thickness and annealing and the relationship to the crystallographic planes in the Fe₃O₄ lattice. Then we
Characterisation of anti-phase domain boundaries in epitaxial Fe$_3$O$_4$ films

Figure 5.2: TEM dark field images of 12 nm thick films grown at 250 °C and post annealed at 300 °C for: (a) 2 hours and (b) 10 hours. Images were taken near the [001] direction using the 220-type reflection.

present the analysis of the APB shifts and their relationship to the approximate boundary planes.

5.3.2 Directionality and inclination of APBs

The directionality of the APBs was studied using image analysis on dark field images taken close to the [001] zone axis using the 220-type reflection. Fig. 5.3 shows the degree of directionality using rose diagrams for 12 nm thick films post annealed at 300 °C.

The directionality of the APBs is predominantly close to ±[100] and ±[010] and increases with annealing time. It can be seen from Fig. 5.3c and particularly in Fig. 5.3d that the directionality also develops a bias in a direction on either side of these ⟨100⟩, indicated in the figure by dashed lines. The average angle between these lobes and the ⟨100⟩ are approximately 18° once the angular deviation and asymmetry due to tilting away from the exact [001] zone axis is taken into account. These lobes lie close to the ⟨130⟩, which lie at 18.4° either side of the ⟨100⟩. Similar results, were observed at higher post-annealing temperatures.

The increased directionality was also observed with increasing thickness as shown in Fig. 5.1, but is less obvious in the thicker films (> 25 nm) because of the relatively large projected width of the APBs.

The inclination of the boundaries through the films can be determined using the projected width measured near the [001], in conjunction with the thickness of the films. In all of the films the inclination (with respect to the film normal) varied from 2° to 13° with a fairly consistent average of 7.5°. No significant relationship between the projected width and APB direction
5.3. Results

Figure 5.3: Rose diagrams showing the directionality of the APB projections in 12 nm thick films (grown at 250 °C): a) initial, b) 1 hour, c) 2hrs, and d) 10 hrs post annealing at 250 °C. The projection directions are near the [001], but the tilt from the zone axis to obtain a two-beam diffraction condition produces asymmetry in some of the rose diagrams. The ⟨100⟩ directions are indicated by the thick arrows. The dashed lines in d) indicate the ⟨310⟩ directions.

in the film plane was observed.

5.3.3 Shift vector of the anti-phase boundary

The visibility criteria for APBs are equivalent to those of stacking faults, i.e. they are visible when the phase change $\alpha = 2\pi g \cdot R = (2N + 1)\pi$ and otherwise invisible, where $g$ is the operating reflection and $R$ is the shift vector of the APB. The specific shifts can be determined with a series of systematic dark-field images taken close to a two-beam condition, and identifying whether the APB is visible or invisible. The relationship between APB visibility and the diffracting vectors used here are shown in Table 5.1.
Chapter 5. Characterisation of anti-phase domain boundaries in epitaxial Fe₃O₄ films

Table 5.1: The visibility criteria used to identify the APB shifts for the specific indexing shown in the table.

<table>
<thead>
<tr>
<th>Beam direction</th>
<th>Diffracting vector</th>
<th>Shift vector:</th>
</tr>
</thead>
<tbody>
<tr>
<td>[001], [116], [114]</td>
<td>(220)g</td>
<td>1/4[011] V I V I</td>
</tr>
<tr>
<td>[116]</td>
<td>(151)g</td>
<td>1/4[011] V V I V</td>
</tr>
<tr>
<td>[114]</td>
<td>(311)g</td>
<td>1/4[101] V I V</td>
</tr>
<tr>
<td>[114]</td>
<td>(131)g</td>
<td>1/4[110] I I I V</td>
</tr>
<tr>
<td>[114]</td>
<td></td>
<td>1/4[110] I V V I</td>
</tr>
<tr>
<td>[114]</td>
<td></td>
<td>1/2[100] I V V V</td>
</tr>
</tbody>
</table>

In the images shown in Fig. 5.1 and 5.2, only the APBs with out-of-plane shifts are visible. APBs with in-plane shifts become visible by tilting to other zone axes and using different diffracting vectors.

Fig. 5.4 shows dark field TEM images of APBs with an out-of-plane shift and corresponding schematics showing the position of all the APBs for regions in a 25 nm thick film grown at 250 °C. A significant number of the APBs, those shown dashed in the schematics, are not visible in the image taken with the 220-type reflection. When all of the APBs are taken into account the actual domain size is about 0.6 of the apparent size observed when using the 220 reflection.

Presented in Table 5.2 are the proportions of boundary length for each specific shift in the 25 nm thick film. These proportions have been determined by analysing over 530 APBs within an area of 350 x 350 nm. There were very few 1/2[100] shifts, only 0.9%, and the vast majority were the 1/4[110] shifts. The proportions of each of the out-of-plane shifts were similar ranging from 13 to 15.5%. The total proportion of out-of-plane-shifts was 55%, which means that in a dark field TEM taken with the (220) spinel reflection, 55 % of the boundaries are visible. The in-plane shifts were also present in relatively equal proportions of 21 to 22%. The proportion of in-plane shifts was thus greater than the out-of-plane shifts.

5.3.4 Relationship between anti-phase shift and boundary plane

A significant proportion of the APBs with in-plane shifts 1/4[110] and 1/4[110] were found to have boundary planes close to (110) and (110) respectively. This means the boundary planes for these APBs tended to be perpendicular to the shift and vertical through the film.

A correlation between the out-of-plane shifts and their boundary plane was
5.3. Results

Figure 5.4: For a 25 nm thick film grown at 250°C, a) TEM dark field image near the [001] direction using the 220-type reflection that shows all of the out-of-plane APBs and b) a schematic image showing all the APBs with the out-of-plane type as full lines and the in-plane types as dashed lines.

Table 5.2: Proportion of boundary length in a 25 nm thick film for all possible shift vectors.

<table>
<thead>
<tr>
<th>Shift vector</th>
<th>Proportion of shift present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Out-of-plane shifts</td>
<td></td>
</tr>
<tr>
<td>1/4[011]</td>
<td>14.6%</td>
</tr>
<tr>
<td>1/4[011]</td>
<td>13.0%</td>
</tr>
<tr>
<td>1/4[101]</td>
<td>15.5%</td>
</tr>
<tr>
<td>1/4[101]</td>
<td>12.5%</td>
</tr>
<tr>
<td>In-plane shifts</td>
<td></td>
</tr>
<tr>
<td>1/4[110]</td>
<td>22.1%</td>
</tr>
<tr>
<td>1/4[110]</td>
<td>21.4%</td>
</tr>
<tr>
<td>1/2[100]</td>
<td>0.9%</td>
</tr>
</tbody>
</table>

also observed which followed from the directionality and projected widths. The boundary plane tended to lie in the vicinity of the (100) or (010) that was 45° to the shift of the APB. Note that the boundary planes were spread to either side of these planes with preference to the \{130\}. Superimposed on this orientation was a tendency for the boundary plane to be inclined by 2 to 13° towards the shift. The only low index crystallographic planes in the range of directions and inclinations described for the APBs are the (100), (010) and the corresponding (310), (310), (130) and (130), which are all vertical through the film.

5.3.5 High resolution TEM study

In order to obtain more details about the configuration of the boundary, we have also performed a high resolution TEM study of a 12 nm thick
Chapter 5. Characterisation of anti-phase domain boundaries in epitaxial
$\text{Fe}_3\text{O}_4$ films

Figure 5.5: High resolution TEM image of a 12 nm thick film that was post-annealed for 2 hours at 300 °C. The directions and the projection of two $\text{Fe}_3\text{O}_4$ unit cells are indicated in the enlargement. The boundary runs close to [310] and the shift vector is out-of-plane.

A film that was post-annealed for 2 hours at 300 °C. Two high resolution images are shown in Fig. 5.5. A boundary with an out-of-plane shift and a plane that has its projection in the [310] direction, probably the (310) plane, is highlighted in Fig. 5.5b. The boundary is very sharp (half a unit cell). Other boundaries in Fig. 5.5a appear broader. This could be due to a larger projected width, which occurs when the boundary plane is not perpendicular to the foil. The directions of the boundaries visible in the high resolution image are similar to the directions obtained from the image analysis, namely $\langle 100 \rangle$ and $\langle 130 \rangle$. 
5.4 Discussion

In principle all seven of the expected APB shifts should be present in equal proportions. The possible shift vectors are 1/2[100] and 6 different 1/4⟨110⟩ type shifts [36]. The distribution of APB shift vectors is therefore expected to be 14% for 1/2[100] and 86% for 1/4⟨110⟩.

However, our observations show that the 1/2[100] type shift only occurs in very small proportions, < 1%. Anti-phase boundaries have also been reported in other spinel structures, both in single crystals [46, 105, 106] and in thin films [47, 48]. In all of these cases, only shift vectors of 1/4⟨110⟩ were reported. However, in a study by Hesse and Bethge of the defect structure in MgTiO₂ films grown by solid state reactions, it was found that the 1/2[100] shift is present, but seventeen times less than the 1/4⟨110⟩ shifts [84]. The fact that shift vectors of 1/2[100] are hardly observed could mean that these APBs anneal out much faster than the APBs with a 1/4⟨110⟩ shift vector, which would be the case if the former have a higher surface energy than the latter.

A schematic drawing of the APB configuration for 1/2[010] shift and (010) boundary plane is shown in Fig. 5.6. The atomic configuration would be the same if the boundary plane were (100). In the spinel lattice, the oxygen anions surrounding a tetrahedral ions do not touch the other tetrahedra. Octahedral and tetrahedral sites only have a common corner anion. At this boundary, however, octahedral and tetrahedral sites share a common edge which is energetically unfavorable. At the boundaries with a 1/4⟨110⟩ shift the octahedral and tetrahedral sites share a common corner [46], which is energetically more favorable than sharing a common edge. This would explain the high driving force for annealing out the APBs with 1/2[100] shift.

No previous studies on the proportions of the 1/4⟨110⟩ shifts in spinel structures have been reported. There are 6 possible 1/4⟨110⟩ shifts, of which 2 are the in-plane and 4 are the out-of-plane shifts. The expected ratio of in-plane to out-of-plane shifts would thus be 1:2. However, the proportion of in-plane shifts is larger than expected, with a ratio of 0.8:1 for a 25 nm thick film. We will argue that this is due to the observed differences in the relationship between the shift vector and the boundary plane for both kinds of shifts and the effect on the relative energies of the boundaries.

Other studies on spinel structures have reported several relationships between the shift vectors and the boundary planes. In single crystals of MgAl₂O₄, the boundary plane is either (100) at 45° to the shift [105], or {110} perpendicular to the shift [106]. Single crystals of lithium ferrite also have {110} type boundary planes perpendicular to the shift [46]. In thin films of nickel ferrite the boundary planes are also {110} type perpendicular to the shift vector [47], whereas in lithium and cobalt ferrite films the boundary planes are either {110} perpendicular to the shift or {310} [48].
Chapter 5. Characterisation of anti-phase domain boundaries in epitaxial Fe$_3$O$_4$ films

Figure 5.6: Schematic drawing of a boundary with a 1/2[010] shift and (010) boundary plane. The three dimensional projection of the iron sublattice is shown in a), where octahedral and tetrahedral sites share a common edge. b) shows the first oxygen layer with octahedral sites and the tetrahedral sites directly above and below this plane and c) shows the second layer. The third and fourth layers (not shown) are similar to the first and second layers. Examples of magnetic super-exchange interactions across the boundary are indicated as grey lines and their numbers are explained in the text.

making an angle of 42° to the shift.

Several arguments for the observed relationship between the shift and the boundary plane have been given, by comparing the energy of all cases, i.e. when the shift vector and plane are parallel, perpendicular or make an angle of 45°. The lowest energy will be achieved when the introduction of the fault does not change the stoichiometry of the crystal [46]. For a shift parallel to the boundary plane, the crystal will remain stoichiometric. When
Figure 5.7: Schematic drawing of a boundary with a $1/4[110]$ shift and (110) boundary plane. a) shows the first oxygen layer with octahedral sites and the tetrahedral sites directly above and below this plane and b), c) and d) show the second, third and fourth layer respectively. Examples of magnetic superexchange interactions across the boundary are indicated as grey lines.

A shift does not lie in the boundary plane, this is not necessarily the case, because a certain fraction of the unit cell has to be either removed or inserted to form this particular boundary. If a non-stoichiometric amount of material is inserted, the boundary is called non-conservative and will posses a higher energy [107]. However, in spinel structures the crystal does remain stoichiometric when the $1/4(110)$ shift lies perpendicular to the boundary plane [46]. To determine which configuration will have the lowest energy, only the number of nearest neighbours and the distances between them has
to be considered. The lowest energy configuration will then be obtained when both of these parameters are least changes with respect to the bulk. Van der Biest and Thomas [46] have shown that this is the case when the shift is perpendicular to the boundary plane.

This is also what we observed for many of the in-plane shifts 1/4[110] and 1/4[110]. However, for the out-of-plane shifts, the boundary plane is not perpendicular to the shift. In contrast, the boundary planes are close to {100} or {120} at 45° and 42° respectively to the shift. The former family of planes was also observed in MgAl₂O₄ single crystals [105] and the latter was also observed for cobalt ferrite thin films [48]. The energy of these configurations is higher than for a {101} boundary plane due to smaller distances between nearest neighbors. One the other hand, the area of the {100} and {120} boundary planes is less than for a {101} type plane which makes an angle of 45° to the foil. The total energy of an APB will depend on its area through the film and on its crystallographic orientation. The minimization of energy seems to be an important factor, as we observed a strong domain growth at relatively low temperatures (125 °C to 350 °C). Also, the curvature of the APBs is strongly reduced upon annealing. As explained above, we would expect all shifts (and possibly also all boundary planes) to occur initially and APBs with the highest energy to anneal out the fastest.

There are two observations that support this view. First, the APBs with 1/2[100] shift vector seem to anneal out much faster. Second, the boundaries with an in-plane shift and a boundary plane perpendicular to the foil (with minimum surface area) are present in larger proportions. There indeed seems to be an anisotropy in APB energy with crystallographic planes, as observed by the increase in directionality shown by the rose diagrams in Fig. 5.3.

Compared to other studies of spinels, the most notable difference in the APB morphology in our epitaxial Fe₃O₄ films is that the boundary planes are not well defined crystallographic planes. The APBs in our study are formed when neighboring domains touch one another and they are able to migrate via a diffusive process at relatively low temperatures. The cobalt and lithium ferrite thin films [47, 48] were grown by chemical vapour deposition at high temperature (1600°C). Consequently, at these much higher temperatures the diffusivities are much larger, enabling the APBs to migrate to proper crystallographic planes. The thermal history indeed seems to have an influence on the boundary configuration, as in MgAl₂O₄ single crystals, grown using a large temperature gradient, the boundary plane was not always a crystallographic plane [105]. This was interpreted as APB lying on arbitrary planes that change their configuration so that their energy can be reduced via cation diffusion, causing the APB to have a folded configuration.
5.4. Discussion

Figure 5.8: Magnetic configurations for a boundary with a $1/4[110]$ shift and $(110)$ boundary plane. This figure shows the magnetic moments for both a ferromagnetic alignment in between the two domains in a) and b) and an anti-ferromagnetic alignment in c) and d).

5.4.1 Magnetic exchange interactions at the APB

The configuration of the APB is important to understand because it will influence the magnetic coupling across the APB and this can effect the physical properties of the epitaxial Fe$_3$O$_4$ films. For instance, magnetic domain walls can be pinned at the APB [108, 23]. An anti-ferromagnetic coupling will have a strong influence on the magnetisation [23] and on the magneto-resistance properties [29].

Before we discuss the interactions across the boundaries, a brief review of the literature on exchange interactions in spinels is appropriate. The exchange interactions to consider in the bulk are: super-exchange between octahedral (iron)-oxygen-tetrahedral (iron), which is anti-ferromagnetic (AF) [49, 50, 51], super-exchange between octahedral-oxygen-octahedral (90°)
and double exchange between octahedral iron ions, which both result in a ferromagnetic coupling (FM) between the octahedral ions [52, 42]. These three exchange interactions have been indicated in Fig. 5.6b as grey lines labelled I, II and III respectively. The interaction between tetrahedral sites can be ignored, because of the large distance between these sites [49]. The anti-ferromagnetic exchange interaction is the strongest one and is responsible for the ferrimagnetic coupling in Fe$_3$O$_4$.

Across the boundary, there can be new octahedral-oxygen-octahedral interactions (180°, AF and strong, labelled IV), additional octahedral-oxygen-octahedral interactions (90°, FM and weak plus additional double exchange interactions between the octahedral iron ions, both labelled V), new tetrahedral-oxygen-tetrahedral interactions (AF and strong, labelled VI), new octa-
5.4. Discussion

Table 5.3: Magnetic exchange interactions across anti-phase boundaries in epitaxial Fe₃O₄ films on MgO, listed according to their relative strength.

<table>
<thead>
<tr>
<th>Exchange interaction</th>
<th>Type and angle</th>
<th>Strength and sign</th>
<th>Presence</th>
</tr>
</thead>
<tbody>
<tr>
<td>oct-oct</td>
<td>super, 180°</td>
<td>AF, strong</td>
<td>at APB</td>
</tr>
<tr>
<td>tet-oct</td>
<td>super, ~140°</td>
<td>AF, strong</td>
<td>at APB</td>
</tr>
<tr>
<td>oct-oct</td>
<td>super, ~120°</td>
<td>AF, strong</td>
<td>bulk and at APB</td>
</tr>
<tr>
<td>oct-oct</td>
<td>super, 90°</td>
<td>FM, weak</td>
<td>bulk and at APB</td>
</tr>
<tr>
<td>tet-oct</td>
<td>super, ~70°</td>
<td>AF, weak</td>
<td>at APB</td>
</tr>
<tr>
<td>tet-tet</td>
<td>direct</td>
<td>AF, weak</td>
<td>at APB</td>
</tr>
<tr>
<td>oct-tet</td>
<td>direct</td>
<td>FM, weak</td>
<td>at APB</td>
</tr>
</tbody>
</table>

Hedr-octahedral-tetrahedral interactions (FM and weak, labelled VII), additional octahedral-oxygen-tetrahedral interactions (AF and strong, labelled VIII), direct exchange interactions between tetrahedral sites (AF and weak, labelled IX), tetrahedral-oxygen-tetrahedral 70° (AF and weak, labelled X). All these interactions, their relative strength and presence have been summarised in table 5.3.

These interactions are all competing across the boundary and not all of them can be minimised simultaneously, leading to competition. The competition mainly results from the anti-ferromagnetic coupling between octahedral-oxygen-octahedral interactions and between octahedral-oxygen-tetrahedral interactions.

We will explain this by examining the structure and magnetic coupling for a 1/4[110] shift with (110) boundary plane (i.e. the shift is perpendicular to the boundary plane, as has also been observed experimentally). Fig. 5.7 shows a schematic drawing of the configuration of a 1/4[110] shift with a (110) boundary plane. In order to represent all the nearest neighbour interactions, we have drawn an oxygen-octahedral plane with the tetrahedral sites below and above this plane. This has been done for all four monolayers in the unit cell. Examples of super-exchange interactions across the boundary are indicated as grey lines. In the first monolayer (Fig. 5.7a) there are new octahedral-oxygen-tetrahedral interactions between an octahedral iron ion in the boundary plane and tetrahedral iron ions on both sites of this plane. This is a strong anti-ferromagnetic interaction. However, the coupling between the octahedral iron can not be anti-ferromagnetic to both of the tetrahedral ions at the same time when the two domains have an overall anti-ferromagnetic alignment. This is illustrated in Fig. 5.8, where the magnetic configuration is drawn for the first two monolayers of this type of boundary. In Fig. 5.8a) and b) the first two monolayers are
Chapter 5. Characterisation of anti-phase domain boundaries in epitaxial Fe$_3$O$_4$ films

Figure 5.10: Schematic drawing of a boundary with a $1/4[101]$ shift and (130) boundary plane. a) shows the first oxygen layer with octahedral sites and the tetrahedral sites directly above and below this plane and b), c) and d) show the second, third and fourth layer respectively. Examples of magnetic superexchange interactions across the boundary are indicated as grey lines.

...drawn with an overall ferromagnetic alignment between the domains. In Fig. 5.8 c) and d) the same monolayers are drawn with an overall anti-ferromagnetic alignment between the domains. When the overall alignment is ferromagnetic, the coupling of the octahedral ion at the boundary can be anti-ferromagnetic with both of the tetrahedral ions on either side. But a ferromagnetic alignment leads to a problem in the second monolayer, where the octahedral-oxygen-octahedral superexchange interaction...
dictates an anti-ferromagnetic coupling between those ions. The number of octahedral-oxygen-tetrahedral interactions that can not be minimised simultaneously for an anti-ferromagnetic alignment between the domains is equal to the number of octahedral-oxygen-octahedral interactions that can not be minimised when the alignment between the domains is ferromagnetic. These superexchange interactions are both strong, and the octahedral-oxygen-octahedral interactions are probably slightly stronger due to the larger angle of 180°. From these considerations one could deduce that an anti-ferromagnetic alignment is slightly more favourable. However, in case of anti-ferromagnetic alignment between the domains there are also octahedral-octahedral interactions that can not be minimised, as this interaction favours a ferromagnetic alignment (this interaction is illustrated by a grey line in Fig. 5.8c). Therefore, both configurations are probably very similar in energy and the resulting alignment will depend on interactions with other neighbouring domains as well.

A similar analysis has been performed for the 1/2[010] shift with a (010) boundary plane using Fig. 5.6. Most super-exchange interactions can be minimised when the magnetic alignment between the domains is anti-ferromagnetic.

All four monolayer with the tetrahedral sites above and below the planes for a 1/4[011] shift with a (010) boundary plane is shown in Fig. 5.9a-d. Applying the same criteria as above, it is concluded that a ferromagnetic coupling between the domains has a lower energy than an anti-ferromagnetic coupling.

As observed experimentally, the boundary planes can also be close to \{310\}.

All four monolayers with the tetrahedral sites above and below the monolayers for a 1/4[101] shift with a (130) boundary plane are shown in Fig. 5.10a-d. In this case, the anti-ferromagnetic coupling between the domains has the lowest energy.

### 5.5 Conclusions

We have grown epitaxial Fe₃O₄ films on MgO and studied the configuration of anti-phase boundaries occurring in these films. The APBs occur as growth defects and the possible shift vectors are 1/2[100] and 1/4⟨110⟩. We studied the distribution of shift vectors, the relation between the shift vector and the boundary plane and the directionality of the APBs. At some of these APBs an anti-ferromagnetic coupling is present and the APBs have a strong influence on resistivity, magnetism and magneto-resistance properties of these films. The 1/2[100] shift was hardly observed, less than 1% was of this type. This probably means the APBs with 1/2[100] shift vectors anneal out quickly because they posses a higher APB energy than APBs with
1/4⟨110⟩ shift. APBs with an in-plane shift vector, 1/4[110] and 1/4[110]
have their boundary planes perpendicular to the shift vector, (110) and
(110) respectively. In this case, the magnetic alignment between the two
domains can be either ferromagnetic or anti-ferromagnetic and 45% of the
boundaries are of this type. The four possible out-of-plane shift vectors were
also expected have the boundary planes perpendicular to the shift. This was
however not the case, but the boundary plane was either close to \{100\} or
\{310\} which was related to a reduction in APB energy by minimizing the
total boundary area. The magnetic coupling across these boundaries is fer-
romagnetic when the boundary plane is \{100\} and anti-ferromagnetic when
the boundary plane is \{310\}.