

Searching Room Temperature Ferromagnetism in Wide Gap Semiconductors

Fe-doped Strontium Titanate and Zinc Oxide



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Abstract

Scientific findings in the very beginning of the millennium are taking us a step further in the new paradigm of technology: *spintronics*. Upgrading charge-based electronics with the additional degree of freedom of the carriers spin-state, spintronics opens a path to the birth of a new generation of devices with the potential advantages of non-volatility and higher processing speed, integration densities and power efficiency. A decisive step towards this new age lies on the attribution of magnetic properties to semiconductors, the building block of today's electronics, that is, the realization of ferromagnetic semiconductors (FS) with critical temperatures above room temperature. Unfruitful search for intrinsic RT FS lead to the concept of **Dilute(d) Magnetic Semiconductors (DMS)**: ordinary semiconductor materials where 3d transition metals randomly substitute a few percent of the matrix cations and, by some long-range mechanism, order ferromagnetically.

The times are of intense research activity and the last few years were astonishingly prolific. Room temperature ferromagnetism has already been reported for a number of such systems based on wide band gap semiconductors. Whereas low-temperature ferromagnetism, e.g. in GaMnAs, can be well described on the basis of carrier-mediated mean-field models, the nature of the high temperature ferromagnetism in wide band gap semiconductors is poorly understood. Indeed, such exotic new materials represent new unexplored grounds of condensed matter physics as dilute ferromagnetic semiconductors with Curie temperatures well above 300 K and large ordered moments per magnetic atom challenge our understanding of magnetism in solids.

This work addresses the main topic of ***search for new above room temperature and giant moment DMSs: Fe ion implanted ZnO and SrTiO₃***. The giant moment FM state was observed in the whole investigated temperature ranges, up to 300 K and 100 K, respectively, with strong indications of a much higher T_C for both systems, along with ***evidence of the diluted configuration of the implanted Fe***. Additionally, a simplified picture of defect-related magnetic ordering is forwarded. Special effort was devoted to SQUID measurements for magnetic characterization and to electron emission channeling (EC) experiments for lattice location of the implanted impurities. Furthermore, the lattice dynamics of Fe:SrTiO₃ was studied by means of Raman spectroscopy and some selected samples were analyzed by means of RBS/C and PIXE for complementary structural characterization.

The demonstrated potential of ion implantation to produce FM layers in commercially available semiconductor materials takes semiconductor industry a step closer to the realization of above room temperature DMSs for a variety of new multifunctional phenomena in spintronic devices. Together with the forwarded insight over the mechanisms involved, it strongly motivates further thorough research.

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Introduction

One shouldn't work on semiconductors, that is a filthy mess; who knows whether any semiconductors exist?

WOLFGANG PAULI [1]

Almost a century later, technology makes elegant use of that once unreliable sensitivity of semiconductor properties to impurities. Integrated circuits and high-frequency devices using the charge of electrons in semiconductors have built the world we live in, from those tinny building blocks that process and communicate information.

Processing speed and integration density of silicon chips have been increasing following the well known “Moore’s law”, which postulates that transistor density on integrated circuits doubles about every two years. However, as this packing endures, the currently used materials are reaching functional limits [2].

Moore's Law is dead. It can't continue forever. In terms of size [of transistor] you can see that we're approaching the size of atoms which is a fundamental barrier, but it'll be two or three generations before we get that far...

GORDON E. MOORE [3]

The end of the road is thus foreseen, but only for today’s technology, operating on the same basic principle of controlling the flow of charges by an applied voltage that was used in the first transistor more than fifty years ago [4]. Rendering devices multifunctional, i.e. introducing the capability of nonvolatile storage and data processing in the same device, one may tackle this atomic barrier to size and speed. Among the nonvolatile physical phenomena, the most appealing is that of ferromagnetic hysteresis. *Ferromagnetism offers high speed and unlimited magnetization reversal, so it is perfect for transistor applications* [5]. A major breakthrough has already been accomplished with the use of the spin degree of freedom in data storing devices. Spin-valves based on the giant magnetoresistance (GMR) effect, which awarded this year’s Noble Prize in Physics to Albert Fert and Peter Grünberg, store nonvolatile bits in hard disks of everybody’s PCs.

With the discovery of GMR and its application in HDRs, one of the first real applications of the promising field of nanotechnology was accomplished. Spintronics had been born making use of localized spins. In a future to come, either adding the spin degree of freedom of the carriers to conventional charge-based electronics or using their spin alone, spintronic devices have the *potential advantages of nonvolatility and increased processing speed, power efficiency and integration densities compared with conventional semiconductor devices* [6]. Nonvolatile digital units that retain logic states when switched on and off would revolutionize the principles of device design. The mode of operation of today’s conventional electronics would be obsolete as these new devices could actually be turned off most of the time. This would allow *year-long operation of mobile electronics and ultrahigh-density integrated circuits free from heat generation problems* [5] just to name a few imaginable possibilities.

In today’s *state of the art* devices, localized magnetic moments store information, charge currents carry and process it and light beams transmit it, but the technology of the future may combine magnetism and semiconductivity in one spintronic device that exploits both charge and spin to process, store and transmit the information. To successfully incorporate the spin degree of freedom into existing charge-based electronics, it is necessary to develop efficient injection, transport, control, manipulation and detection of spin polarization as well as spin-polarized currents. *Semiconductor lasers fed by spinpolarized currents will have better mode stability and lower critical currents. Similarly, a spin transistor consisting of a conductor sandwiched between ferromagnetic contacts is expected to be faster*

and more efficient than a standard field-effect transistor [7]. Furthermore, these new materials would not be restricted to spintronics applications. Indeed, the tackling of speed and size limits could go even further, as they would enable the *efficient injection of spin-polarized current into semiconductors to control the spin state of carriers, which may allow to carry out qubit (quantum bit) operations required for quantum computing* [9, 10].

Because semiconductors are the base of nowadays charge-based electronics, the straightforward approach would be to use semiconductor materials that are intrinsically magnetic. This has not been realized so far because the semiconductors currently used in integrated circuits, transistors and lasers, such as silicon (Si) and gallium arsenide (GaAs), do not contain magnetic ions and are nonmagnetic. On the other hand, ferromagnetic materials used in digital storing devices, such as iron (Fe), cobalt (Co), nickel (Ni) and their alloys are not semiconductors. Moreover, the crystal structures of magnetic materials are usually quite different from that of the semiconductors used in electronics, which makes both materials incompatible with each other when one tries to build functional heterostructures [9]. The obvious solution is to find new *semiconducting materials that display electrically tunable ferromagnetism at temperatures well above room temperature and that can be incorporated into complex integrated circuits* [8]. Back since the 1960s that has been tried with absolutely no success at room temperature (liquid helium temperatures only) [28, 29]. The next (less) obvious solution is to tailor the compounds. Fortunately, Pauli's advice underestimates the capabilities of semiconductors, whose sensitivity to impurities is once more put to test. An approach similar to the electronic doping, which renders *p*- or *n*-type semiconductivity, can be followed to introduce magnetic elements into nonmagnetic semiconductors to make them magnetic. A new concept has emerged and attracted the attention of condensed matter and material science physicists: **dilute(d) magnetic semiconductors (DMS)**, i.e. alloys of standard semiconductors and a few atom-percent of magnetic dopants. However, DMS are useful only if the semiconducting properties "conspire" with the diluted magnetic cations to install ferromagnetic order, which in turn must be attained up to room temperature, if this technology is to be used in everyday applications. Room temperature ferromagnetism has already been reported in a number of DMS material systems. However, if their semiconducting and magnetic properties are indeed dependent of each other, that has not been proved so far.

This manuscript results from a study on such DMS material systems, namely iron (Fe) doped zinc oxide (ZnO) and strontium titanate (SrTiO₃) prepared by ion implantation. The first chapter motivates and introduces the DMS concept, overviews past research and summarizes its current state. The part I, that follows, describes the project working tools. It comprehends four chapters which correspondingly motivate and survey the selected material systems, the magnetic doping method and the characterization techniques, one of which, electron emission channeling, is described in more detail in a devoted chapter not only because it is a non-standard technique but also because the training and understanding of its theoretical and technical trends constituted one of the main efforts of this work. In part II, the results from each technique are presented and discussed. The manuscript finishes with a crossed discussion of the results, global conclusions from the work and a rather exhaustive description of the work that will follow.

Work objectives

- Produce thin layers of diluted magnetic semiconductors by means of ion implantation of Fe into commercially available single-crystalline ZnO and SrTiO₃;
- Characterize the implanted layers properties by means of SQUID (macroscopic magnetic moments), emission channeling (lattice location of implanted Fe) and ion beam channeling (elemental analysis, structural characterization and damage recovery studies);
- Explore the nature of the related magnetism;
- Pinpoint strategies for a subsequent wider research on room temperature DMSs based on wide gap semiconductor nanolayers magnetically doped by means of ion implantation.

Chapter 1

Diluted Magnetic Semiconductors (DMS)

1.1 Motivation and Concept

Either adding the spin degree of freedom to conventional semiconductor charge-based electronics or using the spin degree of freedom alone will add substantially more capability and performance to electronic devices. The advantages of these new devices would be nonvolatility, increased data processing speed, decreased electric power consumption, and increased integration densities compared with conventional semiconductor devices [4-9]. Major challenges in this field of spintronics that are addressed by experiment and theory include the optimization of electron spin lifetimes, the detection of spin coherence in nanoscale structures, transport of spin-polarized carriers across relevant length scales and heterointerfaces, and the manipulation of both electron and nuclear spins on sufficiently fast time scales [4-9]. It is envisioned that the merging of electronics, photonics, and magnetics will ultimately lead to new spin-based multifunctional devices such as spin-FET (field effect transistor), spin-LED (light-emitting diode), spin RTD (resonant tunneling device), optical switches operating at terahertz frequency, modulators, encoders, decoders, and quantum bits for quantum computation and communication [4-9].

Ferromagnetism and semiconducting properties indeed coexist in a few magnetic semiconductors. Among the most extensively studied ferromagnetic semiconductors were europium chalcogenides (e.g. EuSe, EuS, EuO) and chromium chalcogenide spinels (e.g. CdCr_2Se_4 , CdCr_2S_4) that have a periodic array of magnetic elements. In these magnetic semiconductors, which were extensively studied in the late 1960s to early 1970s [28, 29], exchange interactions between the electrons in the semiconducting band and the localized electrons at the magnetic ions lead to a number of peculiar and interesting properties, such as the red shift of band gap when ferromagnetism sets in. Unfortunately, the crystal

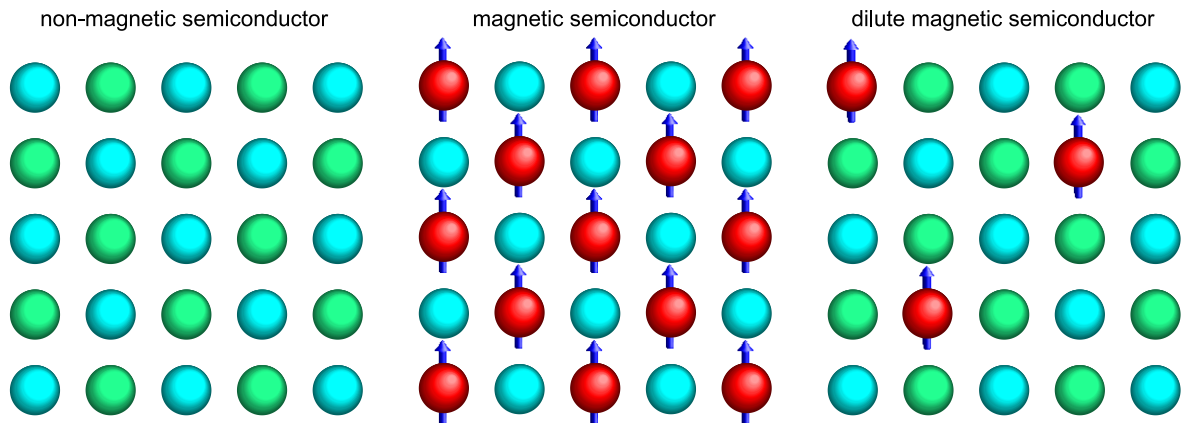


Figure 1.1.1: Representation of different types of semiconductors in this context: non-magnetic, magnetic and dilute magnetic semiconductor (DMS).

structure of such magnetic semiconductors is quite different from that of Si and GaAs. In addition, the crystal growth of these compounds is notoriously difficult - to obtain even a small, single crystal requires weeks of preparation and growth [29]. Furthermore, very low Curie temperatures hampered applications along with the research relevance.

Fortunately however, semiconductors have the particular feature of allowing one to tailor their properties by doping, usually to p - or n -type (electrical doping). This approach is followed to introduce magnetic elements into nonmagnetic semiconductors to make them magnetic. This category of semiconductors, called *diluted magnetic semiconductors*, are alloys of nonmagnetic semiconductor and magnetic elements which randomly substitute a few percent of the host matrix atoms, giving rise to localized magnetic moments in the semiconductor matrix (see figure (1.1.1)). Usually, magnetic moments originate from the unfilled $3d$ or $4f$ shells of transition metals or rare earths, respectively. The usefulness of DMS material systems is constrained in a two-folded manner: (1) by some long range mechanism, the introduced magnetic moments must order ferromagnetically and this FM state must be attained up to maximum typical temperatures of junction operation (~ 500 K); (2) furthermore they must exhibit a spinpolarized conduction band¹, in order to allow, for example, the control of magnetization by an electric field or the use of these semiconductors as spin-polarized current injectors. Indeed, *confirmation of a spin-polarized semiconductor band is the litmus test of the existence of a magnetic semiconductor* [5].

1.2 Past Research

The first DMS generation appeared in the early 1980s, based on II-VI and IV-VI compounds [28].

The $A_{1-x}^{II}Mn_xB^{VI}$ compounds (e.g. $Cd_{1-x}Mn_xTe$, $Cd_{1-x}Mn_xSe$, $Hg_{1-x}Mn_xTe$) were seen as interesting for a number of reasons:

- Their ternary nature allows the tuning the lattice constant and band parameters by varying the composition of the material [30]. Moreover, the substitutional Mn atoms in $A^{II}B^{IV}$ lattice are characterized by highly efficient electroluminescent, which makes the alloys important in the context of optical flat panel display applications.
- The strong exchange interactions between sp band electrons and d electrons associated with $A_{1-x}^{II}Mn_xB^{VI}$ compounds resulted in interesting optical and electrical properties like giant Faraday rotation and magnetic field induced metal-insulator transition [30].
- In these materials the valence of cations matches that of common magnetic ions like Mn. This phenomenon makes this type of DMS relatively easy to make in bulk and thin epitaxial layers.

Fundamental studies were performed on these systems but application was restricted to optical isolators [28]. The magnetic interactions in these DMS are dominated by the antiferromagnetic coupling of Mn spins, which results in paramagnetic, antiferromagnetic or spin glass behaviour [28]. A ferromagnetic DMS based on II-VI materials could not be realized until recently ($T_C \sim 2$ K) [33]. Additionally to such low T_C values, II-VI based DMSs have been difficult to dope either p - or n -type, which made them less attractive for applications [29].

The IV-VI based DMSs (e.g. $Pb_{1-x}Mn_xTe$ and $Ge_{1-x}Mn_xTe$) also attracted attention due to their free carrier induced magnetism. Unlike II-VI DMS, these materials can be grown with higher concentration of free band carriers and their magnetic properties controlled by modifying the carrier concentration through control of native defects. The effect of carrier concentration on the magnetic properties was demonstrated in δ -doped $PbSnMnTe$ [36]. Recently, a ferromagnetic transition temperature as high as 100 K was reported in Fe doped $GeTe$ films [34], but still far from the room temperature goal.

The second DMS generation, compatible with the semiconductors used in present-day electronics, was based on III-V compounds. The III-V semiconductors such as GaAs and InAs have major markets IR LEDs and lasers and magnetic sensors and are applied in a number of electronic and optoelectronic devices, such as mobile phones (microwave transistors), compact disks (semiconductor lasers), and in many other applications. Magnetic III-V semiconductors would therefore introduce magnetic capabilities into well established optical and electrical devices [32]. However, the lack of

¹Of course, a straightforward approach to produce semiconductor material systems exhibiting a FM hysteresis would be to spread FM particles (e.g. high T_C Fe clusters) in the matrix. It would certainly fulfill requirement (1) but very hardly would it exhibit the properties described in (2).

material technologies for magnetic doping of III-V compounds [33] hampered DMS research in these materials. The equilibrium solubility of transition metal atoms into these semiconductors is as low as $\sim 10^{18} \text{ cm}^{-3}$ [35] or less. Above a certain doping concentration, surface segregation and even phase separation occurs precluding further (diluted) incorporation of magnetic ions into the crystals. Therefore, preparation of DMS ternary alloys of III-V semiconductors was an extremely difficult task. No DMS based on these materials was realized until ferromagnetism in epitaxial films of $\text{In}_{1-x}\text{Mn}_x\text{As}$ grown by Molecular Beam Epitaxy (MBE) was reported in 1992 and $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ ($T_C \sim 110 \text{ K}$) in 1996 [37, 38]. The low temperature crystal growth of MBE technique prevents the formation of a secondary phase and these systems have been investigated extensively in an attempt to increase the ferromagnetic transition temperature to more practical limits. So far, the highest reported Curie temperature in Mn δ -doped GaAs is $\sim 172 \text{ K}$ [31].

Room temperature ferromagnetism was additionally reported (2000) in a II-IV-V₂ type chalcopyrite compound CdGeP_2 doped with Mn [28]. Also a group IV ferromagnetic semiconductor $\text{Mn}_x\text{Ge}_{1-x}$ was reported in 2002 [39]. It followed a prediction based on mean field solution of Zener model that ferromagnetic (FM) order can be stabilized in group-IV semiconductors like Si, Ge and $\text{Si}_{1-x}\text{Ge}_x$. The single crystal $\text{Mn}_x\text{Ge}_{1-x}$ films on Ge and GaAs (001) substrates have Curie temperatures varying linearly with the Mn concentration from 25 K to 116 K.

Finally, in 2000, DMS research (theoretical and experimental) received large momentum from the theoretical predictions² of **above room temperature ferromagnetism** in DMS systems based on Mn doped wide band gap semiconductors, namely ZnO and GaN.

1.3 State of the Art

Room temperature ferromagnetism has already been reported for a number of DMS systems based on the wide band gap semiconductors GaN and ZnO [13-19, 24]. However, also the semiconducting oxides SrTiO_3 , BaTiO_3 , KTaO_3 , TiO_2 and SnO_2 are actively investigated and very promising in that respect [13-18]. Recently, also the rare earth (RE) element Gd incorporated into GaN has been observed to exhibit *colossal* magnetic moments at room temperature [20, 21].

Whereas low-temperature ferromagnetism, e.g. in Mn doped GaAs, can be well described on the basis of carrier-mediated mean-field models [11, 12], the nature of the high temperature ferromagnetism in wide band gap semiconductors, in some cases with large ordered moments per transition-metal//rare-earth cation, is poorly understood. Super-exchange, which is predominantly antiferromagnetic and short-ranged, cannot be invoked because the magnetic order appears already at concentrations of magnetic cations of a few percent. In any case, the average net moment per magnetic cation in ferromagnetically ordered superexchange systems is rarely much more than one Bohr magneton. The ferromagnetic double-exchange mechanism, as described by Zener with reference to mixed-valence manganites, can produce large moments, but it is also a nearest-neighbor interaction. In response, it has been proposed that, in high- k dielectrics with degenerate or thermally activated n -type semiconductivity, ferromagnetic exchange is mediated by shallow donor electrons forming bound magnetic polarons which overlap to create a spin-split impurity band [17]. However, the symptomatic observation of a magnetic moment per impurity atom exceeding the spin-only value, the so called *giant* moment, points towards the magnetism arising from the interplay of the magnetic impurities with crystalline defects which play the twofolded role of somehow activating the magnetism of the impurities and contributing directly for the total magnetic moment [17, 20, 21, 26, 27]. Such defect-mediated magnetic interaction would constitute a new type of ferromagnetism.

On the other hand, one of the key unanswered questions is whether the materials under question indeed contain uniformly distributed transition-metal elements or contain clusters, precipitates or second phases that are responsible for the observed magnetic properties [15, 16]. This is a common criticism towards the reported RT DMSs not only because the magnetic properties vary greatly for samples of the same nominal composition prepared by different groups but also because it seems that virtually any TM doped semiconductor/oxide material exhibits a FM state in some concentration and temperature regime. Indeed, there even appeared a report of room-temperature ferromagnetism of pure HfO_2 [23], which contains no magnetic ions at all.

Consequently, methods establishing lattice location or chemical state have been proposed in order to give more insight into possible mechanisms for the observed ferromagnetism [15, 19]. It has

²By a mean-field model of ferromagnetism mediated by delocalized or weakly localized holes in zinc-blende and wurtzite diluted magnetic semiconductors [11, 12].

consistently been pointed out that a successful explanation cannot be reached without a detailed understanding of the structural properties of the doped materials, and a wide range of analytical techniques are required in order to reach a comprehensive picture in that respect [13-19, 24].

For most studies reported in the literature, dilute magnetic semiconductors have been produced by introducing the dopant during growth, for instance during bulk crystal growth, by means of molecular beam epitaxy or metal-organic chemical vapor deposition of single crystalline layers, sputter deposition or pulsed laser deposition of thin polycrystalline layers. However, ion implantation is becoming an increasingly important tool in that respect and some encouraging results from ion implanted Cr:GaN, Gd:GaN, Co:ZnO, Mn:ZnO and Fe:ZnO have recently been reported in the literature [14, 15, 16, 19, 21, 26, 27]. The advantage of ion implantation is that it is less likely to suffer from the formation of second phases and hence may be superior with respect to the realization of single-crystalline magnetic nanolayers. As was already mentioned, there are strong indications that the occurrence of ferromagnetism in certain transition-metal or rare-earth doped wide bandgap semiconductors is related to the interaction with defects present in the material [17, 20, 21, 26, 27]. Instead of being detrimental, the role of defects may thus be beneficial or even necessary for the occurrence of ferromagnetism in these materials. In that respect, defects which are specifically introduced in ion implantation might even play a crucial role in order to achieve the ferromagnetism. The relation between defects and magnetic impurities thus needs to be clarified.

As a final important remark, despite the encouraging high- T_C ferromagnetism reported in a number of different dilute magnetic semiconductors, no evidence for coupling between magnetic and semiconductor properties has so far been reported.

Part I

Project Description

Chapter 2

Material Systems

Wide band gap semiconductors (WBGs) can be roughly defined as semiconductors with an energy gap E_G corresponding to the blue or ultraviolet (UV) range of the optical spectrum, i.e. above 2.5 eV. Typical examples are SiC ($E_G = 2.4\text{--}3.2$ eV, depending on polytype), ZnSe (2.8 eV), GaN (3.4 eV), diamond (5.5 eV), AlN (6.2 eV), **ZnO** (3.4 eV) and **SrTiO₃** (3.2 eV). There exist already many technological applications for WBGs, such as light emitting diodes or lasers in the blue and UV, visible-blind detectors for UV light, high-temperature high-power transistors, or gas sensors. Recently, WBGs have also appeared in the field of multiple-color electroluminescent devices suitable for displays. Along with the fact that WBGs are seen as the best candidates for room temperature DMS behavior, such technological context looms a new generation of spintronic materials.

In the following, the WBGs materials ZnO and SrTiO₃, selected for this work research, are presented. The most relevant physical properties and technological applications are described and a short overview of the relevant DMS-related literature is given. Iron (Fe) was chosen as the magnetic dopant for these material systems. This choice was somewhat arbitrary, as no selectivity among the *3d* TMs is clearly evidenced in the literature.

2.1 Strontium Titanate Perovskite

For a long time, perovskite type oxides have attracted attention regarding their electrical, magnetic and optical properties, such as superconductivity, colossal magnetoresistance and ferroelectricity. Currently, many investigations are underway to enlarge the ability to tune these properties and to create new materials for oxide electronics applications.

Among the perovskite oxides, strontium titanate SrTiO₃ (usually referred as ST or STO) has been amongst the most popular materials, as it exhibits a set of unusual electronic and structural properties, such as the anti-ferrodistorsive phase transition at 110 K, incipient ferroelectricity, polar soft mode behaviour which have generated an intense research activity in the last decades, specially regarding lower than cubic symmetry lattice geometries: tetragonal, orthorhombic and even (possibly) rhombohedral.

Concerning the applications, its high dielectric permittivity, that increases on cooling following the Curie-Weiss law between 100 K and 240 K, and its low microwave (MW) losses, makes STO the most attractive material for tunable MW (low temperature) electronics devices such as phase shifters, filters, delay lines and tunable oscillators. Moreover, STO has attracted a great deal of interest in the world of oxide electronics, not only as a high dielectric insulator, but also as a wide-gap semiconductor (band gap of approximately 3.2 eV).

Strontium titanate yields *n*-type semiconductivity when doped with oxygen vacancies (reduction) or impurities (Nb or Ta on the Ti sites and La on the Sr sites). This allows STO to be used as channel layer in a field effect transistor (FET). Furthermore, by combining a wide gap insulator with undoped SrTiO₃, it is possible to produce metal-insulator-semiconductor (MIS) heterostructures where STO plays the role of semiconductor. The availability of high-quality single crystal SrTiO₃ substrates makes it an attractive material to grow such MIS structures. Although the existence of *p*-type SrTiO₃ has so far not been confirmed, one can envisage its usefulness. It would become a wide-gap semiconductor diode in the blue-light region, of major relevance in semiconductor industry. Moreover, it is well known that *p*-type perovskites accommodate protonic conductivity. The protonic conductors are important

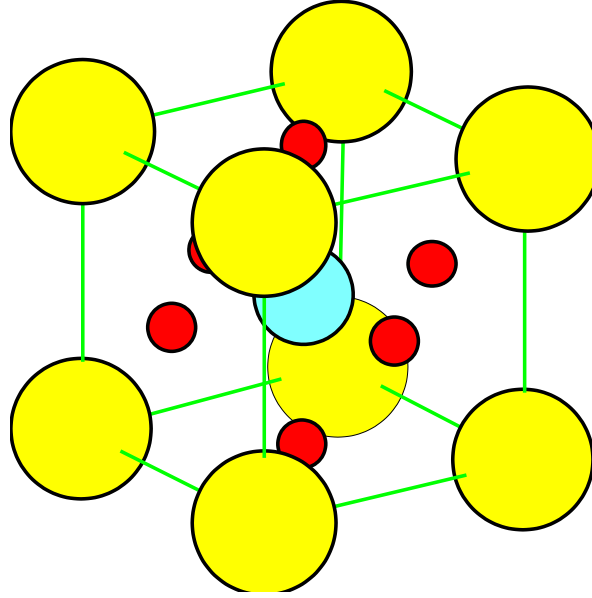


Figure 2.1.1: Perovskite unit cell of Strontium Titanate (SrTiO_3). Here, titanium atoms are represented as blue, strontium as yellow and oxygen as red circles.

materials for a wide variety of electrochemical applications such as fuel cell and hydrogen sensor in the renewable energy-source industry.

Furthermore, the ability to control the conductivity of SrTiO_3 is important to design semiconductor/semiconductor device applications such as the metal oxide semiconductor field effect transistor (MOSFET). The functionality of these devices is optimized by the choice of semiconductor substrate and a controlled doping, which can easily be achieved by ion implantation. MOSFETs are the basis of nowadays technology and are currently made of a Si semiconducting substrate and an insulator which is its corresponding oxide, SiO_2 . This system has a number of advantages: the structural quality of the interface (low defect and imperfection density) and its high mechanical and chemical stability in a broad range of external conditions have contributed to the success of traditional MOSFETs to date. However, with the shrinking of MOSFETs and consequently the effective gate oxide thickness up to the atomic level, the conventional SiO_2 oxide is quickly approaching its fundamental scaling limit due to severe direct tunneling leakage. Among the possible routes to overcome this limitation allowing the development of a new generation of nanotransistors, the most promising is the substitution of the SiO_2 insulating layer with a higher- k dielectric material like STO. The lattice mismatch between STO ($a_0 = 3.905 \text{ \AA}$) and Si ($a_0 = 5.431 \text{ \AA}$) is fairly small ($\sim 1.7\%$) when the SrTiO_3 unit cell is rotated 45° around Si surface normal $[001]$ axis. This high degree of structural compatibility of STO with Si makes molecular beam epitaxy (MBE) possible. The key to exploit alternative materials (oxides) is the possibility to grow high quality interfaces between the various device components. In the last decades, this has been made possible thanks to the vast development of MBE growth techniques of highly ordered interfaces between silicon and crystalline oxides¹.

STO and DMS research

All these characteristics make STO a perfect candidate for the new generation of spintronic materials if DMS capabilities can be incorporated. However, the literature on magnetic properties of TM doped STO is almost nonexistent and can be summarized in the following.

The TMs Co [40] or Mn [41] were implanted, at high temperatures, into single-crystal SrTiO_3 . Following annealing at 700°C , ferromagnetic behaviour was observed over a broad range of concentrations with magnetic ordering temperatures above 300 K and coercivities $\leq 70 \text{ Oe}$, with the exception

¹For device applications, high quality epitaxial oxide films are expected to offer better uniformity, lower leakage and higher reliability than amorphous and polycrystalline materials.

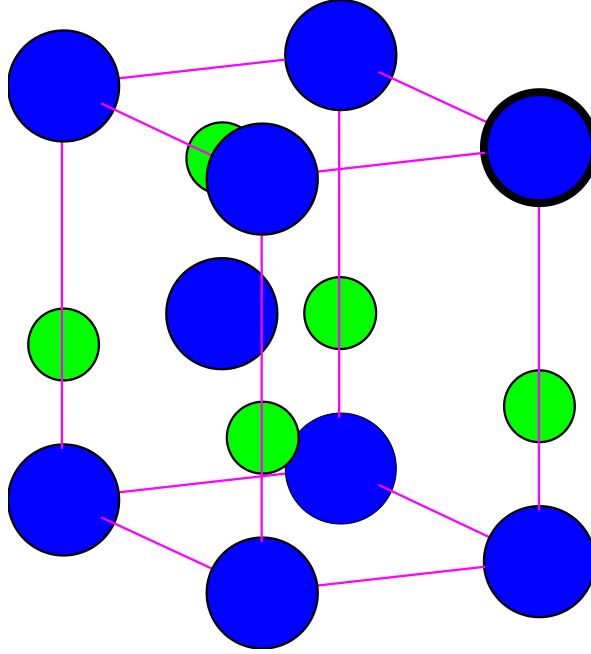


Figure 2.2.1: Wurtzite unit cell of zinc oxide (ZnO) with the oxygen atoms (green) forming a *hcp* lattice and the zinc atoms (blue) occupying half of the tetrahedral positions.

that, at high Mn concentrations (≥ 5 at.%), Mn:SrTiO₃ was no longer ferromagnetic. No secondary phases were detected within the sensitivity of high-resolution X-ray diffraction.

Thin films of 0.5% and 1% Nb:SrTiO₃ doped with 2 at.% of the 3d TMs Cr, Co, Fe, Mn were also examined for ferromagnetism [42]. X-ray diffraction, Rutherford backscattering ion channeling, scanning transmission electron microscopy Z-contrast imaging, and electron energy loss spectroscopy techniques established high crystalline quality of the films with no impurity phases and highly uniform dopant distribution. Although the film conductivity improved dramatically by Nb doping, no ferromagnetism was found in any of the samples over the temperature range of 365 K down to 5 K.

To our knowledge, there are no other reports on DMS related studies of TM doped STO in the literature and, therefore, a whole new and promising ground is yet to be explored.

2.2 Zinc Oxide Wurtzite

The technological relevance of ZnO is recognized for a long time. Characterized by high potential for functionalities utilizing wide band (3.3 eV) gap in the UV region, piezoelectricity and the large exciton energy (60 meV), it has wide applications in electronic devices such as transparent conductor, thin film gas sensor, varistor, surface acoustic wave (SAW) devices, optical wave-guides, acousto-optic modulators/deflectors, ultraviolet LASER source, and ultraviolet detectors.

In the last decade, great development of the growing techniques was achieved, namely by metal organic vapor deposition (MOCVD), molecular beam epitaxy (MBE), hydride vapor phase epitaxy (HVPE) and laser ablation, which in turn allowed scientific work in the field of the physical properties, among which the optical characterization. Zinc oxide is a II-V semiconductor oxide and crystallizes in the wurtzite structure (hexagonal, with $a = 3.25 \text{ \AA}$ and $c = 5.12 \text{ \AA}$) with the oxygen atoms forming a *hcp* lattice and the zinc atoms occupying half of the tetrahedral positions. The ionic radii ratio is 0.53 and only 44% of the unit cell volume is “occupied”, which means that ZnO has a relatively open structure, being relatively easy to dope. This characteristic also affects the nature of the defects, which has been a matter of great controversy in the past few years. With intrinsic defect levels laying approximately 0.05 eV below the conduction band, it is an *n*-type semiconductor with room temperature hall mobility (in single crystals) of the order of $200 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. The *n*-type doping via defects originates from Zn interstitials and p-type conductivity was argued to be induced by using a co-doping technique [25], which has not been well established so far.

Emerging interest on ZnO is related to its tunable conductivity, good optical transmission, hardness and low toxicity, features of privilege when compared with other II-VI compounds. Of particular relevance are the recent advances in the fabrication of ZnO based LEDs which may be superior to the ones based on nitrides. Compared with other semiconductor lasers, ZnO emission has the advantage of being observed in all directions. This makes it of particular interest towards flat panel display applications, with the possibility of low cost device production, which certainly would have great impact in the market.

ZnO and DMS research

In many regards, ZnO is the archetypical wide-bandgap semiconductor. Compared with other oxides that have been investigated as DMSs (for example, TiO_2 and SnO_2), ZnO is relatively well behaved from an experimental point of view, affording the possibility for extensive systematic experimentation and data analysis.

Along with GaN, ZnO was the precursor of a new age of intense research on DMS systems, for its potential to high Curie temperatures and the relative lack of ferromagnetic second phases in the material. Indeed, theoretical predictions suggested that room temperature carrier-mediated ferromagnetism [11] should be possible in ZnO (albeit for the *p*-type material) which resulted in a major outburst of research in this material (and GaN). *Ab initio* calculations also predicted ferromagnetism in the n-type ZnO doped with most transition metal ions [43]. Moreover, ZnO is the typical host material in Coey's alternative model of RT DMS [17].

After the work of Dietl *et al.* in 2000 [11], which pointed ZnO based DMSs (albeit strongly *p*-type) as the most promising to exhibit above room temperature ferromagnetism, it became one of the most studied materials in the field of DMS. Indeed, ferromagnetism has already been reported on a number of different systems, prepared by different techniques, under different conditions and the reader is referred to thorough reviews on the subject [13-16, 22].

A new chapter of ZnO based DMSs history is, however, in its first pages. Ferromagnetic Co:ZnO, grown by direct current reactive magnetron co-sputtering, has been recently observed to exhibit a magnetic moment per impurity atom of $6.1 \mu_B$, exceeding the spin-only value of Co [24]. This new phenomena points towards magnetism arising from the interplay of magnetic impurities with crystalline defects and challenges present concepts for a theoretical modeling of room temperature ferromagnetism in DMS materials.

Chapter 3

Sample Preparation

3.1 Ion-Implantation

Ion implantation is a standard technique to incorporate impurities (foreign atoms) into a host material. It follows a simple principle: atoms or molecules are ionized in an ion source, extracted, and accelerated by a high-voltage electrode. Subsequently the ion beam is mass-separated in an analyzing magnet and finally is steered in order to impinge on the desired material.

Ion implantation offers several advantages which motivate its application to DMS production:

- Being a non-equilibrium technique, allows doping above equilibrium solubility limits to which some other techniques are limited. Although it is observed that for DMS production such high concentrations of the magnetic dopant are not required, it may be important if co-doping with other elements is necessary for FM enhancement or multifunctional purposes (electrical doping etc.).
- At least in the RT range, this technique is not prone to dopant precipitation allowing a relatively homogeneous implantation, vital for the required intrinsic FM in DMS. This is due to the fact that during the implantation process itself the ions have a very low probability for reacting with each other while the formation of clusters during thermal annealing can be controlled by optimizing the thermal budget *vs.* the diffusion coefficients of the implants.
- Unrivalled versatility, allows the implantation of virtually any dopant into any material.
- The collision processes inherent to the ballistic implantation are prone to the production of defects, which might play an important role in the stabilization of the ferromagnetic state in all of the theoretical pictures presently proposed¹. Acceptor defects and (shallow) donor defects are favorable to the models of Dietl *et al.* [11, 12] and of Coey *et al.* [17], respectively, and vacancies of particular elements may actually be the main magnetic entities in some DMSs while the TM dopants play the role of mere FM trigger [95, 94].
- Ion implantation technique is widely used in semiconductor industry. Therefore, any conclusions drawn from these studies are particularly close to device application.
- Indeed, it is becoming an increasingly important tool for DMS production with some encouraging results: Cr:GaN, Gd:GaN, Co:ZnO, Mn:ZnO and Fe:ZnO have recently been reported in the literature [14, 15, 16, 19, 21, 26, 27].

Another advantage is the fact that ion implantation is the preferred technique to incorporate radioactive probes into crystals for emission channeling experiments (section 5) and thereby the compatibility of results is assured. In turn, this preference arises from several specific advantages:

- Ion beam implantation allows fast incorporation of the produced isotopes and following measurement, which is specially vital when short-lived isotopes are used.

¹However, for this to be a complete advantage the defect production should be monitored somehow e.g. by positron annihilation spectroscopy.

- The analyzing magnet ensures that only the desired isotope is implanted, thereby avoiding contamination with other particle emitting isotopes, which would perturb the emission channeling pattern.
- The depth profile can be accurately controlled by the acceleration energy. Knowledge of this depth is necessary for the simulation of the theoretical emission channeling patterns (see section (5.4.1)).
- The integration of the beam current allows exact control of the probe atoms fluence.
- The lateral profile can be manipulated by collimation of the beam or by masking of the sample. A coned implantation spot is required in order to obtain a good angular detection resolution (see section 5.3.2).
- As mentioned above, ion implantation is widely used in semiconductor industry using stable ions. Therefore, emission channeling experiments with implanted radioactive isotopes (of relevant electrical, optical and magnetic dopants) give important feedback on the lattice sites occupied by implanted species in real devices.

In the process of ion implantation, the impinging ions collide with the host atoms displacing them from their lattice sites. The displaced atoms can then collide with other host atoms, thus creating a *collision cascade*. The amount of damage that is created depends on a number of factors: the host material, the ion fluence and energy, the mass of the implanted ions, the substrate temperature, the implantation geometry (relative to the crystal structure), etc. In the limiting case, it can lead to the amorphization of the implanted layer if the collision cascades from different ions overlap significantly². Because of the sensitivity of the electron emission channeling technique, typical fluences of only 10^{12} to 10^{13} cm^{-2} are necessary. In this range, only a small amount of crystal damage is usually observed.

The industrial 200 kV high-current Danfysik implanter of Instituto Tecnológico e Nuclear (ITN), able to implant with energies ranging from 30 to 200 keV (or even 400 keV when double charged ions can be produced with sufficiently high yields), was used for the stable implantation.

3.2 Radioactive implantation at CERN's facility ISOLDE

For the emission channeling experiments (see chapter 5) the implantations with radioactive probes were performed at ISOLDE [56]. This CERN facility is equipped with two radioactive on-line isotope separators: GPS (general purpose separator) and HRS (high resolution separator). The layout of both separators is essentially the same, except for the magnet system. HRS is equipped with two magnets for superior mass resolution, while GPS has only one. A schematic layout of ISOLDE is shown in figure 3.2.1.

The radioactive isotopes are produced in nuclear reactions caused by a 1.4 GeV proton beam impinging on a target. Different target materials are used at ISOLDE, depending on the desired isotopes to be produced. The next step is the ionization of the radionuclides. Heating the target enables the out diffusion of the isotopes towards the ion source. The standard ion source is based on the principle of atom ionization when in contact with a high-temperature metallic surface. This so-called *surface ion source* consists of a metal tube, usually tungsten, that can be heated up to 2400° C. The weakness of this approach is the lack of chemical selectivity, which can lead to a large contamination with unwanted elements. When a large isobaric contamination precludes the desired beam purity or when the desired elements cannot be efficiently ionized by other types of ion sources, use is made of another type of ion source: *resonant laser ion source*. In this case, the ionization is achieved through the stepwise excitation, by laser light that is tuned to the corresponding energies, of two or three atomic transitions, leading to auto-ionizing states or directly to the continuum.

After ionization, the radioactive ions are extracted and accelerated up to an energy of 60 keV by an electrode. The beam is then focused by electrostatic quadrupole elements and mass separated by an analyzing magnet. Subsequently the ions are steered into one of the several beam lines, where they are further focused, collimated, and finally implanted into the desired host material.

The radioactive implantation was performed in a simple implantation chamber that is connected to one of the ISOLDE beam lines. Up to eight samples can be mounted simultaneously on a sample

²The standard method to restore the crystal structure after implantation is high-temperature annealing.

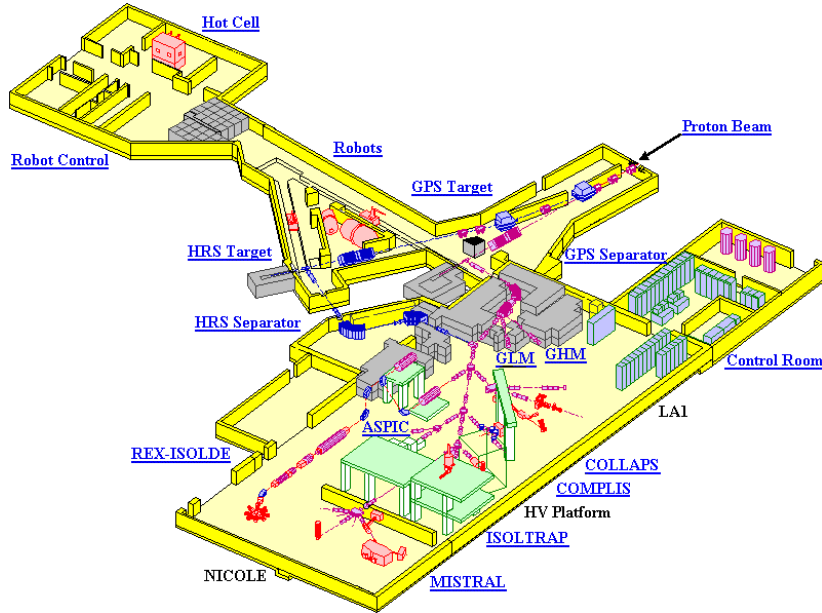


Figure 3.2.1: Layout of ISOLDE facility (CERN).

holder, allowing multiple implantations without breaking the vacuum. The surface normal of the sample holder (usually corresponding to [100] for cubic and to [0001] for hexagonal crystals) was tilted by 7° with respect to the beam to minimize channeling of the ion beam. A collimator with a hole of 1 mm diameter was placed in front of the sample holder, at a distance of a few centimeters³. The implantation fluence is determined by integrating the beam current measured on the sample holder. A voltage of 200 V is applied during implantation to a suppressor plate in front of the sample holder in order to minimize the emission of secondary electrons from the sample, which would otherwise contribute to the beam current readout. Typical radioactive beam currents at ISOLDE range from 3 to 100 pA.

3.3 Impurity and damage profiles

The ion beam fluence (number of ions per unit area) is controlled during implantation. Furthermore, conventional analytical techniques determine total concentrations (e.g. by chemical methods) or, in the best case, local fluences (e.g. by ion beam analysis). In order to complete the knowledge of the local distribution of implanted impurities, which is of particular importance for DMS research, one usually relies on numerical simulations to determine the depth profiles.

Conventional methods used to calculate ion ranges are based on the binary collision approximation (BCA). In these methods the movement of ions in the implanted sample is treated as a succession of individual collisions between the recoil ion and atoms in the sample. For each individual collision the classical scattering integral is solved by numerical integration. The most popular BCA simulation program is TRIM/SRIM (short of TRAnsport of Ions in Matter / in more recent versions called Stopping and Range of Ions in Matter), which is based on the ZBL (Ziegler, Biersack, Littmark) electronic stopping and interatomic potential. Although fast, this code does not take in account the crystalline structure of the material as, for example, MARLOWE code. However, when the beam is not aligned with a low index crystal axis (the reason for the 7° tilt of the samples during implantation) TRIM calculations are quite reliable.

TRIM/SRIM code

SRIM is a group of programs which calculate the stopping and range of ions into matter using a quantum mechanical treatment of ion-atom collisions (assuming a moving atom as an "ion", and all target atoms as "atoms"). It results from the original work by J. P. Biersack on range algorithms [47]

³Collimation of the beam is required to obtain the desired angular resolution of the EC measurements (see section 5.3.2).

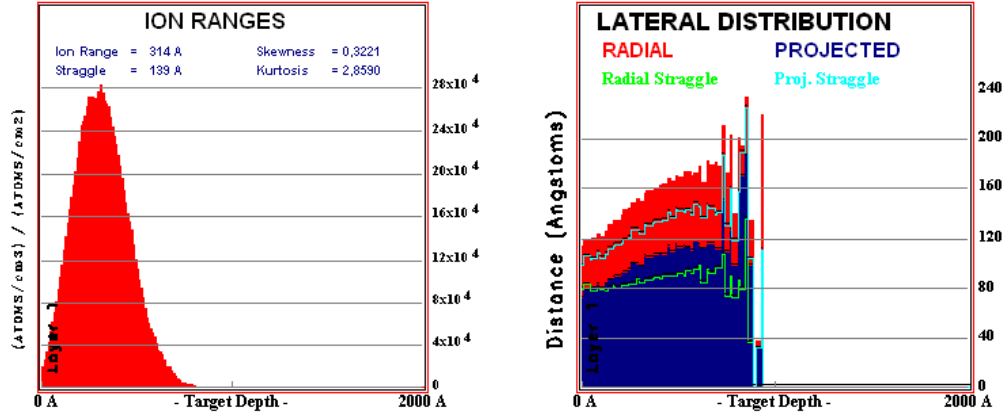


Figure 3.3.1: Longitudinal and lateral ion range profiles simulated by TRIM code for a 60 keV Fe^+ ion beam impinging into SrTiO_3 .

and the work by J. F. Ziegler on stopping theory [46]. A full description of the calculation is found in [55].

This calculation is made very efficiently by the use of statistical algorithms which allow the ion to make jumps between calculated collisions and then averaging the collision results over the intervening gap. During the collisions, the ion and atom describe a screened Coulomb collision, including exchange and correlation interactions between the overlapping electron shells. The ion has long range interactions creating electron excitations and plasmons within the target. These are described by including a description of the target collective electronic structure and interatomic bond structure when the calculation is setup (tables of nominal values are input parameters). The charge state of the ion within the target is described using the concept of effective charge, which includes a velocity dependent charge state and long range screening due to the collective electron gas of the target.

TRIM (TRAnsport of Ions in Matter) is the most comprehensive of the programs included. It accepts complex targets made of compound materials with up to eight layers. It calculates both the final 3D distribution of the ions and also all kinetic phenomena associated with the ions energy loss: target damage, sputtering, ionization, and phonon production. It has default parameters for all ions in all materials up to an ion energy of 1 GeV⁴.

Depth profiles

As an example, TRIM simulated longitudinal and lateral ion ranges in STO material, for a 60 keV beam, are shown in figure 3.3.1. Since the beam sweeps the whole sample surface during implantation, one expects a homogeneous lateral distribution. Thereby, the relevant output parameters refer only to the approximately Gaussian depth profile: the average depth and its standard deviation (*ion range* and *straggle* in the program⁵), plotted in figure 3.3.2 as a function of beam energy. It should be noted that this dependence is not an handicap of the technique but a bonus. Indeed, by means of multiple-energy implantation, it adds some degree of freedom to the implanted layer design, overcoming the true handicap of a constrained shape (and thickness) when single-energy implantations⁶ are performed.

The simulated depth profiles are usually very accurate for standard conditions. However it must be noted that annealing at relatively high temperatures (depending on the material and and implanted element) may change them in some extent due to short-range diffusion of the implanted ions.

⁴At very high energies (larger than several hundreds of MeV per nucleon), nuclear reactions and (especially for electrons) *bremsstrahlung* and *Cerenkov* radiation contribute to the slowing down of all charged particles and are not implemented in the code. Nevertheless, typical implanters (for semiconductor application/industrial purposes) are in the hundreds of keV range.

⁵In fact, the program calculates the *straggle*, the *skewness* and the *kurtosis*, quantities related to the second, third and forth moments of the ion distribution.

⁶This approach has not been used in this work, but is intended to, in the future work. In particular, these samples would exhibit larger magnetic signals for a given concentration, which is of major relevance for the magnetic characterization, since the low fluence magnetic layers prepared by single energy implantation are usually near in the SQUID sensitivity limit.

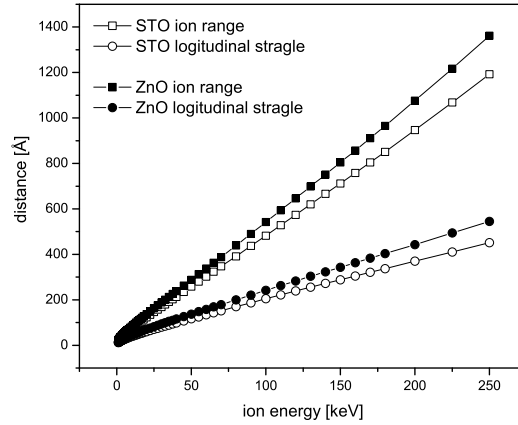


Figure 3.3.2: Ion ranges and longitudinal straggle as a function of beam energy calculated by TRIM code for a Fe^+ ions impinging into ZnO and SrTiO_3 .

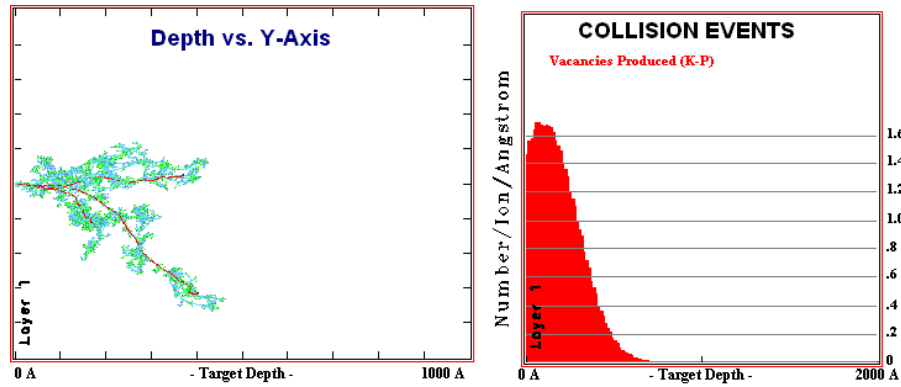


Figure 3.3.3: (Left) Collision cascades of (three) Fe^+ ions (60 keV) impinging into ZnO simulated by TRIM code: trajectories of Fe ions are red and of Zn (removed from their lattice sites when struck by the Fe ion) are green.

Figure 3.3.4: (Right) TRIM simulated depth profile of vacancies produced by implantation of Fe^+ ions (60 keV) into STO.

Collision cascades and damage

Another important parameter is the damage created during the implantation, i.e. the defects introduced into the crystal. In the beginning of the slowing-down process at high energies, the ion is slowed down mainly by electronic stopping and it moves almost in a straight path. When the ion has slowed down sufficiently, the collisions with nuclei (the nuclear stopping) become more and more probable, finally dominating the slowing down. When atoms of the solid receive significant recoil energies when struck by the ion, they will be removed from their lattice positions, and produce a cascade of further collisions in the material. These collision cascades are the main cause of damage production during ion implantation in metals and semiconductors. To incorporate this phenomena into the simulations, one specifies the threshold energy above which the atom from the host matrix is removed⁷. The most straightforward estimate is the cohesive energy: the energy required to break the atoms of the solid into isolated atomic species, (i.e, the energy difference between the lattice configuration *vs.* isolated atoms). It can be experimentally measured or determined by *ab initio* calculations (see [48] for ZnO and [49] for STO). This approach is however rather artificial, considering the non-equilibrium character of implantation damage. An alternative approach is to use is the threshold displacement energy

⁷This is the energy that a recoil needs to overcome the lattice forces and to move more than one atomic spacing away from its original site. If the recoiling atom does not move more than one lattice spacing, it is assumed that it will hop back into its original site and give up its recoil energy into phonons.

thesis name	original name	^{56}Fe fluence [cm $^{-2}$]	^{56}Mn fluence [cm $^{-2}$]	ion range [nm]	straggle [nm]	maximum at. %
STO_VG	STO virgin	-	-	-	-	-
STO_EC	STO Fe #236	-	3×10^{14}	31.4	13.9	0.2
STO_LF	STO Fe #257	1×10^{15}	2×10^{14}	31.4	13.9	2.5
STO_HF	STO Fe #256	5×10^{15}	1×10^{14}	31.4	13.9	11
ZNO_VG	ZnO virgin	-	-	-	-	-
ZNO_LF	ZnO Fe #233	1×10^{15}	-	29.1	13.4	2.0
ZNO_MF	ZnO Fe #255	5×10^{15}	2×10^{14}	29.1	13.4	8.8
ZNO_HF	ZnO Fe #254	1×10^{16}	2×10^{14}	29.1	13.4	17

Table 3.4.1: List of samples and implantation specifications.

(TDE), i.e. the minimum kinetic energy transferred to an atom in the lattice from an impinging particle necessary to permanently displace an atom from its lattice site, thus generating a stable defect. Although better suited for describing radiation damage, it implies the extra complexity that different defects may be produced (Frenkel pairs, antisites...), each one with a different TDE. For the case of TDE, DFT calculations are preferred over experimentally determined values, given the difficulty to distinguish effects from different types of defects. Typical values range from a few to a hundred eV ([50] for ZnO and [51] for STO). Furthermore, the TDE value provides a lower limit of the particle kinetic energies that must be considered in molecular dynamics (MD) simulations of radiation damage (more accurate than the BCA approach used by TRIM).

Another source of complexity, regarding the estimation of implantation induced damage from TRIM simulation, is related with the process of dynamic annealing, i.e. the recombination of created primary defects during or shortly after the evolution of a displacement cascade. For ZnO, in particular, the damage can be avoided to a large extent as this compound was found to display a very efficient *dynamic annealing* [52]. This conclusion follows directly from the observation that the experimentally measured lattice disorder is much less than that predicted by ballistic calculations, e.g. by TRIM which only takes into account collision processes and neglect defect diffusion and annihilation. Even for heavy ions and high energies, fluences in excess of 10^{17} cm^{-2} are needed to completely amorphize the implanted layer.

As a result of such uncertainties, the estimated damage in the samples prepared for this work ranges from a few to hundreds of vacancies per implanted ion (for both systems). When the ion concentration is in the at. % range any of these estimations would imply amorphization of the crystal, which shows the important role of dynamic annealing.

Nevertheless, the simulations indicate that the concentration of vacancies in the implanted layer should be at least of the same order as the implanted Fe and additionally give an idea of their spacial distribution (although not in absolute terms). Figure 3.3.4 shows the simulated depth profile of the vacancies after Fe^+ (60 keV) implantation in STO. Notice that a non-negligible fraction, sitting close the surface, does not overlap significantly with the implanted ions (see figure 3.3.1).

Notice that these profiles refer to the as-implanted state only. Temperature treatments are applied in order to reduce or completely anneal out the implantation induced damage.

3.4 Prepared samples

All three SrTiO_3 samples were cut from a commercially available 0.5 mm thick wafer grown by Crystal GmbH Inc. by *Verneuil* solid state reaction. The wafer is single crystalline, [100] oriented with one side polished. The ZnO samples were cut from a commercially available 0.5 mm thick wafer grown by CrysTec Inc. by hydrothermal method. The wafer is single crystalline and [0001] oriented with one side polished.

Table 3.4.1 lists the implanted ZnO and SrTiO_3 samples, the respective (radioactive and stable) ion fluences and simulated ion ranges, longitudinal straggle and concentration maximum (at the center of the Gaussian distribution).

The implantations (stable and radioactive) were performed at room temperature with a 60 keV beam of Fe^+ ions, tilted by a 7° angle towards the surface normal in order to avoid channeling effects.

Chapter 4

Characterization Techniques

In this chapter, an overview of the experimental techniques used in this work is given, with the exception of electron emission channeling, to which the next chapter is dedicated. The context of application, the relevant experimental details and references to detailed descriptions are given.

4.1 SQUID Magnetometry

The magnetic characterization of the implanted thin layers required the most sensitive magnetometry. With the typical magnetization curves requiring a resolution of at least 10^{-6} emu, use was made of a commercial SQUID (Superconducting Quantum Interference Device) from Quantum Design (resolution 10^{-7} emu) installed at IN-IFIMUP.

The SQUID in the MPMS system does not detect the magnetic field from the sample directly. The measurement is performed in the MPMS instrument by moving the sample through the superconducting detection coils, which are located at the center of the superconducting magnet outside the sample chamber. The detection coils are connected to the SQUID through superconducting wires, allowing the current from the detection coils to inductively couple to the SQUID sensor. As the sample moves through the detection coils, the magnetic moment of the sample induces an electric current in the detection coils. The detection coils, the connecting wires and the SQUID input coil form a closed superconducting loop. Any change in the magnetic flux in the detection coils produces a change in the persistent current in the detection circuit, proportional to the change in magnetic flux. Since the SQUID functions as a highly linear current-to-voltage converter, the variations in the current in the detection coils produce corresponding variations in the SQUID output voltage which are proportional to the magnetic moment of the sample. In a fully calibrated system, measurements of the voltage variation as the sample is moved through the detection coils provide a highly accurate measurement of the sample magnetic moment. The system can be accurately calibrated using a small piece of material having a known mass and magnetic susceptibility.

The *Quantum Design* instrument with a superconducting magnet can be operated using fields up to 5.5 T and measurements can be performed at temperatures ranging from 1.7 to 350 K. Isothermal magnetization as a function of applied field, $M(H)$, and constant field magnetization as a function of temperature, $M(T)$, were performed¹.

The samples were mounted in plastic straws and held by white cotton string². The measurements were carried out with in plane applied magnetic field.

Details on the measurement scheme and experimental apparatus can be found in [80, 81].

4.2 Raman Scattering Spectroscopy

Raman relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. When the laser light interacts with phonons or

¹For $M(T)$ measurements, it would be desirable to perform Zero Field Cooling (ZFC) and Field Cooling (FC) procedures, but the preliminary character of this work postponed such time spending studies to the thorough investigation that will follow.

²Both the plastic straws and the cotton string (white to avoid any magnetic particles from the pigment) were characterized and shown no significant magnetic response besides a small DM contribution, which can be easily subtracted from the experimental curves.

other excitations in the system, the energy of the photons are shifted up or down [44]. This shift in energy gives information about the modes, i.e. the lattice dynamics, of the system.

Raman spectra were excited using the polarized light of an Ar^+ laser Coherent Innova 90 ($\lambda = 514, 5\text{nm}$) in a right-angle scattering geometry. The scattered light was analyzed using a Jobin Yvon T64000 spectrometer equipped with a CCD and a photon counting detector, in the spectral range of $20 - 950\text{cm}^{-1}$. The spectral slit width was about 1.5cm^{-1} and the diameter of the laser spot was estimated as $3 - 4\mu\text{m}$. The samples were placed in a closed-cycle helium cryostat with a temperature stability of about $\pm 0.2\text{K}$ controlled by a Lakeshore DRC-93CA temperature controller with an accuracy better than 0.05K . The actual sample temperatures were estimated to differ by less than 1K from the temperature measured with a silicon diode attached to the sample holder. The temperature homogeneity in the sample was achieved with a copper mask set-up.

Details on the measurement scheme and experimental apparatus can be found in [82, 83].

4.3 Ion-beam Analysis

4.3.1 Rutherford Backscattering and Ion Channeling (RBS/C)

Rutherford backscattering spectrometry is a non-destructive powerful technique to determine the composition and thickness of thin films. Combined with channeling it can also provide information on the crystal quality of single-crystals or epitaxially grown thin films, and on the lattice location of impurities. It is based on Rutherford's famous experiment. Charged particles are generated in an ion source and accelerated to an energy of several MeV. A fraction of the impinging particles is backscattered and detected. By determining the number of backscattered particles as a function of their energy, a backscattering spectrum can be composed. This gives information on the target composition as a function of depth if the energy scale is converted to a depth scale by means of the stopping power.

The RBS/C measurements were performed using the set-up available at Instituto Tecnológico Nuclear (ITN), using a 1mm collimated $2\text{MeV } ^4\text{He}^+$ beam provided by a 3.0MV Van de Graaf accelerator. The samples were mounted in the available RBS/C chambers (I and II) equipped with computer controlled two-axes goniometers, having an angular accuracy of 0.01° , and surface barrier detectors placed in distinct geometries. Chamber I had two detectors placed in CORNELL geometry at 160° and 180° scattering angles with solid angles of 1.7msr and 15msr and energy resolutions of 13keV and 16keV , respectively. These two detectors were used to analyze virgin and implanted samples after annealing. The rest of the samples, in the as-implanted state, were analyzed at chamber II. In this chamber, the backscattered particles were detected by two surface barrier silicon detectors placed at 140° and close to 180° scattering angles in IBM geometry and with energy resolutions of 13 and 18keV and solid angles of 3.4msr and 19msr , respectively.

4.3.2 Proton Induced X-ray Emission (PIXE)

Proton induced x-ray emission (PIXE), is a powerful non-destructive elemental analysis technique. Bombardment with ions of sufficient energy (usually MeV protons) produced by an ion accelerator, cause inner shell ionization of atoms in a specimen. Outer shell electrons drop down to replace inner shell vacancies through allowed transitions. A X-ray spectrum characteristic of the element is thus emitted. An energy dispersive detector is used to record and measure these x-rays and the intensities are then converted to elemental concentrations. Compared to electron based X-ray analytical techniques such as energy dispersive spectroscopy (EDS), PIXE offers better peak to noise ratios and consequently much higher trace element sensitivities. In this work it was used to determine possible impurities from accidental contamination of the samples and to confirm the implanted fluence.

PIXE measurements were performed using the 3MV Van de Graaff Accelerator of ITN, with a $2.15\text{MeV } \text{H}^+$ beam and the X-rays were detected with a Gresham Scirus detector with 155eV energy resolution placed at 110° to the beam direction and at a distance of 25mm from the samples. The PIXE spectra were de-convoluted using the AXIL code [86]. Both PIXE and RBS data were simulated using the NDF code [85].

Chapter 5

Electron Emission Channeling (EC)

The starting point to understand any impurity related phenomena is the knowledge of the lattice site(s) it occupies. Particularly when studying DMS material systems, *methods (...) that establish lattice location or chemical state should be applied in order to give more insight into possible mechanisms for the observed ferromagnetism*[15]. Given its unrivaled efficiency and sensitivity for lattice location of impurities in single-crystal materials and epitaxial thin films¹, electron emission channeling (EC) studies are thereby essential for any DMS related research.

This chapter is devoted to a relatively more detailed description of electron emission channeling, not only because it is a non-standard technique but also because the training and understanding of the theoretical and technical trends constituted one of the main efforts in this work. A detailed description of the experimental apparatus and measurement principles can be found in [57, 58, 59]. A thorough survey of the rather multidisciplinary theoretical and technical aspects can be found in [60].

5.1 Principle

Simply looking at a lattice from particular directions (a “random” orientation in contrast to a crystal axis or plane, see figure 5.3.1), keeping in mind that the motion of energetic charged particles in a solid is mainly determined by their coulomb interaction with the screened nuclear lattice charges, dramatically different behaviors are readily expected. *Channeling* thereby refers to the effect of atomic rows and planes² acting as guides that steer energetic particles along the major crystal axes and planes.

In 1965, Lindhard published his theory on channeling, which still remains the foundation of channeling analysis [61]. This classical approach does not describe quantitatively electron emission chan-

¹The efficiency of EC is roughly four orders of magnitude higher than with conventional ion beam methods (RBS/C). RBS/C requires typical impurity fluences above $10^{14} - 10^{15} \text{ cm}^{-2}$ whereas for EC a fluence of $10^{10} - 10^{11} \text{ cm}^{-2}$ is sufficient. Additionally, RBS relies on the elastic recoil, which considerably limits the study of light elements but does not apply to EC.

²The following will be strict to axial channeling, planar channeling will not be discussed.

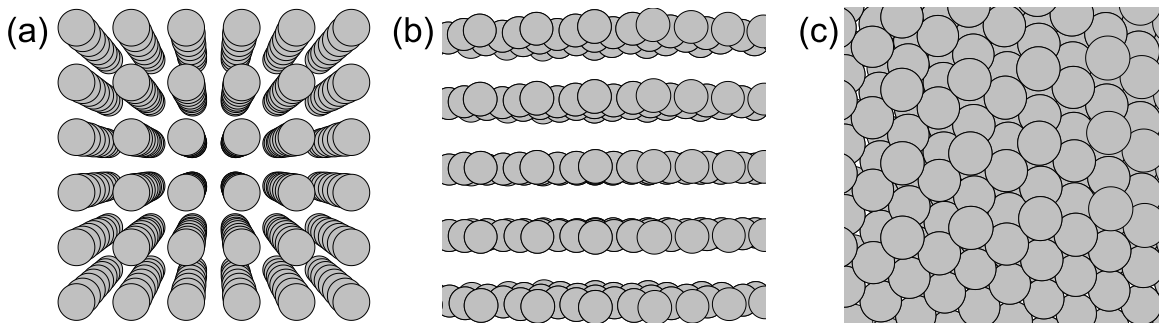


Figure 5.1.1: Three categories of orientations: (a) along a crystallographic axis; (b) aligned with a crystal plane; (c) random orientation.

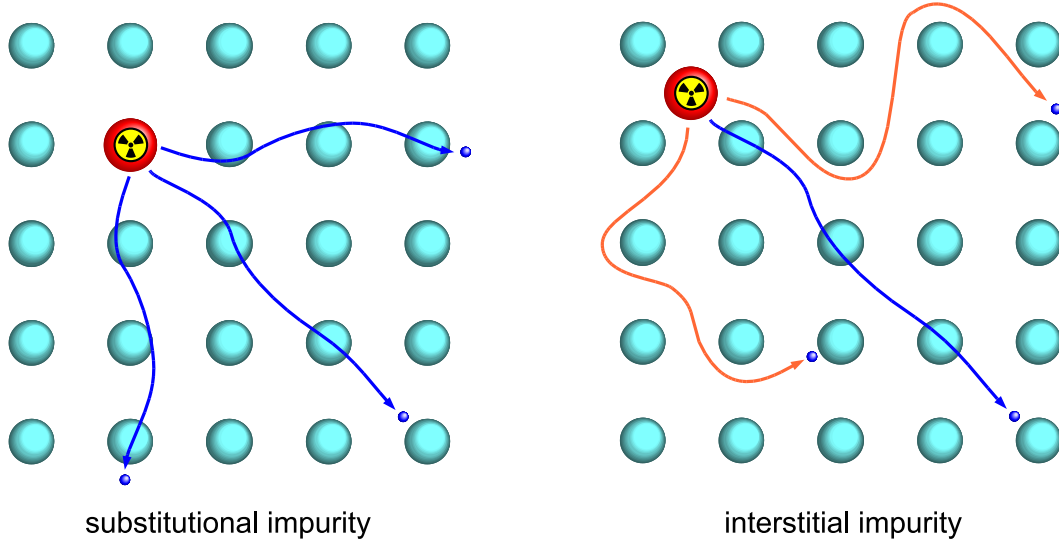


Figure 5.1.2: Artistic view of channeling (blue arrows) and blocking (orange arrows) effects for negatively charged particles emitted by substitutional and interstitial impurities along different crystal directions.

neling, in which quantum effects must be taken in account, but allows for intuitive insight over the elementary phenomena.

Lindhard showed that positively charged particles moving along directions aligned with a crystal axis, can be steered by multiple small-angle collisions with the crystal atoms (figure 5.4.3). There are three elementary requirements for the channeling of a positively³ charged particle. [62]First, the particle must find an open channel between the rows of atoms - *transparency*. This means that the particle should be emitted in a direction that is nearly aligned with a given crystal axis. Furthermore, the screened positive potential (Coulomb repulsion) of the nuclei that make up the rows of atoms must be able to steer the particle towards the middle of the channel - *steering*. The third and final requirement of *stability* means that the particle must not approach the rows of atoms too closely, otherwise the gentle steering effect of many glancing collisions will be replaced by a wide angle deflection in one or more violent head-on collisions with individual atoms⁴. These large non-correlated deflections constitute the so called *blocking* effect. As represented in figure 5.4.3, the competition between channeling and blocking effects is mainly determined by the initial position and direction of the particle and thus gives a signature of the lattice site from which the particle was emitted.

The charged moving particles that are emitted from impurity sites as represented in figure 5.4.3 can have different sources, e.g the reaction of an external ion beam with the impurities, like backscattering of H or He ions in Rutherford backscattering spectrometry (RBS), or nuclear reactions in nuclear reaction analysis (NRA). The principle of emission channeling is, however, different. *Radioactive isotopes* of the impurities under study are introduced into the crystal and emit energetic charged particles during the decay.

The emission channeling experiments performed for this work can be summarized as: (1) radioactive electron (β^- or conversion electrons) emitting isotopes are implanted in a single crystal occupying certain lattice site(s); (2) some of the emitted electrons are channeled along a few strong-channeling crystal axes and leave the sample surface describing anisotropic emission patterns, characteristic of the emission site and the channeling axis, which are recorded by a position-sensitive detector around selected axes; (3) by fitting these 2D experimental patterns to theoretically calculated ones, the lattice site of the impurities is determined. Relevant aspects are discussed in more detail throughout this chapter, starting with a short overview of the theoretical aspects and a somewhat more detailed description of the technical and analysis-related trends.

³The same applies to negatively charges. Only, these “see” as channels the rows of atoms instead of the empty space in between.

⁴In this case, the path of the particle is almost unaffected by the material structure like it was moving in a random (amorphous) system, losing all information concerning its initial direction.

5.2 Theoretical framework

The classical theory of Lindhard is appropriate for particles with masses equal or greater than the proton mass. For light particles like electron and positrons, however, quantum effects may become dominant. Typical energies of electrons and positrons emitted in nuclear decay and used in emission channeling experiments are between about 50 keV and several MeV. The rule of thumb is that quantum effects are of importance in particle motion when the De Broglie wavelength is comparable to the dimensions of the potential governing it. The De Broglie wavelengths for electrons and positrons under these conditions are well in the sub-Å range, while the typical dimensions of the potential inside a solid are in the Å range. One could hence assume that at these high (essentially relativistic energies) the particle movement can be entirely described by (relativistic) classical mechanics. However, the approximate number of bound states for electrons and positrons at energies up to the MeV range, for the main axial directions in typical solids, is relatively low and therefore requires the (quantified) quantum-mechanical description. Only for several MeV, the number of bound electron states becomes so high that a classical description might be appropriate⁵.

With the quantum mechanical approach thus motivated a short overview of the equations governing the electron⁶ channeling effect is given in the rest of the section.

5.2.1 From the relativistic Klein-Gordon to the transverse Schrodinger equation

As described, electron channeling is associated with a relatively small number of quantum states and a quantum-mechanical treatment is hence required. On the other hand, the electron energies are sufficiently high so that a relativistic approach must be made as well. Therefore, neglecting spin dependent terms is the Hamiltonian, the starting point is the basic wave equation of relativistic quantum mechanics for spinless particles, the time-dependent Klein-Gordon equation

$$\left\{ (\hbar c)^2 \Delta + \left[i\hbar \frac{\partial}{\partial t} - V(x, y, z) \right] - m_0^2 c^4 \right\} \Psi(x, y, z) = 0. \quad (5.2.1)$$

A characteristic of the channeling effect is that the component of the motion along the channeling axis is much larger than the off-axis components and that it essentially remains constant while the particle propagates throughout the crystal. One hence uses the wave function *ansatz* expressed as the product of a plane wave along the z -direction (which is supposed to account for practically all of the kinetic energy of the particle) and a time-independent function $\psi(x, y, z)$ accounting for the details of the interaction with the lattice atoms⁷. In order to further simplify, one uses the *continuum approximation* for the potential⁸, i.e. the three-dimensional dependent potential is replaced by its average $U(x, y)$ along the channeling direction. Some algebra and the necessary approximations result in the following Schrodinger-like equation:

$$-\frac{\hbar^2}{2\gamma m_e} \Delta \psi + U(x, y) \psi = i\hbar v \frac{\partial}{\partial z} \psi \quad (5.2.2)$$

where γ is the Lorentz factor and v is the electron velocity. Since the potential $U(x, y)$ is only a function of x and y , the coordinates perpendicular to the channeling direction and does not depend on z , the equation can be simplified by separating the variables with the *ansatz*:

$$\psi(x, y, z) = \phi(x, y) e^{-i \frac{E_{\perp} z}{\hbar v}}. \quad (5.2.3)$$

One is thus left with the so called *transverse Schrodinger equation*, a time-independent (or “stationary”) Schrodinger equation in two dimensions where only the electron rest mass m_e has been replaced by the relativistic mass γm_e :

⁵A quantum-mechanical approach always gives the correct results, but if the number of states involved is very high, as is the case when a classical movement is described quantum-mechanically, the computational requirements are impossible to fulfill with nowadays processing capabilities.

⁶The formalism is equivalent for positrons. However, they are not treated here since their use in emission channeling is less firmly established than electrons.

⁷For the region outside the crystal the solution of Klein-Gordon equation is a trivial plane wave and boundary conditions, matching both wave functions, are applied once the highly nontrivial solution inside the crystal is found.

⁸Based on the fact that, for typical ratios of transverse to axial motion energies, the moving particles are deflected by “collisions” with a large number of lattice nuclei.

$$\left[-\frac{\hbar^2}{2\gamma m_e} \Delta_{x,y} + U(x,y) \right] \phi^j(x,y) = E_{\perp}^j \phi^j(x,y) \quad (5.2.4)$$

where $E_{\perp}^j$ is thus identified with the eigenvalue of the transverse energy of the eigenstate $\phi^j(x,y)$ (the j indexes account for the discreteness of the bound states).

5.2.2 Fourier expansion in the reciprocal lattice

In order to find the solutions, use is made of the fact that any (finite) function $f(x,y)$ with the same periodicity as the crystal lattice can be expanded into a Fourier series with respect to the reciprocal lattice vectors. Thereby, with $\mathbf{r} = (x,y)$, the continuum potential is given by:

$$U(\mathbf{r}) = \sum_{nm} U_{nm} e^{i\mathbf{g}_{nm} \cdot \mathbf{r}} \quad (5.2.5)$$

where U_{nm} are the conventional Fourier coefficients and $\mathbf{g}_{nm} = n\mathbf{g}_a + m\mathbf{g}_b$, with $\mathbf{g}_a$ and $\mathbf{g}_b$ the basis vectors of the two-dimensional reciprocal lattice.

According to Bloch theorem, the Fourier expansion of each energy eigenstate ϕ^j can be written in the form:

$$\phi^j(\mathbf{r}) = e^{i\mathbf{k}_{\perp} \cdot \mathbf{r}} \sum_{nm} C_{nm}^j e^{i\mathbf{g}_{nm} \cdot \mathbf{r}} \quad (5.2.6)$$

where C_{nm}^j are dimensionless complex coefficients. Substituting both the wave function 5.2.6 and the continuum potential 5.2.5 into the transverse Schrodinger equation 5.2.3 and integrating over the two-dimensional unit cell, the result is the matrix equation:

$$\left[\frac{\hbar^2 (\mathbf{k}_{\perp} - \mathbf{g}_{nm})^2}{\gamma m_e} + \sum_{klm} \delta_{kn} \delta_{lm} U_{n-n', m-m'} \right] C_{nm}^j = E_{\perp}^j C_{nm}^j. \quad (5.2.7)$$

This is an eigenvalue problem and the solutions are the sets of j eigenvectors in the form of complex matrices C_{nm}^j . One have thus transformed the problem of solving the analytical Schrodinger equation into finding the algebraic solution of a matrix eigenvalue problem. The algebraic eigenvalue problem is solved numerically by considering a finite number of Fourier components only (thereby giving approximate eigenfunctions), which is called the *manybeam* approach. If the same number of Fourier components is used, from $-M$ to M , in both dimensions in order to expand the potential into the $(2M+1) \times (2M+1)$ component matrix U_{nm} , the wave functions are represented by complex matrices of size $(M+1)^2 \times (M+1)^2$. The integer number M is called the *number of beams*. A number of beams from $M = 10$ to $M = 24$, comprising the relevant range of incidence angles, is typically suited to get sufficiently precise results ($\sim 1\%$ accuracy of electron flux), corresponding to 21×21 to 49×49 matrices for U_{nm} and 121×121 to 625×625 matrices for C_{nm}^j . For a fixed $\mathbf{k}_{\perp}$, an M -beam calculation yields $(M+1)^2$ eigenvalues $E_{\perp}^j$ corresponding to $(M+1)^2$ orthogonal wave functions ϕ^j .

5.2.3 Doyle-Turner potentials

In order to use equation 5.2.7 one needs to specify the interaction potentials between the electrons and the atoms of the solid. Since channeled electrons can be bound in states close to the crystal atoms, it is evident that the calculated wave function must strongly depend on the approximation one chooses. It was found that the thermally averaged Doyle-Turner (DT) potential energy gives the best agreement⁹. The essence of the DT approach is to create interaction potentials which are particularly suited with respect to electron scattering problems from approximations to atomic potentials calculated using first-principle Hartree-Fock methods. Furthermore, It was also found [63] that the inclusion of thermal vibrations of the lattice atoms turns out to be very significant in order to get a good agreement between theory and experiment. DT potentials, basically, a sum of four (sometimes five) Gaussian terms, do that by including a projected two-dimensional root mean square thermal displacement u_1 of the crystal atoms¹⁰ and the coefficients U_{nm} in expansion 5.2.5 become:

⁹DT potentials are particularly well-suited in order to describe electron interactions with single crystals due to the fact that their Fourier transform is very simple, and they are widely used, e.g. in electron microscopy or in reflection high energy electron diffraction (RHEED).

¹⁰One assumes a simple Einstein model for the lattice vibrations, i.e. each atom vibrating independently from the others in a harmonic potential. In principle this approach also allows to incorporate anisotropic vibrations with $u_x \neq u_y$ but for simplicity it is assumed here that the atom vibrations are isotropic in space, i.e. $u_x = u_y = u_1$.

$$U_{nm} = -\frac{2\pi a_o e^2}{V_{2d}} \sum_{\alpha} e^{i\mathbf{g}_{nm} \cdot \mathbf{r}_{\alpha}} \sum_{i=1}^4 a_{i\alpha} e^{-\frac{1}{4}\mathbf{g}_{nm}^2 (B_{i\alpha} + 2u_{1\alpha}^2)} \quad (5.2.8)$$

where the first sum runs over the different atom strings α in the two-dimensional unit cell, with $a_{i\alpha}$ and $B_{i\alpha}$ the i th Doyle-Turner coefficients¹¹ belonging to atom species α , with V the “volume” of the two-dimensional unit cell¹², a_o the Bohr radius, and $u_{1\alpha}$ the rms displacement of atom species α . These Fourier expansions can now be inserted into equation 5.2.7.

5.2.4 Emission Probability function

Solving the eigenvalue problem 5.2.7 numerically gives the $(M+1)^2$ eigenvalues $E_{\perp}^j$ corresponding to the $(M+1)^2$ orthogonal wave functions $\phi^j(\mathbf{r})$. The actual transverse wave function inside the crystal is a superposition of the eigenfunctions $\phi^j(\mathbf{r})$ in equation 5.2.6 and the respective amplitudes are found by matching the transverse wave function inside the crystal to a transverse plane wave outside.

The probability P_T of hitting a thermally displaced impurity atom at a position (x, y, z) , which by Lindhard’s *reversibility rule* is equivalent to the corresponding emission probability from this site, can thus be shown to be:

$$P_T(\mathbf{r}, z) = \sum_{ij} C_{00}^i C_{00}^{j*} e^{-i(E_{\perp}^i - E_{\perp}^j) \frac{z}{\hbar v}} \sum_{nm pq} C_{nm}^i C_{pq}^{j*} e^{-i(\mathbf{g}_{nm}^i - \mathbf{g}_{nm}^j) \cdot \mathbf{r}} D_{nm pq} \quad (5.2.9)$$

where the first imaginary exponential describes the oscillations in depth and the second the variations in intensity in the transverse plane. The Debye-Waller factor $D_{nm pq}$, accounting for the thermal displacement of the emitter¹³ is given by:

$$D_{nm pq} = e^{-\frac{1}{2} |\mathbf{g}_{nm}^i - \mathbf{g}_{nm}^j|^2 u_1^2}. \quad (5.2.10)$$

5.2.5 Dechanneling

The electron flux in a channeling experiment can be divided in two categories: the *channeled beam*, for which the probability of close encounter is almost zero and the *random beam* for which the same probability is almost unity. By describing the interaction with the crystal by a thermally averaged continuum potential, inelastic scattering by electrons and phonons that leads to incoherence of the electron wave function (incoherent scattering) has been neglected. In our picture of a twofold beam, this so called *dechanneling* occurs when a *channeled* electron becomes *random*. The dechanneling contribution is treated as a perturbation to the derived wave function. The most significant causes are:

Thermal vibration of the lattice nuclei induces incoherent scattering disrupting the correlation between successive “soft” collisions, via large momentum transfers. Since the channeled electrons are closely bound to the atom rows, the effect can be very prominent.

Inelastic electronic scattering due to inelastic interaction processes with the (core and valence) electron gas. The main contribution comes from the excitation of plasmons and is usually much smaller than thermal incoherent scattering.

Scattering by crystal defects which in emission channeling experiments are created in considerable amounts, since the electron emitters are incorporated by ion implantation. Note that this dechanneling contribution was not used in the calculations presented in this work and any possible influence of defect scattering in our experiments is discussed in page 56.

These different scattering processes can be incorporated into expression 5.2.9 by means of a total dechanneling length λ_i (equivalent to a mean free path) for an eigenstate i depending on thermal, electronic and defect coherence lengths contributions through the relation

¹¹Tabulated by Doyle and Turner, determined by fitting the function that defines the DT coefficients to the results of atomic Hartree-Fock calculations.

¹²The area A of the 2D unit cell (from the integration that gives the Fourier coefficients) times the periodicity d along the string (from the averaging integration of the continuum approximation).

¹³Similar to what is done to account for the vibration of the “steering” atoms, here is to account for the emitter atoms vibration.

$$\frac{1}{\lambda_i} = \frac{1}{\lambda_{thi}} + \frac{1}{\lambda_{el}} + \frac{1}{\lambda_D}.$$

The initial (channeled beam) eigenstates are thereby depopulated exponentially with increasing z , and correspondingly, the free states yield (random beam) increases. The final depth-dependent scattering yield $P_T(\mathbf{r}, z)$ thus becomes:

$$\begin{aligned} P_T(\mathbf{r}, z) = & \sum_{ij} C_{00}^i C_{00}^{j*} e^{-\frac{z}{2}(1/\lambda_i - 1/\lambda_j)} e^{-i(E_{\perp}^i - E_{\perp}^j) \frac{z}{\hbar v}} \\ & \times \sum_{nm pq} C_{nm}^i C_{pq}^{j*} e^{-i(\mathbf{g}_{nm}^i - \mathbf{g}_{pq}^j) \cdot \mathbf{r}} e^{-\frac{u^2}{2} |\mathbf{g}_{nm}^i - \mathbf{g}_{pq}^j|^2} \\ & + \sum_i |C_{00}^i|^2 (1 - e^{-z/\lambda_i}). \end{aligned} \quad (5.2.11)$$

5.2.6 Angle-dependent electron flux

According to the reciprocity theorem, equation 5.2.11 yields the flux of electrons with an energy E emitted from a position $(\mathbf{r}, z)$ within a crystal towards a detector positioned at an angle (θ, ϕ) . These angles are, respectively, the polar and azimuthal angles of the electron momentum vector $\mathbf{k}$ with respect to the z -axis. Since the electron emitters are incorporated by means of ion implantation, the probes are distributed in depth according to an approximately Gaussian implantation profile. The calculated emission yield $P_T(\mathbf{r}, z)$ for a fixed emitter position $\mathbf{r}$, therefore, has to be folded with the appropriate emitter concentration profile as determined from TRIM [45]. The resulting function $\chi_{\mathbf{r}, E}(\theta, \phi)$ gives the angle-dependent emission yield for an electron with energy E emitted by an impurity at position $\mathbf{r}$ inside the crystal.

In electron emission channeling experiments, the implanted radioactive probe emit either conversion electrons, β^- particles, or both. Conversion electrons are orbital electrons that are ejected out of the atom during the electromagnetic de-excitation of an excited nucleus and therefore have well-defined energies. In the case where there is only one prominent conversion electron line in the energy spectrum, the theoretical angle-dependent emission yield $\chi_{\mathbf{r}}(\theta, \phi)$ is equal to $\chi_{\mathbf{r}, E}(\theta, \phi)$, with E equal to the energy of the conversion electron line. However, for most probe nuclei the energy spectrum is more complicated: there could be more than one conversion electron line present, e.g. due to the presence of several nuclear transitions. Additionally, a β^- decay has a continuous energy spectrum, which in addition might have conversion electron lines superposed. In these cases the emission yield $\chi_{\mathbf{r}, E}(\theta, \phi)$ is calculated for a set of discrete energies E_i . The final theoretical angle-dependent emission yield for an emitter probe at position $\mathbf{r}$ is then given by

$$\chi_{\mathbf{r}}(\theta, \phi) = \sum_i I_i \chi_{\mathbf{r}, E_i}(\theta, \phi) \quad (5.2.12)$$

where I_i is the normalized conversion electron branching ratio or the β^- intensity at energy E_i , so that $\sum_i I_i = 1$.

Hofsass and Lindner [64, 65, 66] developed the computer program *manybeam* based on the formalism developed above for the theory of electron emission channeling. U.Wahl [76] introduced modifications to the code resulting in a program of high accuracy and performance for the calculation of angle-dependent emission channeling yields for any lattice position of emitter impurities channeled in any direction. The patterns thus calculated would be the end of the story if the detectors were “looking” at one single channel. But since the diameter of the implantation beam spot in the sample is about 1 mm, a large number of rows are therefore contributing and consequently it is required to convolute the 2D patterns with a Gaussian-like implantation lateral profile¹⁴. This can be seen as a finite angular resolution which as a further contribution from the finite size of the detector pixels. These and other details are described, for the ZnO and SrTiO₃ manybeam simulations, in section 5.4.1.

The output yields of this program are used to fit to the experimental emission patterns, allowing an accurate lattice location of the impurities and respective occupancy fractions. The fitting routine is described in section 5.4.2.

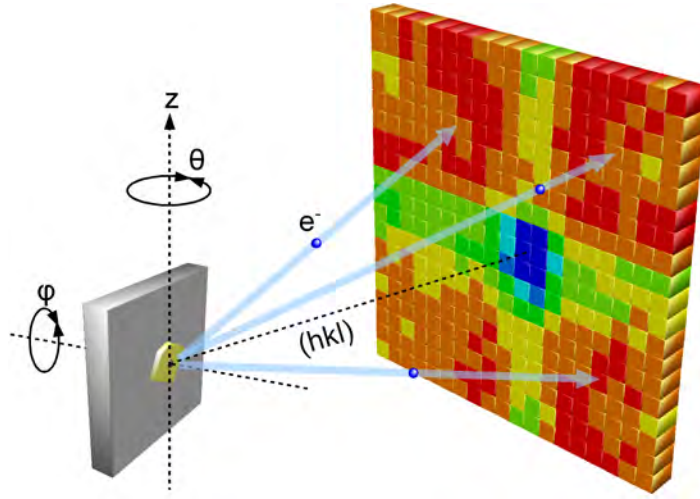


Figure 5.3.1: Artistic view of the sample holder and the 22×22 pads Si PSD of used at ISOLDE to collect electron emission channeling patterns. The z , φ and θ represent, respectively, the translation and polar and azimuthal rotation degrees of freedom of the goniometer. The direction (hkl) refers to the crystallographic axis under study. The color of each pad/pixel accounts for the number of detected particles.

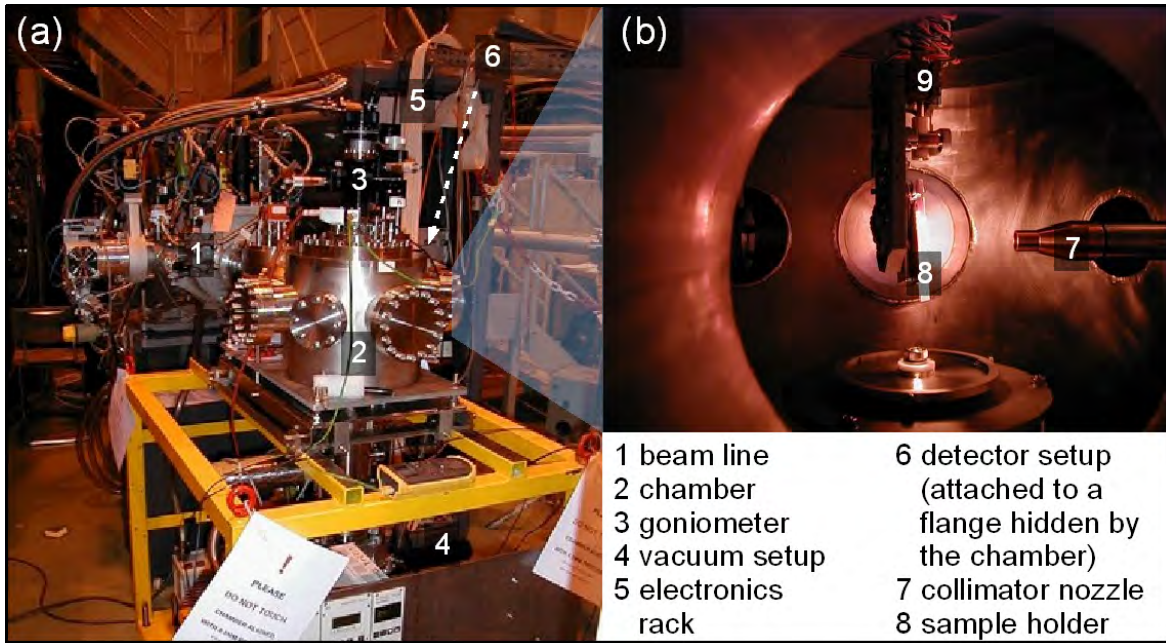


Figure 5.3.2: Pictures of the latest EC setup assembled at ISOLDE: (a) On-line (the measurements are performed in the same chamber as the implantation) and with count rates up to several kHz (it is equipped with the new self-triggering readout chips for the Si pad detectors), extends the technique applicability to shorter-lived probes (e.g. ^{27}Mg with $t_{1/2} = 9.46$ min). (b) Chamber interior during annealing.

5.3 Experimental details

5.3.1 Emission channeling experimental setup

After implantation with the radioactive probe isotope, the sample is transferred to an electron emission channeling setup. The concept of such a setup is very simple and relies on the ability to detect electrons coming out of the sample as a function of the angle towards some crystallographic axis. The three essential components are: a high-vacuum chamber, a goniometer to rotate the sample holder, and an electron detector.

High vacuum chamber Inside a chamber, the sample is mounted vertically on a sample holder, in front of the detector, oriented in such a way that electrons arising from the sample's surface parallel to the measured crystallographic axis reach the center of the PSD. The measured 2D pattern represents the emission yield as a function of solid angle of emission (see figure 5.3.1). A combined system pumping system produce high vacuum of typical pressures around 10^{-6} mbar.

Goniometer The two-axes goniometer allows the movement of a sample in one direction and around two axes of rotation (φ and θ in figure 5.3.1), with a typical angular precision around 0.05° - 0.1° . Note that, since 2D position-sensitive detectors are used, the accuracy of the goniometer does not determine the quality of the measurements¹⁵. The sample holder is equipped with a tungsten wire (resistive) heating device, which allows the *in-situ* vacuum annealing of samples up to 900°C , or the measurement of samples at elevated temperatures¹⁶. One of the goniometer setup is furthermore, equipped with a helium continuous flux cryostat allowing low temperature measurements down to 10 K.

Position-sensitive detector Technological developments¹⁷ allowed the upgrade of the 0-dimensional detectors to (2D) position-sensitive detectors (PSDs), better suited to measure the angular dependent emission yield, increasing the detection efficiency by about two orders of magnitude[67, 68]. The principle of operation of these detectors is based on integrating an array of separate detector cells (pads or pixels) on a single Si chip and individually contacting them on the surface by a pattern of conducting and insulating layers. The square-shaped sensitive area is $28.6 \times 28.6 \text{ mm}^2$ and consists of 22×22 pixels (thus each of $1.3 \times 1.3 \text{ mm}^2$). The multiplexed readout of all pads is triggered if the signal on the detector back plane, which is common to all pads, exceeds an externally set lower threshold. This readout procedure limits the count rate of the device to a maximum of about 250 events/s. This is, however, sufficient for typical experiments with long-lived (half-life above a few few hours) radioactive isotopes, implanted at low to moderate fluences. The energy resolution for electrons is 5-6 keV, and is mainly due to energy loss and straggling in the detector entrance window and electronic noise. Concerning the position resolution of the detector σ_d , note that, besides the lower limit posed by the pad size of 1.3mm, the lateral straggling of the electrons in the detector is a natural limit. The lateral straggling leads to events where the charge is shared among several pads. Its magnitude is comparable to the thickness required to completely stop all electrons, which in Si is around $7 \mu\text{m}$ at 30 keV, $350 \mu\text{m}$ at 300 keV, and 2 mm at 1 MeV.

5.3.2 Angular resolution

The experimental angular resolution is a key parameter in the quantitative analysis of channeling and blocking patterns. For a position-sensitive detection system it depends on the distance between sample and detector, the position resolution of the detector which may vary with energy and nature of

¹⁴Defined in the two 2D implantation plane (normal to the implantation direction). Different from the 1D depth Gaussian profile.

¹⁵If a 0-dimensional detector (1-pad detector) is used, the sample is moved in order to perform the scans, and thereby the accuracy of the measurements would be determined by the accuracy of the goniometer. Actually, this method was used for a variety of lattice location experiments in metals and semiconductors up until the 90's [64, 66].

¹⁶Limited by the detector temperature tolerance

¹⁷In case of MeV α particles, suitable PSD systems were developed already in the 70's and are commercially available from several suppliers. However, alpha emitting isotopes are mainly found, with few exceptions, at masses above $\sim 150 \text{ a.m.u.}$ On the other hand, beta and conversion electron emitters exist for almost all elements of the periodic system. Position-sensitive detectors were developed at CERN for collision experiments and medical X-ray imaging and were found to be extremely efficient detecting electrons. Since then, this type of detectors are being used to perform electron EC to (successfully) determine lattice location of several impurities on semiconductors.

the incoming particles and on the size and shape of the projected beam spot¹⁸. Assuming that both the position resolution of the detector and the projected beam spot distribution can be approximated as two-dimensional isotropic Gaussian distributions with standard deviations σ_d and σ_b , respectively, the total angular resolution is given by

$$\sigma_{ang} \approx \arctan \left(\frac{\sqrt{\sigma_d^2 + \sigma_b^2}}{d} \right) \approx \frac{\sqrt{\sigma_d^2 + \sigma_b^2}}{d} \quad (5.3.1)$$

where d is the distance between sample and detector which, was chosen to be around 30 cm¹⁹ in order to cover an angular range of 5°-6°, the relevant range of EC patterns. With the distance d thus fixed and since the detector resolution σ_d is limited by the size of the pixels, the angular resolution can only be manipulated through the beam spot σ_b . From 5.3.1, it makes no sense to achieve a beam spot which is much smaller than the detector resolution or vice-verse. Thereby, the implanted spot should be around 1,3 mm, the size of the pixels, which requires beam collimation during implantation. As a trade-off between position resolution and beam transmission²⁰, a 1 mm beam spot is chosen. Assuming that the standard deviations associated with the beam spot and the pixels are about half of their sizes, the overall angular resolution is $\sigma_{ang} \approx 0.16^\circ$.

5.4 Data analysis procedures

5.4.1 *Manybeam* simulations

In order to fit the experimental 2D emission patterns, theoretical emission yields were calculated using the *manybeam* program with the theoretical background described in section 5.2.

An important input parameter is the vibration amplitude of the crystal atoms. The one-dimensional root mean square (rms) vibration amplitude u_1 can be determined experimentally from the Debye-Waller factors in X-ray absorption or diffraction experiments. Published values are used as input for *manybeam* calculations.

The relation between the one-dimensional rms vibration amplitude u_1 and the Debye temperature Θ_D is given by [77]:

$$u_1^2 = \frac{3\hbar T}{Mk_B\Theta_D^2} \left[\varphi \left(\frac{\Theta_D}{T} \right) + \frac{\Theta_D}{4T} \right] \quad (5.4.1)$$

where M is the mass of the element in question, k_B the Boltzmann constant, Θ_D the Debye temperature and $\varphi(x)$ the Debye function defined as

$$\varphi(x) = \frac{1}{x} \int_0^x \frac{t dt}{e^t - 1} \quad (5.4.2)$$

Within the Debye model, the rms vibration amplitude of a *mass defect*, like a substitutional foreign emitter atom which is bound to its neighbors with the same elastic constants as the lattice ions²¹, can be estimated from the effective Debye temperature of the emitter Θ_D^{imp} [69, 70, 78] as:

$$\Theta_D^{imp} = \Theta_D \sqrt{\frac{M}{M'}} \quad (5.4.3)$$

where Θ_D and M denote the Debye temperature and the mass of the host atom that is substituted by the foreign atom, while M' is the mass of the impurity. The rms vibration amplitude u_1 of the impurity atom can thus be calculated by equation 5.4.1 if one replaces the mass M by the impurity mass M' and uses the effective Debye temperature Θ_D^{imp} . These impurity vibration estimates are reference values. The actual displacement amplitudes are obtained from fitting to experimental patterns the theoretical yields simulated for a set of different rms displacement values.

For each experiment, the electron emission yield is calculated for the emitter atom located on several possible lattice sites: substitutional and typical interstitial sites and, for each of these, for the perfect position and a set of statically displaced positions within the meaningful range. These

¹⁸The area on the sample from which the charged particles are emitted, projected onto the detector under the angle of detection.

¹⁹Some geometric details like distance d are slightly different among setups.

²⁰The amount of beam that is lost due to collimation with that size of aperture amounts to 50-70%.

²¹In this approximation, the foreign atom behaves as if a purely isotopic substitution would have taken place.

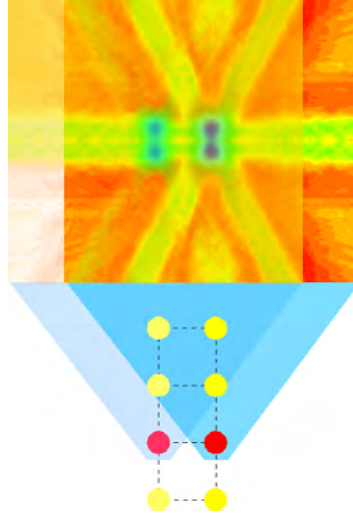


Figure 5.4.1: Schematics of the superposition of EC patterns from different atoms rows in the beam spot. The distance between patterns is exaggerated; the true effect is a Gaussian weighted smoothing of about 0.1° standard deviation (see figure 5.2.5).

simulations are performed for the reference vibration amplitude given by equations 5.4.1 and 5.4.3 and several others. The fitting determines which one is correct and from which should the calculated fractions be accepted.

5.4.2 Fitting procedures

The *manybeam* simulations result in two-dimensional patterns of electron emission probability for different emitter positions and, for each of these, for different rms displacement values. These patterns are smoothed using a Gaussian with $\sigma \simeq 0.1^\circ$ to account for that part of the experimental angular resolution due to the 1 mm beam spot on the sample²² (see figure 5.2.7). In fact, the initial set of simulated patterns were smoothed for several values of $\sigma = 0.1^\circ; 0.15^\circ; \dots; 0.55^\circ; 0.6^\circ$ in order to investigate other possible broadening sources like crystal mosaicity and extended damage due to high fluence implantation (see section 5.5). The size and shape of the detector pads is taken into account by averaging over the simulated yield falling within the angular range $(0, 26^\circ \times 0, 26^\circ)$ of one pixel, resulting in the final $\chi^{theo}(\theta, \phi)$.

The program *Fdd* was developed by U.Wahl [79] to perform the quantitative analysis of the experimental 2D patterns $\chi^{exp}(\theta, \phi)$ by fitting a linear combination of the calculated yields $\chi^{theo}(\theta, \phi)$. The fitting routines allow up to three site occupation per measured axis according to:

$$\chi^{exp}(\theta, \phi) = S \left[f_{rand} + \sum_{i=1}^3 f_i \chi_i^{theo}(\theta, \phi) \right] \quad (5.4.4)$$

where S is a scaling factor and f_i denotes the fraction of emitter atoms occupying i th site. The random fraction f_{rand} accounts for emitter atoms which do not contribute significantly to the anisotropy of the pattern, i.e. which are located on sites with very low crystal symmetry or heavily damaged (amorphous) surroundings or have a random occupation of lattice sites²³ and is thus given by:

$$f_{rand} = 1 - \sum_{i=1}^3 f_i.$$

Using non-linear least squares fitting routines, the best fit $S, f_1, f_2, f_3, x_0, y_0$ and ϕ_0 parameters, where the last three denote the axis position in the detector and an azimuthal rotation angle of the pattern in respect to the channeling axis, can be determined simultaneously. While S, x_0, y_0 and ϕ_0 are always allowed to vary in order to provide correct normalization of the experimental spectra

²² Assuming that the implantation profile projected in the plane normal to the observation direction is reproduced by a Gaussian of standard deviation given by half the beam spot diameter.

²³ Statistically, it is not expected that *all* the implanted ions occupy *only* three different preferred sites.

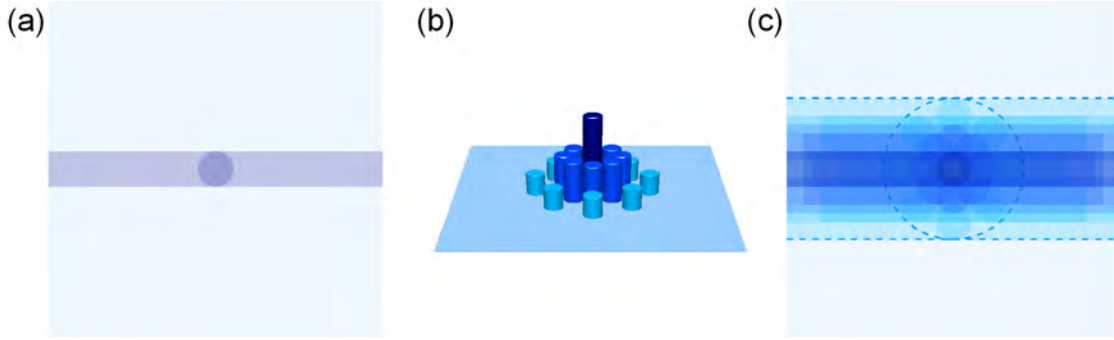


Figure 5.4.2: Artistic view of (a) the convolution of a simple “axial+planar” channeling pattern with (b) a Gaussian-like orientation distribution resulting in (c) a smoothed (actually broadened, when the angular spread is significant) pattern.

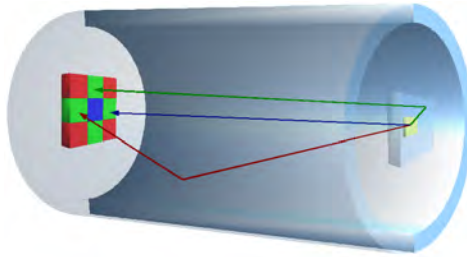


Figure 5.4.3: Simplified schematics of the EC chamber interior showing the different types of trajectories an electron can trace from the sample to the detector: direct electrons (blue), electrons backscattered inside the sample or sample holder (green) or electrons that are scattered by parts of the setup (red).

and to achieve optimum translational and azimuthal orientation with respect to the detector, usually only one or two different site fractions f_1 and f_2 are considered²⁴. The set of simulated patterns (and combinations) are fitted to each of the experimental patterns. The best fit determines the lattice site (or combination of sites) of the impurities while the occupancy fractions are calculated. A well behaved *best fit* dependence on rms and σ values allows their simultaneous estimation.

5.4.3 Scattered electron background correction

One can estimate the number of the electrons (β^- and CE) that are emitted with initial direction close the detection axis, the *direct electrons*. This is given by the ratio between the solid angle Ω spanned by the detector relative to the beam spot and the full 4π solid angle into which all the electrons are (almost) isotropically emitted, i.e. $\Omega/4\pi$ of the total number of decays. In a real experiment, however, the number of detected electrons is always significantly larger than this estimate. The additional fraction is caused by electrons that initially are not emitted towards the detector, but still reach it after being scattered. The scattering event can occur inside the sample, when an electron is scattered by the host atoms, or outside the sample by parts of the setup (see figure 5.4.3). These scattered electrons represent an additional isotropic background in the experimental angular emission yields which is not accounted for in the theoretical framework of channeling that is presented in 5.2. Without any quantitative knowledge about this effect, it is impossible to deduce accurate fractions from the fitting procedure²⁵. Although there exist experimental investigations where the backscattering of electrons from a substrate was investigated as a function of angle, energy and substrate material [71], the scattering by parts of the setup will depend on its the exact geometry and therefore cannot be deduced as easily from literature values. Furthermore, the problem is totally different for CE and β^- particles:

²⁴Not only because usually it is enough to reduce the random fraction to conceivable values but also because the fitting routines loose sensitivity when too many sites are allowed.

²⁵In fact, if the scattering background is completely neglected in the analysis, the fractions will always be underestimated.



Figure 5.5.1: Schematics of *tilt* (white) and *twist* (blue) components of the mosaic effect in columnar domains.

Conversion electron decay It is possible to deduce the total scattering background of a pure conversion electron decay from the experimental energy spectrum: for direct electrons it consists of a set of narrow peaks at well defined energies while scattered electrons form tails below these peaks (due to the energy lost in the scatter process). It is possible to correct for this scattering background by estimating (integrating the counts in the tails) and subtracting it to the experimental yields.

Beta decay Such a simple estimate is not possible for β^- decays, due to the continuous nature of their energy spectra. Therefore, another approach is necessary. The computer program *Pad* was developed in order to simulate, by means of Monte-Carlo method, the background contribution for β^- decays [84]. From the simulated energy spectra, it is possible to calculate the number of scattered electrons, the number of direct electrons, and the total number of electrons. A background correction factor f can then be calculated according to:

$$f = \frac{\text{total electrons}}{\text{total electrons} - \text{scattered electrons}} = \frac{\text{total electrons}}{\text{direct electrons}}. \quad (5.4.5)$$

This f factor can be used to correct the experimental patterns or, equivalently, as a rescaling factor of (multiplying by) the fractions calculated from the fitting procedure²⁶.

5.5 Effects of external parameters

The theoretical description given in section 5.2 assumes a perfect crystal. The approach is still reasonable when point defects are present, if they only cause isotropically enhanced dechanneling. However, long-range disorder of the crystal (e.g. mosaicity) and implantation related effects (e.g. crystal damage) are not taken in account. In this section, the description of electron emission channeling technique, presented above in a well fundamented mathematical and physical formalism, is extended with a rather qualitative discussion of three external parameters which must be taken in account during the analysis: mosaicity and fluence and implantation geometry dependence.

5.5.1 Implications of mosaicity

Depending on the compound and growth technique and conditions, mosaic domains may occur. These grains are slightly misoriented with respect to each other and the substrate, with slightly different crystallographic orientation, giving rise to large dislocation densities at their boundaries. The domain misorientation can be split up into *tilt* (out-of-plane, polar) and *twist* (in-plane, azimuthal) components, as shown in figure 5.5.1, depending on the type of dislocations present at the interface or grain boundary. The magnitude of the mosaic tilt and twist can be determined, for example, from X-ray diffraction rocking curves²⁷.

Every domain is a good quality single-crystal on its own, but has a slightly different orientation than the others. The channeling effect coming from only one grain can therefore be described accurately by the theory for a perfect crystal, assuming that the grains are large enough so that most channeling particles will only travel through one grain. The influence of mosaicity inside one grain will then be

²⁶ During the fitting, this isotropic *setup-scattered* yield contributes for the random fraction determined, but it is not truly part of the above discussed random occupancy fraction, since these electrons can actually be emitted from the i th fitted lattice sites.

²⁷ However, such experiments are very difficult to accomplish with a standard X-ray diffractometers. The reason for this is that they require a grazing incident and exit beam, which results in weak scattering and extensive beam spill-off from the sample. Therefore, such experiments must be carried out at synchrotron facilities.

limited to a rotation of the channeling axis with respect to the substrate by the corresponding tilt and twist angles of the grain. Since these domains are very small, a real channeling experiment (beam spot diameter 1 mm) will probe a large number of domains simultaneously. The orientation distribution that is usually used is given by the line-shape of the XRD rocking curves, which are well described by a pseudo-Voigt function, a linear combination of a Gaussian and Lorentzian function.

The superposition of tilt and twist components, for each measured crystal axis (depending on the samples specific distribution of components magnitudes and grain size), is a rather complex problem and, since no such measurements were performed for this work, the discussion here will be limited to general arguments.

First of all, *twist* and *tilt* concepts are relative to the on-surface direction. Looking from other directions, given that these two “components” (the *twist* is completely specified by one angle but the *tilt* two) span every rotation in 3D space, for each measured axis, one can project the mosaic effect in a *new tilt* component that changes the channeling center and a *new twist* component that rotates the pattern²⁸ (see figure 5.2.6). Since the measured channeling pattern is a superposition of contribution from all grains within the beam spot, the theoretical channeling yields for a perfect crystal should be convoluted (weighted average) with the orientation distribution (of the new/projected tilt and twist) of each measured channeling axis (see figure 5.2.5). The effect of the *projected twist* component is about two orders of magnitude below the *projected tilt* (the distance between detector and sample is two orders of magnitude above the detector dimension). Nevertheless, these projected components are combinations of the initial *tilt* and *twist* (relative to the on-surface directions) and since these two components are typically of the same order of magnitude, both are important when several directions are measured.

If the *tilt* and *twist* distributions FWHMs are known, this effect can be modeled by a smoothing of the simulated patterns, i.e. by an extra contribution to σ , depending on the *projected* tilt distribution FWHM_{*ptilt*}:

$$\sigma_{ptilt} = \frac{\text{FWHM}_{ptilt}}{2\sqrt{2\ln(2)}} \simeq \frac{\text{FWHM}_{ptilt}}{2.35} \quad (5.5.1)$$

which is introduced in the fitting procedure as a fixed value. If these distributions are unknown, the alternative approach is to produce several sets of patterns for different values of total σ in a suited range and search for the best fit within. Typical tilt and twist FWHM values in the $0.1^\circ - 0.5^\circ$ range give an expected σ_{ptilt} from 0.04° to 0.2° .

5.5.2 Fluence dependence

Another external parameter studied in [84] is the effect of high-fluence implantation. The majority of the EC experiments carried out so far have been focused on low-fluence implantation (up to 10^{13} cm^{-2}), which is excellently suited to investigate the interactions of an isolated impurity with the surrounding crystal host. However, high fluences are usually desired for device applications, and therefore it is equally important to understand what lattice sites are occupied by the impurities after incorporation in large concentrations, for which the interactions between impurity atoms and other defects may become relevant.

The typical effect is the broadening of the axial channeling peaks. For the high-fluence experiments done so far (up to $1 \times 10^{15} \text{ cm}^{-2}$), the effect was only evidenced for the off-surface directions (of the wurtzite GaN). Typically, the poor fit quality of the theoretical patterns causes the fractions estimated for sites along these directions to be much lower than the fraction calculated from the [0001]. The conventional explanation for such a discrepancy is that a considerable fraction of impurities are situated on a third lattice position that is located along the c-axis atomic rows. But quantitatively, it must be checked if (1) it accounts for the determined fractions, i.e. if the sum of the (now) split site-fractions reproduce the un-split value determined from the [0001] direction; (2) the multi-fraction theoretical patterns indeed reproduce the broadening of the experimental ones; (3) additionally, if previous lattice location experiments (RBS/C, EXAFS etc.) have identified such sites or if theory supports it. If these fail, the horizontal broadening (and the resulting poor fit quality and low fitted fractions) must have another source. Moreover, if these effects are not evidenced in low-fluence experiments, they should be related to the higher implantation fluence.

²⁸The angles of spread are very small so the distortion effects due to the patterns projection in the detector plane are negligible.

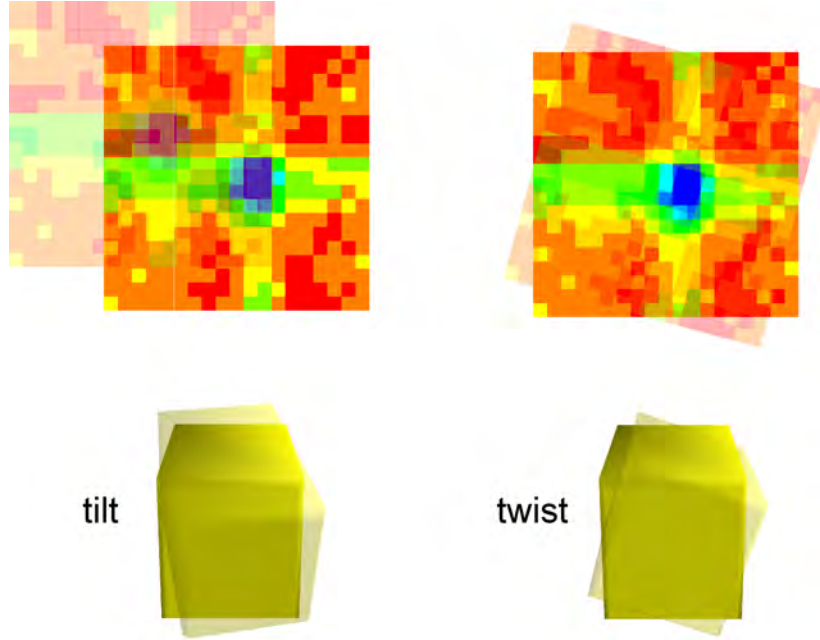


Figure 5.5.2: Artistic view of the effects of (projected) tilt and twist components of mosaicity in emission channeling patterns.

Based on the fact that ion implantation to fluences of $10^{14} - 10^{15} \text{ cm}^{-2}$ introduces considerably larger amounts of lattice defects²⁹ compared to low-fluence implantation, an explanation for the broadening effect was forwarded in [84] (for $1 \times 10^{15} \text{ cm}^{-2}$ Fe:GaN).

The large amount atoms displaced to interstitial sites during implantation resulted in a lattice expansion of the implanted layer. The lattice expansion was investigated in the pre-implanted sample by means of X-ray diffraction and a satellite peak appeared that originates from the strain induced in the implanted region. In the implanted layer, the lattice a -parameter was unaffected and the c -parameter suffered a variation up to $\sim 2\%$. This leads to an uncertainty in the inclination angle for an off-normal crystal direction of the order of 0.6° . The spread is, of course, expected to influence channeling along off-normal crystal directions. Accurate modeling within the manybeam formalism for emission channeling is very difficult, since the strain varies continuously as a function of depth throughout the implanted layer. Nevertheless, the influence on the channeling effect is expected to be of the same order of magnitude as the spread in orientation, and should act mainly on the horizontal direction.

5.5.3 Implantation geometry dependence

Implantation geometry refers to the direction of the ion beam relative to the crystal and can be divided into two categories: *channeled implantation* along a low-index crystallographic axis and *random implantation*, in the limiting case, along a non-aligned direction. It is a well known fact [74, 75, 72] and clear from the *gentle deflections* vs. *head on collisions* characteristic of *channeling* vs. *blocking* effects, that the former is characterized by a larger penetration power and smaller degree of defect creation than the latter. While random implantation at low fluences³⁰ mainly introduces damage (accumulation of point defects from the collision cascades) very close to the surface, channeled implantation, characterized by a smaller probability of nuclear collisions and thereby by a larger penetration depth, produces a lower (and more evenly spread) defect concentration and degree of surface sputtering. This enables a higher degree of damage anneal out for “channeled-implanted” samples. In fact, for the

²⁹ As a consequence of the (more or less efficient, depending on the material) dynamic annealing process this is only of limited importance for low fluences, but becomes increasingly more important in the high fluence range.

³⁰ At high fluences the problem is not straightforward. For example, the damaged surface (or a part) can end up being sputtered out of the sample.

case of random implantation, denser surface damage can even cause its further degradation at high annealing temperatures [54]³¹.

This picture is qualitatively confirmed by experiment. The dependence of channeling on implantation geometry was recently studied in [84]. It was observed that, from the as-implanted state and up to a 400 °C annealing step, the lattice location results are similar for channeled and random implantation within the experimental error. However the difference increases noticeably from that temperature onwards: whereas the randomly implanted sample shows a nearly constant substitutional fraction or even a minor decrease as a function of annealing temperature, the channeled-implanted fraction increases monotonously.

³¹A damaged surface layer will cause an apparent decrease in the substitutional fractions as a result of the enhanced dechanneling of electrons.

Part II

Results

Chapter 6

Lattice Location

Electron emission channeling experiments were performed on three of the prepared samples: ZNO_MF, ZNO_HF and STO_LF. The complete analysis and the discussion of ZnO related data are presented. For STO, despite the author's active participation in the experiments and analysis, only a short overview on preliminary results is presented (complete description and analysis will be found in [87]). The situation is similar regarding the ion-beam analysis (RBS/C and PIXE) on STO samples. Therefore, there is no dedicated section and the relevant results are presented whenever needed to guide the analysis or the discussion.

6.1 ^{59}Fe in Zinc Oxide

A previously published emission channeling experiment with the ^{59}Fe probe in ZnO, has already shown that after low-fluence implantation ($2 \times 10^{13} \text{ cm}^{-2}$) between 90% and 100% of the Fe atoms occupy substitutional Zn sites with rms displacements in the range of $0.06 - 0.17 \text{ \AA}$ [88]. In order to investigate whether Fe is still incorporated on S_{Ga} sites after high-fluence implantation, two samples were pre-implanted with stable ^{56}Fe to a fluence of $5 \times 10^{15} \text{ cm}^{-2}$ (ZNO_MF: 8.8%) and $1 \times 10^{16} \text{ cm}^{-2}$ (ZNO_HF: 17%). Subsequently, these samples were implanted at ISOLDE to a fluence of $2 \times 10^{14} \text{ cm}^{-2}$ with an isotopically clean beam¹ containing radioactive ^{59}Mn ($t_{1/2} = 4.6 \text{ s}$). This precursor isotope decays to ^{59}Fe , during which the Fe nucleus receives a recoil energy between 150 and 200 eV. Since this exceeds the maximum threshold energy of 65 eV (estimated for [0001] oriented ZnO[50]) that is needed to create a Zn displacement, the recoil energy should be sufficient to effectively re-implant ^{59}Fe in the ZnO crystal. The β^- particles emitted by this isotope were then used to determine the lattice sites of Fe in ZnO. The results are presented and discussed in this section.

6.1.1 Experiment

The probe isotope ^{59}Mn was produced at ISOLDE by the nuclear reactions caused by a 1.4 GeV proton beam impinging on a UC2 target. Subsequently, the isotopes were ionized by a resonant laser Mn ion source tuned to the atomic transitions of Mn. An isotopically clean ^{59}Mn ion beam was then produced by extracting the Mn ions (at 60 keV) and by mass-separating them in an analyzing magnet. Using

¹Through the use of a Mn laser ion source.

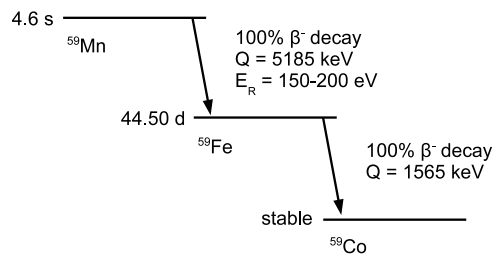


Figure 6.1.1: Decay scheme of ^{59}Mn precursor isotope that decays for ^{59}Fe probe.

this beam, the ZnO samples were implanted at room temperature with ^{59}Mn ions to a fluence of $2 \times 10^{14} \text{ cm}^{-2}$ using a beam spot of 1 mm diameter. During implantation, the sample was tilted by an angle of 7° in order to minimize channeling of the implantation beam. The radioactive isotope ^{59}Mn decays through the emission of β^- particles with an endpoint energy of 5.2 MeV to ^{59}Fe (see figure 39). After implantation at ISOLDE, each sample was transferred to an off-line emission channeling setup, where the β^- angular distribution patterns were measured along the [0001], $[\bar{1}102]$, $[\bar{1}101]$ and $[\bar{2}113]$ axes. The same angular yields were measured after 10 min *in-situ* isochronal vacuum ($< 10^{-5}$ mbar) annealing steps at 200, 400, 600, 700 and 800 °C in order to determine the influence of temperature on the lattice site of ^{59}Fe , giving a total of 48 experimental patterns. From the experimental datasets, which contain the energy and position of every recorded particle, emission channeling patterns were extracted for the β^- energy window of 10-500 keV.

6.1.2 Simulations

In order to analyze the experimental recorded patterns, theoretical angular distributions were calculated by the *manybeam* program. The simulations were carried out for the emitter atom ^{59}Fe on different lattice sites: Zn and O substitutional, main interstitials (bond-centered, anti-binding, wide open interstitials and “hexagonal”, in figure 6.1.2) and statically displaced sites between specific pairs of the formers. Figure 6.1.3 shows the theoretical emission patterns along the [0001], $[\bar{1}102]$, $[\bar{1}101]$ and $[\bar{2}113]$ axes for 100% of ^{59}Fe atoms situated on substitutional Zn sites (SA), substitutional O sites (SB), and the interstitial T, HA, and O sites.

Since both Zn and O atoms are located in the same c-axis atomic rows, they give rise to the same emission pattern along this direction. In addition, there are also interstitial sites (e.g. the T site) along the c-axis rows, which also lead to the same angular emission yield as for the substitutional sites. Since the HA, HB and O sites are all centered in the hexagon spanned by the c-axis atomic rows, they also produce the same channeling pattern (but different from that of SA, SB and T) of hexagonal symmetry along the [0001] direction. In order to discriminate between these sites, emission patterns along other crystalline directions should be inspected. In this work, as usual for wurtzite lattice materials, the $[\bar{1}102]$, $[\bar{1}101]$ and $[\bar{2}113]$ axes were chosen. As can be seen from 6.1.3, there is, for every site, at least one angular yield which significantly differs from the others, which already demonstrates the specificity of the emission channeling technique. Combining the results obtained along different crystal axes, one thus obtain an accurate lattice site determination of the probe atoms.

6.1.3 Fitting the experimental patterns

Figure 6.1.6 shows emission pattern measured along the [0001] direction in the as-implanted state. Comparing with the patterns from figure 6.1.3, the axial channeling effect and the intersecting planar effects already suggest that ^{59}Fe is situated along the c-axis atomic rows. More quantitative data (not only the lattice site(s) but also the fractions and rms displacements of the impurity atoms) can be extracted by performing a least-squares fit of this experimental pattern to a set of theoretically calculated patterns (see section 5.4.1). The fractions were subsequently corrected for electron scattering. A correction factor of 1.6 was used, estimated by means of Monte-Carlo simulations [84] (described in section 5.4.1).

The symptomatic pronounced broadening effect is already observed in the lower fluence sample (ZNO_MF) patterns and even more for the highest fluence (figures 6.1.6, 6.1.7, 6.1.8 and 6.1.9 for MF sample and 6.1.10, 6.1.11, 6.1.12 and 6.1.13 for HF sample). This broadening is conventionally attributed to crystal mosaicity (during growth) or structural disorder (related to strain fields induced by a high concentration of defects, whether impurities and/or implantation damage) as discussed in section 5.5. To model these effects, the simulated patterns of the initial set were smoothed with additional Gaussian σ values, ranging from 0.1° , which accounts only for the angular resolution due to the finite beam spot, to 0.6° . Half a degree is around one sixth of the pattern side, so for higher values of σ , the border *cut-off* effect propagates to a significant fraction of the fitted data. Therefore, higher values of smoothing σ do not produce reliable patterns. It should be noted that this procedure is acceptable to model the mosaic spread but is much less adequate to simulate the high fluence effect. In fact, the (highly non-trivial) mechanisms responsible for this fluence dependent broadening effect are still to be studied; after all this is one of the first high fluence emission channeling experiments.

The simple fact that the broadening effect gets worse with higher fluence for these two samples (supposedly with the same crystallinity) and the experience from other low *vs.* high(er) fluence EC

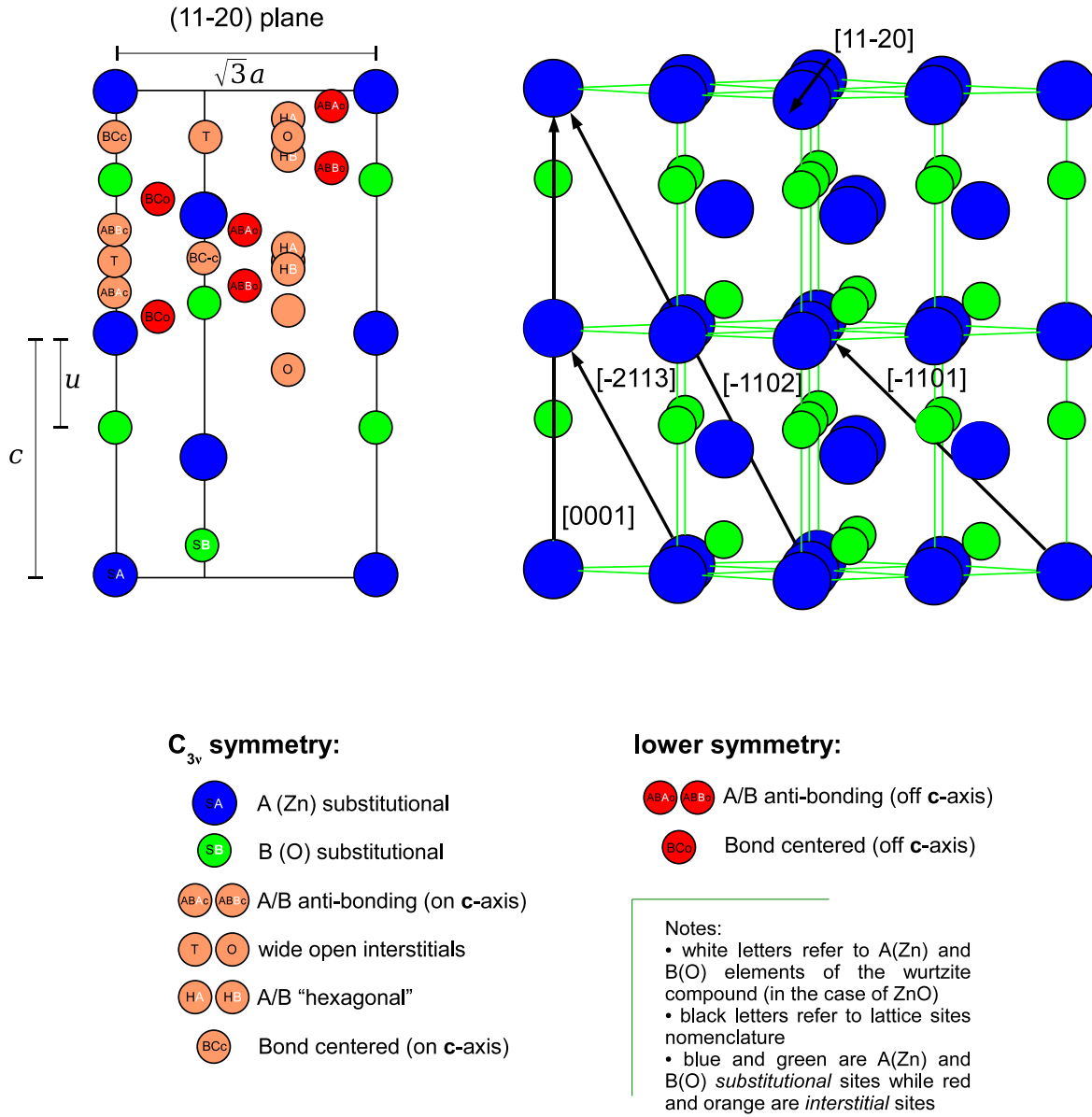


Figure 6.1.2: (Left) Cross-section of the ZnO wurtzite lattice along the $(11\bar{2}0)$ plane, showing Zn and O substitutional and main interstitial sites. All sites located along the c -axis and in the center of the interstitial region (in orange) are sites of trigonal (C_{3v}) symmetry, while the sites shown in red have lower than trigonal symmetry. (Right) Projection of the ZnO wurtzite lattice along the (near) $[11\bar{2}0]$ direction, showing the channeling axes used in this work.

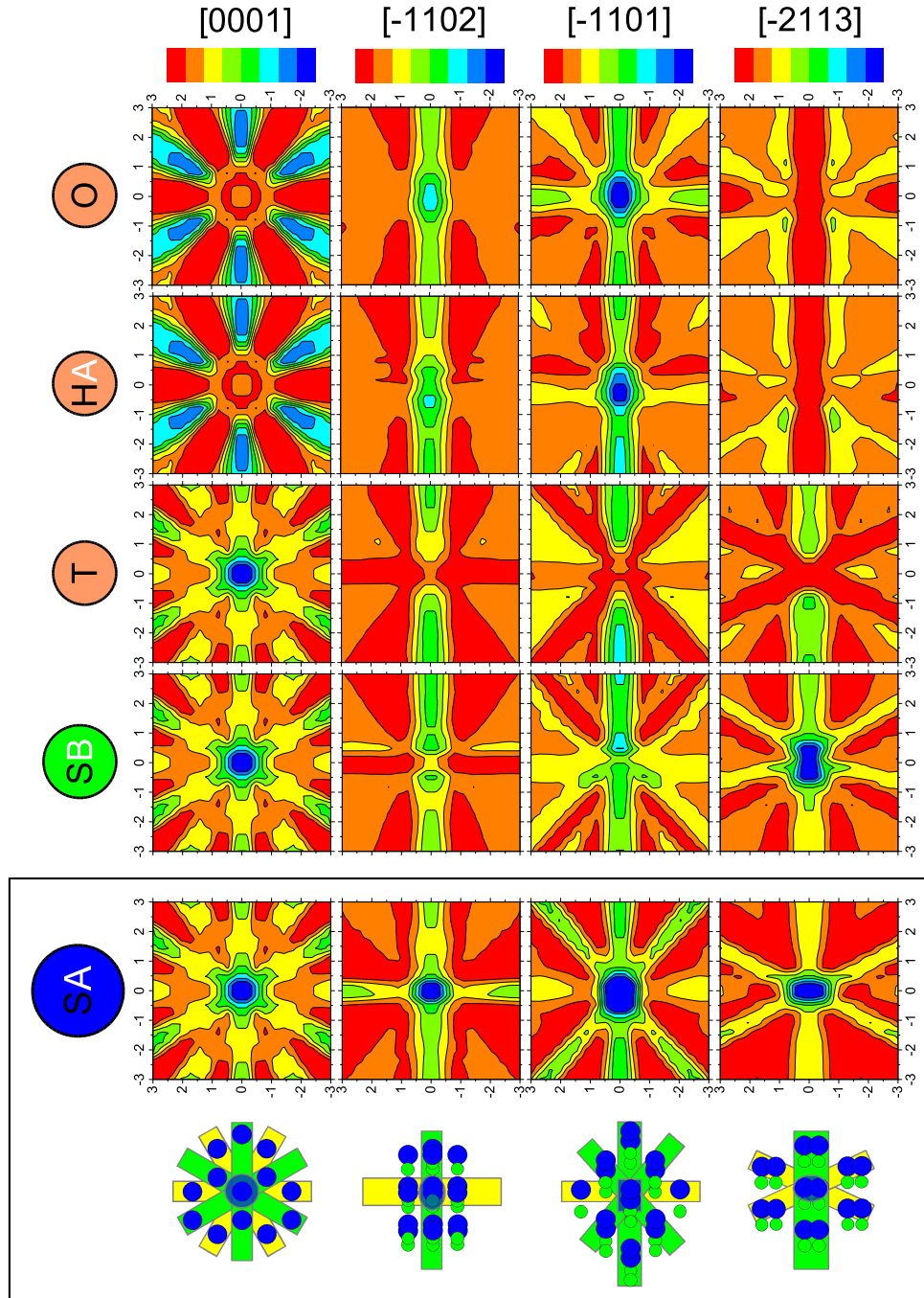


Figure 6.1.3: Some of the simulated patterns: 100% of emitter atoms (^{59}Fe) on substitutional Zn sites SA, substitutional O sites SB, and the interstitial T, HG, and O sites. For SA site the lattice projection along each direction evidences the correspondence between the strong channeling axis/planes and the axes/planes of high ionic density.

experiments clearly evidence the cause-effect relation, as discussed on page 33. Although not ideal, the Gaussian smoothing is the current approach to simulate these effects. Thereby, all experimental patterns were fitted to the whole range of σ values (from 0.1° to 0.6° with a 0.05° step). For each σ , a best (two fraction: one site plus random²) fit scenario, in terms of fitted lattice sites and respective rms displacements, was found³. Plotting fit quality as a function of σ , a nice *V* shaped curve pointed unambiguously the best fit σ from which the fitted parameters should be taken (both the fraction and the rms values are very sensitive to σ). However, for more than half of the patterns ([0001] patterns of MF sample and all the patterns of HF), the maximum $\sigma = 0.6^\circ$ was not sufficient⁴ (the fit kept improving). Thereby, it was necessary to apply a more complex (although less objective) criteria of physically meaningful parameters and the intuition and experience accumulated from other EC experiments. The results are compiled in figures 6.1.4 and 6.1.5 for the MF and HF samples, respectively. For MF sample, the criteria gave a fixed $\sigma = 0.1^\circ$ for [0001] pattern. For the HF sample the σ values are not displayed because they were fixed as 0.3° for [0001] patterns and 0.6° for the others. It should be noted that, although the σ values used for the [0001] direction are lower (in both samples) than for the other directions, the broadening effect is actually more pronounced. This somehow contrasts with what was found in [84], where high fluence GaN:Er ($5.2 \times 10^{14} \text{ cm}^{-2}$) layer suffered a lattice expansion only in the [0001] direction⁵, thereby affecting only the off surface channeling directions. However, for the MF and HF samples, the fluence is one order of magnitude above, which can result in a more complex behavior, such as lattice expansion in more than one preferred direction. Along with other subjective choices, this made clear the inadequacy of the Gaussian smoothing approach and the necessity to develop a suited modeling approach⁶.

Despite the difficulties related with the high fluence intangible effects, a way was found tackling the unknowns and in the following, after a quantitative discussion of the results, a qualitative picture is formulated.

6.1.4 Discussion

For the MF sample (see figure 6.1.4), around 85% of the implanted Fe is located on Zn substitutional sites⁷, already in the as-implanted state, with the remainder situated at random sites⁸. The σ values are well above the usual which is attributed, as justified above, to the high fluence effect. Fraction, rms displacement and σ values, all stay approximately constant up to 400°C annealing. From 600°C on, σ monotonically decreased indicating that, by temperature enhancement of atomic mobilities, some kind of “accommodation” of the crystal to the defects (impurities and damage) took place. This is specially evident after 700°C annealing, with the rms displacements of the implanted Fe, determined from all 4 directions, decreasing and converging to the Zn value, an evident mark of structural stability. However, also the S_{Zn} fraction decreases and for 800°C it falls to less than half. This is rather usual in EC experiments, and can have a number of reasons:

- ⁵⁹Fe diffusion. The implanted impurities might diffuse out of the sample (short-range diffusion), but that was not the case for this experiment, since the activity measured in the sample before and after the annealing was approximately the same. They can also diffuse to deeper regions inside the sample⁹, but in order to produce such a decrease in the fitted fractions, it should be a quite long range diffusion, not accounted for in the literature for any ion in ZnO, for these

²Motivated by the low fluence experiment results which located between 90% and 100% of the Fe in perfectly Zn substitutional sites [88].

³In practice, the tendency from $\sigma = 0.1^\circ$ was found to be reliable for the following sets, reducing the analysis effort, that otherwise would have been more than 5 times the usual.

⁴The maximum $\sigma = 0.6^\circ$ was determined as a compromise between the gain in fit quality and the *cut-off* border effect.

⁵This expansion is caused by the formation of interstitial atoms (these can be both lattice or dopant atoms) in the GaN lattice during implantation. As a consequence of the efficient dynamic annealing process this is only of limited importance for low fluences of 10^{13} cm^{-2} , but becomes increasingly more important in the fluence range of $10^{14} - 10^{16} \text{ cm}^{-2}$.

⁶Although absolutely non-straightforward. Indeed it is a mind-breaking task, the attempt to incorporate the complex beauty of the physics of defects in systems of high structural disorder into an approach (*manybeam*) which is half of the way between *ab initio* and the simple modeling.

⁷The significant difference between fraction values calculated from different channeling directions is an artifact from the use of different sigmas. It was observed during the fitting that larger σ values lead to larger fractions, which relates perfectly with the results in figure 6.1.4. A suited (and thereby more precise) approach to model the fluence effect may approximate the fitted fractions.

⁸These random sites correspond to low-symmetry sites, or sites with very disordered or amorphous surroundings.

⁹Diffusion to near surface regions would, in principle, enhance the fitted fractions.

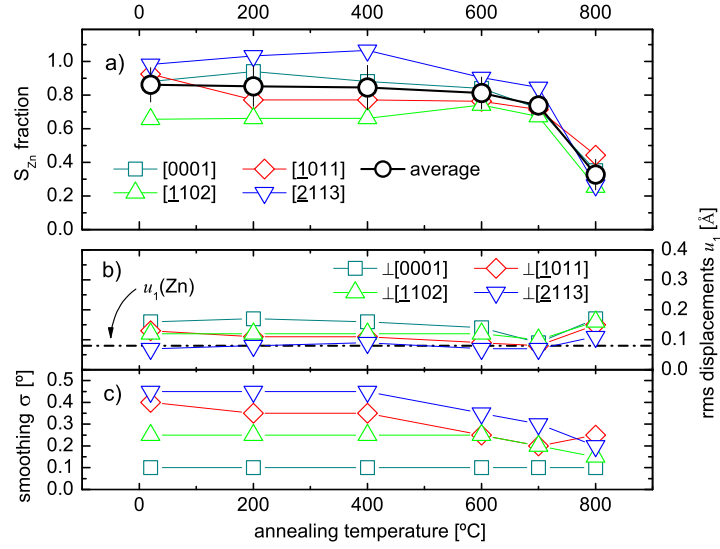


Figure 6.1.4: Compiled results for the MF sample ($5 \times 10^{15} \text{ cm}^{-2}$), as a function of isochronal annealing temperature: (a) fractions of ^{59}Fe on substitutional Zn sites determined from each axis (the black circles display the average and the error bars correspond to the standard deviations; the remainder of ^{59}Fe is considered to be located on random sites), (b) root mean square displacements from the ideal substitutional site, perpendicular to the respective measurement axis (the dashed line indicates the room temperature thermal vibration amplitude of Zn in ZnO, $u_1(\text{Zn}) = 0.082 \text{ \AA}$) and (c) standard deviation of the smoothing Gaussian.

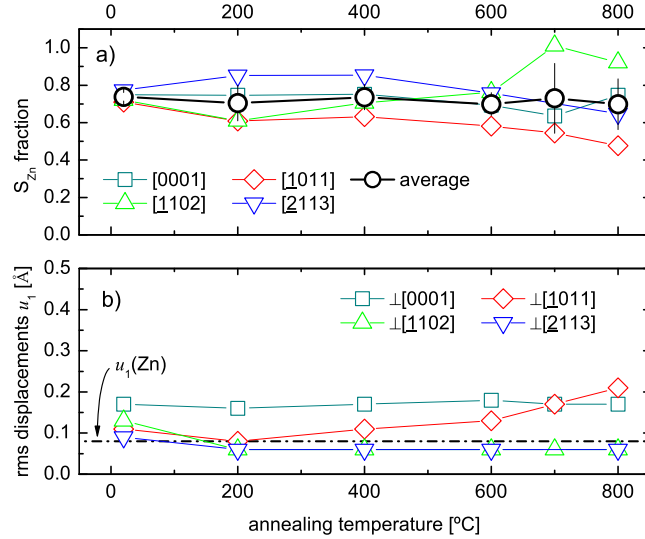


Figure 6.1.5: Compiled results for the HF sample ($1 \times 10^{16} \text{ cm}^{-2}$), as a function of isochronal annealing temperature: (a) fractions of ^{59}Fe on substitutional Zn sites determined from each axis (the black circles display the average and the error bars correspond to the standard deviations; the remainder of ^{59}Fe is considered to be located on random sites) and (b) root mean square displacements from the ideal substitutional site, perpendicular to the respective measurement axis (the dashed line indicates the room temperature thermal vibration amplitude of Zn in ZnO, $u_1(\text{Zn}) = 0.082 \text{ \AA}$).

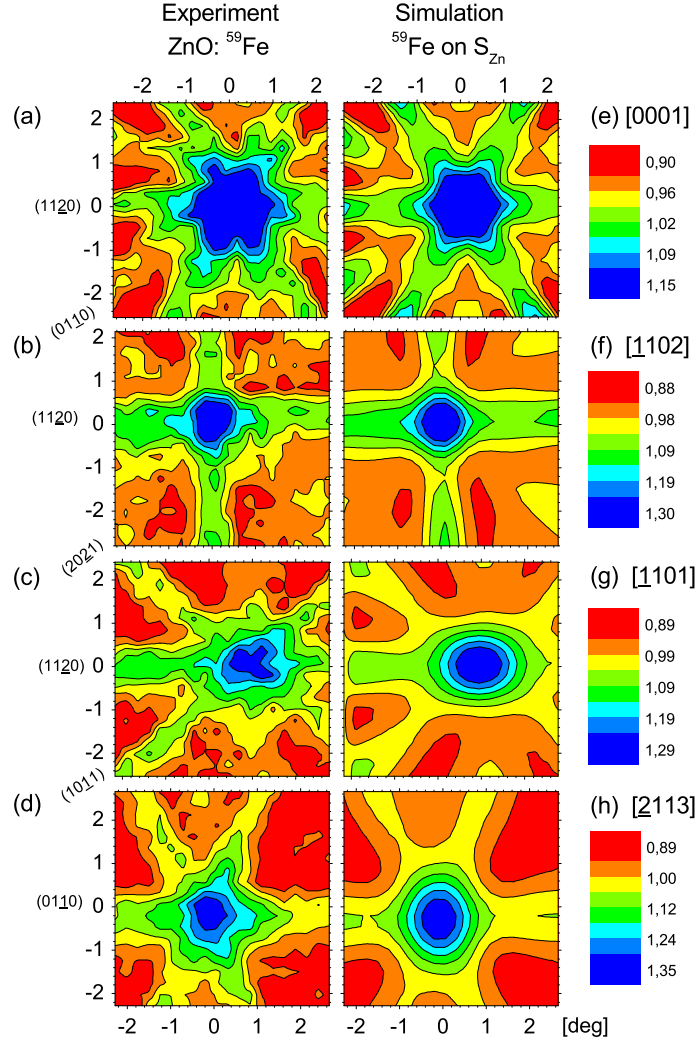


Figure 6.1.6: Experimental angle-dependent β^- emission yields from ^{59}Fe in ZnO (MF sample: $5 \times 10^{15} \text{ cm}^{-2}$) after room-temperature implantation (as-implanted) around the (a)[0001], (b)[$\bar{1}102$], (c)[$\bar{1}101$] and (d) [$\bar{2}113$] axes. (e)-(h) Best fits of simulated channeling patterns for SA (S_{Zn}) sites to the experimental yields, corresponding to 88%, 65%, 92% and 98% of ^{59}Fe on S_{Zn} sites with rms displacements of 0.16, 0.12, 0.13 and 0.07 Å and σ values of 0.10°, 0.25°, 0.40° and 0.45°, respectively.

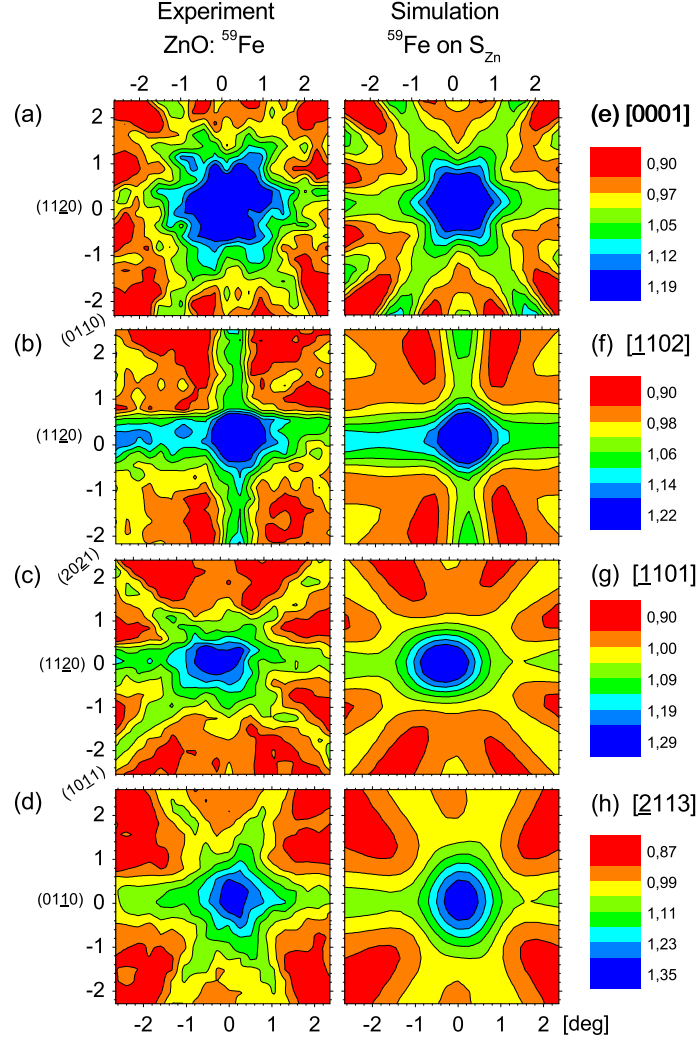


Figure 6.1.7: Experimental angle-dependent β^- emission yields from ^{59}Fe in ZnO (MF sample: $5 \times 10^{15} \text{ cm}^{-2}$) around the (a) [0001], (b) $[\bar{1}102]$, (c) $[\bar{1}101]$ and (d) $[\bar{2}113]$ axes following 200°C vacuum annealing. (e)-(h) Best fits of simulated channeling patterns for SA (S_{Zn}) sites to the experimental yields, corresponding to 94%, 66%, 77% and 100% of ^{59}Fe on S_{Zn} sites with rms displacements of 0.17, 0.12, 0.12 and 0.08 Å and σ values of 0.10° , 0.25° , 0.35° and 0.45° , respectively.

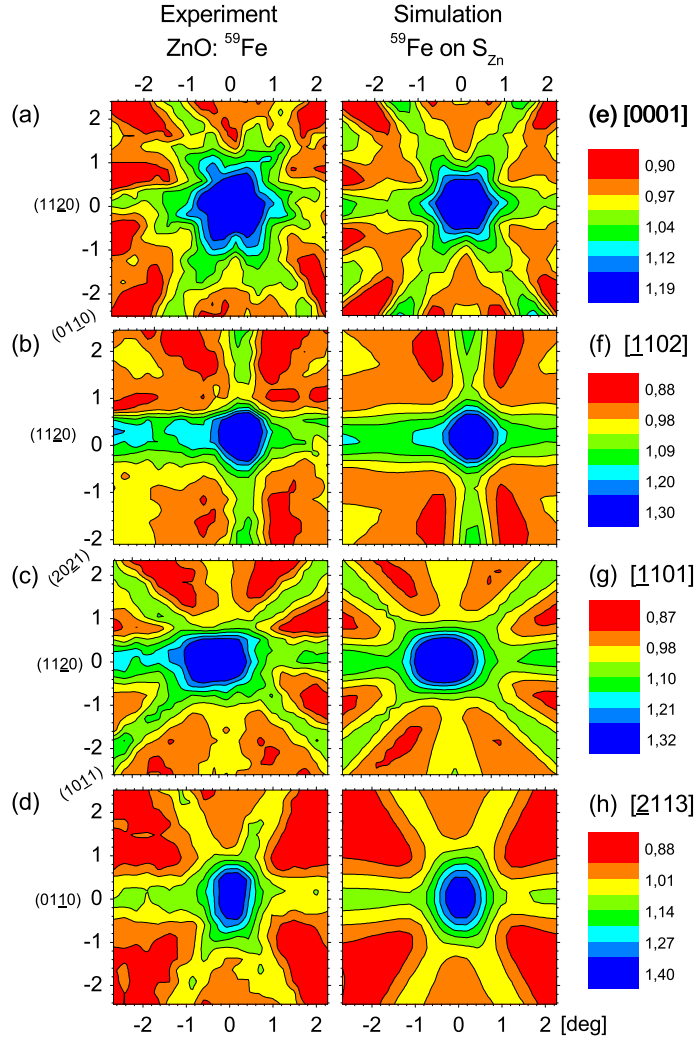


Figure 6.1.8: Experimental angle-dependent β^- emission yields from ^{59}Fe in ZnO (MF sample: $5 \times 10^{15} \text{ cm}^{-2}$) around the (a)[0001], (b)[1102], (c)[1101] and (d) [2113] axes following 700°C vacuum annealing. (e)-(h) Best fits of simulated channeling patterns for SA (S_{Zn}) sites to the experimental yields, corresponding to 98%, 66%, 77% and 106% of ^{59}Fe on S_{Zn} sites with rms displacements of 0.16, 0.12, 0.12 and 0.09 Å and σ values of 0.10°, 0.20°, 0.20° and 0.30°, respectively.

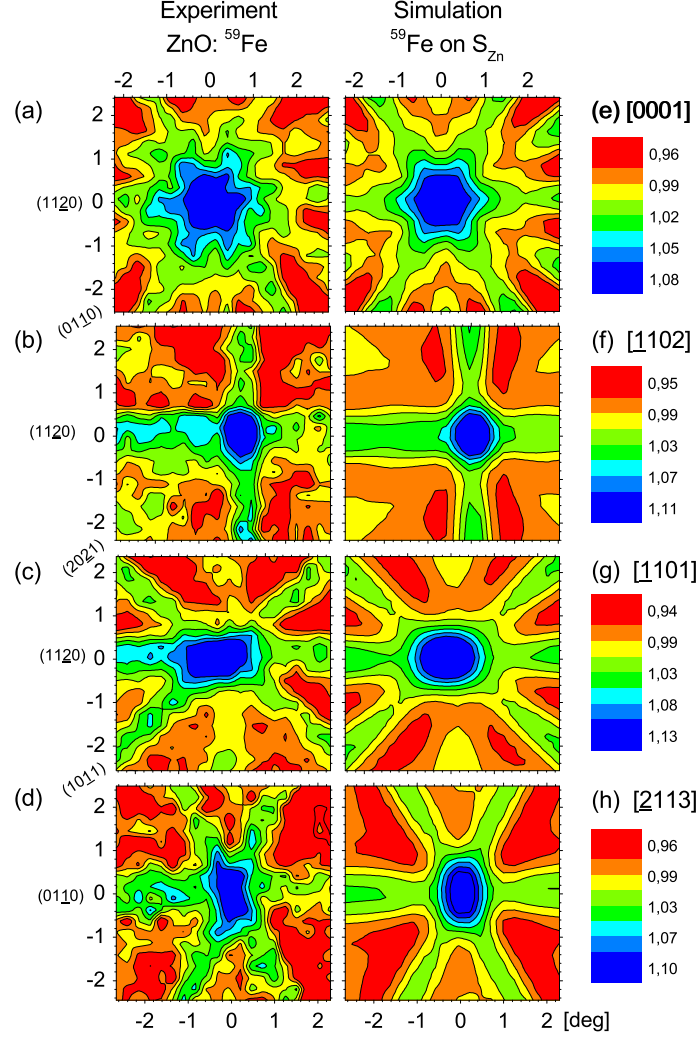


Figure 6.1.9: Experimental angle-dependent β^- emission yields from ^{59}Fe in ZnO (MF sample: $5 \times 10^{15} \text{ cm}^{-2}$) around the (a)[0001], (b)[$\bar{1}102$], (c)[$\bar{1}101$] and (d) [$\bar{2}113$] axes following 800°C vacuum annealing. (e)-(h) Best fits of simulated channeling patterns for SA (S_{Zn}) sites to the experimental yields, corresponding to 35%, 25%, 44% and 26% of ^{59}Fe on S_{Zn} sites with rms displacements of 0.17, 0.16, 0.16 and 0.11 Å and σ values of 0.10° , 0.15° , 0.25° and 0.20° , respectively.

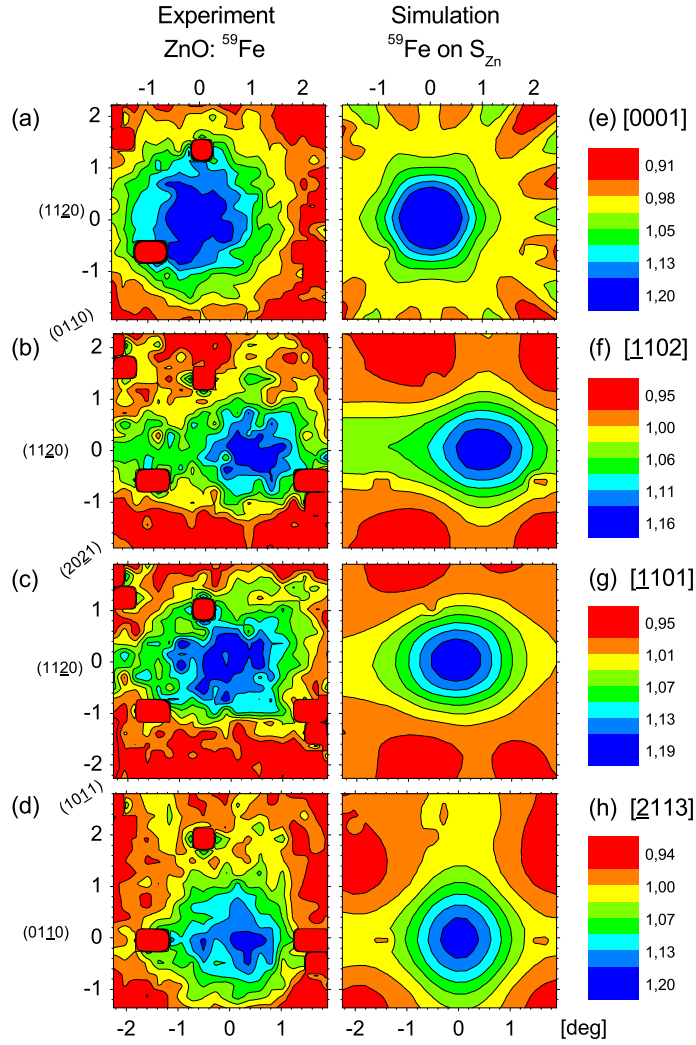


Figure 6.1.10: Experimental angle-dependent β^- emission yields from ^{59}Fe in ZnO (HF sample: $1 \times 10^{16} \text{ cm}^{-2}$) after room-temperature implantation (as-implanted) around the (a)[0001], (b)[$\bar{1}$ 102], (c)[$\bar{1}$ 101] and (d) [$\bar{2}$ 113] axes. (e)-(h) Best fits of simulated channeling patterns for SA (S_{Zn}) sites to the experimental yields, corresponding to 75%, 71%, 72% and 77% of ^{59}Fe on S_{Zn} sites with rms displacements of 0.17, 0.13, 0.11 and 0.09 and 0.07 Å and σ values of 0.30°, 0.60°, 0.60° and 0.60°, respectively. The small red regions common to all patterns refer to *dead* pixels, and were not taken in account during the fitting.

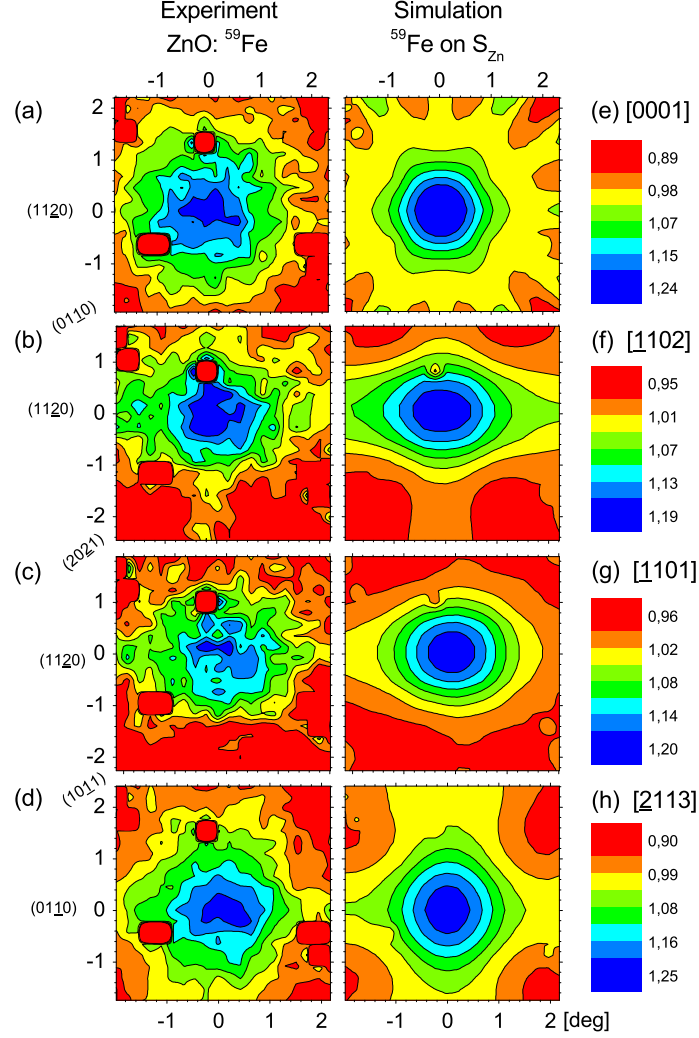


Figure 6.1.11: Experimental angle-dependent β^- emission yields from ^{59}Fe in ZnO (HF sample: $1 \times 10^{16} \text{ cm}^{-2}$) around the (a)[0001], (b)[1102], (c)[1101] and (d) [2113] axes following 200°C vacuum annealing. (e)-(h) Best fits of simulated channeling patterns for SA (S_{Zn}) sites to the experimental yields, corresponding to 75%, 61%, 61% and 85% of ^{59}Fe on S_{Zn} sites with rms displacements of 0.16, 0.08, 0.06 and 0.06 Å and σ values of 0.30°, 0.60°, 0.60° and 0.60°, respectively. The small red regions common to all patterns refer to *dead* pixels, and were not taken in account during the fitting.

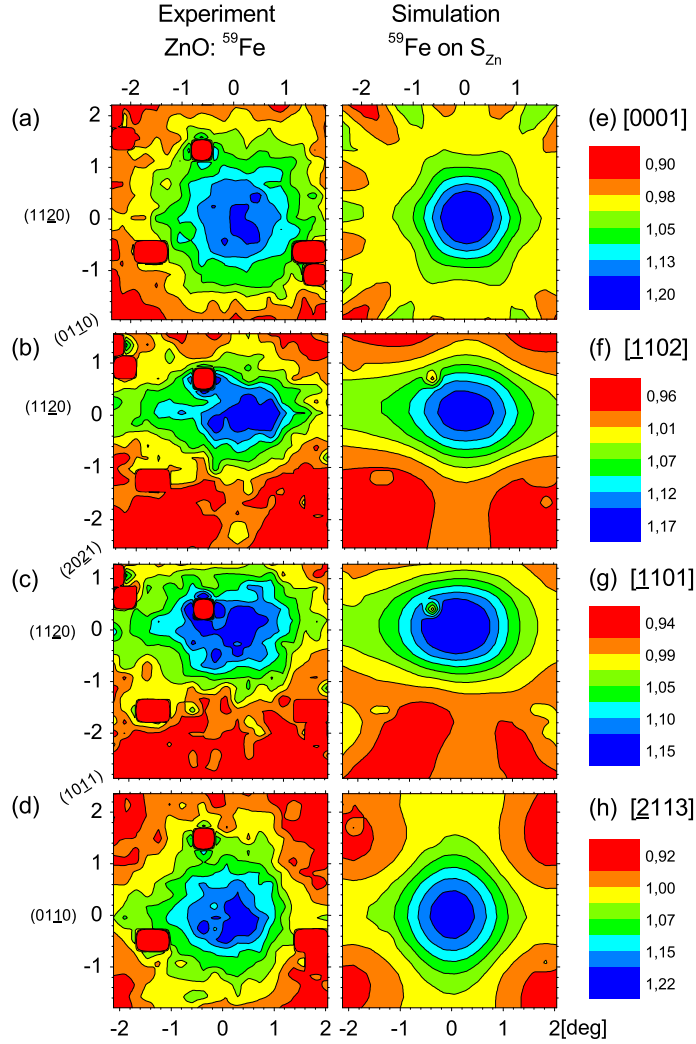


Figure 6.1.12: Experimental angle-dependent β^- emission yields from ^{59}Fe in ZnO (HF sample: $1 \times 10^{16} \text{ cm}^{-2}$) around the (a)[0001], (b)[$\bar{1}102$], (c)[$\bar{1}101$] and (d) [$\bar{2}113$] axes following 700°C vacuum annealing. (e)-(h) Best fits of simulated channeling patterns for SA (S_{Zn}) sites to the experimental yields, corresponding to 63%, 100%, 54% and 76% of ^{59}Fe on S_{Zn} sites with rms displacements of 0.17, 0.17, 0.06 and 0.06 Å and σ values of 0.30°, 0.60°, 0.60° and 0.60°, respectively. The small red regions common to all patterns refer to *dead* pixels, and were not taken in account during the fitting.

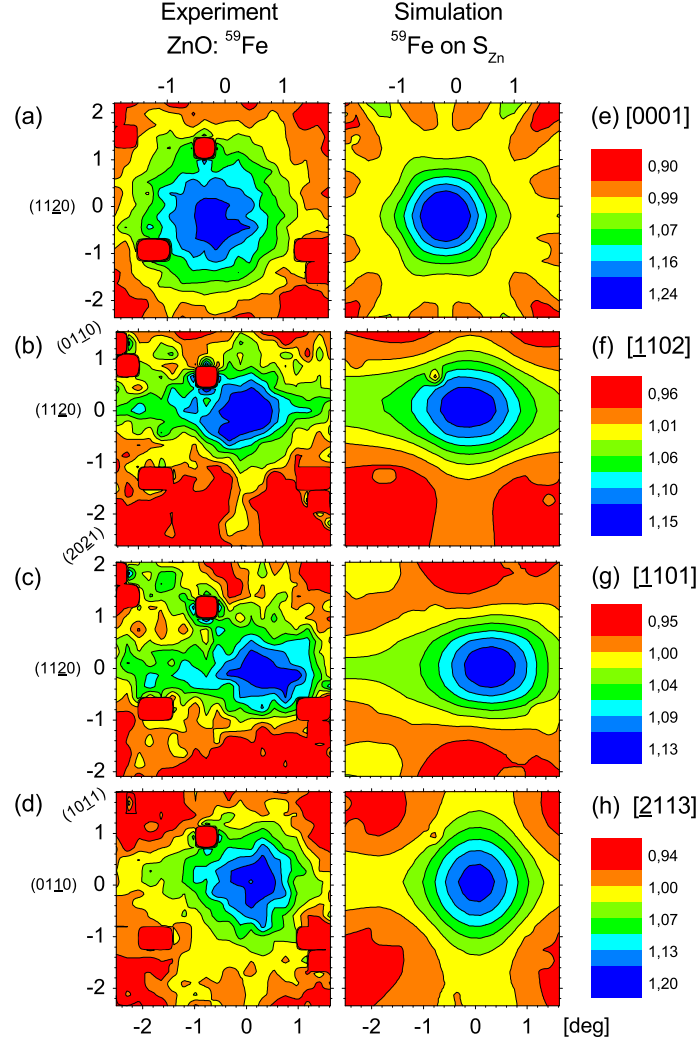


Figure 6.1.13: Experimental angle-dependent β^- emission yields from ^{59}Fe in ZnO (HF sample: $1 \times 10^{16} \text{ cm}^{-2}$) around the (a)[0001], (b)[$\bar{1}102$], (c)[$\bar{1}101$] and (d) [$\bar{2}113$] axes following 800°C vacuum annealing. (e)-(h) Best fits of simulated channeling patterns for SA (S_{Zn}) sites to the experimental yields, corresponding to 75%, 92%, 48% and 65% of ^{59}Fe on S_{Zn} sites with rms displacements of 0.17, 0.21, 0.06 and 0.06 Å and σ values of 0.30° , 0.60° , 0.60° and 0.60° , respectively. The small red regions common to all patterns refer to *dead* pixels, and were not taken in account during the fitting.

annealing temperatures. Moreover, while (inwards) diffusion is expected to influence the fitted fractions, it does not have a pronounced influence on the identification of the rms displacements. The opposite behaviour, a consistent decrease with temperature, was observed in this experiment. Therefore, diffusion of the implanted ⁵⁹Fe should not be the reason for the decrease in the fitted fraction.

- Precipitation of the Fe or reaction with other elements in the matrix. If the Fe starts forming clusters or secondary phases, the symmetry of the atoms sites is different than for the simulated (ZnO) lattice, thereby decreasing the fitted fractions. But if this was the case, the effect should be even more noticeable for higher fluences, since the average distance between two Fe atoms diminishes and a larger fraction of the Fe would react or precipitate. The results for the HF sample point precisely in the opposite direction (figure 6.1.5)¹⁰ and thus these clustering/reacting processes should not be the reason for the decrease in the fitted fraction neither.
- Loss of crystallinity. In the high-fluence regime, the implantation-induced defects can, as was observed in [84] for Fe:GaN, form larger point defect clusters and a dense network of planar defects (dislocations and stacking faults)¹¹. At the same time, it was observed that the sample surface can act as a *nucleation* region for point defects, which eventually leads to the formation of an amorphous or polycrystalline surface layer. Both defect types will drastically influence the local crystal structure. As a consequence, an increasingly large fraction of the impurity atoms sits on lattice sites with highly damaged surroundings, leading to an increase in the random fraction at the expense of the substitutional fraction. Although no RBS was performed on these samples, [89] reports on such a study on $1 \times 10^{16} \text{ cm}^{-2}$ Fe:ZnO (the same as the HF_ZNO) prepared under very similar conditions (100 keV ion implanted Fe⁺) and showed no formation of extended damage in the surface, further confirming the knowledge of the damage resistance of ZnO.
- Migration and accumulation of point defects into the near surface layers. During highest temperature annealing, point defects, such as vacancies, present in relatively high concentrations due to the implantation, may diffuse to the surface¹² as argued in [88]. Also oxygen vacancies are very likely to be produced in the near surface layers, since the annealing was performed in vacuum. Such concentrations of damage, although below the loss of crystallinity limit, result in an enhanced dechanneling. Some of the electrons emitted from ⁵⁹Fe atoms in substitutional sites may thus loose anisotropy being detected as coming from the random fraction.

Nothing seems to rule out the latter hypothesis. In fact, at least part of the decrease is explained by an immaterial effect of the use of a lower σ (see figure 6.1.5 b), which as already pointed, is not an accurate approach to model the structural disorder produced by the high fluence implantation. Assuming that the explanation lies entirely on these two facts, the decrease is thus only *apparent* and since no other site provided a better fit (which was obvious since no significant change was observed in the patterns), one concludes that between 80% and 90% of the implanted Fe in ZnO is located in the Zn substitutional site for the whole annealing temperature range.

For the high fluence sample everything seems very similar. The Fe is still located in Zn substitutional sites although 10% less than the lower fluence sample. This might be a real decrease of substitutional *vs.* random occupancy. In fact, that would be consistent with a ZnO:Cu EC experiment¹³, where the same anti-correlation between substitutional fraction and implanted dose was evidenced [96]. However, this decrease can be attributed to the fact that the σ 's used for the fitting were lower than the best fit values (the fit kept improving up the maximum value allowed), which, as already pointed, has the consequence of an apparent lowering of the fitted fractions. Another difference is the suppression of the fraction abrupt decrease for 800 °C annealing. This is inconsistent with the explanation forwarded above of accumulation of point defects in the near surface layers, since more damage is produced in higher fluence implantations. Some discussion could be made around a possible source of this apparent suppression¹⁴, but just by looking at the experimental patterns (figures 6.1.10 to 6.1.13) it is evident that the sensitivity of the fitting is very limited in the case of

¹⁰In the second part of the discussion it is argued that the fractions actually decrease after the 800 °C annealing of the HF sample too, but still somewhat less than for the MF sample.

¹¹GaN is also a wurtzite crystal structurally very similar to ZnO, thus being an interesting material to compare with.

¹²This remark is of major importance in the qualitative discussion below.

¹³Cu is a 3d as Fe is, so similar properties are expected in ZnO:Fe and ZnO:Cu in some extent.

¹⁴Since different directions give very different behaviors of $f(\text{S}_{\text{Zn}})$ as a function annealing temperature (see figure 6.1.5), one can try to point the most reliable one. The fitting was performed always from lower to higher values of σ and

this higher fluence experiment. Thereby, the only reliable conclusion from the HF experiment is that the majority of the implanted Fe is located on Zn substitutional sites.

After this quantitative discussion a more insightful (although more qualitative) picture is presented in the rest of the section.

6.1.5 Near-substitutional sites

A refinement of the analysis was motivated by two details of the experimental patterns:

- The strengthening of the channeling along the $[11\bar{2}0]$ plane in the $[\bar{1}102]$ axis pattern (in the MF sample¹⁵, figures 6.1.6 to 6.1.9), which could have several sources, from lattice expansion in particular directions to occupancy of other lattice sites.
- The consistently different values of rms displacement determined from different axes (again for the MF sample only, for the same reasons), indicating possible anisotropy of preferred displacement directions.

The possibility of lattice expansion in preferred directions is related with high fluence effects on channeling, but was not investigated, since the available theoretical patterns had been simulated for a perfect ZnO lattice, being left for a future work. Nevertheless, combining both observations, the most natural explanation would be a non-negligible occupancy of other lattice sites. Several combinations of interstitial and intermediate¹⁶ sites were fitted and, although the experimental patterns quality (or the inadequacy of the Gaussian smoothing approach) did not allow significant sensitivity, a general tendency was observed: when only Zn substitutional sites (varying rms displacement values and static displacement towards particular interstitials) were fitted, the fit improved significantly (in the % range) with the total $f(S_{\text{Zn}}) + f(S_{\text{Zn}}^{\text{disp}})$ being kept approximately the same as determined for perfect S_{Zn} . Moreover it was made clear that the S_{Zn} population was divided somewhat equally between two categories: perfect S_{Zn} with large ($\approx 0.15 \text{ \AA}$) rms displacements and S_{Zn} displaced $\approx 0.15 \text{ \AA}$ towards the ABAC interstitial¹⁷ (Zn anti-bonding along the c-axis) with rms displacements of $\approx 0.08 \text{ \AA}$ (approximately the Zn thermal vibration amplitude). Static displacements towards the BCc interstitial, i.e. the closest O, was also tried (using the same combinations) giving worst agreement than for perfect S_{Zn} only. Some geometric discussion could be forwarded around these displacements but the available simulated patterns do not span the whole range of possible preferred displacement directions. Moreover, the perfect S_{Zn} fraction with large rms displacements can be interpreted as a superposition of displacement towards nonequivalent directions. Imagine a row of atoms in which the emitting Fe atoms (substituting Zn) were displaced to Zn sites of the nnn or $nnnn$ shells (with radii differing only by $\sim 1\%$) along different directions. Such a superposition of small static displacements would in principle be very similar to an isotropic rms displacement (notice the same $0.15 \text{ \AA}$).

Although rather qualitative, these observations point to a displacement of the implanted Fe (substituting Zn) to the surrounding Zn sites. However, the covalent sizes of Fe and Zn covalent radii are very close and thereby this displacement is not explained, in principle, by simple size mismatch. It points more clearly to the formation of impurity-defect complexes. For instance, the strain caused by a nearby interstitial atom (e.g. the Zn atom that was substituted) or the strain de-compensation due to a nearby vacancy atom will displace the impurity atom from the perfect substitutional Zn site.

the following behaviour was consistently observed. Below some kind of threshold value, the fitted rms displacement was constrained to the minimum $0.06 \text{ \AA}$. When the σ approached the *best fit* one, the fitted rms displacement abandoned that value, monotonically increasing with σ . The only channeling axis for which this happened was the $[\bar{1}101]$, promoting it to the most reliable one. In fact, the $f(S_{\text{Zn}})$ curve as a function annealing temperature of the $[\bar{1}101]$ direction has a very similar shape to the average f of MF sample, with the same significant decrease at 800°C . That decrease should be even larger than for the MF sample (and it is not), since a larger amount of damage (which can accumulate at the surface) is produced. Indeed, that is what is expected from the following. Since the fitted rms displacement values increase from 200°C to 800°C annealing, which was not observed in the lower fluence samples, this line of thoughts furthermore points to the crystal accommodation to the defects with increase of annealing temperature, as expected and already seen in the MF sample. Since this makes the best fit σ to decrease with temperature while one used the same, the difference between the correct and the actually fitted fractions should also decrease with annealing temperature. Thereby, the actual difference between $f(S_{\text{Zn}})$ values at 200°C and 800°C would be larger than it appears to be, which allows the possibility for it to be equal or larger than for the MF sample, as expected.

Note that this only supports that the abrupt decrease of the fitted fractions at 800°C is only apparent.

¹⁵For the HF sample, the low quality of the patterns precludes any refinement.

¹⁶Substitutional sites with static displacements towards specific interstitials.

¹⁷Displaced S_{Zn} site along the c-axis towards the furthest O (see figure 6.1.2).

6.1.6 Impurity-defect complexes

In principle, in an ideal EC experiment (which is not the case) it would be possible to deduce what native defects bind to the impurities, by measuring the direction and magnitude of the static displacement(s). In practice, it is usually rather difficult to extract reliable values for such small static displacements. The reason for this is that a change in the rms displacement amplitude (i.e. an isotropic displacement) has almost the same effect on the channeling spectra as a small static displacement. This is especially true for displacements from the substitutional Zn site, where the crystal potential is almost rotationally symmetric. It can get even more complex, if there are several defect complexes (or of different symmetry relative to the channeling axis) involved, each displacing the impurity atoms along different crystalline directions. As already stated, such a superposition of small static displacements would in principle be very similar to an isotropic impurity displacement.

It is therefore necessary to cross these observations with results obtained from other techniques. However, ion implantation is not an equilibrium process and the relative abundances of the different types of defects do not necessarily correspond to the thermodynamically most favorable situation that can be deduced simply from the formation energies of those defects. These specificities reduce in a large extent the reported results that can be used.

Fortunately, a very insightful experiment was performed simultaneously at ISOLDE on Fe ion implanted ZnO also in the context of DMS research [95]. The analytical power and sensitivity of ⁵⁷Fe Mossbauer spectroscopy was used to gain atomic-scale information on room temperature ferromagnetism. They found evidences of magnetic ordering in the local atomic vicinity of substitutional Fe_{Zn}³⁺ with ordering temperatures $\gg 600$ K, which was attributed to the formation of (magnetically ordered) impurity-defect complexes. These are formed when the impurity (Fe) atom bind (and magnetically couple) to lattice defects in the atomic surroundings, with the Zn vacancies (abundantly created during the implantation) as the strongest candidate. These magnetic complexes were observed to be stable up to 600 K (although the population decay behaviour was not described). This motivated (theoretical) *ab initio* calculations [94] which confirmed the stability of these complexes (for Zn vacancies; Fe_{Zn}-V_O are not stable) relative to isolated Fe_{Zn} and Zn vacancies, due to the magnetic coupling interaction. Also, by positron annihilation spectroscopy (PAS) performed on ZnO after room temperature e⁻-irradiation (producing the same kind of defects as ion implantation) the Zn vacancy was observed to be associated in a complex with an unknown defect [93]. Furthermore, the already mentioned RBS study on $1 \times 10^{16} \text{ cm}^{-2}$ Fe ion implanted ZnO [89], showed that temperature treatments up to 600 °C only slightly annealed the damage (RBS is specially sensitive to Zn interstitials, which must relate in number with Zn vacancies). After 900 °C annealing an abrupt decrease was observed but still some damage was present. Crossing these with the EC results (specially from the MF sample, which provides more sensitive information) a qualitative description of what happened in the samples during the various annealing steps is given in the following.

After implantation, the majority of Fe occupied the Zn substitutional site, as is clearly evidenced by the EC results. In the process, dense collision cascades resulted, as is well known, in a large amount (at least of the order of magnitude of the implanted Fe dose, see section 3.3) of Zn vacancies in the implanted layer and the region between it and the surface. The Zn vacancy, is stable presumably only up to room temperature. But it seems that in the presence of a sufficiently high concentration of impurities (Fe in this case, but there are indications spread over the literature that equally point to other elements) these are able to bind, forming impurity defect complexes (Fe_{Zn}-V_{Zn} in this case), precluding the anneal out of this part of the damage up to 600 °C since the Zn interstitials do not recombine as long as the Zn vacancies are stabilized in complexes. This is supported by theory [94] and by experiment: ⁵⁷Fe Mossbauer spectroscopy [95] identified these complexes up to 600 K, in samples of much lower fluence (two orders of magnitude at least); these EC results indirectly indicate that these complexes are stable up to higher temperatures (≈ 600 °C); RBS on ZnO:Fe samples with similar characteristics but even higher fluence ($1 \times 10^{16} \text{ cm}^{-2}$) indicate that only a small fraction of the Zn interstitials recombine [89] during annealing steps up to 600 °C, corresponding in principle to the Zn vacancies which were not captured by the Fe ions. During the 700 °C and 800 °C annealing, these complexes are ruptured. A significant part of the thus freed Zn vacancies recombine (about half of the damage anneals [89]) or migrate to the surface layers which act as nucleation centers for defect clustering (resulting in enhanced dechanneling and the consequent apparent abrupt decrease of fitted fractions and increase of rms displacement after 800 °C) and the thus freed Fe atoms occupy perfect substitutional Fe sites (explaining why the overall rms displacements decrease approaching

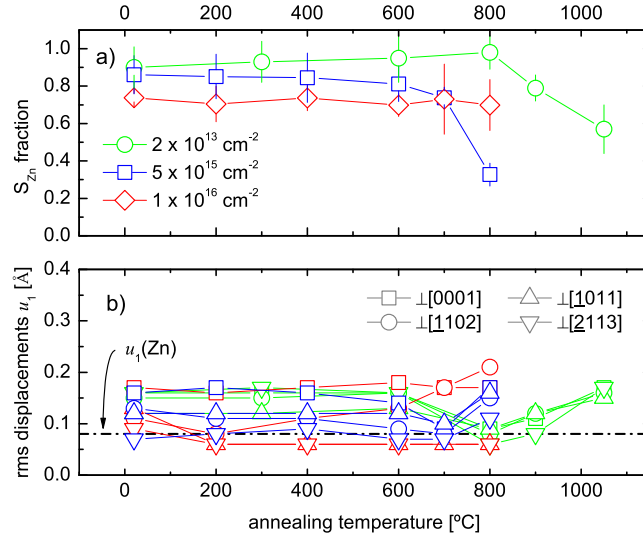


Figure 6.1.14: Compiled EC results of Fe ion implanted ZnO: low fluence ($2 \times 10^{13} \text{ cm}^{-2}$) [88], LF sample $5 \times 10^{15} \text{ cm}^{-2}$ and HF sample $1 \times 10^{16} \text{ cm}^{-2}$.

the Zn value for 700 °C annealing¹⁸, figure 6.1.4). In the end, a significant fraction of the implanted Fe (about half, at least) must still be forming complexes with the Zn vacancies, since even 900 °C annealing [89], did not totally anneal the implantation damage, and the static displacement is still evidenced in the EC patterns. Damage recovery studies on nominally equal (to MF and HF) samples are required to confirm the hypothesis.

6.1.7 Conclusions

In this section, results of a study on lattice location of Fe in high fluence ion-implanted Fe:ZnO, using the electron emission channeling technique, are presented. It was found that 80% to 90%, in MF sample and that 70% to 80%, in the HF sample, of the implanted Fe occupies (near-)substitutional Zn sites. The deviation from perfect substitutional occupancy is attributed to static displacements towards the surrounding Zn sites. The displacement is in turn explained by the binding of the Fe atoms to Zn vacancies, forming the so-called impurity-defect complexes. The observed thermal stability is in accordance with reported theoretical [94] and experimental [89, 95, 93] results. There are strong indications that a significant part of the implanted Fe is forming these complexes even after the last (800 °C) annealing treatment.

As a final remark regarding the technique itself, it was observed that the Gaussian averaging approach reaches a limit for which it no longer reproduces the effect of high fluence implantation on the channeling yields. Below a certain value of standard deviation, the smoothing reproduces very well the broadening of the channeling center peak observed in the experimental patterns. Above it, however, in order to reproduce the broadening of the strong channeling axes, the averaging reduces the anisotropy of the rest of the pattern much more than what is observed. This indicates that the effects of the large amount of damage introduced by high fluence implantation is not restricted to *structural disorder* i.e. the strain fields deforming the crystal which is sufficiently well implemented by the smoothing. The selective *cut-off* of the channeling peaks indicate that an *enhanced de-channeling* is caused in those regions of the patterns by defect scattering e.g. by vacancies (in large concentrations) sitting along certain crystal axes. This is not implemented in the simulations (such contribution to de-

¹⁸ A conventional explanation for the fitted fraction sudden decrease at high annealing temperatures is that the impurities reacted or precipitated forming secondary phases or clusters. If this was the case, the rms displacements should gradually increase indicating the growing instability. This is observed in other EC experiments where it is argued that the necessary short range diffusion took place [96], but not in this one.

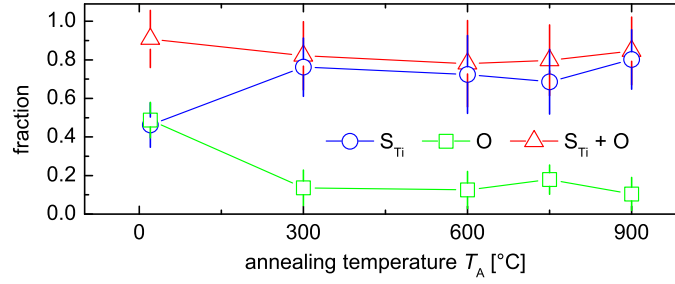


Figure 6.2.1: Average (over the four measured directions) ^{59}Fe fractions in sample STO_EC sample ($1 \times 10^{15} \text{ cm}^{-2}$) as a function of isochronal annealing temperature. The curve referring to substitutional Ti sites is in fact a sum of two contributions: perfectly substitutional and statically displaced towards the substitutional O (oxygen) site (the ratio is between 1:1 and 1:2). Note that “O” site (green) does not refer to the substitutional oxygen site but to the octahedral interstitial site.

channeling is only important in the case of the now starting high fluence experiments) and represents a possible up-grade to the code.

Nevertheless, although precluding sensitive fitting, it still produces reliable overall determinations: the lattice sites and approximate estimations of the respective occupancy fractions. That is attested not only by the highlighted (indirect) agreement with results from other techniques in the same material system, but also by the accordance of the overall behaviour of the fraction curves as a function of fluence with the EC results on ZnO:Cu [96] in the comparable annealing temperature range.

6.2 ^{59}Fe in Strontium Titanate

The experimental details of Fe:ZnO and Fe:STO experiments are equivalent. Since for STO only a short overview of the STO_EC sample results is presented, experimental considerations were omitted. The complete description and analysis (of the complete set of STO samples) will be found in [87].

Figure 6.2.1 displays the fitted fractions as a function of the annealing temperature analysis of the STO_EC sample. It was found that the majority of the Fe atoms are sitting on S_{Ti} sites after the first annealing step at 300 °C. From these, between 30% and 50% are sitting on perfectly substitutional sites (with approximately the same rms as Ti, indicating good stability) with the rest being statically displaced towards the substitutional oxygen site ($0.2 - 0.8 \text{ \AA}$).

RBS was performed on both LF and HF samples, as-implanted and after the 900 °C annealing. In the as-implanted state, both samples evidenced amorphized regions comprising the implanted layer. But while the temperature treatment recovered the crystallinity of the LF sample significantly, for the HF the damage only increased. Extrapolating the tendency to the STO_EC sample, this might bring some light over the interesting process of occupancy commutation (from O to S_{Ti}) from the as-implanted to the first (300 °C) annealed state. Indeed, the octahedral interstitial O site occupancy (see figure 6.2.1) in the as implanted state should be a consequence of heavily damaged surroundings of the implanted Fe atoms¹⁹, which is annealed out during the first annealing. Indeed, already after the first annealing step, the Fe is found almost entirely in the substitutional Ti site, the same lattice position it occupies up to the last (900 °C) annealing step. Combining both the RBS and EC results one may thus argue that a significant recovery of the crystal occurred already during the 300 °C annealing.

Regarding the observed static displacement of the (Ti site) substitutional Fe towards the O site, it is attributed, similarly to Fe:ZnO, to the formation of impurity-defect complexes. Indeed, $\text{Fe}_{\text{Ti}}\text{-V}_{\text{O}}$ complexes are very well known in Fe doped STO, e.g. they were observed by in-situ EPR spectroscopy [104].

¹⁹Thereby, not characteristic of perfect Fe:SrTiO₃.

Chapter 7

Magnetic Characterization

For the magnetic characterization of the samples, measurements were performed by means of SQUID magnetometry of magnetic dipole moment μ as a function of field H and as a function of temperature T , referred in the following as $\mu(H)$ and $\mu(T)$, respectively. The main purposes of this characterization are:

Identification of the implanted layers magnetic states Besides the diamagnetism from the substrate, different states from the implanted layer may be identified, depending on the distribution of the magnetic impurities:

1. *Diluted impurities.* If the implanted impurities are homogeneously distributed, a paramagnetic behaviour would be naturally expected, since, in this diluted limit of implantation, the magnetic ions are sitting a few lattice constants apart from each other in a non-magnetic matrix. However they may order ferromagnetically below a transition temperature T_C due to some long range mechanism.
2. *Clusters.* Although it is expected that ion-implantation produces an homogeneously implanted layer, the impurities may precipitate¹ forming clusters of different sizes. These magnetic particles may evidence superparamagnetic or ferromagnetic behavior.
3. *Secondary phases.* The impurities may also react with one or more of the matrix elements forming compounds which may be magnetic.

Determination of T_C and moment per implanted atom Whenever a FM state is identified, besides the relevance of these parameters for application purposes, their values provide insight over the phenomena, particularly they may allow to pinpoint the mechanisms responsible for the magnetic states.

All samples except ZNO_MF and ZNO_HF were characterized. As previously mentioned, the purpose of the reported experiments is an informed planning of a wider research on DMS to follow. Therefore, the set of samples, the measurements and results do not aim an extensive and conclusive investigation, but the discussion and training which necessarily comes before it.

This section starts with the description of the analysis method developed for the magnetic characterization of the typical samples of this study, followed by its application to SQUID data for ZnO and SrTiO₃, separately.

7.1 Method of analysis

A quick look at $\mu(H)$ and $\mu(T)$ experimental curves indicates the presence of different magnetic phases. The $\mu(H)$ curves, figure 7.0.1, evidence the substrate diamagnetism, linear in applied field, and possible FM and/or SPM (below blocking temperature) hysteretic signatures. Here, the identification of a PM phase is not straightforward: at 100 K, a *Brillouin* like PM response is practically linear in the

¹Specially during the high temperature annealing treatment

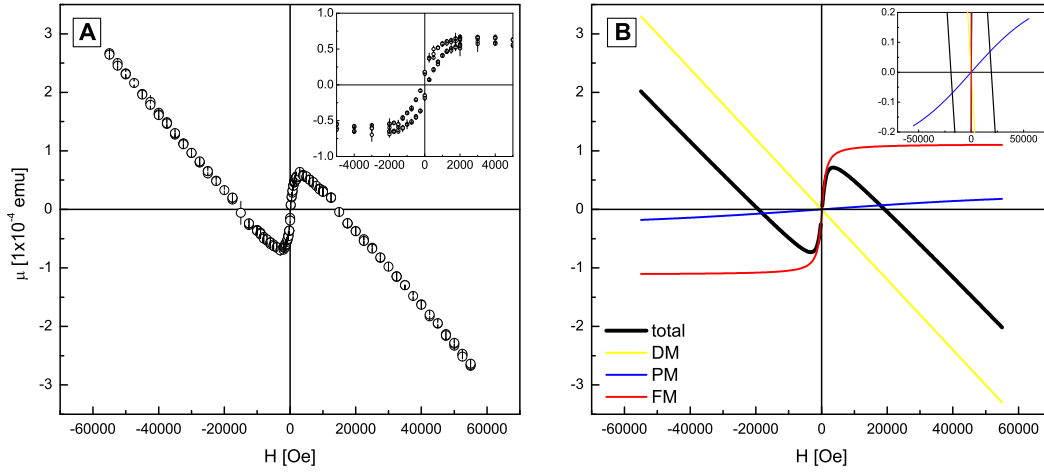


Figure 7.0.1: (Left) Typical $\mu(H)$ experimental curve (STO_HF at 10 K); *Inset* - Zoomed detail revealing the hysteretic signature. (Right) Curve deconvolution in different contributions from some *a priori* estimated magnetic phases: substrate diamagnetism, typical (Brillouin-like) paramagnetic behaviour of implanted impurities and phenomenological hysteresis to account for the observed coercivity; *Inset* Zoomed detail showing the non-linearity of the simulated PM contribution.

investigated field range, adding a small positive slope to the DM response; at 10 K, however, a non-linearity appears, as evidenced in the inset of figure 7.0.1 B. In turn, $\mu(T)$ curves, figure 7.1.1, clearly evidence a *Brillouin* like PM contribution added to the negative constant DM contribution and, if present, the smaller FM contribution (approximately constant if T_C is above enough the measured range).

Since the final purpose is to isolate the hysteresis, a procedure was developed to subtract the DM and PM contributions from the $\mu(H)$ curves. The DM contribution (from the DM substrate and the linear term of the PM response) is easily determined by a linear fit to the high field region, where the FM behaviour was observed to be saturated² and thereby is unaffected by this operation. But subtracting the non-linear terms of the PM contribution is not as straightforward. To do so, a model of the PM is required. The simplest picture for a PM phase is the one of isolated magnetic dipoles³ in a non magnetic and perfectly symmetric matrix governed by a Hamiltonian whose magnetic terms reduce to the Zeeman term $-\mu \cdot B$ and where the orbital moment is assumed to be *quenched*, as expected for transition metal ions in lattice sites of high symmetry⁴.

In this simplified picture, the total magnetic moment due to the PM phase is then given by:

$$\mu_{PM} = Ng_s\mu_B S B_S(y) \quad (7.1.1)$$

where N is the number of magnetic dipoles, g_s is the spin g-factor, μ_B is the Bohr magneton, S is the spin quantum number and $B_S(y)$ is the *Brillouin function*:

$$B_S(y) = \frac{2S+1}{2S} \coth\left(\frac{2S+1}{2S}y\right) - \frac{1}{2S} \coth\left(\frac{y}{2S}\right) \quad (7.1.2)$$

² All high temperature $\mu(H)$ experimental curves showed constant negative slope above ~ 20000 Oe. Since for these temperatures the PM is linear over the entire field range, the FM, if present, must therefore be saturated (in the high field range) or in the linear region (in the entire measured range). The shape of the curves clearly supports the former and the subsequent analysis confirms that this conclusion can be extrapolated for low temperature $\mu(H)$ curves.

³ The denomination of *magnetic dipoles* was preferred over *magnetic impurities* since there is the possibility that the implanted ions are not the dipole entities by themselves but may be coupled with some other dipole in the matrix in the form of impurity-defect complexes. Nevertheless, the number of dipoles must be the same as the implanted magnetic ions.

⁴ Since such symmetry is not assured, specially because of the massive damage (defects) produced by the implantation, the moments may not be totally quenched and a more refined method of analysis should allow a non-vanishing orbital moment. However, it is shown that in this case the experimental data available does not allow a consistent fitting when such subtleties are taken in account.

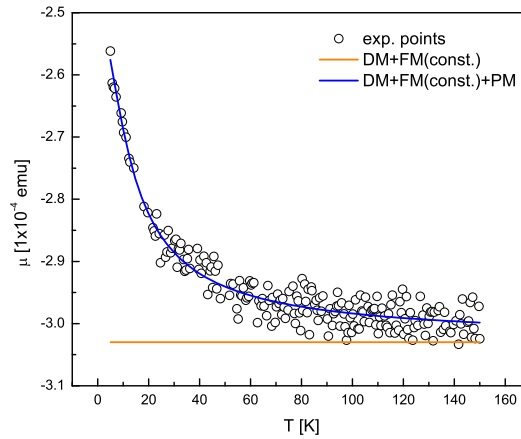


Figure 7.1.1: Typical $\mu(T)$ experimental curve (STO_HF at 55000 Oe) and possible deconvolution in constant DM and FM contributions and *Brillouin* like PM.

$$y = \frac{g_S \mu_B S B}{k_B T} \quad (7.1.3)$$

where $B = H + 4\pi M$ is the magnetic flux density, with H the magnetic field strength and M the magnetization⁵.

For typical values of N and S , it can be shown that equation 7.1.1 reproduces the PM phase behaviour evident from the experimental curves. In particular, it can be shown that the non-linearity in $\mu_{PM}(H)$ curves can be ignored already for $T \sim 100 K$. This means that for the temperature range suited to study the PM-to-FM phase transition, the PM response is linear in H and its contribution for the $\mu(H)$ curves can easily be subtracted along with the DM of the substrate with a simple linear fit. Nonetheless, it is worth the mind-breaking task of fitting $\mu(T)$ curves with:

$$\mu(T) = \mu_{DM+FM} + \mu_{PM}(T) \quad (7.1.4)$$

where μ_{DM+FM} is a free parameter accounting for the DM and FM contributions⁶ and $\mu_{PM}(T)$ is given by equation 7.1.1 with S and N as two more free parameters⁷. Besides allowing the correct PM correction for low temperature $\mu(H)$ curves this approach gives estimates⁸ of:

- The spin state of the dipoles (fit parameter S) which contributes with an additional insight over the mechanisms responsible for the FM, assuming that the FM and PM dipoles are of the same nature, only differing in average *next neighbor* distance;
- The number of PM dipoles (fit parameter N) which together with the known number of implanted magnetic ions N_i and the saturation moment of the FM hysteresis loops ($\mu(H)$ curves corrected for the DM and PM) μ_{FM}^{sat} allows to confirm the moment per magnetic dipole μ_{eff} and the PM and FM populations measured in number of dipoles, N_{PM} and N_{FM} , respectively.

Summarizing, there are three experimentally determined parameters (N , S and μ_{FM}^{sat}) and three unknowns (N_{FM} , N_{PM} , and μ_{eff}), all related by:

$$\mu_{eff} = g_S \mu_B S, \quad (7.1.5)$$

⁵In this picture of isolated atoms in the diluted limit, the interaction between dipoles can be ignored i.e. $M \simeq 0$.

⁶Taken as constant since the FM should be saturated (if the applied field and the temperature range are high and low enough, respectively) and the PM and FM phases are assumed not to significantly exchange population with temperature.

⁷It would be interesting to confirm the parameters thereby determined by fitting the $\mu(H)$ curves with a superposition of the same kind of equation 7.1.4 but in this case, it is impossible to separate the PM contribution from the others, whether due to similar dependencies in field or due to the masking of the relatively small PM contribution by the experimental uncertainties (dominated by the DM signal, around two orders of magnitude above the PM one).

⁸Nothing more than an estimate since the overly simplified equation 7.1.1 is not expected to accurately reproduce the PM behaviour.

Sample	$\mu(T)$	$\mu(H)$
STO_VG	$T = 5 \rightarrow 100 \text{ K}$	$H = -55000 \rightarrow 55000 \rightarrow -55000 \text{ Oe}$
	$H = 55000 \text{ Oe}$	$T = 10 \text{ K and } T = 100 \text{ K}$
STO_LF	$T = 5 \rightarrow 150 \text{ K}$	$H = -55000 \rightarrow 55000 \rightarrow -55000 \text{ Oe}$
	$H = 55000 \text{ Oe}$	$T = 10 \text{ K and } T = 100 \text{ K}$
STO_HF	$T = 5 \rightarrow 150 \text{ K}$	$H = -55000 \rightarrow 55000 \rightarrow -55000 \text{ Oe}$
	$H = 55000 \text{ Oe}$	$T = 10 \text{ K and } T = 100 \text{ K}$

Table 7.2.1: Measurement parameters for STO samples.

$$N_{FM} + N_{PM} = N_i, \quad (7.1.6)$$

$$\mu_{FM}^{sat} = \mu_{eff} N_{FM}. \quad (7.1.7)$$

The fitting is carried out by a *least square method* based on the widely used Leveberg-Marquardt algorithm. Although fast, it is unable to perform a converging fit when both N and S are left as free parameters. The solution found was to perform different fits for each discrete value of S followed by the evaluation of the best fit by comparison of the respective χ^2 values, a measure of the deviation of the fit curve from the fitted data.

Up to this point, only the a DM substrate and the *implanted* impurities were discussed. In order to isolate the magnetic signal of the implanted layer, the DMS part of the sample, it is necessary to subtract the contributions from the rest of the sample. It was assumed that the macroscopic magnetic properties were constant along the material *batch* from which the substrates were cut, so the characterization of a non-implanted substrate followed by its mass-normalized subtraction from the curves of the implanted samples would be enough. That is the procedure followed, although it is made clear that this starting assumption fails and a characterization of all substrates before implantation is necessary in the future work.

This analysis of the SQUID data from the virgin samples, as just described, does not aim a conclusive investigation of the dipoles nature, but simply to produce a fit curve that can be re-parametrized (if the experimental parameters are not the same) and normalized in order to be correctly subtracted from the curves of the implanted samples. Additionally, it may allow some degree of cross checking with the data of other characterization techniques.

Being particular for each of the STO and ZnO systems, the rest of the method details are presented in the following along with the analysis itself.

7.2 Strontium Titanate samples

The STO samples were characterized according to table 7.2.1. A virgin sample was characterized not only to allow for the subtraction of the magnetic background from the substrate but also to investigate possible effects of the implantation, more complex than just the addition of a magnetic layer to a much thicker DM substrate.

7.2.1 The $\mu(T)$ curves

The experimental $\mu(T)$ curve (figure 7.3.1) of the virgin sample evidences a magnetic phase transition between 75 K and 85 K that does not appear in the implanted samples. Such an abrupt change could be related with a decrease in DM susceptibility due to the well known cubic-to-tetragonal structural phase transition of SrTiO_3 around 110 K [109]. In fact, from the $\mu(H)$ curves, this (linear in field) DM susceptibility decrease was estimated and supported the suspicion. However there is no trivial reason why the same effect should not appear in the implanted samples $\mu(T)$ curves. Even assuming that the Fe implantation produces dramatic changes in the sample structural behavior, the fact is that this should not be responsible for the suppression of the transition, since it only affects a layer of vanishingly small thickness ($\sim 300 \text{ \AA}$ of damaged surface plus $\sim 200 \text{ \AA}$ of implanted layer) compared with the whole substrate (half a millimeter thick), which was confirmed by the Raman spectroscopy results (see section 8). Besides the iron doping, the only difference between implanted and virgin samples is that the former were annealed up to 900°C while the later was not. Nevertheless it is not expected that an annealing treatment suppresses the effect of the structural transition in the DM

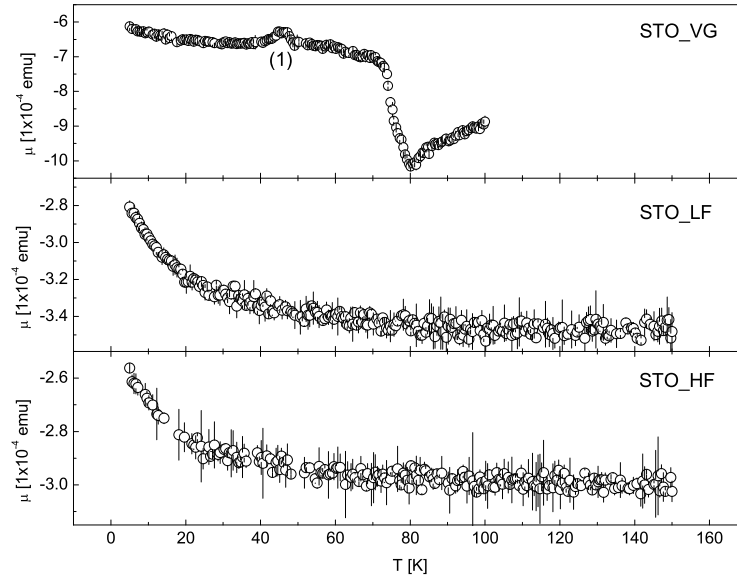


Figure 7.2.1: Experimental $\mu(T)$ curves of STO samples (full temperature range). An oxygen contamination was identified (1).

susceptibility. This subject will be addressed in future work.

The described method of analysis of the PM phase was applied to sample STO_VG experimental $\mu(T)$ curve for the low temperature (approximately constant DM and FM) and contamination free range (figure 7.2.2). With a best fit for $S = 5/2$, it was calculated a number of dipoles around $1,5 \times 10^{15}$. It seems to relate with the $1,1 \times 10^{15}$ Cu contamination measured by PIXE (Cu is not magnetic but Cu^{2+} is). In fact, if the unquenching of the Cu^{2+} ions is allowed, Hund's rules give a $J = 5/2$. However, with the necessary changes in the fit function to account for the respective S and L values of Cu^{2+} , N increases even further⁹. Nevertheless this PM signal can have other origins (e.g some magnetic contaminant invisible to PIXE) and a further discussion would not contribute to this study purposes. Assuming that this contamination is reasonably homogeneous¹⁰, it is possible to use this fit curve to correct the data from the implanted samples and consequently isolate the PM contribution from the implanted Fe.

For the case of sample STO_LF, figure 7.2.3, after subtraction of the PM background from the virgin sample, the fit was done considering the *full temperature range* available (5-150 K), which has the statistical convenience of larger amount of data and the following inconveniences and corresponding solutions:

- The FM contribution in 7.1.4 was considered as constant. Taking such a wide temperature range, this may not be the case and the precise behavior is unknown. Nevertheless, the hysteretic $\mu(H)$ curves (figure 7.2.8 on page 66) show an approximately constant saturation magnetization from 10 to 100 K, supporting the assumption.
- Since the data is homogeneously spaced, the fit is overweighting the constant (high temperature) region of the curve, when it should overweight the low temperature range, which tells more about the PM, specially regarding the S value. To do so, the data was plotted as $\mu(T^{-1})$ and smoothed by means of a Savitzky-Golay method, with homogeneously spaced values of T^{-1} (figure 7.2.4)¹¹. This has the added bonus of allowing a visual test for the quality of the fit and the significance of

⁹Still, the difference could still be explained by an (undesired) inhomogeneity of the contamination, since the PIXE spot is of submillimeter scale and the sample surface is $0,5 \text{ cm}^2$.

¹⁰A PM contribution should come from diluted contaminants, both expected to be reasonably homogeneously distributed over a wafer.

¹¹It should be noted that the straightforward procedure of performing a linear fit to $\mu(T^{-1})$ in the high temperature region is useless in this case, since it collapses N and S in a single free parameter accounting for the slope, precluding their separate determination.

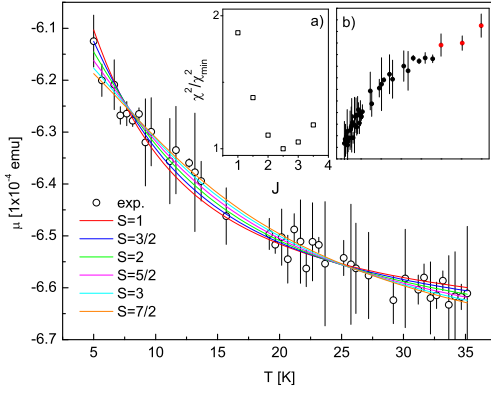


Figure 7.2.2: (Left) Experimental $\mu(T)$ of sample STO_VG for the low temperature and contamination free range and fit curves for different values of S . a) Normalized deviation (χ^2/χ^2_{min}) giving $S = 5/2$ as best fit. b) Experimental $\mu(T^{-1})$ for the same temperature range.

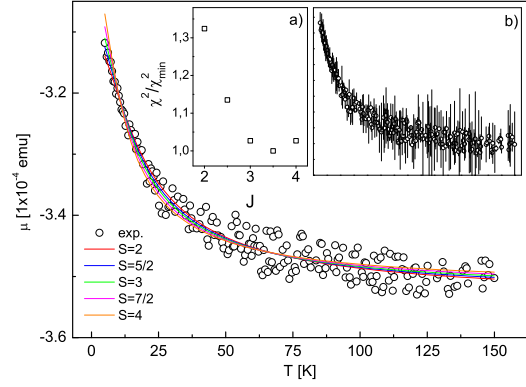


Figure 7.2.3: (Right) Experimental $\mu(T)$ of sample STO_LF subtracted of the PM contribution determined from the virgin sample and fit curves for different values of S . a) Normalized deviation (χ^2/χ^2_{min}) giving $S = 7/2$ as best fit. b) Same $\mu(T)$ curve with experimental error bars.

the choice of the S value (the fit curve for $S = 7/2$ reproduces almost perfectly the fitted one, the others do not). Furthermore, it compresses any non-negligible variation of the FM contribution in a very narrow T range, giving more reliable information about the PM phase.

Remarkably, both approaches - fitting $\mu(T)$ or $\mu(T^{-1})$ - give exactly the same $S = 7/2$ **unprecedented for any TM:STO based DMS**. Moreover, the N value determined from the two approaches converges for that value (figure 7.2.5), supporting the approach and thereby the results.

It should be noted that this alternative approach besides unnecessary for the virgin sample, since there is no direct interest on studying the detail of the PM contamination, it is not as easy (nor objective) to apply¹².

Summarizing, both the (unprecedented) S value and the (weakly fundamented) model used, find very good support, specially through the following three facts:

1. The agreement between the two approaches regarding the determined best fit S value;
2. The perfect convergence of N between the two approaches (figure 7.2.5);
3. The perfect (visual) reproduction of the $\mu(T^{-1})$ curve by the model for $S = 7/2$, in contrast with the others¹³.

However, the determined number of dipoles in the PM phase ($N = 6,9 \times 10^{14}$) does not reproduce the implanted Fe dose ($N_i = 4,3 \times 10^{14}$)¹⁴. Allowing for an unquenched orbital angular momentum L , some degree of agreement can be recovered. For non-vanishing orbital moment, the previous equations are adapted:

- S is substituted J , total angular momentum, given by:

$$J = L + S, L + S - 1, \dots |L - S|;$$

- g_S is substituted by the Landé g-factor g_J given by:

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}.$$

¹²The best fit S value is very sensitive to different choices of the low temperature points - red points in figure 7.2.2 b.

¹³Otherwise it could be argued that the used fitting curves were simply too flexible.

¹⁴There is no unquestionable justification for it to reproduce. But keeping the assumptions that the implanted ions are in the diluted (isolated) configuration, even if they couple with other magnetic dipoles in the matrix (e.g. Oxygen vacancies) there should still be a one-to-one relation.

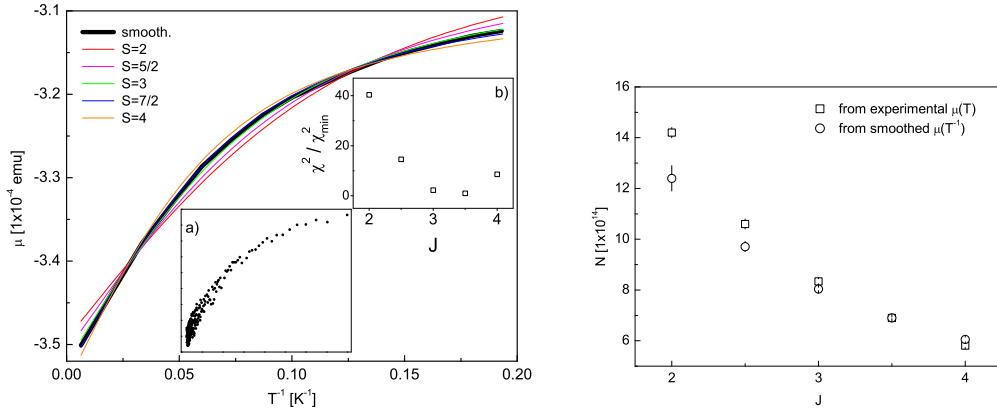


Figure 7.2.4: (Left) Savitzky-Golay smoothing (homogeneous spacing) of experimental $\mu(T)$ from sample STO_LF (after background correction) and the fits for different values of S . a) Experimental points showing the validity of the smoothing. b) Normalized deviation (χ^2/χ_{min}^2) giving $S=7/2$ as best fit.

Figure 7.2.5: (Right) Calculated N (number of PM dipoles) from fit to experimental $\mu(T)$ (squares) and to smoothed $\mu(T^{-1})$ (circles). Converges to the same value at $S=7/2$ both from lower and higher values of S .

The complexity of such relations precludes any attempt to extract one single solution (set of parameters) from the available data. But it can be shown that such a simple model has potential to correctly reproduce all the experimental data (including N_i) and thereby contribute with insight over the physics of the phenomena. Playing with L and S keeping $J=7/2$, for simplicity, which in practice simply means changing the value of g_J used in the fit function, N can, in fact, be made equal to N_i .

Of course, the degeneracy increases even further if the coupling with other magnetic dipoles that might be in the matrix is allowed. In this case, the total angular momentum can have contributions from the orbital and spin angular moments from the magnetic ion and the coupled dipole(s). Therefore, searching for solutions based on this macroscopic is fruitless. Nevertheless, two conclusions can be forwarded for the low fluence sample:

1. All (or almost) implanted Fe ions form a PM phase.
2. The magnetic dipoles in this phase have an angular moment above the Fe spin-only value.

The same method was applied to the high fluence sample - figure 7.2.6. The best fit to the experimental $\mu(T)$ is again for $S=7/2$ but the dispersion of $\mu(T^{-1})$, figure 7.2.6 b, invalidates the alternative approach for this sample data. Moreover, the determined $N=2.1 \times 10^{14}$ (which can be even less by a factor up to $\sim 1/2$, from the experience with sample STO_LF), around 15% of the implanted dose $N_i=1.4 \times 10^{15}$, indicating that *the majority of the implanted Fe do not form a PM phase*.

The above conclusions can thus go further:

1. All (or almost) Fe ions implanted in STO_LF form a PM phase.
2. Less than 15% of Fe ions implanted in STO_HF form a PM phase.
3. The magnetic dipoles in the PM phase behave as having an angular momentum above the Fe spin-only value.

The analysis of $\mu(H)$ completes the picture.

7.2.2 The $\mu(H)$ curves

The idea is to isolate a possible hysteresis from a FM phase formed by the implanted Fe. The straightforward approach is the simple subtraction of the (mass normalized) STO_VG experimental

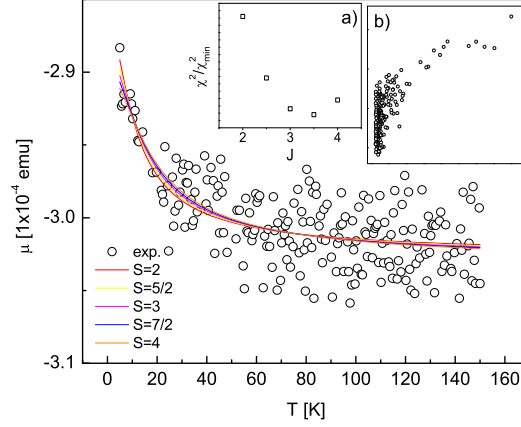


Figure 7.2.6: Experimental $\mu(T)$ of sample STO_HF subtracted of the PM contribution determined from the virgin sample and the fits for different values of S . a) Normalized deviation (χ^2/χ_{min}^2) giving $S = 7/2$ as best fit. b) Experimental $\mu(T^{-1})$ for the same temperature range, evidencing non-validity of the alternative approach.

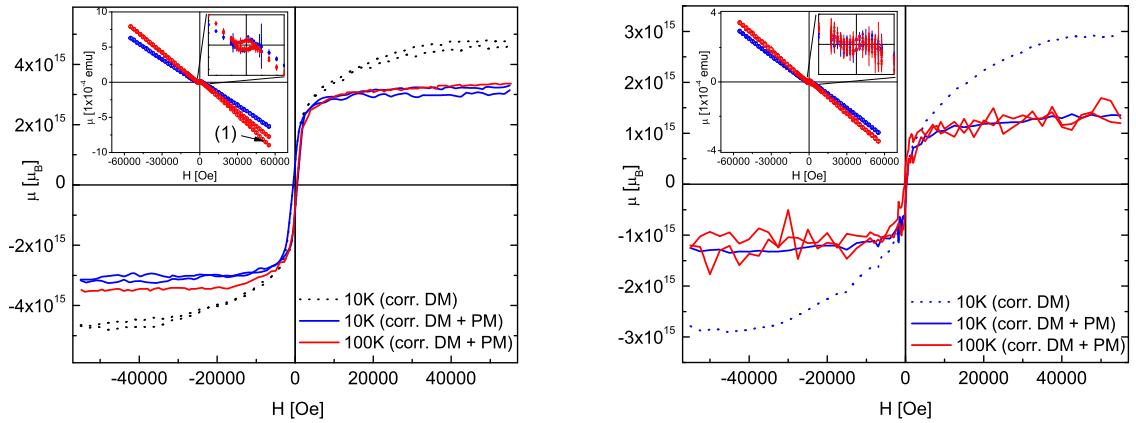


Figure 7.2.7: (Left) Experimental $\mu(H)$ of sample STO_VG subtracted of: linear DM e linear term of contaminant PM at 10 K (blue dots); linear DM and contaminant PM estimated from the model and fit parameters above (blue lines); linear DM and linear PM at 100 K (red lines). *Inset*: As measured experimental $\mu(H)$ - the 100 K decreasing field curve is not included in the analysis because of the strangely different slope in the positive region (1).

Figure 7.2.8: (Right) Experimental $\mu(H)$ per implanted Fe of sample STO_LF subtracted of: linear DM e linear term of contaminant PM at 10 K (blue dots); linear DM and contaminant+implanted Fe PM estimated from the model and fit parameters above (blue lines); linear DM and linear PM at 100 K (red lines). *Inset*: as measured experimental $\mu(H)$.

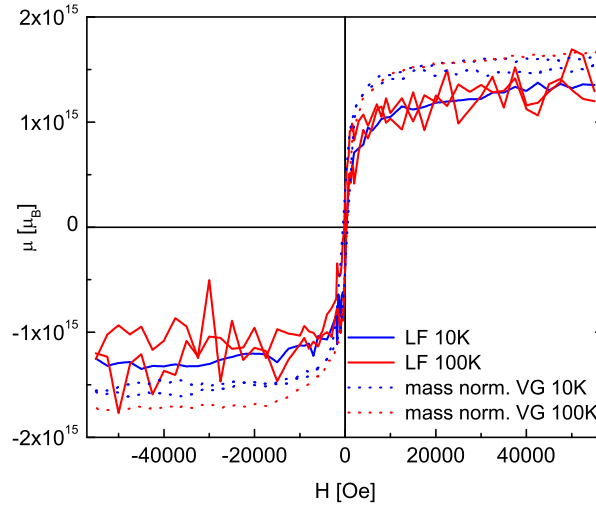


Figure 7.2.9: Comparison between the resulting hysteresis from samples VG and LF (the former normalized to the last).

$\mu(H)$ from the implanted sample curves, which would correct, in principle, any magnetic signal coming from any region but the implanted layer¹⁵. However, the inhomogeneity¹⁶ of the FM background between substrates from the same wafer, among other subtleties of the analysis, motivate a more careful approach.

The following treatment of the virgin sample $\mu(H)$ is based on the starting assumption that the FM, if present in the virgin sample due to some contamination, is saturated for an applied field of 4 T¹⁷:

1. Linear fit to the high field region ($55000 > |H| > 40000$ Oe) of experimental $\mu(H)$ and its subtraction. At 100 K, the modeled PM is linear up to 55000 Oe (the non-linear contribution is negligible). Such subtraction thereby eliminates not only the DM from the substrate¹⁸ but also the PM from diluted magnetic impurities. At 10 K, however, the non-linearity of the PM becomes important, as evidenced in figure 7.2.7.
2. Subtraction of non-linear terms of the PM contribution at 10 K, calculated from equation 7.1.1 with N and S parameters determined above.

The resulting curves, red and blue lines in figure 7.2.7 are thus the magnetic signal of the virgin sample with a different origin than the substrate (DM) and the diluted contaminant impurities (PM). In fact, they reveal a hysteresis with a constant saturation magnetization from 10 to 100 K indicating a much higher T_C which in turn points to metallic origin. From this and the reduced number of dipoles (of the order of 1×10^{15}) necessary to account for the observed hysteresis, this contamination can easily be attributed, for example, to FM contamination from metallic handling equipment or to incorporation of FM particles during growth. The former is specially undesirable, since it is not expected to cause a reproducible contamination among different samples, invalidating any attempt of FM background correction using the available data. Although a special care was devoted to avoid FM contamination during handling, it may still have occurred. It is shown that there actually is a strong indication of a non-homogeneous FM contamination among these different samples and thus it was made clear that a magnetic *pre*-characterization of every substrates followed metal free handling until implantation and *post*-characterization is vital.

Once characterized the virgin sample, it is possible to compare with (or correct) the experimental $\mu(H)$ from the implanted samples and thereby obtain the magnetic signal from the implanted layer.

¹⁵The implanted layer thickness is negligible comparing with the whole substrate.

¹⁶Concluded after this study and thereby after the implantation. Logistic constraints made impossible to repeat the measurements.

¹⁷The assumption is clearly confirmed by the shape of the resulting hysteresis.

¹⁸The DM contribution from any impurity is negligible.

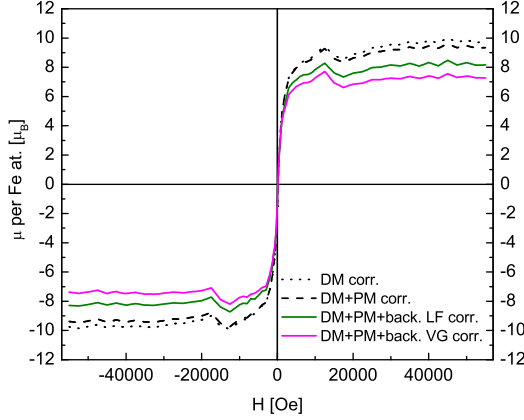


Figure 7.2.10: (Left) Example of $\mu(H)$ curves at 10 K resulting from different corrections (subtractions): DM (or, to be more precise, DM + linear term of PM) - linear fit to the high field region; PM (or, to be more precise, non-linear terms of PM) - non-linear terms of the modeled PM both from the contaminants and the implantation with the calculated parameters; back. LF/VG - background hysteresis of the LF/VG sample.

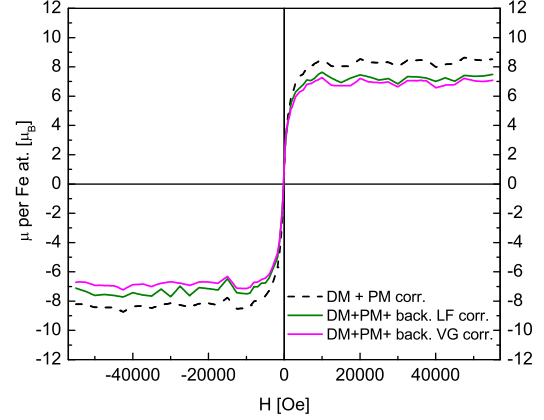


Figure 7.2.11: (Right) Example of $\mu(H)$ curves at 100 K resulting from different corrections (subtractions): DM+PM - linear fit to the high field region; back. LF/VG - background hysteresis of the LF/VG sample.

The following method is applied, based on the starting assumption that the FM, if present in the implanted samples, is saturated for an applied field of 4 T¹⁹:

1. Linear fit to the high field region ($55000 > |H| > 40000$ Oe) of experimental $\mu(H)$ and its subtraction.
 - (a) At 100 K, the modeled PM is linear up to 55000 Oe (the non-linear contribution is negligible). Thereby, such subtraction eliminates:
 - i. the PM contribution from diluted contaminants;
 - ii. the PM contribution from the implanted impurities;
 - iii. the DM contribution from the substrate²⁰.
 - (b) At 10 K the non linear terms of the PM contribution are non-negligible. Such subtraction thereby eliminates:
 - i. the linear term of the PM contribution from diluted contaminants;
 - ii. the linear term of the PM contribution from the implanted impurities;
 - iii. the DM contribution from the substrate.
2. Subtraction of the non-linear terms of the PM contributions at 10 K both from the diluted contaminants and the implanted impurities calculated from equation 7.1.1 with N and S parameters determined in section 7.2.1.

Applying the method to the low fluence sample, the resulting curves are the magnetic moment of some phase other than the DM substrate, the PM contaminants, and the PM fraction of the implanted Fe (figure 7.2.8)²¹.

Comparing²² these resulting curves with the ones of the same kind from the virgin sample (figure 7.2.9) it may be concluded that the FM signal in the LF sample comes from the same kind of contamination as in the VG sample, and *the implanted layer in the LF sample is therefore non-ferromagnetic*.

¹⁹The assumption is clearly confirmed by the shape of the resulting hysteresis.

²⁰the DM of any impurities is negligible

²¹Once again, a the nicely saturated FM hysteresis recovered by a correction based on the forwarded PM model.

²²It was preferred to directly compare instead of subtracting, given the close magnitudes and the relatively large noise.

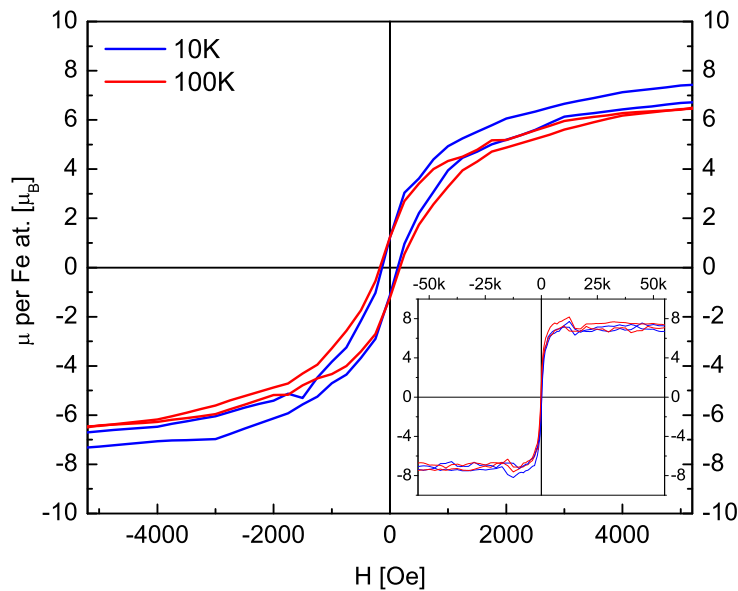


Figure 7.2.12: Completely corrected (DM + PM + contaminant FM) $\mu(H)$ curves of sample STO_HF at 10 K and 100 K. *Inset*: Plot of the entire measured field range.

For the case of the high fluence sample²³, the subtraction of the background is possible and more natural than a comparison between curves as was done for the LF sample. However, it was observed that the hysteresis loops of the LF sample may be due to contaminant background. Consequently, it is not obvious which of the two slightly different backgrounds (determined from the VG and LF samples) should be subtracted to the HF curve (since all the substrates come from the same wafer) - see figure 7.2.10 as example for the 10 K curves and figure 7.2.11 as an example for 100 K curves. A joint criteria of best saturation behavior and best agreement between saturation values indicate that the VG sample correction is more reliable and thereby is used in the following.

The result of all the corrections to $\mu(H)$ curves of sample STO_HF are well behaved hysteresis (figure 7.2.12). Both a quantitative and qualitative analysis can be made:

- The giant moment²⁴ of $7.5 \mu_B$ per Fe atom in the non-PM phase (the saturation value for the lowest temperature curve) supports the already determined above spin-only value (conclusion 3. on page 65).
- The small squareness (ratio between the remanence and saturation magnetization) of ~ 0.13 supports the picture of a FM state of magnetic nano-domains percolating (contrasting with conventional ferromagnets).
- The hysteretic shape indicates a FM state of some part of the implanted layer. A key question remains: *what is the origin of the hysteresis?*
 - *FM secondary phases?* There is no known secondary phase of the available elements in the samples to account for the observed hysteresis (namely, their giant saturation moment).
 - *Fe clusters?*
 - * Single domain (SD) particles have a typical hysteresis with a quite different shape than the observed²⁵.

²³Wherever “per Fe atom” appears referring to the STO_HF sample it should be read “per implanted Fe atom of the FM phase”, meaning that the normalization was not performed to the total implanted atoms but to that minus the amount in the estimated PM phase.

²⁴Average magnetic moment per atom larger than the atomic value.

²⁵In fact, this is a question repeated in every report of FM in DMS. Despite the wide range of experimental techniques used, including transmission electron microscopy and extended X-ray absorption fine structure spectroscopy (EXAFS), such precipitates were not detected in the majority of the reported FM in DMS. Any ferromagnetic particles must be very

- * Multiple domain (MD) or pseudo single domain (PSD) particles²⁶ can account for the observed hysteresis but it is not clear if ion implantation may produce particles with the necessary size (a few atoms) although at such high annealing temperature the Fe atoms may diffuse and precipitate. Nevertheless, such a giant moment cannot be explained singly by these phases.
- *FM state of diluted Fe?* The forwarded conclusion, although such macroscopic data does not allow a definite answer. Further local probe studies are required. Nevertheless, in this work some extra insight over this particular question is given: the EC results locate the implanted Fe mainly in Ti substitutional sites, supporting the diluted configuration. Although
- The very small decrease in saturation moment (7.5 to $6.8 \mu_B$ per Fe atom in the FM phase) with temperature (10 to 100 K) indicates that the PM to FM transition temperature, T_C , must be much higher than 100 K.
- The coercivity H_c (magnitude of applied field necessary to flip the magnetization) increases (130 to 170 Oe) with temperature (10 to 100 K). Although unusual, this can easily be explained with a simple picture. With increasing temperature the interaction radius of the dipoles is expected to decrease. Since the dipoles are not sitting periodically in the matrix, a FM single phase can break in smaller FM phases with increasing temperature, depending on the relative distances between sets of close sitting dipoles, as represented in figure ???. This mechanism can have the effect of increasing the coercivity with temperature, since, it requires lower fields to translate domain walls in a single FM phase (energetically easy process) than to rotate the magnetization of daughter FM particles (energetically more difficult process). Nevertheless, whatever mechanism(s) may be responsible for such an increase, it competes with the opposite effect of decreasing coercivity with increasing temperature. Which one dominates, for a given temperature, depends on the particular characteristics of a sample.

At this point, a remark should be made regarding the low fluence sample. The conclusion that this sample FM comes from the contaminant background was based on the closeness of the saturation magnetization value with the unimplanted sample and the assumption that this background is relatively homogeneous. But looking at a more characteristic parameter of the origin of a FM signature, the coercivity, the opposite could be concluded. Figure 7.2.13 indicates that the FM of the implanted samples are of the same type (similar coercivities) and not of the type of the background FM. This brings some degree of doubt over the conclusion (in the following section) that the maximum local concentration of Fe achieved throughout the implanted layer of sample STO_LF is below the percolation threshold, and further confirms that a pre-characterization of all substrates before implantation is absolutely necessary for further conclusive studies.

7.2.3 Crossed discussion

Based on the results from the $\mu(T)$ and $\mu(H)$ a schematics of the phases present in the samples is given in figure 7.2.14:

- The substrate (DM) has two types of magnetic contaminants:
 - Isolated dipoles, possibly Cu^{2+} , with PM behaviour and a concentration n_C around 0.5 ppm.
 - Unidentified FM particles.
- The implanted Fe forms two phases differing in relative distances between dipoles (isolated Fe, Fe coupled with defects, ...):
 - FM phase: the dipoles sitting in the high density region of the Gaussian depth profile (above the percolation threshold) are close enough to order.
 - PM phase: the dipoles sitting in the tails of the Gaussian behave as isolated dipoles.

small indeed to escape detection. “As ultrasmall particles would normally be expected to display superparamagnetism, that is, non-correlated orientations of magnetic moments when thermal energy exceeds anisotropy energy, another interesting question is raised: does the semiconductor environment enhance magnetic anisotropy, and if so, how? This is a timely issue that may provide clues for overcoming the superparamagnetic limit in magnetic recording media.”[99]

²⁶Any mixed state between MD and SD.

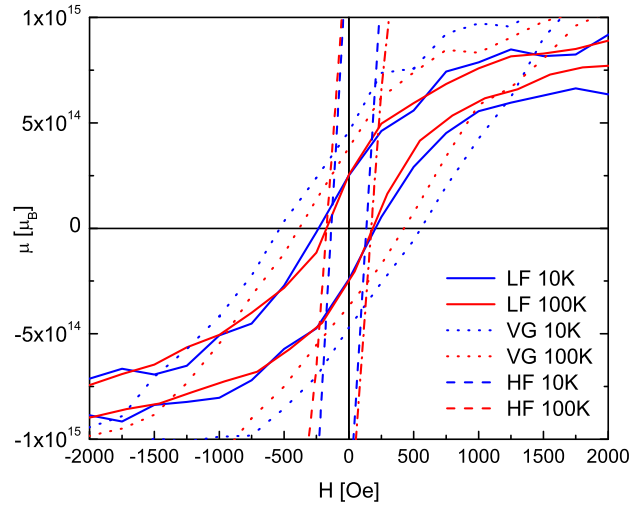


Figure 7.2.13: Comparison between coercivities, H_C , of the three STO samples, indicating a common origin of the FM of the implanted samples, different from unimplanted one.

- The existence of any kind of secondary phase or precipitates cannot be definitely excluded based on these macroscopic magnetic measurements. However, EC results (section 6.2) point in that direction.

Assuming the simulated implantation depth profile and that it is not altered by any mechanism (e.g. Fe diffusion), the estimated PM phase in the HF sample gives a threshold concentration of Fe, n_{th} , around 2.5% (0.025 Fe atoms per unit cell, i.e. per Sr or Ti atom). This is consistent with the observation that the LF sample has no FM phase (the maximum concentration is 2.5% there)²⁷.

Regarding the magnitude of the magnetic moments of the implanted Fe, it can be shown that, in order to account for both the results from the $\mu(T)$ and $\mu(H)$ results, giving $J \simeq 7/2$ and $\mu(\text{Fe}) \simeq 7.5 \mu_B$, respectively, some possible explanations are forwarded:

1. *The Fe atoms are unquenched.* It is well known that in a perfect STO lattice the Fe ions (substituting Ti) are in a high-spin state of $S=2$. Being a $3d$ TM the maximum value would in any case be $S=5/2$. Therefore, to account for such a high angular momentum of singly a Fe ion, the unquenching must be considered. In fact it is not expected a total quenching since all the damage produced by the implantation (that survived the annealing [89]) must perturb the symmetry of the Fe sites. Nevertheless, to account for the estimated J and $\mu(\text{Fe})$ the value of the orbital moment should be at least 2, which is actually the d -shell value, making this possibility very unlikely since this would require that *all* the Fe ions were in a unquenching environment.
2. *The nonmagnetic host matrix is magnetically polarized in the vicinity of the Fe atoms.* This behavior was never reported for strontium titanate and such a large magnetization of a non magnetic matrix is highly unexpected.
3. *The Fe atoms couple with some other(s) magnetic dipole(s) in the matrix.* Impurity-defect complexes form when one or more point defects with non-vanishing magnetic moment (e.g. oxygen vacancies) bind to a impurity (Fe) atom. In fact, it is expected that a significant amount of these defects (see section 3.3) are sitting in the vicinity of the Fe atoms, since the implantation produces considerable damage and a part of it survives the 900 °C annealing (see section 6.2). Indeed, these Fe(Ti)-V(O) complexes were observed in Fe : SrTiO₃ by *in situ* EPR spectroscopy [104], which makes this a strong possibility.

7.3 Zinc Oxide samples

The ZnO samples were characterized according to table 7.3.1.

²⁷ This is a clear example of the importance of the time spending analysis of the $\mu(T)$ curves by the developed method.

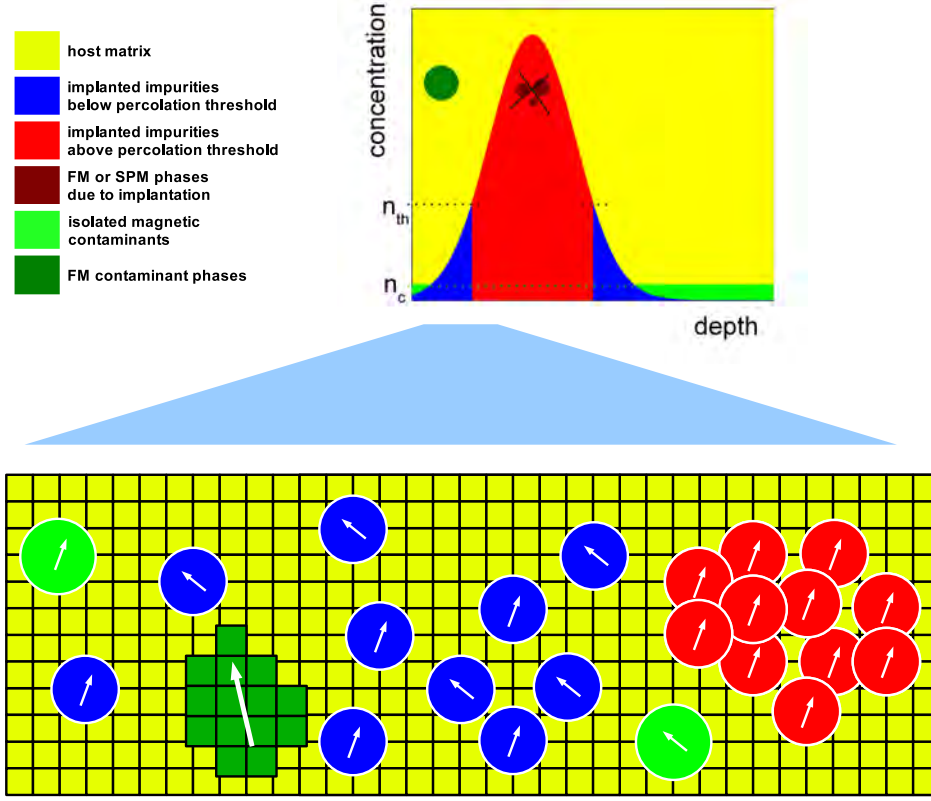


Figure 7.2.14: Representation of the possible phases in the samples.

Samples	$\mu(T)$	$\mu(H)$
ZNO_VG	$T = 2 \rightarrow 300$ K $H = 20000$ Oe	$H = -20000 \rightarrow 20000 \rightarrow -20000$ Oe $T = 5$ K and $T = 300$ K
ZNO_LF	$T = 2 \rightarrow 300$ K $H = 5000$ Oe	$H = -5000 \rightarrow 5000 \rightarrow -5000$ Oe $T = 5$ K and $T = 300$ K

Table 7.3.1: Measurement parameters for ZnO samples.

7.3.1 The $\mu(T)$ curves

The experimental $\mu(T)$ curve (figure 7.3.1) of the virgin sample evidences a magnetic phase transition around 250 K that does not appear in the implanted sample. The shape of the curve in the transition region is very similar to the case of sample STO_VG, but for ZnO there is no candidate phenomena to account for this behaviour. Since this transition suppression must not come from the implantation but from the annealing²⁸ it is out of the scope of this work, justifying however a future investigation.

²⁸Since the implantation affects a layer of vanishingly small thickness (~ 300 Å of damaged surface plus ~ 200 Å of implanted layer) compared with the whole substrate (half a millimeter thick) it is not expected such a macroscopic influence considering that whatever the nature of the transition may be, it must occur in the whole (relatively homogeneous) sample.

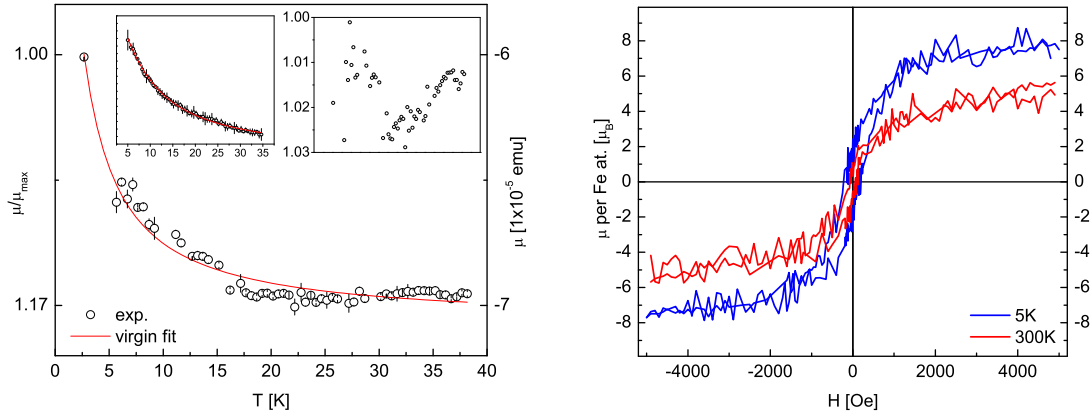


Figure 7.3.2: (Left) Experimental $\mu(T)$ of sample ZNO_LF for the low temperature and contamination free range (circles) and fit to the $\mu(T)$ of ZNO_VG reparametrized to reproduce the different measurement conditions (line), evidencing a perfect match. a) ZNO_VG experimental $\mu(T)$ and fit. b) Experimental $\mu(T)$ of sample ZNO_LF corrected for the PM determined from the ZNO_LF sample supporting the observation that if the PM introduced a PM phase it must be so small that is masked by the experimental noise.

Figure 7.3.3: (Right) Corrected (DM + contaminant PM) $\mu(H)$ curves of sample STO_HF at 5 K and 300 K. The noise is much bigger than for the STO measurements only because the experimental statistics used was considerably lower.

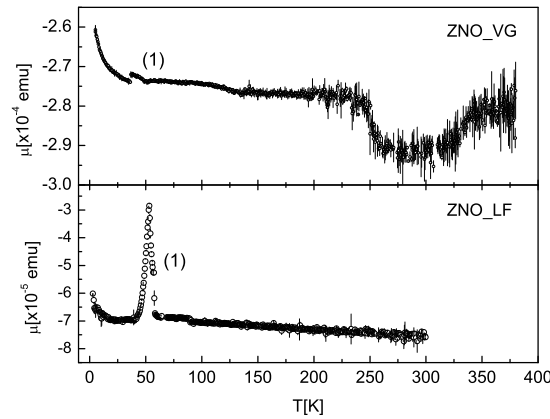


Figure 7.3.1: Experimental $\mu(T)$ curves of ZnO samples (entire temperature range). An oxygen contamination (possible condensation in the sample) was identified (1).

The analysis, as for STO samples, of the low temperature region of $\mu(T)$ curves (figure 7.3.2) detected no PM phase due to implantation. At least a very small phase must exist in the tails of the Gaussian depth profile, given what was concluded from the STO samples, but may be masked by the experimental noise (figure 7.3.2 b).

7.3.2 The $\mu(H)$ curves

The $\mu(H)$ curve of the virgin sample shows no hysteretic signature. Therefore, the analysis of the implanted sample follows straightforward with the linear correction (linear fit to the high field region) and subsequent non-linear PM correction (contaminant PM contribution estimated by the analysis to the $\mu(T)$ curves) - see figure 7.3.3. The correction again results in well behaved hysteresis and a qualitative and quantitative analysis follows, as for STO samples:

- The giant moment of $7.5 \mu_B$ per Fe atom in the non-PM phase (the saturation value for the lowest temperature curve) is, very interestingly, exactly the same as for STO.
- The small squareness of ~ 0.1 is, within experimental error, the same as for STO, indicating a common origin of the hysteresis.
- Again, the hysteretic shape evidences the FM nature of some part of the implanted layer and the key question and discussion regarding its origin are the same as for STO.
 - *FM secondary phases?* Some FM secondary phases may form - $(\text{Zn}, \text{Fe})_3\text{O}_4$ and ZnFe_2O_4 . However, the required preparation conditions and the fact that these compounds (weak FM) cannot account for the measured saturation magnetization makes this possibility very unlikely²⁹. Moreover, the shape of the hysteresis and its characteristic parameters are incredibly similar to the case of STO and so both hysterical behaviors must have the same origin.
 - *Fe clusters?* The same as for STO, with the further supporting observation that only high temperature (far above RT) implantation of Fe in ZnO results in small Fe particles [101] (ZNO_LF sample was implanted at RT).
 - *FM state of diluted Fe?* Again, it is the forwarded conclusion. Although such macroscopic data does not allow a definite answer EC results support the diluted configuration (see section 6.1). Since no PM phase was detected within the experimental resolution, it is not possible to estimate the threshold concentration for Fe:ZnO. Nevertheless, from the magnitude of experimental noise (figure 7.3.2 b), its superior limit can be estimated to be 0.3%.
- The coercivity H_c decreases (160 to 70 Oe) with temperature (5 to 300 K). For ZnO sample, it seems that the conventional mechanism of thermally enhanced magnetization rotation dominates the one forwarded to account for the opposite behavior of the STO sample.

Regarding the origin of the giant magnetic moment of the implanted Fe ($7.5 \mu_B$), the discussion is similar discussion to STO results. In this case, the Fe(Zn)-V(O) complexes were already observed in Fe:ZnO by Mossbauer spectroscopy [95] and subsequent *ab initio* calculations [94] supported the results.

7.4 Conclusions

In this section, results of magnetic characterization of ion-implanted Fe:ZnO and Fe:SrTiO₃ by means of SQUID magnetometry are present. The magnetic behaviour of the implanted layers was isolated from the other contributions. The result, for the high fluence sample of Fe:SrTiO₃ and the implanted sample of Fe:ZnO, were hysteretic $\mu(H)$ curves in the entire investigated temperature range, attributed to a FM state of diluted dipoles, although the possibility of a different origin, namely Fe clusters or FM secondary phases, is not totally excluded. In these dipoles, it is argued that the Fe ion may be bound and magnetically coupled with some other magnetic dipoles in the matrix. This suspicion is based on the above spin-only angular momentum and the giant magnetic moment of $7.5 \mu_B$ per dipole in both systems, hardly explained singly by unquenched angular momentum of Fe or magnetization of the host matrices. The reported giant moment is *unprecedented* for any TM:SrTiO₃ and for Fe:ZnO (a giant moment up to $18.9 \mu_B$ was recently reported for Co:ZnO prepared by pulse-injection metal organic chemical vapor deposition [98]). For Fe:SrTiO₃/Fe:ZnO, the Curie temperature was observed to be higher than 100 K/300 K (for the particular concentration profiles of the studied samples), the maximum investigated temperatures, presumably much higher than that because of the small 9%/27% decrease in saturation magnetization from 10-100 K/5-300 K. The room temperature character of the FM of ion implanted Fe:ZnO/Fe:SrTiO₃ is thereby proved/suspected. The threshold concentration of Fe (bellow which, the dipoles are too far apart to order) was estimated to be around 2.5% for Fe:SrTiO₃ and bellow 0.3% for Fe:ZnO. It should be noted that these values refer to the specific conditions under which the samples were prepared, as does the defect creation which is believed to trigger the FM state.

²⁹ For example, ZnFe_2O_4 particles in ZnO show a SPM behavior down to 20 K with vanishing coercivity and saturation magnetization per Fe atom one and two orders of magnitude below the measured values here, making them non-plausible candidates to explain these hysteresis [100].

The continuation of the study is required for refinement and completion. For example, the samples should be measured for $\mu(H)$ with further increasing temperatures in order to determine the full range behaviour of saturation magnetization and consequently the T_C of each system. Also, FC and ZFC measurements are necessary to investigate for SPM behaviour, since any small single domain (or pseudo single domain) FM particles will be SPM at a given temperature range. It is also clear in the literature that the magnetic characterization must be performed in different annealing steps, since a significant effect on the magnetic properties is generally observed [102, 103]. Furthermore, some of the observations require confirmation by means of other techniques, namely, local probe techniques to investigate the possible origin of the FM in clusters or secondary phases and, if confirmed the intrinsic origin (in the diluted dipoles), to investigate the local constituents and structure of these dipoles and the possibility of unquenched orbital momentum and matrix magnetization. Regarding the dipoles nature, some extra insight is already given in this thesis by *electron emission channeling* results (section 6) which indicate the association of the Fe ions to zinc/oxygen vacancies in ZnO/STO samples. These Fe(Ti)-V(O) complexes were already observed in Fe:SrTiO₃ by means of *in-situ* EPR spectroscopy [97] and the Fe(Zn)-V(O) complexes in Fe:ZnO by means of Mossbauer spectroscopy [95] (subsequent *ab initio* calculations [94] supported the results). The studied samples are specially prone to the formation of these impurity-defect complexes, given that a significant amount of damage (defects) is produced during the implantation.

As a final remark, this magnetic characterization was part of a preliminary study with the main objective of allowing for an informed planning of a future wider research on DMS, as stated above. Not only it fulfilled those purposes - as an example, the trivial but crucial experimental detail regarding the necessary pre-characterization of any substrate before implantation was pointed - but it exceeded them, with some unprecedented results.

Chapter 8

Lattice Dynamics of STO samples

The study of STO samples by means of Raman scattering spectroscopy was motivated by the observation (see page 62) of a magnetic phase transition between 75 K and 85 K in the virgin sample (that did not appear in the implanted samples) that could be related to the well known anti-ferrodistorsive phase transition of SrTiO_3 (around 110 K [109], depending on growth technique and conditions). The bottleneck for the application of the technique to this type of samples is that only a layer of vanishingly small thickness ($\sim 200 \text{ \AA}$ sitting at a depth of $\sim 300 \text{ \AA}$) compared with the whole sample (half a millimeter thick) consists of actual Fe:SrTiO_3 , while it is expected that, since the samples are transparent, the laser probes a depth that is more than 1 order of magnitude larger than that (it is expected that the laser penetrates a few wavelengths). Thereby, the measured spectra should in principle be a superposition of the two phases, dominated by pure single crystalline strontium titanate. This is in fact a major drawback if one wanted to study the implanted layer. But another, maybe even more important (and definitely much more interesting), question can still be addressed: *since the transition (in the magnetic signal) was suppressed in the implanted samples, could the implantation¹ have some kind of effect over a significantly larger fraction of the material?* In the following, only a preliminary analysis of the obtained Raman spectra is presented, since this particular question is out of the scope of this work, which is the investigation of the implanted layer properties.

Already during the measurements, the intense glow in the whole sample indicated that the laser was probing a fraction of macroscopic dimensions. A rough comparison of the three samples spectra (figure 78) confirms it, since no significant differences are observed besides an apparent TO_4 mode enhancement and the appearance (or enhancement) of a 123 cm^{-1} mode (attributed to the impurity/dopant presence). One is thus in the position to answer the question forwarded above. Among several modes that could be identified [107], our attention is drawn to the spectra region that can tell us about the anti-ferrodistorsive phase transition: in all the samples, the weak band emerging at low frequencies and hardening on cooling was identified as the A_{1g} mode (figure 79) following the power law

$$\omega_{A_{1g}}(T) \propto (T_a - T)^\beta$$

where $\beta \simeq 1/3$ [107, 108] and T_a is the anti-ferrodistorsive phase transition temperature. Figure 79 shows how T_a decreases from the virgin sample (119 K, acceptable value for pure single crystal SrTiO_3) to the low fluence (115 K) and high fluence (103 K) implanted samples. While this decrease with impurity concentration is expected for STO samples in which the dopant occupies the Ti substitutional site (supporting the EC results, chapter 5), it brings back the question of how large the probed sample fraction is after all. Two strong observations support the hypothesis that it is at least of the order of the laser wavelength (514.5 nm): the sample was glowing during the measurements and no significant effects are observed in the implanted samples spectra (while a broadening of some modes should be

¹Another difference between samples is that the implanted ones were annealed up to 800 °C but that is expected to further improve the crystalline quality, which points in the opposite direction.

It could be argued that this high temperature annealing makes the iron to diffuse. However, there are no accounts in literature of long-range diffusion of implanted ions for such annealing temperatures. Furthermore, while it would spread over a larger fraction of the probed sample, its concentration would fall with the inverse of that, along with its effects on the lattice dynamics.

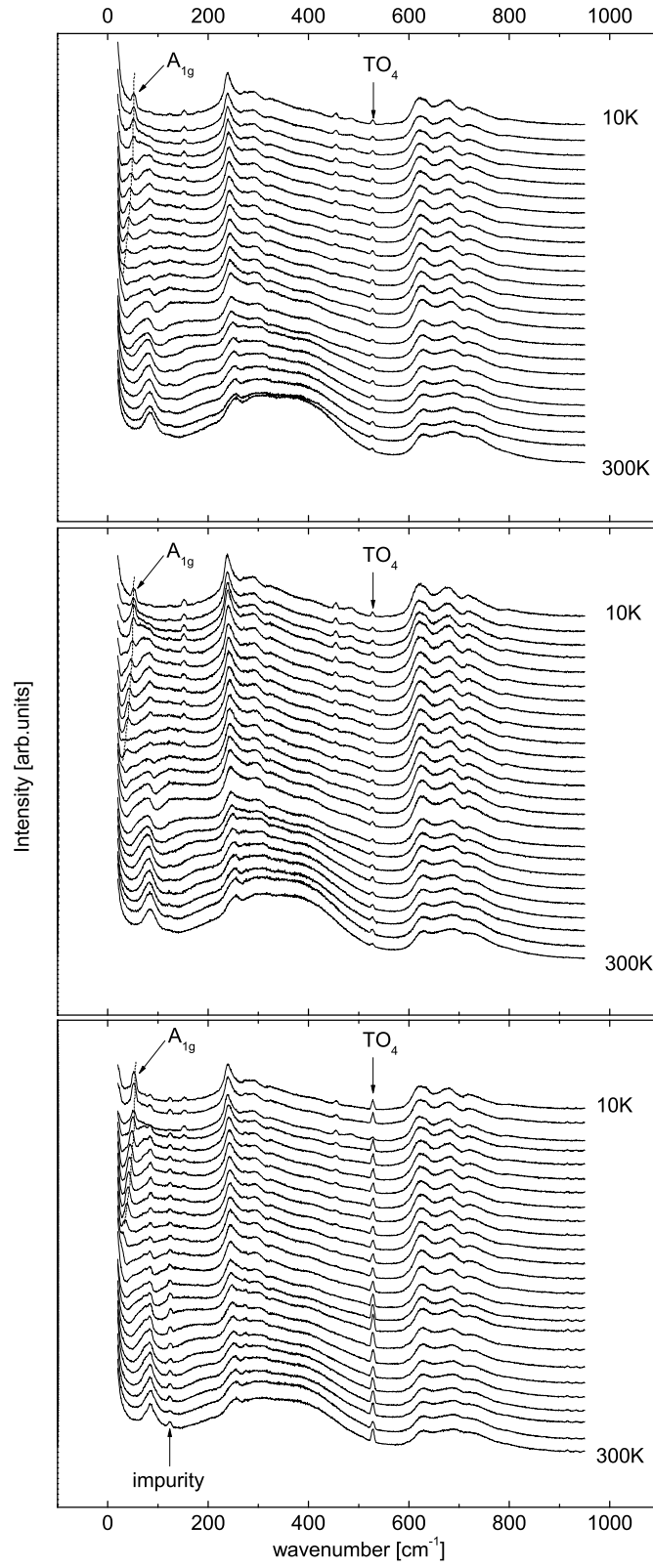


Figure 8.0.1: Unpolarized Raman spectra for the iron implanted strontium titanate VG (virgin), LF (4%) and HF (20%) samples.

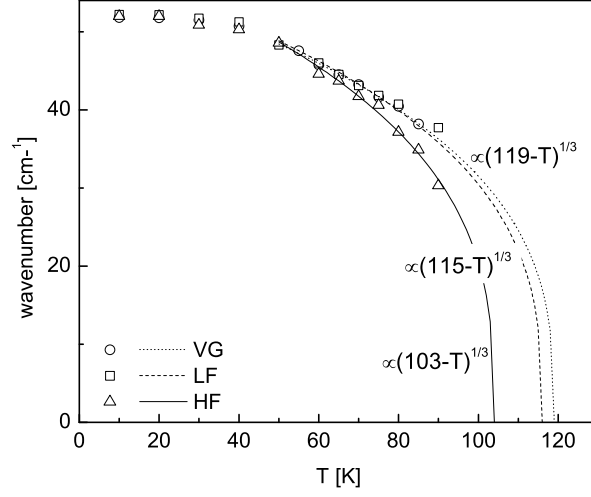


Figure 8.0.2: Frequency variation of the A_{1g} soft mode with temperature for the iron implanted strontium titanate VG (virgin), LF (2.5%) and HF (11%) samples. The lines represent the fitting functions $\omega_{A_{1g}}(T) \propto (T_a - T)^{1/3}$ with $T_a = 119$ K, 115 K and 103 K respectively.

evidenced, for example, if the implanted layer was a significant part of the probed volume²). These results thus indicate that the implanted layer (of a few nanometers) induced a significant change in the temperature behaviour of the anti-ferrodistorsive phase transition of an amount of pure SrTiO_3 at least one order of magnitude larger.

Even though it did not definitely answer the starting question concerning the nature of the magnetic phase transition, these results motivate the completion and refinement of the analysis in a future work of a slightly different scope: instead of the implanted layer isolated properties, its overall effects in the sample³.

²Because of the significant structural disorder induced by the impurities and the damage (a density of defects of the same order) introduced by the implantation.

³As an example, the same implanted samples should be measured with the laser facing the unimplanted side.

Discussion

Fe:ZnO

Emission channeling results evidenced the diluted configuration of the implanted Fe in the ZnO matrix. With the majority of the Fe in Zn substitutional site, a small ($\approx 0.15 \text{ \AA}$) displacement was strongly indicated. Supported on theoretical and experimental reported results [94, 95], it was argued that such displacement was due to the formation of impurity-defect complexes, namely $\text{Fe}_{\text{Zn}}\text{-V}_{\text{Zn}}$. Furthermore, SQUID measurements evidenced a room temperature FM state of the implanted layer with a giant moment of about $7.5 \mu_B$ per implanted Fe. Combining the EC results with the fact that any precipitate or secondary phase, matrix magnetization or even unquenching of the angular momentum could not, in principle, account for the characteristics of the observed hysteresis (particularly the giant moment), the FM state is attributed to the $\text{Fe}_{\text{Zn}}\text{-V}_{\text{Zn}}$ complexes. The magnetic moment added to the spin only value of Fe would originate from the Zn vacancies (between 1.6 and $1.8 \mu_B$ [94, 112] per vacancy), which is in agreement with theoretical DFT calculations which predicted such magnetic coupling [94]. The limited range of the presented magnetic characterization measurements is very well balanced by reported results on *Fe ion-implanted ZnO* (although no indication of the FM mechanism is forwarded there). Indeed, summarizing the relevant SQUID measurements reported on this system, it was found that the saturation magnetization decreases with annealing treatment: 40% from the as-implanted to the 700°C annealed state [110] and vanishes from the 700°C to the 900°C annealing steps [110]. This decrease in saturation magnetization is in perfect agreement with the forwarded hypothesis of FM impurity-defect complexes created during implantation which start to rupture at a given temperature (between 300°C and 700°C) and monotonically decrease in population from that temperature on, vanishing completely between 800°C and 900°C . Precise transition temperatures cannot be deduced from the available results. Actually they are expected to vary considerably, depending on the amount of defects produced, i.e. fluence and beam energy.

The forwarded mechanism of ferromagnetic state stabilization is further motivated by the fact that none of the proposed and currently accepted models, namely the one of Dietl *et al.* [11, 12] and the one of Coey *et al.* [17], accounts for the observed phenomena. The samples do not fulfill the requirements for hole mediated ferromagnetic correlation [11, 12], namely the high impurity concentration (the threshold concentration was estimated one order below the typical values for this model) and the strong *p*-type semiconductivity (the samples were not electronically doped), neither is the model able to explain the observed giant moment. The alternative model of donor impurity band exchange [17] predicts a TM threshold concentration in ZnO around 5%, while it is shown that in ZNO_MF sample it must be at least one order of magnitude below.

Taking the hypothesis a bit further, one may estimate that an average of two to four vacancies bind to each of the Fe atoms. This represents about half of the six *nnn* and *nnnn* Zn sites (with shell radii differing by less than 1%), which is rather high. This may bring some light to the unavoidable question of why did not other groups obtain the same giant moment values in similar samples, prepared under similar conditions, i.e. Fe ion-implanted ZnO. In [110], a fluence of $5 \times 10^{16} \text{ cm}^{-2}$ Fe was implanted at 200 keV into single crystalline ZnO, giving a maximum concentration of 26% and showing a magnetic moment per Fe atom of $0.13 \mu_B$. In [111] a fluence of $3 \times 10^{16} \text{ cm}^{-2}$ Fe was implanted at 80 keV , giving a maximum concentration of 34%. Although no estimate of magnetic moment per Fe atom is given, from the saturation magnetization and the typical size of the samples, it should be of the same order as [110]. The local concentration is thereby, the only tangible difference between the samples of this work and the ones produced by other groups (with moment per Fe atom one order of magnitude below). Although limited, these results may be seen to point in the following direction: higher concentrations may lead to growing dopant-dopant association and/or sharing of the available vacancies by different impurity atoms, thus reducing the moment per impurity atom. Moreover, it is

argued in [94] that the complex formation energy is indeed correlated with Fe concentration, which agrees with a decrease in the population with increasing Fe concentration.

Regarding the nature of the ordering mechanism, the very small threshold concentration⁴ estimated (less than 0.3%) indicates a long range ordering interaction between the complexes. It was predicted [94] that $\text{Fe}_{\text{Zn}}\text{-V}_{\text{Zn}}$ complexes induce a spin polarization at the surrounding oxygen atoms ($0.14 \mu_B$ per O atom), which may thus form a “polaron-like” chain linking the Fe atoms. However, for that to produce long range order, the Fe atoms would have to be sitting in neighboring unit cells. Thereby, such a mechanism, as envisioned in [94], is insufficient to explain ferromagnetic order in the tenths of at. % range. A more complex order mechanism must be responsible for the collective FM state demonstrated here and further development is required.

As a final remark, despite the beauty of such an exotic new material, from the physics point of view, if magnetic and semiconductor properties existed independently of each other, it would be of no use for device applications. The essence of magnetic semiconductor resides in the mutual interaction between magnetic and semiconducting properties which enables the control of magnetization by electrical potential or the control of semiconductor optical characteristics by magnetic field, for example. Indeed, *ab initio* calculations [94] determined that these complexes present a fully polarized SDOS at Fermi energy and indicated that this property should be maintained up to quite high temperature. In fact, at 0 K, the Fermi energy is near the top of the minority spin valence band, while the minority band gap is larger than 1 eV. Thereby, possibly up to quite high temperatures, the electrons can be thermally excited only to majority spin states while the system maintains the property that conduction electrons have a fully spin polarized SDOS. These predictions, if confirmed by experiment, make this compound promising for displaying the referred desired interaction between magnetic and semiconducting properties.

Fe:SrTiO₃

For strontium titanate, an equivalent picture could be presented. However, the limited literature on STO based DMS precludes such a detailed discussion. Nevertheless, the hypothesis of ferromagnetically ordered $\text{Fe}_{\text{Ti}}\text{-V}_{\text{O}}$ complexes in Fe:STO finds support on this work results. The EC experiment locate the implanted Fe at displaced substitutional Ti sites (of STO lattice symmetry, not secondary phases or Fe clusters) and the SQUID results evidence the high J value of the magnetic dipoles. Since such an high degree of orbital unquenching seems to be ruled out, and assuming that the extrapolation of the STO_EC to the STO_HF sample is possible, the combination of these two observations strongly support the hypothesis of ferromagnetically ordered impurity-defect complexes, i.e. Fe impurity bound and magnetically coupled to one or more O vacancies.

Furthermore, in the final stages of this work, a suspicion was raised which points in another very interesting direction, both from the applications and the physics point of view. A ferroelectric relaxor state can be induced in incipient ferroelectrics with FE soft mode behaviour (as SrTiO₃) by the presence of random-site electric dipoles [105]. If the $\text{Fe}_{\text{Ti}}\text{-V}_{\text{O}}$ complexes are polar, as they are expected to be due to the observed displacement of the Fe ion from its symmetry center, one could thus expect that the STO_HF sample (assuming that it evidences the same impurity-defect complexes as the STO_EC sample) exhibits both ferromagnetic and ferroelectric relaxor states. Moreover, the two phenomena would originate from the same entities, the $\text{Fe}_{\text{Ti}}\text{-V}_{\text{O}}$ complexes. Although highly hypothetical and without a clear possible application (specially because the FE relaxor state is not expected to be attained up to room temperature), this strongly motivates a further study of a wider scope.

⁴The impurity concentration below which the dipoles do not order anymore.

Conclusions

In this work, the potential of ion implantation technique to produce ferromagnetic layers in industrially viable semiconductors was demonstrated. Magnetic characterization, by means of SQUID magnetometry, evidenced the FM state of Fe:SrTiO₃/Fe:ZnO layers and threshold Fe concentrations around 2.5% / below 0.3%. The Curie temperature was observed to be above 100 K/300 K, the highest investigated temperatures, presumably well above. The room temperature character of the FM state was thereby suspected/proved. A magnetic moment of $7.5 \mu_B$ per Fe atom was estimated for both systems. This giant moment is unprecedented for any TM:SrTiO₃ and for Fe:ZnO. Furthermore, it is hardly explained singly by unquenched angular momentum of the Fe atom or magnetization of the host matrices. By means of electron emission channeling technique, the dilute configuration of the implanted Fe was demonstrated, an important prerequisite for intrinsic DMS behaviour.

Towards the understanding of the mechanism that stabilizes the FM state, EC results provide extra information. In SrTiO₃/ZnO the Fe was located almost entirely on Ti/Zn substitutional sites with small (tenths of Å) displacements towards the O/Zn site. This was attributed to the formation of impurity-defect complexes (bound Fe impurities and O/Zn vacancies), already identified in SrTiO₃/ZnO [104]/[95], which additionally accounts for the observed giant moment. For Fe:ZnO, the magnetic properties of these complexes, when isolated, had already been investigated [95, 94] and the potential for ferromagnetic long range ordering was suspected (along with possible spin injector capabilities, of major relevance for spintronic applications). This work thus strongly corroborates these expectations for Fe:ZnO and furthermore extends the phenomena to a rather different material system Fe:SrTiO₃.

The groundbreaking character of the hypothesis forwarded in this work is very well summarized in [95]:

The occurrence of defect-related local magnetic ordering on an atomic scale appears an attractive hypothesis also for an explanation of ferromagnetism under other experimental conditions in ZnO as well as in other DMSs and it challenges present concepts for a theoretical modeling of room temperature ferromagnetism.

Future work

Given the short-term character of this work, the studies presented in this report were very limited. On going studies are thereby extending the variables ranges, always with the two-folded objective of DMS system optimization *and* understanding, which certainly are not independent. Such extension spans full range characterization and preparation parameters.

The implantation parameters span a wide range of implantation temperatures, energies and fluences, annealing temperatures, duration and atmosphere and magnetic/electronic co-doping combinations (both with the two-folded contribution to semiconductor and magnetic properties). The aim is to identify optimum implantation and annealing parameters with respect to producing samples that show ferromagnetic behaviour. In a second stage, the conditions can be further optimized e.g. by implanting the dopants at multiple energies in order to create broader profiles of transition metal ions with a specific concentration in the semiconductor (with the added bonus of larger measurable magnetic signal). In particular one can produce e.g. two ferromagnetic semiconductor layers buried in the semiconductor substrate and separated by a few nanometers (1-3 nm) and study the magnetic inter-layer coupling. This would be a breakthrough towards the production of more complex nanostructures (spin-valve like) relevant for applications.

Regarding the characterization of the thus produced samples, an extensive roll of techniques are available within a collaboration that involves the universities of Porto, Aveiro and Lisboa, ITN, CERN (Switzerland) and IKS (Belgium). The conventional structural characterization of virgin and implanted samples will be accomplished by means of X-ray diffraction (XRD), Rutherford Backscattering/ Channeling (RBS/C), Proton Induced X-ray Emission / Channeling (PIXE/C). Furthermore, while the emission channeling method provides direct information on the lattice sites of implanted impurities, hyperfine interaction methods available within the collaboration such as Mossbauer spectroscopy (MS) or the perturbed angular correlation (PAC) techniques are in many cases suitable in order to investigate the local environment around probe atoms and can hence be applied in a complementary way. In order to distinguish between magnetic properties arising from a doped semiconductor layer and from possible ferromagnetic clusters of the implanted elements (given that dynamic effects depend on the nature of the magnetic entities in the system), selected samples shall be investigated by time-dependent magnetization measurements, e.g. magnetic viscosity as a function of temperature, or by AC susceptibility measurements in a broad range of frequencies. The magnetic intrinsic properties (e.g. spin-polarized semiconductor bands) shall be investigated in selected samples using Magneto-optical Faraday (for transparent samples) or Kerr effect (MOKE, in reflection) measurements as a function of temperature and magnetic field. The inter-layer coupling of the two layer (spin-valve like) structures mentioned above, can be studied by means of SQUID and MOKE in order to access the inter-layer coupling and layer switching fields. Since most of these characterization techniques are nondestructive, it is possible in many cases to characterize the same samples with different techniques. Also, the annealing procedures can in many cases be applied sequentially, i.e. followed by suited sample characterization after each annealing step.

A very assertive experiment addressing the role of defects on the inset of the FM state was also envisaged. Sequential magnetic characterization of a sample epitaxially grown (thereby only with primary/intrinsic defects) that is repeatedly RT e^- -irradiated (which produces an increasing amount of damage of the same kind as ion-implantation) and defect-characterized at each step by positron annihilation (PA), allows one to find the precise correlation between defects and magnetic properties. To produce samples with the same diluted nature as with ion-implantation, one could use molecular beam epitaxy (MBE). It is a thin-film growth technique that allows one to work far from equilibrium, i.e., since the crystal is grown at low temperature, there is not enough thermal energy available to form secondary phases, allowing the epitaxial growth of a single-crystal alloy.

Other techniques, not so easily accessible, could be applied to optimized samples, in order to further investigate the nanoscopic phenomena governing these material systems. The use of synchrotron radiation or neutrons would allow the investigation of secondary phases and precipitates in the atomic size limit and the local probing of the magnetic interactions.

Furthermore, the research covers other technologically relevant and scientifically promising materials. GaN is a special case, not only for its DMSs potentialities, but also because of its closeness to semiconductor industry (LED technology), unrivaled among the most intensively studied (DMS related research) semiconductor materials. Also, other semiconductor oxides (KTaO_3 , TiO_2 and AlO_3) and other magnetic dopants (the 3d TMs Mn, Fe, Co and Ni and some promising REs like Eu, Gd, or Tb) are part of the planned studies.

Bibliography

- [1] L. Hoddeson, E. Braun, J. Teichmann and S. Weart, *Out of the Crystal Maze: Chapters from the History of Solid-State Physics*, Oxford Univ. Press, Oxford, 1992.
- [2] S. A. Chambers, *Materials today* (April 2002) 34.
- [3] M. Dubash, *Operating Systems and Servers News* (13 April 2005) Techworld.
- [4] S. J. Pearton, *Nature Materials* **3** (2004) 203.
- [5] K. Ando, *Science* **312** (2006) 1883.
- [6] S. A. Wolf *et al.*, *Science* **294** (2001) 1488.
- [7] T. Dietl, *Nature Materials* **2** (2003) 646.
- [8] A. H. Macdonald, P. Schiffer and N. Samarth, *Nature Materials* **4** (2005) 195.
- [9] H. Ohno, *Science* **281** (1998) 951.
- [10] D. P. DiVincenzo, *Science* **270** (1995) 255 .
- [11] T. Dietl *et al.*, *Science* **287** (2000) 1020.
- [12] T. Dietl, H. Ohno and F. Matsukura, *Phys. Rev. B* **63** (2001) 195205.
- [13] W. Prellier, A. Fouchet, and B. Mercey, *Journal of Physics: Condensed Matter* **15** (2003) R1583-R1601.
- [14] S.J. Pearton *et al.*, *Materials Science and Engineering R* **40** (2003) 137-168.
- [15] S.J. Pearton, W.H. Heo, M. Ivill, D.P. Norton, and T. Steiner, *Semiconductor Science and Technology* **19** (2004) R59-R74.
- [16] C. Liu, F. Yun, and H. Morkoç, *Journal of Material Science: Materials in Electronics* **16** (2005) 555-597.
- [17] J.M.D. Coey, M. Venkatesan, and C.B. Fitzgerald, *Nature Materials* **4** (2005) 173-179.
- [18] S.A. Chambers, *Surface Science Reports* **61** (2006) 345-381.
- [19] S.J. Pearton *et al.*, *Journal of Electronic Materials* **36** (2007) 462-471.
- [20] S. Dhar, O. Brandt, M. Ramsteiner, V. F. Sapega, and K. H. Ploog, *Physical Review Letters* **94** (2005) 037205/1-4.
- [21] S. Dhar, T. Kammermeier, et al., *Applied Physics Letters* **89** (2006) 062503/1-3.
- [22] S.J. Pearton *et al.*, *Journal of Electronic Materials* **36** (2007) 462.
- [23] M. Venkatesan, C. B. Fitzgerald, J. M. D. Coey, *Nature* **430** (2004) 630.
- [24] C. Song *et al.*, *Phis. Rev B* **73** (2006) 024405.
- [25] Joseph M., Tabata H. and Kawai T., *Japan. J. Appl. Phys.* **38** (1999) L1205.
- [26] E. Biegger *et al.*, *Journal of Applied Physics* **101** (2007) 073904/1-6.

- [27] P. Wu, G. Saraf *et al.*, Applied Physics Letters **89** (2006) 012508/1-3.
- [28] G. A. Medvedkin, T. Ishibashi, T. Nishi and K Hayata, Jpn. J. Appl. Phys. **39** (2000) L949.
- [29] H. Ohno, F. Matsukura, Solid state. Comm. **117** (2001) 179.
- [30] J.K. Furdyna, J. Appl. Phys. **64** (1988) R29.
- [31] M. Nazmul, S.Ahsan, & Tanaka, Cond-mat (2003), 0208299.
- [32] S.J. Pearton *et al.*, Mat Sc. And Engg., R 40 (2003), 137.
- [33] A. Haury *et al.*, Phys. Rev. Lett. **79** (1997) 511.
- [34] Y. Fukuma *et al.*, Journ. Of Appl. Phys. **93** (2003) 7667.
- [35] H. Munekata *et al.*, Phys. Rev. Lett. **63** (1989) 1849, 54.
- [36] T. Story, R.R. Galazka, R.B. Frankel, P.A. Wolff, Phys. Rev. Lett. **56** (1986) 777.
- [37] H. Ohno *et al.*, Phys. Rev. Lett. **68** (1992) 2664.
- [38] H. Ohno *et al.*, Appl. Phys. Lett. **69** (1996) 363.
- [39] Y. D. Park *et al.*, Science, 95 (2002) 651
- [40] Norton D. *et al.*, Electrochem. Solid-State. Lett. **6** (2003) G19.
- [41] Lee J. S. *et al.*, Electrochem. Solid-State. Lett. **6** (2003) G31.
- [42] Zhang *et al.*, Appl. Phys. Lett. **89** (2006) 012501.
- [43] Sato K. and Katayama-Yoshida H., Japan J. Appl. Phys. **39** (2000) L555.
- [44] Gardiner, D.J., *Practical Raman spectroscopy*, Springer-Verlag, 1989.
- [45] J. F. Ziegler, J. P. Biersack and U. Littmark, *The Stopping and Range of Ions in Solids*, by Pergamon Press, New York, 1985.
- [46] J. P. Biersack, *The Stopping and Range of Ions in Matter*, volumes **2** - **6**, Pergamon Press (1977-1985).
- [47] J. P. Biersack and L. Haggmark, Nucl. Instr. and Meth. **174** (1980) 257.
- [48] J. E. Jaffe, J. A. Snyder, Z. Lin, and A. C. Hess, Phys. Rev. **B 62**, (2000) 1660.
- [49] S. Thevuthasan, W. Jiang, V. Shutthanandan, W.J. Weber, Nuc. Instr. & Meth. in Phys. Reserch. Sec. B - Beam Int. with Mat. and At. **206** (2003) 162-165.
- [50] K. Lorenz *et al.*, Appl. Phys. Lett. **87** (2005) 191904.
- [51] B.S. Thomas, N.A. Marks and B.D. Begg, Nuclear Instruments and Methods in Physics Research **B 254** (2007) 211-218.
- [52] Coskun C., Look D.C., Farlow G.C., Sizelove J.R., Semiconductor Science and Technology **19** (2004) 752-754.
- [53] S. M. Hogg, B. Pipeleers, A. Vantomme, and M. Swart, Appl. Phys. Lett. **80** (2002) 4363.
- [54] S. Kucheyev, J. S. Williams, and S. J. Pearton, Mater. Sci. Eng. R **33** (2001) 51.
- [55] J. F. Ziegler, J. P. Biersack, and U. Littmark, *The stopping and range of ions in solids*, vol. 1, Pergamon Press, New York, 1985.
- [56] E. Kugler, The ISOLDE facility, Hyperne Interact. **129** (2000) **23**.
- [57] U. Wahl, Hyperfine Interactions **129** (2000) 349-370.
- [58] U. Wahl *et al.*, Nuc. Instr. & Meth. in Phys. Reserch. Sec. B - Beam Int. with Mat. and At. **136** (1998) 744-750.

- [59] H. Hofsas, U. Wahl, S. G. Jahn, Hyperfine interactions **84** (1994) 27-41
- [60] U. Wahl, *Emission channeling: charged particle-solid interaction, detection and lattice location methods - Masters Course*, Univ. de Lisboa, Lisboa, 2006.
- [61] J. Lindhard, Mat. Fys. Medd. Dan. Vid. Selsk. **34** (1965), 14.
- [62] D. V. Morgan, Channeling, John Wiley & Sons, 1973.
- [63] J. U. Andersen *et al.*, Nucl. Instrum. Meth. **194** (1982), 209.
- [64] H. Hofsass and G. Lindner, Phys. Rep. **201** (1991), 121.
- [65] H. Hofsass, U. Wahl, and S. G. Jahn, Hyperne Interact. **84** (1994), 27.
- [66] H. Hofsass, Hyperne Interact. **97-98** (1996), 247.
- [67] P. Weilhammer *et al.*, Nucl. Instrum. Meth. A **383** (1996), 89.
- [68] U. Wahl *et al.*, Nucl. Instrum. Meth. A **524** (2004), 245.
- [69] O. H. Nielsen *et al.*, Z. Phys. B - Cond. Matter **52** (1983), 99.
- [70] U. Wahl, Phys. Rep. **280** (1997), 145.
- [71] H. H. Seliger, Phys. Rev. **88** (1952), 408.
- [72] B. Pipeleers, S. M. Hogg, and A. Vantomme, J. Appl. Phys. **98** (2005), 123504.
- [73] S. Kucheyev, J. S. Williams, and S. J. Pearton, Mater. Sci. Eng. R **33** (2001), 51.
- [74] A. Vantomme *et al.*, Nucl. Instrum. Meth. B **175-177** (2001), 148.
- [75] J. Nord, K. Nordlund, B. Pipeleers, and A. Vantomme, Mater. Sci. Engin. B **105** (2003), 111.
- [76] U. Wahl *et al.*, Phys. Rev. Lett. **79** (1997) 2069.
- [77] B.T.M. Willis, A.W. Pryor, The thermal vibrations in Crystallography (1975) Cambridge University Press, Cambridge.
- [78] P.G. Dawer R.G. Elliot, Proc. Roy. Soc. London, A273 (1963) 222.
- [79] U. Whal, Ph. D. Thesis, Konstanz Univ., Konstanz (1992).
- [80] B. G. Almeida, Ph. D. Thesis, Univ. do Porto, Porto (1998).
- [81] M. M. P. de Azevedo, Ph. D. Thesis, Univ. do Porto, Porto (1999).
- [82] R. Chaves, H. Amaral. and S. Ziolkiewicz, Physique **41** (1980) 259.
- [83] A. Almeida *et al.*, Ferroelectrics **294** (2003) 49.
- [84] Bart De Vries, Ph. Thesis, Katholiek Uni. Leuven, Leuven, 2006.
- [85] N.P. Barradas, C. Jeynes, R.P. Webb, Appl. Phys. Lett., Appl. Phys. Lett. **71** (1997) 291.
- [86] P. van Espen, *AXIL v3.0 Computer Code Manual*, 1990.
- [87] Ana Marques, Ph. D. Thesis, Univ. de Lisboa, Lisboa (unpublished).
- [88] E. Rita *et al.*, Appl. Phys. Lett. **85** (2004) 4899.
- [89] T. Monteiro *et al.*, J. Appl. Phys. **93**, (2003) 11.
- [90] S.O. Kucheyev *et al.*, Phys. Rev. **B 67** (2003) 094115.
- [91] D.C. Look, C. Coskun, B. Claflin and G.C. Farlow, G. C., Physica **B 340-342**, 32-38 (2003).
- [92] L.S. Vlasenko and G.D. Watkins, G. D., Phys. Rev. **B 72** (2005) 035203.
- [93] F. Tuomisto, K. Saarinen, D.C. Look, and G.C. Farlow, Phys. Rev. **B 72** (2005) 085206.

- [94] A. Debernardi and M. Fanciulli, Appl. Phys. Lett. **90** (2007) 212510.
- [95] G. Weyera, H.P. Gunnlaugssona, R. Mantovanb, D. Naidoo, R. Sielemann, K. Bharuth-Ramd, M. Fanciullib, T. Agnef, (unpublished).
- [96] U. Wahl *et al.*, Superlattices and Microstructures **39** (2006) 229-237 .
- [97] R. Merkle and J. Maier, Physical Chemistry Chemical Physics **11** (2003) 2297-2303.
- [98] Zukova A. *et al.*, Appl. Phys. Lett. **89** (2006) 232503.
- [99] Dietl *et al.*, Nature **423**, 850-853 (2003).
- [100] G.F. Goya and E.R. Leite, J. Phys. Condens. Matter **15** (2003) 641-655.
- [101] K. Potzer *et al.*, Appl. Phys. Lett. **88** (2006) 052508.
- [102] Song Y. Y. *et al.*, Journal of the Korean Physical Society **50** (2007) 1706-1710.
- [103] Wu P. *et al.*, Appl. Phys. Lett. **89**, 012508 (2006).
- [104] R. Merkle and J. Maier, Physical Chemistry Chemical Physics **11** (2003) 2297-2303.
- [105] George A. Samara, J. Phys.: Condens. Matter **15** (2003) R367-R411.
- [106] Almeida A., *et al.*, Ferroelectrics **318** (2005) 147-153.
- [107] Petzelt J. *et al.*, Phys. Rev. B **64** (2001) 184111.
- [108] P A, Fleury. J. F, Scott, and J. M. Worlock, Phys. Rev. Lett. **21** (1968) 16.
- [109] S. A. Hayward and E. K. H. Salje, Phase Transitions **68** (1999) 501.
- [110] Wu *et al.*, Appl. Phys. Lett. **89** (2006) 012508.
- [111] N. H. Hong *et al.*, Appl. Phys. Lett. **89** (2006) 042503.
- [112] N. A. Spaldin, Phys. Rev. B **69**, 125201 (2004).

List of Communications

Oral communications by invitation

1. L. Pereira, J.P. Araújo, U. Wahl, *Diluted Magnetic Semiconductors*, Seminar at IKS - Instituut voor Kern & Stralingsfysica, Leuven, Belgium, June 2007.

Other oral communications

1. L. Pereira, J.P. Araújo, U. Wahl, *Spintrónica de Semicondutores Magnéticos Diluídos*, III Jornadas do IFIMUP Departamento de Física, Faculdade de Ciências da Universidade do Porto, Portugal, May 2007.
2. L. Pereira, J.P. Araújo, U. Wahl, A. C. Marques, *Doping ZnO and SrTiO₃ with Fe by ion implantation: magnetism and impurity lattice site location*, XIX International School of Physics and Chemistry of Condensed Matter: Physics and Chemistry of Magnetic Materials, Białystok/Białowiesza, Poland, July 2007.
3. A. C. Marques, U. Wahl, J. G. Correia, E. Rita, C. Marques, E. Alves, J. P. Araújo, L. Pereira, M. R. Silva, J. C. Soares, *Lattice site location of implanted Fe in SrTiO₃ and lattice damage recovery studies*, ISOLDE workshop and users meeting 2006/2007, Geneva, Switzerland, February 2007.

Posters in conferences

1. L. Pereira, J.P. Araújo, U. Wahl, A. C. Marques, *Indication of high temperature ferromagnetism with giant magnetic moment in SrTiO₃*, DyProSo XXXI - 31st International Symposium on the Dynamic Properties of Solids, Porto, Portugal September 2007.