Spin-dependent transport across anti-phase boundaries in magnetite films
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Chapter 2

Theoretical concepts

2.1 Introduction

The subject of this chapter is twofold. In the first half, we discuss the structure and electronic- and magnetic properties of Fe$_3$O$_4$. In §2.2 we do this for bulk material, while in §2.3 the formation and structure of anti-phase domain boundaries (APBs) in epitaxial films will be discussed. A good knowledge of the structure of the films and the magnetic interactions resulting from the presence of APBs is necessary to describe the magneto-resistance behaviour of these films. In the second half of this chapter, we focus on the electrical conductivity. In §2.4, we will discuss the fundamental theoretical concepts needed to understand the nature of the spin-polarised transport in Fe$_3$O$_4$. To describe the resistivity behaviour in bulk and epitaxial films we have adopted the small polaron hopping model using the single electron approach, which will be discussed in §2.5. Even though Fe$_3$O$_4$ is a many electron system, this approach gives a good description of the conductivity. A many electron description of the conductivity is well outside the scope of this thesis, but the effect of neglecting the fact that Fe$_3$O$_4$ is a many electron system on the spin polarisation will be discussed in §2.6. This chapter only describes the basic fundamental concepts; the detailed magneto-resistance behaviour of magnetite films will be discussed in chapter 7.

2.2 Structure and properties of bulk Fe$_3$O$_4$

Bulk Fe$_3$O$_4$ exhibits the inverse spinel structure with a lattice constant of 8.397 Å [35, 37]. The inverse spinel structure consists of a face centred cubic oxygen lattice, with Fe$^{3+}$ ions filling 1/8 of the available tetrahedral sites
Figure 2.1: The inverse spinel structure of Fe$_3$O$_4$, consisting of an fcc oxygen lattice and Fe$^{3+}$ ions filling 1/8 of the tetrahedral sites and equal amounts of Fe$^{3+}$ and Fe$^{2+}$ ions filling half of the octahedral sites. Electron exchange between these two ions results in an average charge of Fe$^{2.5+}$ on the octahedral sites.

Figure 2.2a: A schematic drawing of a (001) plane is shown in Fig. 2.2a. Electron hopping between Fe$^{2+}$ and Fe$^{3+}$ ions occurs at the B sites and results in a high conductivity and an average charge of Fe$^{2.5+}$. Fe$^{3+}$ has 5 d-electrons, which are parallel to each other as dictated by Hund’s rule, forming a filled sub shell. Fe$^{2+}$ has an additional spin-down electron which can easily hop to a neighbouring Fe$^{3+}$ site if their spins are parallel. In the magnetically ordered state only the spin-down electron can easily move, resulting in spin-polarised electron transport. The electron transport is restricted to the B sites. B site spins are oriented ferromagnetically because of their mutual anti-ferromagnetic coupling to the A site spins. The magnetic coupling will be further discussed below. Around 120 K the so called Verwey transition ($T_v$) occurs [12]. At this transition the structure distorts from cubic symmetry [13] and a charge ordering occurs at the B sites [39] thus reducing the conductivity by two orders of magnitude. The
exact transition temperature depends on the purity of the crystal [40, 41].

**Magnetic exchange interactions**

The magnetic exchange interaction between two neighbouring spins is described by the Heisenberg exchange Hamiltonian:

\[ H_{ex} = - \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \]  

(2.1)

The sign and strength of the effective exchange integral \( J_{ij} \) depends on the distance, angle, spin and electronic configuration of the neighbouring moments and can result from cation-cation interactions and cation-anion-cation interactions. The latter type of interaction is referred to as superexchange. A good description of many of the possible exchange interactions is given by Goodenough [42].

In Fe\(_3\)O\(_4\), there are several magnetic exchange interactions that have to be taken into account. The magnetic ions in Fe\(_3\)O\(_4\) are Fe\(^{3+}\) and Fe\(^{2+}\) and their electron configurations are \( d^5 \) and \( d^6 \) respectively. They are both in the high spin state, which means that the 5 \( d \)-electrons form a closed sub shell. The spin of the extra electron on Fe\(^{2+}\) is opposite to the other 5 \( d \)-electron spins.

**Cation-cation interactions.** The most important interaction between the iron ions on the octahedral site is the double exchange interaction [52]. This interaction is based on the electron transfer between Fe\(^{2+}\) and Fe\(^{3+}\). Because the spin of the extra electron of Fe\(^{2+}\) is oppositely directed to the electrons of Fe\(^{3+}\), electron transfer is only possible when both ions are aligned ferromagnetically. This then increases the band width or delocalisation of the extra electron, thereby decreasing its kinetic energy and favouring a ferromagnetic alignment.

**Cation-oxygen-cation interactions (superexchange).** The strength and sign of this exchange interaction depends on the angle between the ions and on the filling of the orbitals. Exchange between the two iron ions via the intervening oxygen requires overlap of the orbitals. Overlap only occurs between orbitals with similar symmetry. On the oxygen ions three \( p \)-orbitals contribute, of which 2 have a \( \pi \)-type symmetry and one has \( \sigma \)-type symmetry [43, 42]. Of the 5 \( d \)-orbitals of iron, 3 posses a \( \pi \)-type symmetry (the 3 \( t_{2g} \)-orbitals) and 2 a \( \sigma \)-type symmetry (the 2 \( e_g \)-orbitals). The \( e_g \)-orbitals thus overlap with the oxygen \( p \)-orbitals with \( \sigma \)-type symmetry and the \( t_{2g} \)-orbitals with the oxygen \( p \)-orbitals with \( \pi \)-type symmetry. Because \( \sigma \)-overlap is generally larger than \( \pi \)-overlap [42], the \( \sigma \)-exchange is stronger. In Fe\(_3\)O\(_4\) the following superexchange interactions are important:

- 125 degree iron-oxygen-iron exchange between the iron ions on the octahedral sites and on the tetrahedral sites. These interactions are indicated
Figure 2.2: Schematic Drawing of a (001) plane in $\text{Fe}_3\text{O}_4$. The octahedral sites run in the [110] direction and in a plane, alternating strings are occupied. The magnetic exchange interactions are indicated in the figure. Thick black line: $90^\circ$ superexchange interaction at the octahedral site. Thick dashed line: superexchange interaction between iron ions on the octahedral and tetrahedral lattice. Thick gray line: double exchange between iron ions on the octahedral lattice.
2.3. Structure and properties of epitaxial Fe\textsubscript{3}O\textsubscript{4} films

Substrates

The epitaxial Fe\textsubscript{3}O\textsubscript{4} films have been grown on both cleaved and polished magnesium oxide, MgO (001) substrates (see chapter 3 for details about the growth process). The almost perfect epitaxial relationship between Fe\textsubscript{3}O\textsubscript{4} and MgO is due to the common fcc oxygen sublattice. MgO possesses the rock-salt crystal structure as shown in Fig. 2.3a and belongs to the space group Fm\textbar3m. The lattice constant of MgO is 4.212 Å [35, 37]. The lattice mismatch with Fe\textsubscript{3}O\textsubscript{4} is only -0.3% so MgO has extensively been used as a substrate for the growth of Fe\textsubscript{3}O\textsubscript{4} films.

The Fe\textsubscript{3}O\textsubscript{4} films were also grown on MgAl\textsubscript{2}O\textsubscript{4} substrates. MgAl\textsubscript{2}O\textsubscript{4} has the normal spinel structure and the lattice constant is 8.08 Å, see Fig 2.3b. This results in a larger mismatch of 4 %. In the normal spinel structure the Mg\textsuperscript{2+} ions occupy the tetrahedral sites and the Al\textsuperscript{3+} ions occupy the octahedral sites.

Formation of anti-phase domain boundaries on MgO

In the first stages of growth, islands of Fe\textsubscript{3}O\textsubscript{4} are deposited on MgO. However, because of the difference in unit cell parameter and crystal symmetry, the different islands can be related by a shift vector which is not a lattice translation vector. This results in so-called anti-phase boundaries (APBs) [23, 24, 36, 45]. APBs form when islands of Fe\textsubscript{3}O\textsubscript{4} on the MgO surface coalesce and the neighboring islands are shifted with respect to each other [36]. The APB shifts in these films are a consequence of two distinct forms of symmetry breaking between MgO and Fe\textsubscript{3}O\textsubscript{4}. The first is due to the lattice parameter of MgO (0.4212 nm) being half that of Fe\textsubscript{3}O\textsubscript{4} (0.8397 nm) and
Figure 2.3: a) Schematic Drawing of the MgO unit cell, which has the rocksalt structure. The oxygen sublattice is the same as in Fe$_3$O$_4$ (fcc). All the octahedral sites are occupied by Mg$^{2+}$. b) Schematic drawing of the MgAl$_2$O$_4$ unit cell, which has the normal spinel structure. The Mg$^{2+}$ ions occupy the tetrahedral sites and the Al$^{3+}$ ions occupy the octahedral sites.

thus two adjacent Fe$_3$O$_4$ monolayers may be shifted by $1/4[110]$, $1/4[1\bar{1}0]$ or by $1/2(100)$ as shown in Fig. 2.4. The other APB shifts are a result of the lower symmetry of Fe$_3$O$_4$ monolayers compared to the MgO substrate surface, where the former is 2m and the latter is 4m. Consequently, adjacent Fe$_3$O$_4$ islands on the same MgO surface may be rotated by $90^\circ$, also shown schematically in Fig. 2.4. In combination with the screw symmetry element of the spinel structure this gives rise to the $1/4[101]$, $1/4[10\bar{1}]$, $1/4[011]$ and $1/4[01\bar{1}]$ shifts. Growth from regions on the MgO substrate separated by an atomic step of $1/2a_{\text{MgO}} = 0.2106$ nm can also give rise to these shifts.

In this thesis we designate the $1/4[110]$, $1/4[1\bar{1}0]$ and the $1/2[100]$ shifts to be the in-plane shifts (i.e plane of the film) and the $1/4[101]$, $1/4[10\bar{1}]$, $1/4[011]$ and $1/4[01\bar{1}]$ shifts to be the out-of-plane shifts. Note that the oxygen sublattice is more or less undisturbed across the APBs and only the cation lattice is shifted. This type of anti-phase boundary shifts have also been observed in other spinel structures, such as lithium ferrite [46] and nickel- and cobalt ferrite [47, 48].
2.3. Structure and properties of epitaxial $\text{Fe}_3\text{O}_4$ films

Figure 2.4: Schematic illustration showing APB shifts can be formed based on the different translation and rotation symmetry of the first $\text{Fe}_3\text{O}_4$ monolayer and the $\text{MgO}$ surface. Represented on the $\text{MgO}$ surface are unit cells of $\text{Fe}_3\text{O}_4$ monolayers shifted relative to the reference (A) to form the in-plane shifts of (B) $1/2[100]$ and (C) $1/4[110]$, and a rotated monolayer (D) that can form an out-of-plane shift.

The structure at the boundary is determined by the type of shift and by the direction of the shift with respect to the plane of the boundary (whether the shift is parallel or perpendicular to the boundary plane). Some examples of APBs are shown in Fig. 2.5. These and other possible APBs will be extensively discussed in chapter 5.
Figure 2.5: Schematic representation of anti-phase boundaries with $1/4[110]$, $1/2[100]$ and $1/4[101]$ shifts, and the shifts both parallel and perpendicular to the boundary plane. The boundary is indicated by the thick dashed line. Gray lines across the boundary indicate super exchange interactions.
Formation of anti-phase domain boundaries on MgAl$_2$O$_4$

In case of Fe$_3$O$_4$ growth on MgAl$_2$O$_4$, both the substrate and the epitaxial film exhibit the spinel type structure and symmetry. Because of the similar crystal structure and lattice constants, the formation of APBs is not expected, but APBs in these films have nevertheless been observed [53]. If the only restriction for the growth of the epitaxial film is the continuation of the oxygen sublattice, the formation of APBs is indeed possible on MgAl$_2$O$_4$ substrates. The Fe$_3$O$_4$ can then nucleate at 7 non-equivalent sites on the MgAl$_2$O$_4$ substrate, resulting in the same type of shifts as for the films grown on MgO. In that case, the interfacial energy will not be equal for different domains. Kleint et al. have indeed observed anti-phase boundaries in Fe$_3$O$_4$ films grown on MgO and MgAl$_2$O$_4$, but do not mention whether there is a difference in domain size for the two different substrates [53]. Another factor that has to be taken into account is the misfit. Due to the misfit of almost 4% between Fe$_3$O$_4$ and MgAl$_2$O$_4$, the epitaxial films above the critical thickness will be relaxed generating interfacial misfit dislocations which can lead to stacking faults. Other spinel films (MnFe$_2$O$_4$ and CoFe$_2$O$_4$) with a similar lattice constant to Fe$_3$O$_4$ grown on MgAl$_2$O$_4$ show a grain structure, which has been related to the misfit [54, 55].

Magnetic exchange interactions at the APB

The structure at the boundary influences the magnetic coupling over the boundary. Across the boundary there can be superexchange interactions that are not present in bulk Fe$_3$O$_4$. For instance in case of the 1/4⟨110⟩ type shifts there are 180 degree superexchange interactions that are antiferromagnetic. Note that in case of the 1/2[100] shift there are only ferromagnetic superexchange interactions across the boundary.

Of course these drawings are only schematic and in reality the boundaries need not be atomically sharp or the lattice may have reconstructed due to the charge at the boundary. This will be further discussed in chapter 5, where high resolution TEM images of the boundary will be shown. Which types of APB shifts are present and their corresponding ratios will also be discussed in chapter 5.

2.4 Conductivity in bulk Fe$_3$O$_4$

2.4.1 Band calculations using the single electron approach

The electronic structure in bulk Fe$_3$O$_4$ has been intensively calculated [2, 15, 16]. Cullen and Callen [15, 16] have described the electronic structure using a band model. The Fe$^{3+}$ ions have a closed shell configuration with
S=5/2. The extra electron of the Fe$^{2+}$ ions is in a spin-down t$_{2g}$-band at the B sites which is separated from the occupied spin-up t$_{2g}$-band by a gap of around 3.5 eV [17]. Due to the trigonal symmetry of the crystal field at the B sites the t$_{2g}$ orbitals of the d-level split into two doublets and a singlet, which has the lowest energy. Overlap of the wave-functions broadens these singlet levels into bands. The Hamiltonian for d-electrons in the singlet state is:

$$H = \sum_{i,j} \epsilon_{ij} a_i^\dagger a_j + \sum_{i,j} U_{ij} n_i n_j.$$  \hfill (2.2)

where $\epsilon_{ij}$ is the nn transfer integral, $a_i^\dagger$ and $a_j$ are the electron creation and annihilation operators, $U_{ij}$ is the coulomb repulsion and $n_i$ is the electron occupation number, such that the first term describes the nearest-neighbour (nn) hopping and the second term the Coulomb repulsion. This Hamiltonian is treated in the Hartree Fock approximation, i.e. the electron-electron repulsions are treated in an average way [18]. The authors found that the so-called order parameter, or charge difference on alternate sites, depends on the ratio of the Coulomb repulsion and the bandwidth $w$. This means that for different values of $U/w$, different types of order are obtained. Above $T_v$, where $U/w$ is small, only a metallic structure results. At the Verwey transition, multiple ordering occurs. This means there is more than one non-zero order parameter. As $U/w$ increases below $T_v$, only a single order parameter structure exists. The multiple ordering can explain the extra lines observed in Mössbauer and NMR spectra. Due to the ordering, a gap is opened in the band structure reducing the conductivity.

Ihle and Lorenz have calculated the band structure, band gap and conductivity of Fe$_3$O$_4$ using a similar kind of band structure [22]. They take into account the nn Coulomb repulsion, the next nearest neighbour (nnn)
2.4. Conductivity in bulk Fe$_3$O$_4$

Coulomb repulsion, \textit{nn} hopping and electron-phonon interactions. The importance of electron-phonon interactions becomes apparent from the large isotope effect on the Verwey transition temperature \[19, 56\]. Also long-range ordering (LRO) below \(T_v\) and the presence of short-range order (SRO) indicate the importance of electron correlation effects.

These types of order have been described by Anderson \[57\]. In the spinel structure the octahedral sites form a corner sharing network of tetrahedra. Due to the strong \textit{nn} Coulomb repulsion the energy is lowest when each tetrahedron contains two Fe$^{3+}$ ions and two Fe$^{2+}$ ions, as shown in Fig. 2.6. However, there is a macroscopic number of states with this distribution of ions which all have the same (lowest) energy. To obtain LRO an additional interaction (for instance the \textit{nnn} Coulomb repulsion) is necessary to lift this degeneracy and stabilise LRO.

The authors have explained this by using the following model Hamiltonian:

\[
H = \frac{1}{2} \sum_{i \neq j} V_{ij} n_i n_j + \sum_{\mathbf{q} \nu} \omega_{\mathbf{q} \nu} b_{\mathbf{q} \nu}^\dagger b_{\mathbf{q} \nu} + \sum_{\mathbf{q} \nu} A_{\mathbf{q} \nu} e^{i \mathbf{q} \mathbf{R}_i} n_i (b_{\mathbf{q} \nu} + b_{\mathbf{q} \nu}^\dagger) + \sum_{i \neq j} t_{ij} c_i^\dagger c_j
\]

where \(V_{ij}\) are the Coulomb integrals in the absence of phonons, \(b_{\mathbf{q} \nu}^\dagger\) is the phonon creation operator and \(\omega_{\mathbf{q} \nu}\) is the phonon energy, \(A_{\mathbf{q} \nu}\) is the electron phonon coupling, \(t_{ij}\) are the \textit{nn} transfer integrals and \(c_i\) and \(n_i\) are electron creation and occupation number operators respectively. When \(t_{ij}=0\) the ground state of equation 2.3 shows perfect SRO and perfect LRO. In this ground state, each electron is surrounded by two electrons on the \textit{nn} sites and by four electrons on the \textit{nnn} sites. The ground state thus has a fully occupied level at \(2U_1 + 4U_2 = 2U\), where \(U_1\) and \(U_2\) are the \textit{nn} and \textit{nnn} Coulomb repulsions respectively and \(U = U_1 + 2U_2\). In the first excited level an additional electron occupies a site with four electrons as \textit{nn} and eight electrons as \textit{nnn}. This level, which is empty at zero temperature, has an energy of \(4U\). The corresponding band picture is shown in Fig 2.7.

At finite temperature, the SRO is destroyed to some extent which means that the tetrahedra can be occupied by 0, 1, 3 and 4 electrons. This results in the appearance of excited states in the middle of the Coulomb gap. The density of states at the Fermi level depends on the destruction of the SRO and is thus temperature dependent. The LRO remains the same from \(T=0\) to \(T_v\), but vanishes abruptly at \(T_v\). Also the SRO has a small change at \(T_v\), which results in an increase of the density of states in the middle of the bandgap. The Coulomb band gap above \(T_v\) is about half as large as below \(T_v\).

The conductivity behaviour of Fe$_3$O$_4$ can also be explained by this band picture. Conduction takes place within the sub bands and the number of current carriers is proportional to the thermal activation across the Coulomb
2.4.2 Quantitative description of the conductivity

The band description discussed above gives a qualitative description of the conductivity in Fe$_3$O$_4$. Ihle and Lorenz have also performed a quantitative calculation [20, 21]. To do so they used perturbation theory. The Hamiltonian of equation 2.3 is written as: $H = H_0 + H_1$, where $H_0$ contains the intersite Coulomb, the phonon formation and the electron-phonon coupling terms. The transfer term $H_1$ is treated as a small perturbation. Furthermore, it is assumed that the transfer integral is so small that the small polaron (SP) hopping is non-adiabatic. After using a unitary transformation, $H_0$ becomes:

$$H_0 = -E_b \sum_i n_i + 1/2 \sum_{i \neq j} U_{ij} n_i n_j + \sum_{\mathbf{q} \nu} \omega_{\mathbf{q} \nu} \hat{b}^\dagger_{\mathbf{q} \nu} \hat{b}_{\mathbf{q} \nu}$$

(2.4)

where $E_b$ is the small polaron binding energy, $U_{ij}$ the effective SP-SP interaction energies and $\hat{b}_{\mathbf{q} \nu}$ the displaced phonon operators. The perturbation term $H_1$ becomes:

$$H_1 = \sum_{i \neq j} t_{ij} \phi_{ij} \tilde{c}_{ij} \tilde{c}_{ij}$$

(2.5)
where $\tilde{c}_{ij}$ is the small polaron creation operator and $\phi_{ij}$ the vibrational overlap integral. This equation describes the SP transitions from site $j$ to $i$. These transitions can occur without changes in the phonon occupation number (diagonal transition) or with changes in the phonon occupation number (non-diagonal transition). The diagonal transitions give rise to band motion, where $H_b = \sum_{i\neq j} \tilde{t} \tilde{c}_i \tilde{c}_j$. The effective overlap integral $\tilde{t}$ (only nn hopping is considered) is thus reduced with respect to $t$ by the vibrational overlap integral ($\tilde{t}_{ij} = t_{ij} \phi_{ij}$) and decreases with increasing temperature. The non-diagonal transitions result in hopping motion, $H_h = H_1 - H_b$.

The conductivity is then calculated using the Kubo formula. The band conductivity, which is the main contribution to the conductivity below and not too far above $T_v$ then becomes

$$\sigma_b = \frac{t^2 C_b}{kT} e^{-U_1/2kT} e^{4S_0\omega_0/kT}$$

in the limit of small $U_1/2kT$ and large $\omega_0/2kT$. In this equation, the constant $C_b$ contains temperature independent terms, $U_1$ is the $nn$ Coulomb repulsion and $\omega$ is the phonon energy and $S_0$ contains the electron-phonon coupling strength. This equation also shows that the band conduction is thermally activated and increases with temperature. However, as shown in the second line of Eqn. 2.6, $\tilde{t}$ decreases with temperature. This means that the band conduction first increases due to the thermal activation. It then reaches its maximum value after which it starts to decrease due to the decrease of $\tilde{t}$.

With increasing temperature the probability for multi-phonon processes increases and the hopping conduction starts to dominate the conductivity process. The hopping conductivity is given by:

$$\sigma_h = \frac{t^2 C_h}{kT} e^{-U_1/2kT} e^{S_0\omega_0/2kT}$$

The total conductivity is the summation of the band and hopping parts, but below room temperature the band conductivity is the main contribution to the conductivity. As both the band and the hopping conductivity are proportional to $t^2$, the total conductivity is also proportional to $t^2$, i.e. $\sigma_T \propto t^2$.

2.5 Conductivity in epitaxial Fe$_3$O$_4$ films

The previous paragraphs have described the conductivity in bulk Fe$_3$O$_4$. We will now consider the conductivity in epitaxial films. The conductivity in these films is strongly modified due to the presence of anti-phase boundaries (see §2.3).
2.5.1 Blocking of electron transfer due to anti-ferromagnetic boundaries

As was explained in §2.3, epitaxial Fe$_3$O$_4$ films consist of domains separated by anti-phase boundaries. Furthermore, the magnetic coupling over these boundaries can be anti-ferromagnetic. The conductivity is proportional to the square of the transfer integral: $\sigma \propto t^2$ (see §2.4.2).

The transfer integral was shown to depend on the angle between two spins on neighbouring ions [59, 60]. When the angle between the two spins is $\varphi$, the transfer integral is reduced to:

$$t = t_0 \cos \frac{\varphi}{2} \quad (2.8)$$

In case of ferromagnetic alignment, the two spins are parallel and the transfer integral has its maximum value $t$. In the classical limit, the spin-polarisation is 100 % (this will be discussed in more detail in the next paragraph). In case of anti-ferromagnetic alignment the transfer integral becomes zero. This is the case at the anti-phase boundaries when an anti-ferromagnetic coupling is present.

The epitaxial films are thus made up of domains, within which the conduction resembles bulk behaviour, and of boundary regions where the conduction is strongly reduced.

In chapter 6 we will see how the total conductivity in the epitaxial films can be described as a function of the bulk and boundary conductivities. When a magnetic field is applied, the spins at the boundary will align themselves to some degree with the magnetic field so that the electron transfer across the boundaries is increased. This is the cause of the magneto-resistance behaviour observed in these films and will be described in chapter 7.

2.6 Spin polarisation

The band structure calculations described in the previous sections were performed using a single electron Hamiltonian. The justification for doing so was given by the reasoning that the spin-up and spin-down band are separated by several eV. The five $d$-electrons of Fe$^{3+}$ form a closed shell configuration and all occupy the lowest band. The extra electron on Fe$^{2+}$ thus occupies the higher energy level and has an opposite spin. This electron is the mobile one and the conduction electrons are thus completely spin-polarised. From band calculations using the local-spin-density approximation (LSDA), it was found that there is a gap at the Fermi level for the majority electrons, but not for the minority electrons [2, 3, 17]. The band at the Fermi level results from the $t_{2g}$ orbital overlap of the iron ions at the B sites.
Zhang and Satpathy [17] found that the energy gap between the spin-up and spin-down electrons is about 3.5 eV (which was also found from photo-emission spectroscopy [61]) and the crystal field splitting is about 2 eV for B site iron. When the exchange splitting is larger than the crystal field splitting, like in the present case, a high spin state is obtained. This supports the calculations that have assumed the extra electron to be in a separate band with opposite spin to the majority electrons.

However, band theory is not correct in describing the spin-polarisation, because the local spin is not taken into account in the band picture. In the band picture, the z-projection of the spin remains a good quantum number, but the spin itself does not. Band theory treats the local spin as a classical object. Therefore, the spin-polarisation in this classical limit is 100%. If the local spin is treated as a proper quantum number, we obtain a different picture. The spin of the $d^6$ configuration is $S = 2$. If an electron is removed from this configuration, it can be either an spin-up or a spin-down electron. In the classical approximation the former would cost a lot more energy than the latter. However, in the quantum treatment there is a finite amplitude of obtaining the same energy when a spin-up electron is removed as when a spin-down electron is removed [62, 63, 64]. The resulting maximum spin-polarisation is then 66.7% [64, 65].

The spin-polarisation at the Fermi level can be studied by spin-resolved photo-emission. These experiments are strongly surface sensitive, so spin fluctuations at the surface will influence the observed spin-polarisation. The (001) surface of Fe$_3$O$_4$ is reconstructed [66, 76, 67] and can influence the spin-polarisation measured with photo-emission. Indeed, Morton et al. found a strong dependence of the spin-polarisation on the surface treatment [68, 69]. For instance, after treating the surface with ion bombardment the spin-polarisation disappears. This strong surface sensitivity could explain why the observed spin-polarisation was found to be less than the theoretical maximum value.

The electronic and magnetic properties of Fe$_3$O$_4$ can be studied in considerable detail using Mössbauer spectroscopy. By placing a Mössbauer active probe layer, the electronic and magnetic properties of thin films can be studied at any desired depth. This has been performed by Fujii et al., who made epitaxial (111) and (001) oriented films [70, 71]. For (111) Fe$_3$O$_4$, the surface was found to have good stoichiometry, but also a broadened component which possibly results from enhanced thermal fluctuations of the atomic magnetic moments at the surface. Also, the B-site component is broadened because the electronic state at the B-site is very susceptible to structural changes taking place at the surface [71]. For (001) Fe$_3$O$_4$ the surface was found to be slightly oxidised, but electron hopping on the B-sites still occurs [70]. Furthermore, there is a distribution of hyperfine fields which reflects a distribution in electronic states.
As mentioned above, in the quantum treatment, the maximum spin-polarisation is 66.7\% \cite{64, 65}. This spin-polarisation would strongly reduced the magneto-resistance effect in Fe\textsubscript{3}O\textsubscript{4}. However, Dedkov \textit{et al.} have observed a spin-polarisation of 80.5 \% in Fe\textsubscript{3}O\textsubscript{4} (111) films \cite{72}. A high magneto-resistance effect of 500\% has been observed between Fe\textsubscript{3}O\textsubscript{4} nanocontacts \cite{73}, which also indicates a large spin-polarisation. It should be noted however that spin flip scattering events are strongly reduced in nanocontacts.

The conductivity behaviour of the epitaxial films is strongly influenced by the presence of APBs, where the electron transport is blocked when the conduction electrons are perfectly spin-polarised. The polarisation can be reduced if spin-flip scattering occurs at the boundaries and because of the anti-ferromagnetic ordering at some of the boundaries. The spin polarisation of epitaxial Fe\textsubscript{3}O\textsubscript{4} films has been studied \cite{65, 68}. The obtained spectra were quite similar to that found for the bulk \cite{64} so it seems that the polarisation is not significantly reduced with respect to the bulk.