Spin-dependent transport across anti-phase boundaries in magnetite films
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Chapter 1

Introduction

1.1 General properties of magnetite

Magnetite, $\text{Fe}_3\text{O}_4$, is the oldest magnetic material known to man. It is abundantly found in nature (especially in rocks) and was first discovered by man in Greece around 2000 BC. It was found in the region called Magnesia, from which the names magnetite and magnetism were derived. Magnetite is magnetic at room temperature, in fact it is ferrimagnetic with a very high Curie temperature of 858 K [1]. Not only is it magnetic at room temperature, magnetite is also conducting and band calculations predict the conduction electrons to be fully spin polarised [2, 3] making it a very interesting candidate for magnetic recording and spin-valve applications. Interestingly, magnetite also occurs in organisms and is believed to be used as a magneto-receptor [4, 5, 6].

In the following sections, a brief description of the use and ubiquitousness of magnetite will be provided.

1.1.1 Research on naturally occurring magnetite

Magnetite occurs in living creatures such as bacteria [6], trout [4], salmon [7] and tuna fish [5]. The morphology of these magnetite crystals is distinctly different in that small magnetite particles, between 20 and 100 nm in size, are arranged in a chain, with gaps between the crystals. Elongated crystals are aligned along their long axis and the chains are very flexible due to the presence of soft organic material around the chains. The small crystals are single magnetic domains.

The chains of magnetite occur both in bacteria [6], so-called magnetotactic bacteria, and in higher organisms such as those mentioned above [4, 5]. In bacteria, the magnetite chains give rise to a permanent magnetic moment so that the bacteria can align themselves with the earth’s magnetic field. In this way, the bacteria can more easily find optimal oxygen concentrations.
in water columns. In fish, the chains of magnetite are believed to act as detector elements because the interaction between the magnetite particles and the earth’s magnetic field results in a torque on the particles which is measurable by the nervous system, a so called magneto-receptor [4, 5].

In the recently discovered meteorite ALH84001, which comes from Mars, Fe₃O₄ crystals with a similar morphology to the magnetite crystals found in magneto-tactic bacteria have been discovered [8, 9, 10]. Because of the distinctive morphology of biological magnetite, it was concluded that these crystals resulted from a biological origin and therefore from a living organism on Mars. These findings are part of the reasons of NASA’s interest in Mars, even though the validity of the experiments performed by Friedmann et al. has been questioned [11].

1.1.2 Research on single crystals and thin films of magnetite

Naturally occurring magnetite has been used by man for ages. For instance, compass needles were made out of magnetite. Even though the material itself is known for a long time, its properties are still the subject of many investigations. Despite the extensive research some of the properties of Fe₃O₄ are still not understood. One prominent example is the so-called Verwey transition, which occurs around 120 K [12, 13]. Above the Verwey transition Fe₃O₄ has a cubic unit cell. On cooling through the Verwey transition the structure distorts from cubic symmetry. At the transition a so called charge ordering occurs as well, which means the conduction electrons become more localised, causing the conductivity to decrease by two orders of magnitude. The nature of this transition is still not understood [14], nor is there any agreement on the exact nature of the charge ordering. for instance, 16 different Fe sites have been identified in the low temperature phase [39].

Besides the natural abundance of magnetite, it has also been synthesised many times, both as a single crystal and in thin film form. In addition to many experimental studies determining the crystal structure, magnetic properties and electrical conductivity, a lot of theoretical work has been performed in order to understand the band structure [2, 3, 15, 16] and the conductivity properties [19, 20, 21, 22].

Due to the development of ultra-high vacuum techniques, the deposition of thin films has increased strongly. Thin films of Fe₃O₄ have properties that deviate from the bulk ones. The magnetisation does not saturate in high fields [23] and ultrathin films below 5 nm become superparamagnetic [24]. The resistivity is increased with respect to the bulk [25, 26] and epitaxial films show magneto-resistance [122, 27, 29]. These findings led to an investigation of the structure of these thin films.

The relationship between the microstructure and the physical properties is
1.2 Motivation

The electron transport in Fe$_3$O$_4$ is predicted to be fully spin-polarised [2, 3] such that it is half metallic. This, combined with the fact that the Curie temperature is very high, makes Fe$_3$O$_4$ a very interesting candidate for spin-valve applications. Spin-valves have received a lot of attention due to their application in magnetic recording read heads [30, 31]. These spin-valves consist of a multilayer of magnetic materials, separated by a thin non-magnetic material. The current in the magnetic materials is spin-polarised. In their ground state, the magnetic materials are coupled anti-ferromagnetically and the resistance through the structure is high. On application of a magnetic field, the two magnetic layers align ferromagnetically, enhancing the electron transport through the structure and consequently the resistance decreases. The multilayer can thus be applied in read heads, as the resistance of the structure will depend on the magnetisation of the magnetic domains on the hard disk. However, to model the magneto-resistance of such a structure is complicated, because the magneto-resistance is influenced by several effects, such as the band structure of the materials, the presence of magnetic impurities, structural disorder and interface roughness [32, 33]. Attempts to apply Fe$_3$O$_4$ in spin-valves were not very successful up to now, as the observed magneto-resistance effect was very low [34]. A proposed explanation for this behaviour was the presence of a so-called magnetic dead layer at the interfaces [115]. However, a magnetic dead layer was shown not to be present [35, 24]. The low magneto-resistance observed in Fe$_3$O$_4$ spin-valves can be explained by studying the microstructure of the films. The epitaxial films contain a high density of anti-phase boundaries (APBs) [23, 24, 36]. At a significant fraction of these boundaries, an anti-ferromagnetic coupling is present and the APBs thus have a strong influence on the spin-polarised conduction electrons of Fe$_3$O$_4$. Even though the presence of APBs reduces the efficiency of Fe$_3$O$_4$ spin-valve multilayers, they also open up a new type of spin-valve application. The APBs themselves will also act like a spin-valve, giving rise to magneto-resistance within a single layer. The advantage of this type of spin-valve is that it does not require a multilayer structure, thus reducing the number of interfaces and the Fe$_3$O$_4$ domains on both side of the boundary have the same band structure. Furthermore, the domains are structurally intergrown and the magnetic properties of adjacent domains are strongly coupled. The APB are atomically sharp interfaces without a disordered region
Chapter 1. Introduction

with switchable magnetic properties.

The central motivation for the work presented in this thesis is to produce a realistic description of the geometrical and magnetic structure at the anti-phase boundaries and to study and describe their influence on the physical properties of Fe$_3$O$_4$ films. Therefore, the main theme of this work is studying the spin dependent transport across the APBs. Related questions that will be addressed are: How does the presence of the APBs influence physical properties such as resistivity, magneto-resistance and the magnetic properties of these films? What is the exact structure at the boundaries and how can we influence the APB density? What about the thermal stability of the APBs? In order to address all these questions, we have grown various Fe$_3$O$_4$ films and systematically studied their microstructure, their magneto-resistance and their magnetic properties.

1.3 Outline

Having discussed the motivation for this work we now proceed with a detailed description of the separate chapters of this thesis. We have chosen to write the thesis in such a way that every chapter can be read independently, without having to read the previous ones. To prevent excessive repetition cross referencing is used throughout the text. It should be noted that this approach inevitably leads to some redundancy for those reading this work from beginning to end.

Chapter 2. Here we describe the fundamental theoretical concepts used in this work. In order to understand the magneto-resistance properties of epitaxial Fe$_3$O$_4$ films, one needs to understand the structure of bulk Fe$_3$O$_4$, which will be explained in §2.2 after which we turn to the structure of epitaxial films in §2.3, where the formation of anti-phase boundaries and the magnetic exchange interactions across the boundary will be explained. The conductivity in bulk Fe$_3$O$_4$, using the single electron approach, will be discussed qualitatively and quantitatively in §2.4. The influence of the presence of APBs in epitaxial films on the conductivity will be discussed in the next paragraph, §2.5. The conductivity was calculated using the single electron approach which assumes full spin-polarisation. Whether the conduction electrons in Fe$_3$O$_4$ are indeed fully spin-polarised has been a subject of debate and experiments have been performed to answer this issue. These results will be discussed in §2.6.

Chapter 3: This chapter discusses the thin film deposition technique of molecular beam epitaxy, MBE, and the techniques used to analyse the
films. We start in §3.2 with a description of the ultra high vacuum setup and the *in situ* analysis techniques RHEED and LEED. The deposition of Fe$_3$O$_4$ films will also be discussed in this paragraph. Subsequently we discuss the use of Mössbauer spectroscopy to determine the stoichiometry of these films, and their magnetic properties in §3.3. Structural analysis of the films, especially the anti-phase domain structure, has been performed using transmission electron microscopy (TEM). In §3.4 the electron microscope itself will first be explained, after which the operation of the TEM will be explained. In the last paragraph, §3.5, the physical property measurement system (PPMS) used to perform electrical conductance and magneto-resistance measurements will be discussed.

Chapter 4: Because the anti-phase domain structure determines the physical properties of the epitaxial films, a good knowledge of the APB density is necessary. In this chapter we have studied the APB density as a function of film thickness and growth parameters. It was found that the APB are not static, but they are able to migrate at relatively low temperatures. The experiments and results studying this migration behaviour will be discussed as well as the corresponding rate law. From the results of the APB density versus growth parameters, a growth mechanism for the MBE growth of Fe$_3$O$_4$ films is postulated.

Chapter 5: When the APBs are formed, there are seven possible shift vectors. In this chapter we present results of a study on the distribution of these shift vectors, i.e. which shift vectors are present and in which proportion. We have further studied the relationship between the APB shift vector and boundary plane. We also present results on the directionality of the boundaries. The exact nature of the anti-phase boundaries determines the magnetic exchange interaction across the boundary. The exchange interactions will depend on the APB shift vector, on the APB plane and the orientation of the plane with respect to the shift. The magnetic couplings for several different types of APBs are discussed.

Chapter 6: We discuss the relationship between the presence of anti-phase boundaries and the resistivity of epitaxial Fe$_3$O$_4$ films. The resistivity of the films strongly depends on the film thickness as the resistivity increases with decreasing film thickness. In this chapter we will show this can be related to a strong increase in anti-phase boundary density with decreasing film thickness. We have used the effective medium approximation to describe the conductivity of the films, which is a function of both the bulk and boundary conductivities and of the fraction in which both phases are present.
Chapter 7: We address the magneto-resistance properties of epitaxial Fe$_3$O$_4$ films. We also present a model to describe the magneto-resistance. The model describes the spin-polarised electron hopping across an anti-ferromagnetic boundary between two ferromagnetic chains. The model incorporates magnetic anisotropy and the magneto-resistance therefore depends on the orientation of the magnetic field with respect to the film surface, which has also been observed experimentally. The model predicts very high magneto-resistance for a single boundary. However, in the Fe$_3$O$_4$ films the domain size is very small, less than 50 nm, and the magneto-resistance is consequently measured over many boundaries. This greatly reduces the MR effect and complicates the modelling. This will also be discussed as well as the temperature and geometry dependence of the MR.

Chapter 8: This chapter is dedicated to the superparamagnetic behaviour of ultrathin Fe$_3$O$_4$ films. Superparamagnetic behaviour only occurs for very thin films. The reason for this was believed to be the fact that the anti-ferromagnetic coupling is frustrated at most of the boundaries and that for thin films the volume of the domains is small enough such that their magnetic moments are able to fluctuate. We will show that superparamagnetic behaviour can be tuned in thicker films by growing them at lower temperatures such that the domain size is reduced. In this chapter we show that the anti-ferromagnetic coupling is not as prominent as initially assumed and the reason why the thin films become superparamagnetic is that this anti-ferromagnetic barrier height can be overcome.

Chapter 9: This final chapter summarises the main results described in this thesis. Further, some remaining questions and recommendations will be discussed.